

Low-temperature electronic transport of metal
doped carbon nanotube molecular hybrids and
Nitrogen-doped nanocrystalline diamond

University of the Witwatersrand



*A dissertation submitted in fulfilment of the requirements for the degree
of Doctor of Philosophy*

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15 August 2024

Declaration

I declare that this thesis is an original report of my research, has been written by me and has not been submitted for any previous degree. The experimental work is entirely my own work; the collaborative contributions have been indicated clearly and acknowledged. Due references have been provided on all supporting literature and resources.

A handwritten signature in black ink, consisting of a stylized 'S' followed by a horizontal line and a small flourish.

15 August 2024

Abstract

This thesis explores the magnetism and spin-related properties in carbon-based molecular hybrid materials, with a focus on expanding our understanding of low-dimensional carbon structures and their potential electronic applications. The investigation spans from one-dimensional systems, such as carbon nanotubes (CNTs) functionalized with single-molecule magnets (SMMs), to three-dimensional systems like nitrogen-doped ultra nanocrystalline diamond (UNCD). In these carbon structures, electronic transport is intricately tied to microstructural features, such as grain boundaries and impurity clusters, which hold significant potential for the development of all-carbon electronic devices.

The research begins with a detailed examination of the chemical functionalization of multi-walled carbon nanotubes (MWCNTs) through controlled acid treatment to achieve precise metal doping. Using Raman spectroscopy and complementary techniques like ICP-MS and ToF-SIMS, we successfully demonstrate how functionalization levels influence the magnetic properties of CNT hybrids loaded with magnetic metals from the lanthanide series (Gd, Tb, Dy). The study reveals that low percentages of metal doping (0.5% to 1.0%) preserve the magnetic bistability of SMMs post-grafting, while higher doping levels lead to complex magnetic behaviors including superparamagnetism, quasi-ferromagnetism, and potential Kondo lattice behavior in CNT-heavy metal systems.

We also explore the spin-phonon coupling in Gd-filled double-walled CNTs, where the onset of superparamagnetic properties at low temperatures is coupled with phonon mode stiffening observed via Raman spectroscopy. This enhanced coupling offers promising pathways for developing efficient molecular qubits through the modulation

of spin-phonon interactions in one-dimensional systems.

The second part of the thesis investigates into the microwave plasma-assisted chemical vapor deposition (MWCVD) growth of nitrogen-doped nanocrystalline diamond (NCD) thin films on different substrates. By pioneering upgrades to the MWCVD system, I was able to achieve reliable growth of high-quality nanocrystalline diamond thin films. Notably, I observed a novel nanostructure, termed Diaphite—a previously unreported feature, in these NCD films, consisting of nanodiamond grains coherently linked with graphene-like rings. This structure, along with the non-equilibrium growth conditions induced by nitrogen doping and secondary nucleation, presents unique polymorphic features in artificially grown diamonds.

Detailed low-temperature transport measurements on four different samples—ranging from 7.5% to 20% nitrogen doping—uncovered complex transport phenomena such as 3D weak localization (WL), variable-range hopping (VRH), and unusual magnetoresistance (MR) behavior. In particular, the 7.5% N₂-doped UNCD film on quartz exhibited 3D weak localization (WL) at low fields and anti-weak localization (AWL) at higher fields, with distinct magnetoresistance characteristics depending on the direction of the applied magnetic field. The 20% N₂-doped films on both quartz and silicon showed more metallic-like behavior, with magneto-resistance characterized by a $B^{1/2}$ dependence at low temperatures, suggesting an intricate relationship between doping level, microstructure, and electron transport.

These findings significantly expand our understanding of the role that microstructural and chemical modifications play in determining the electronic and magnetic properties of carbon-based materials. This work provides a foundational platform for future research into carbon electronics, offering potential breakthroughs in spintronics, molecular transistors, quantum computing, and other advanced electronic applications.

Acknowledgements

The completion of this doctoral dissertation marks the conclusion of a five-year commitment to low dimensional carbon system and their quantum transport research. Throughout this period, I encountered various challenges and received invaluable support from numerous individuals. I want to express my gratitude, first and foremost, to my advisor, Professor Somnath Bhattacharyya. Beyond being a trailblazer in carbon-based quantum and nano-technology, he has guided our research group with unparalleled enthusiasm and dedication during my relatively brief tenure as a researcher. The establishment of state-of-the-art facilities at the Nano-Scale Transport Physics Laboratory (NSTPL) has provided access to profound and captivating physics, which was largely inaccessible in South Africa at the time of his appointment. I am profoundly thankful to him for granting me the opportunity to delve into such compelling fields, as evident in the research presented here.

I would also like to extend my gratitude to both past and current members of my research group, with special mention to Chris Coleman, Siphephile Ncube, Davie Mtsuko, Sarv Mosse, and George Chimowa. Each of them has been a valuable collaborator, and I have gained significant insights from our collective efforts on various projects. Additionally, I have been fortunate to receive technical assistance from individuals outside our research group, including Daniel Wamwangi, Rudolf Erasmus, Roger Van Rensburg, from University of the Witwatersrand, Prof. Andrew Huxley from University of Edinburgh, and Prof. Charlie Johnson from University of Pennsylvania. Their contributions were instrumental, and much of the work presented in this thesis would not have been possible without their support.

Finally, I want to express my deepest appreciation to my family and friends. The dedication required to complete this body of work has consumed much of my time over the past few years. The moral support and understanding I have received during this period are immensely valued and will be remembered with gratitude.

Preface

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The thesis is primarily based on three scientific articles published in peer-reviewed international journals, along with two manuscript currently in preparation. To aid in the interpretation of the research findings, the publications have been expanded to include additional illustrative figures, supplementary information, and an introductory chapter dedicated to relevant theoretical concepts.

The following publications and manuscript form the core of this thesis:

1. **Sodisetti, V. R.**, and Bhattacharyya, S. (2024). Diaphite: diamond-graphene hybrid nanostructures grown in $\text{CH}_4/\text{H}_2/\text{N}_2$ chemistry. Sci Rep–Under Review.
2. **Sodisetti, V.R.**; Lemmerer, A.; Wamwangi, D.; Bhattacharyya, S. Observation of High Magnetic Bistability in Lanthanide ($\text{Ln} = \text{Gd}, \text{Tb}$ and Dy)-Grafted Carbon Nanotube Hybrid Molecular System. Int. J. Mol. Sci. 2023, 24, 12303. <https://doi.org/10.3390/ijms241512303>
3. Chimowa, G., Flahaut, E., **Sodisetti, V.R.** and Bhattacharyya, S. (2023), Converting Ambipolar Double-Walled Nanotube Bundles to Unipolar Carbon Nanotube Field-Effect Transistor Devices by Inner Functionalization. Phys. Status Solidi A, 220: 2200669. <https://doi.org/10.1002/pssa.202200669>
4. **Sodisetti, V.R.**; Ncube, S.; Coleman, C.; Erasmus, R.M.; Flahaut,

- E.; Bhattacharyya, S. Strong spin–phonon coupling in Gd-filled nanotubes. *J. Appl. Phys.* 7 December 2021; 130 (21): 214301. <https://doi.org/10.1063/5.0067555>
5. Mosse, I.S.; **Sodisetti, V.R.**; Coleman, C.; Ncube, S.; de Sousa, A.S.; Erasmus, R.M.; Flahaut, E.; Blon, T.; Lassagne, B.; Šamořil, T.; et al. Tuning Magnetic Properties of a Carbon Nanotube-Lanthanide Hybrid Molecular Complex through Controlled Functionalization. *Molecules* 2021, 26, 563. <https://doi.org/10.3390/molecules26030563>
6. C. Coleman, **V. R. Sodisetti**, I. S. Mosse, A. S. de Souza, D. Wamwangi, E. Flahaut, S. Bhattacharyya. "Realization of a one-dimensional Kondo lattice in hybrid molecular magnet-carbon nanotube systems." Pending Submission

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Chapter 1

Introduction

Carbon stands as an wonderful element. The James Webb Space Telescope from NASA recently achieved the first detection of a carbon molecular compound, specifically the methyl cation (CH_3^*), situated approximately 1,350 light years distant from Earth in space [1]. Given that carbon and its compounds are recognized as the fundamental building blocks of all known life, this finding sparks human curiosity, offering insights into the origins of life, both on Earth and on distant planets throughout the universe.

The carbon element, initially in the form of coal, played a pivotal role as a fossil fuel during the inception of the first industrial revolution. Coal served as a crucial energy source for heat generation, powering trains, ships, and facilitating the production of iron and steel in factories. Even today, emerging economies continue to rely on coal for electricity generation to meet their energy needs. The discovery of diamond, a carbon allotrope, dates back to 320 - 296 BCE in India, where they were referred to as 'Vajra'[2]. Diamonds were first mined in India's Golconda region, located between the Godavari and Krishna Rivers, around 4,000 years ago. However, the modern diamond market truly burgeoned in the late 1800s following the revelation of diamond mines in Kimberly, South Africa. The recent unveiling of graphene has brought about a revolutionary transformation in the contemporary materials industry. In conclusion, the carbon element permeates every facet of our lives, prompting extensive research efforts to comprehend its fundamental science and harness technological applications.

Notably, there are over 500 hypothetical allotropes of carbon, as indicated by [3], with well-known variants including Fullerene, Carbon nanotube, Graphene, and Diamond (Figure. 1.1).

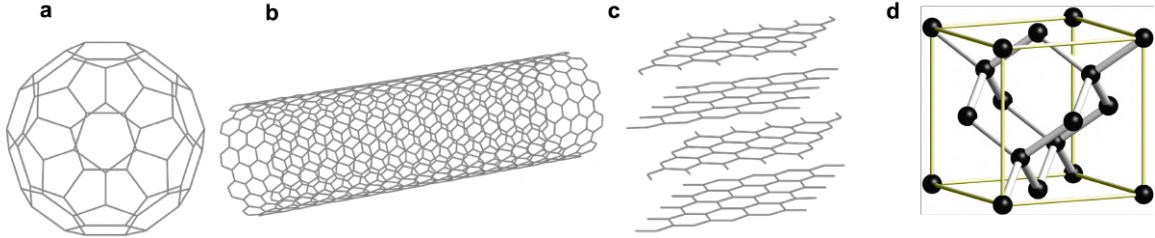


Figure 1.1 *Allotropes of Carbon.* Commonly known four allotropes of carbon. a) Fullerene, b) Carbon nanotube, c) Graphene, and d) Diamond.

Carbon manifests diamagnetic properties due to its negative net magnetic susceptibility (χ). With four valence electrons in its outer orbitals, carbon promptly forms covalent bonds with neighboring carbon atoms, leaving no unpaired electrons. This bonding mechanism results in tightly held electrons within the p -orbitals, generating no net magnetic moment and opposing changes in the electric field induced by an external magnetic field. Consequently, carbon exhibits robust diamagnetism, a characteristic documented in various carbon allotropes such as Fullerene [4], Carbon Nanotubes (CNT) [5], graphene, graphite [6], and diamond [7].

Carbon, known for its exceptional conductivity, presents exciting prospects when magnetism is introduced into the material through factors like disorder, reduced dimensionality, or interfacing with molecular magnets. This opens up new avenues for delving into fundamental physics and advancing technological applications.

1.1 Scope of Thesis

The present thesis/my research work explores the fundamental physics and electronic transport characteristics of a 1D carbon nanotube molecular system interfaced with nanoscale molecular magnets and a 3D carbon system composed of nitrogen doped

ultra-nanocrystalline diamond (N_2 -UNCD) where a disorder parameter introduced through regulated nitrogen doping governs the transport properties.

Segment I: Coupling Magnetism and CNT discrete energy states at a molecular scale

In bulk materials, magnetism arises from the collective behavior of numerous magnetic moments or spins. Below the Curie temperature (T_C), this collective behavior transitions into the formation of magnetic domains within the magnet, where a uniform magnetization is observed [8]. When exposed to an external magnetic field, these domains can be enhanced, propagated, and destroyed until the bulk magnet reaches full magnetization, displaying characteristic hysteresis behavior (refer to Figure 1.2). As the size of the magnet is reduced to the scale of magnetic nanoparticles or molecular clusters, a uniform reversal of magnetization can be observed, typically occurring at around 10^5 Bohr magnetons, as the magnetic field compensates for the magnet's anisotropy energy [9].

Further reducing the size of a magnet to the level of a single molecule results in a decrease in magnetization to just a few Bohr magnetons, rendering the magnet vulnerable to various quantum mechanical phenomena. For instance, in single molecule magnets, there is evidence of quantum tunneling of magnetization (QTM), which manifests as distinct steps in the magnet's hysteresis curve at extremely low temperatures. Owing to their molecular structure, single molecule magnets also exhibit remarkably prolonged relaxation times, extending up to several years, and coherence times of up to a few microseconds at cryogenic temperatures below 1 Kelvin. This characteristic enables the coherent manipulation of molecular spins, rendering single molecule magnets promising candidates for (molecular) spintronic devices and highly suitable for spin qubits[10].

In line with the current trend towards developing more compact and efficient detectors, Ganzhorn and Wernsdorfer et al. (2012) introduced a plan for a supramolecular torque magnetometer employing a carbon nanotube NEMS. This proposed configuration seeks to explore and regulate the magnetic moment (approximately $1 \mu_B$) or force (around

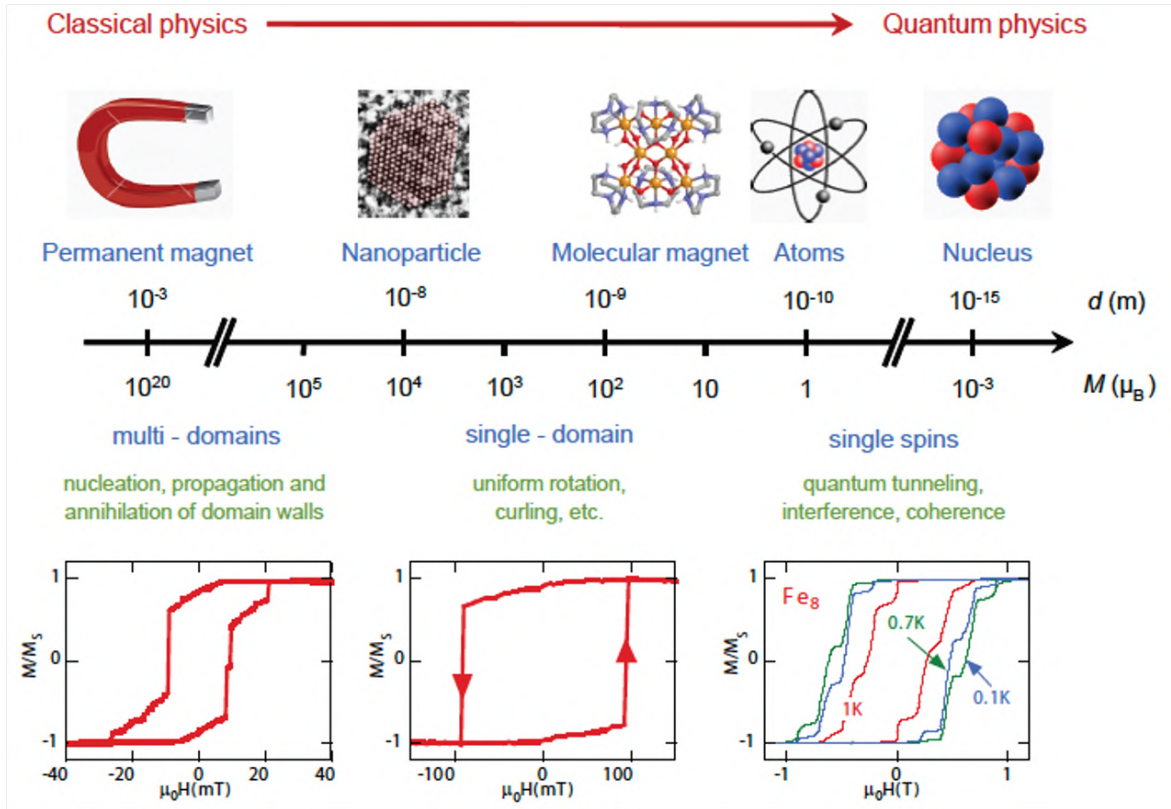


Figure 1.2 *From the perspective of large-scale observations to the realm of quantum mechanics in the study of magnetism. adopted from [11]*

10^{-18} N) of a single molecule magnet at low temperatures. Such a supramolecular spintronic device (depicted in Fig. 1.3 a) would facilitate the detection of an individual electronic spin and potentially even a set of nuclear spins. Both carbon nanotube NEMS and SMMs exhibit characteristics of promising quantum oscillators and spin qubits, respectively. By coupling these quantum systems, it becomes feasible to detect and manipulate a single electron or nuclear spin via quantum oscillation. This coupling would empower molecular spintronic devices to carry out quantum information processing at the level of individual spins or phonons. Such advancements could include entangling two distinct molecular spins or phonons, paving the way for sophisticated quantum computing and communication capabilities.

Carbon allotropes like graphite, diamond, carbon nanotubes, and fullerenes primarily display diamagnetic traits. In simpler terms, this diamagnetic behavior occurs as a response opposing an applied magnetic field. In diamond, this response comes from localized electrons, while in graphite, it arises from delocalized π -band electrons, particularly when the magnetic field is perpendicular to the graphene layers. In

the case of fullerenes and nanotubes, diamagnetic properties result from a blend of diamagnetism from localized electrons and van Vleck paramagnetic contributions. These contributions originate from magnetic dipole interband transitions due to the chemical bond's asymmetry. Consequently, carbon nanosystems are proposed as an ideal platform for coupling and for exploring the quantum state of a single molecule magnet without perturbing its quantum properties.

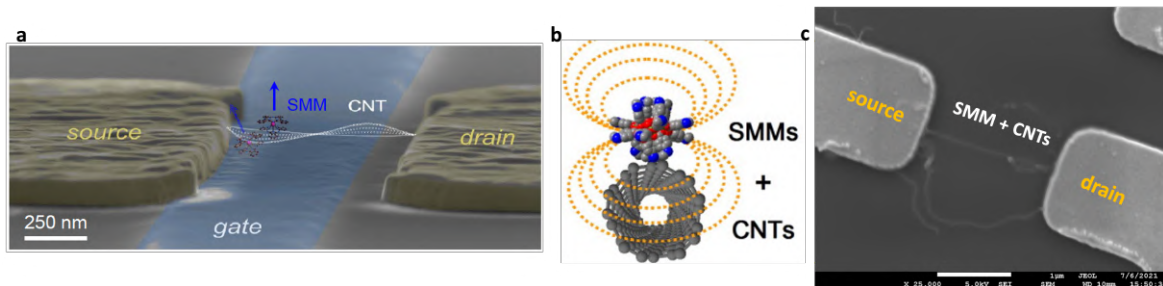


Figure 1.3 *a) A hybrid quantum system composed of a carbon nanotube nano-electromechanical system (CNT NEMS) and a single molecular magnet (SMM). b) Diagram illustrating the interaction between the magnetic properties of a SMM and the quantized mechanical modes of a CNT. c) CNT device prepared at NSTPL - discussed in the chapter 4. adopted from:[12]*

Nevertheless, there remains a necessity for a fundamental understanding of constructing efficient hybrid systems integrating carbon nanotubes (CNTs) and single molecule magnets (SMMs).

- Can we retain the novel magnetic traits of SMMs post their grafting?
- What are the effective ways in accomplishing the novel magnetic traits post their grafting?
- What are the enhanced electronic properties of such hybrid molecular systems?

Chapter 2 explores efficient methods for functionalizing carbon nanotubes, assessing their level of chemical functionalization via Raman spectroscopy, and adjusting their magnetic properties by carefully grafting Gd-DTPA molecular magnets.

Chapter 3 delves into the one-step chemical process of preparing Ln EDTA and conducts crystallographic studies to comprehend the source of slow magnetic

relaxation. Leveraging insights gained from CNT functionalization, these Ln-EDTA magnetic molecules are attached, and their magnetic bistability properties are investigated after being grafted onto the CNT surface.

Chapter 4 delves into the endohedral functionalization of Gd magnetic molecules within a double-walled carbon nanotube (DWCNT). Specifically, it examines the interaction between this magnetic molecule and discrete vibrational modes of the CNT using low-temperature Raman spectroscopy (at liquid nitrogen temperatures).

Additionally, the Kondo Effect in Ln EDTA-grafted MWCNT molecular systems is investigated. Finally, the observation of Kondo lattice phenomena in a heavily doped fermionic system (with doping exceeding 5.8%) is studied.

Segment II: CVD Diamond growth and electronic transport of N₂ doped NCD films

Chapter 5: CVD deposition of diamond thin films.

The Microwave Plasma Enhanced Chemical Vapor Deposition (CVD) reactor plays a crucial role in producing high-quality diamond thin films. Achieving this entails optimizing both the reactor itself and the process parameters involved. In this context, various parameters are examined and discussed. Specifically, nitrogen-doped ultrananocrystalline diamond (UNCD) films were grown on both quartz and silicon (Si) substrates.

Chapter 6 focuses on the chemical vapor deposition (CVD) process for depositing UNCD thin films within a hydrogen-rich plasma environment. Additionally, it explores the creation of novel polymorphs, particularly the Graphene-diamond hybrid superlattice known as Diaphite with regulated N₂ doping

Chapter 7 delves into the electronic transport properties of nitrogen-doped ultrananocrystalline diamond (N₂-doped UNCD) films grown on both quartz and silicon (Si) substrates. Various electronic transport fitting models, including 1D (ES) VRH, 2D VRH, 3D (Mott) VRH, activated conduction, and 3D weak localization,

were employed to study the conduction mechanism. It has been observed that 3D weak localization dominates in all the samples with N₂ doping concentrations greater than 10%. Furthermore, a conductivity crossover from the semiconducting to the metallic regime is observed when the N₂ doping concentration is increased to 20%.

1.2 Background: Molecular Magnetism

1.2.1 Magnetism

Magnetic materials are integral to our daily existence, their significance dating back to the early observations of magnetism by the ancient Greeks. Building upon this knowledge, the Chinese ingeniously employed magnetic forces to develop the "south pointing" compass. Subsequently, the integration of magnetic elements has witnessed a notable increase, with a plethora of gadgets utilizing these materials across diverse fields such as medical equipment, frictionless bearings, magnetic separators, microphones, speakers, sensors, data storage devices, and motors.

Conventional magnetic materials are usually composed of organized arrays of inorganic atoms forming structures in two or three dimensions, commonly incorporating transition metals or lanthanides. The production of these materials typically requires high-temperature procedures and metallurgical methods. Conversely, molecular magnets form a separate class, consisting of organic or hybrid materials derived from organic and inorganic sources. These molecular magnets are constructed from spin units containing metal components.

The distinctive attributes of molecular magnets offer several advantages over traditional magnetic materials. These potential benefits encompass the capability to produce magnetic materials at lower temperatures, improved optical properties, enhanced electro-optomechanical properties, greater control over the magnetic properties of a material, and simplified processing methods. This shift towards molecular magnets opens up new avenues for exploring diverse and customized properties in the development of magnetic materials.

To engineer materials with intriguing magnetic properties on a larger scale, it's imperative to grasp the origins of magnetism in bulk samples. Although a comprehensive understanding of magnetism remains elusive, numerous established principles govern magnetic behavior. These principles encompass the magnetic moments linked with individual atoms, the impact of exchange interactions between adjacent magnetic moments, the role of magnetic domains, the occurrence of magnetic hysteresis, the significance of the Curie temperature in phase transitions, and the influence of magnetic anisotropy on a material's characteristics. While providing a foundational comprehension, continuous research endeavors aim to deepen our understanding and refine our capacity to design materials with specific magnetic attributes.

1.2.2 Fundamentals of Magnetism

Magnetic Moment

The magnetic moment serves as the fundamental unit of magnetism. In classical electrodynamics, a basic magnetic moment is represented by a current loop. When a current (I) circulates around a small, oriented loop with an area $|dS|$, the resulting magnetic moment is expressed as: $|d\mu| = IdS$

Angular Momentum

Angular momentum is a defining attribute of an electron tied to its spin, which remains constant. The common analogy is that the electron rotates on its axis. The spin of an electron is quantized, leading to a spin angular momentum $S = 1/2$. In atoms, the magnetic moment μ associated with an orbiting electron aligns with the electron's angular momentum L and is directly proportional to it:

$$\mu_L = \gamma_L L \tag{1.1}$$

, Where γ_L denotes the gyromagnetic ratio, which is calculated as (e/m_e) , where e stands for the elementary charge and m_e represents the electron's mass. Additionally, the g-factor, a dimensionless quantity describing the magnetic moment relative to the angular momentum, is approximately 2 for electrons.

Spin degree of freedom

The magnetic characteristics observed in solid materials are attributed to electron behavior. A detailed comprehension of magnetism at the microscopic level is grounded in the principles of quantum mechanics governing the angular momentum of electrons. This momentum arises from two primary sources: the orbital motion and the intrinsic spin of electrons. The interaction between these two aspects is facilitated by the spin-orbit coupling. When exposed to a magnetic field, free electrons follow cyclotron orbits, whereas bound electrons undergo Larmor precession, resulting in orbital diamagnetism.

The magnetic moment can be expressed as

$$m = - \left(\frac{e}{m_e} \right) s \quad (1.2)$$

. Here e is the elementary charge, m_e is the mass of the electron, and s stands for the electron's spin. The spin magnetic quantum number, denoted as $m_s = \pm \frac{1}{2}$, permits just two potential angular momentum states. The spin's projection along any axis can be expressed:

$$m_z = - \left(\frac{e}{m_e} \right) m_s \hbar \quad (1.3)$$

, with $m_s = \pm \frac{1}{2}$.

Spin-Orbit Coupling

An electron possesses both spin and orbital angular momentum. When these two properties interact, it results in spin-orbit coupling. it is defined as: $m = \gamma j$ The angular momentum characteristics of a single electron are denoted by the quantum numbers (l, s, j) .

In an isolated many-electron ion, the combination of individual electrons' spin and orbital angular momenta gives rise to total spin (S) and orbital (L) quantum numbers. The subsequent interaction of spin-orbit coupling further impacts the energy levels, causing them to split into J - multiplets. Hund's rules specify the characteristics of the lowest J - multiplet.

For a general value of J the Curie-law susceptibility, represented as $\chi = \frac{C}{T}$ is computed. When incorporated into a solid, the ion experiences a crystal field due to its surrounding charge environment. This crystal field perturbs the spin-orbit coupling, resulting in either S or J as the appropriate quantum number. The crystal field modifies the configuration of the lowest M_S or M_J magnetic sublevels, which then undergo further splitting due to the Zeeman interaction. Additionally, the crystal field introduces single-ion anisotropy.

1.2.3 Types/Classes of Magnetic Materials

Diamagnetism and Paramagnetism

Diamagnetism and paramagnetism are the two primary forms of magnetism present at the atomic level. All other magnetic behaviors observed can be attributed to these fundamental magnetic phenomena.

Diamagnetic characteristics appear as the material's ability to repel an external magnetic field. This behavior results from the interaction between the applied magnetic field and molecular or atomic orbitals containing paired electrons. Temperature changes do not influence this type of magnetism, and the intensity of the interaction typically aligns with the material's molecular weight.

On the contrary, paramagnetism is defined by the inclination of a substance to be drawn toward an external magnetic field. This occurrence stems from the interplay between the applied magnetic field and unpaired electrons within atomic or molecular orbitals. Paramagnetic substances usually harbor one or more unpaired electrons, and the intensity of paramagnetic interactions fluctuates with temperature [13].

Cooperative Magnetism

The collective magnetic behavior arises from interactions among paramagnetic atoms or molecules. These interactions can result in materials exhibiting either magnetic or nonmagnetic properties, depending on the alignment of neighboring magnetic spins([14]).

While magnetic interactions take place in three dimensions, their characteristics and intensity may vary across each dimension. As a result, magnetic materials frequently demonstrate a predominant cooperative interaction type in one dimension and different cooperative interaction types in the other two dimensions. Usually, when different magnetic interactions emerge due to dimensional differences, the material is categorized based on the most dominant interaction.

Generally, the overall magnetic properties of a substance fall into one of four main categories: paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism ([13], [15]). These classifications pertain to the behavior of neighboring magnetic moments at extremely low temperatures. The specific interactions are delineated as follows:

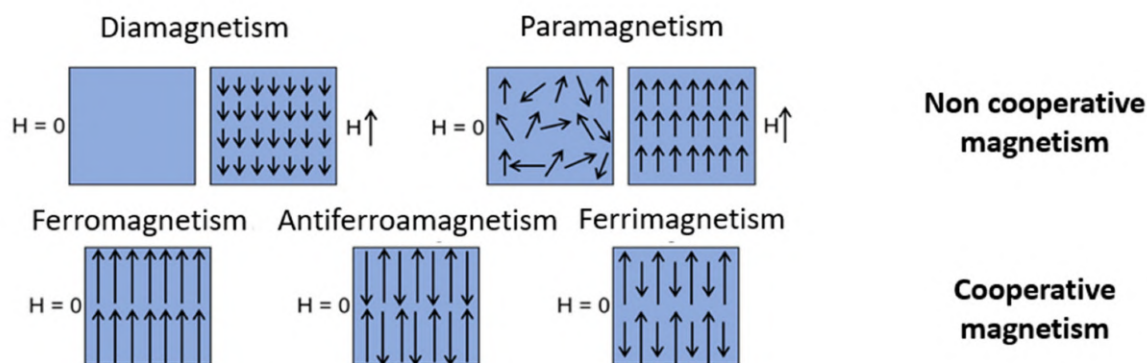


Figure 1.4 *various types of magnetism:* The depiction of the organization of magnetic moments in materials exhibiting various magnetic behaviors, with distinctions made regarding their response to the presence or absence of an external field H adopted from [16]

Paramagnetism: In paramagnetic materials, each electron spin operates independently of its neighbors. When subjected to an external magnetic field, these spins can easily align (refer to Figure 1.4). However, once the field is removed, the

system reverts to a random distribution of magnetic moments.

Ferromagnetism: Ferromagnetism is distinguished by the parallel orientation of neighboring magnetic spins (see Figure 1.4), leading to a significant overall magnetic moment. This alignment is uncommon and happens only in the absence of quantum mechanical overlap between the orbitals containing spins. Ferromagnetic materials retain a net magnetic moment even without an external magnetic field.

Antiferromagnetism: In antiferromagnets, magnetic spins align in an antiparallel manner, resulting in a material with a zero net magnetic moment (see Figure 1.4). At absolute zero temperature, antiferromagnets display a diamagnetic reaction to an external magnetic field. Antiferromagnetism is frequently observed in the overall magnetic behavior of materials, even in substances that may locally exhibit ferromagnetism.

Ferrimagnetism: Ferrimagnetism represents a distinct variant of antiferromagnetism, characterized by a lattice comprising spins of alternating magnitudes (see Figure 1.4). While adjacent spins align antiparallel, the material retains a net magnetic moment even without an external magnetic field, owing to the differing magnitudes of neighboring spins. Ferrimagnetism plays a crucial role in conferring magnetism to substances such as magnetite.

Paramagnets

The thermal and field-dependent traits of an ideal paramagnet are precisely defined and offer significant utility in magnetic characterization. Temperature changes in paramagnetic materials adhere to the Curie law, while the influence of magnetic fields is expounded by the Brillouin function.

Curie Law: The way a material reacts to a magnetic field is determined by its magnetic susceptibility, which is defined as $\chi = M/H$, where M represents magnetization and H is the applied magnetic field. The thermal dependence of magnetic susceptibility in an ideal paramagnet is described by the Curie law.

$$\chi_m = Ng^2\mu_B^2 \frac{S(S+1)}{3kT} \quad (1.4)$$

This equation is typically simplified to the form:

$$\chi_m = \frac{C}{T} \quad (1.5)$$

It's essential to emphasize that the Curie law holds true only under the condition where the ratio of the applied magnetic field to temperature ($\frac{H}{kT}$) is small

Brillouin Function: The Brillouin function describes the magnetization of an ideal paramagnet as a function of applied field and temperature. The function is expressed as:

$$M = Ng\mu_B S \cdot B_s(y) \quad (1.6)$$

$$B_s(y) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}y\right) - \frac{1}{2S} \coth\left(\frac{1}{2S}y\right) \quad (1.7)$$

$$y = g\mu_B SH/kT \quad (1.8)$$

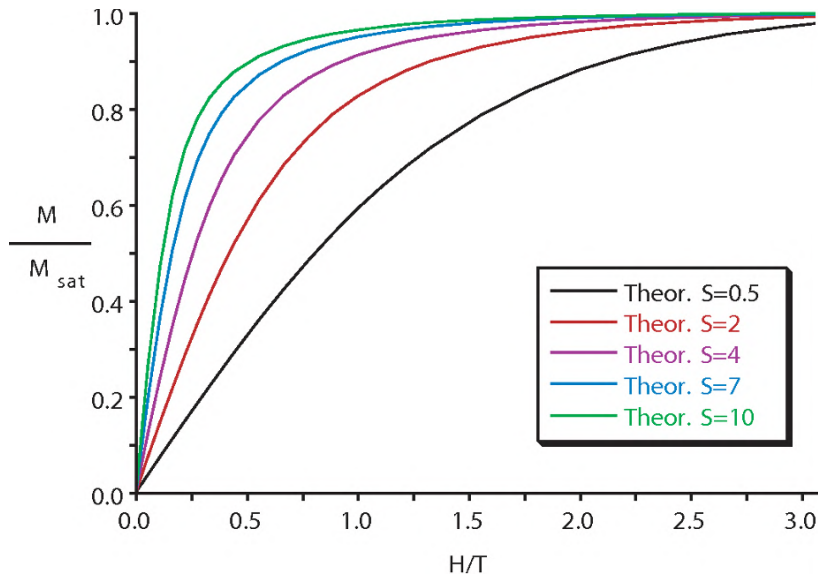


Figure 1.5 Brillouin function curves illustrate the magnetization behavior of an ideal paramagnet with different spin (S) values. adapted from [16]

Figure 1.5 presents a graph illustrating the Brillouin function across various magnetic spin states. Brillouin analysis allows for the determination of a material's spin state without requiring precise knowledge of its chemical composition. This determination is based on observing the magnetization concerning the applied field and the saturation magnetization of the sample.

1.2.4 Temperature dependance of Magnetic Materials

At elevated temperatures, all magnetic materials behave as paramagnets due to thermal energy disrupting alignment and causing spins to move randomly. The critical temperature (T_c) signifies the onset of magnetic order in a material. Bulk magnetism becomes apparent only considerably below the critical temperature.

To explore temperature-dependent magnetism, researchers commonly investigate a material's susceptibility concerning temperature. Analyzing a material's properties involves examining temperature-dependent susceptibility (χ vs T), the susceptibility-temperature product (χT vs T), and the inverse susceptibility (χ^{-1} vs T). These different approaches provide unique perspectives on the bulk magnetism of the material.

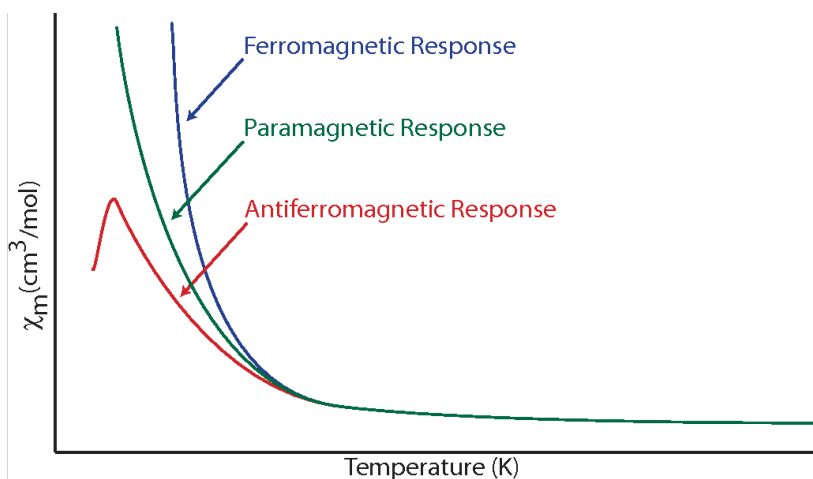


Figure 1.6 A plot illustrating the magnetic susceptibility versus temperature (χ vs T) for paramagnetic, ferromagnetic, and antiferromagnetic materials. adopted from [16]

Figure 1.6 shows the typical trends of magnetic susceptibility as a function of temperature for ferromagnetic, paramagnetic, and antiferromagnetic materials. For

a antiferromagnetic material, that exhibit a maximum at low temperatures, we can obtain information about the strength of magnetic interactions. Additionally, the form of this peak offers insights into the dimensionality of these interactions; rounded peaks suggest one or two-dimensional antiferromagnetic properties, while sharp peaks indicate three-dimensional antiferromagnetic behavior.

Examining the susceptibility-temperature product relative to temperature offers valuable insights into the fundamental interactions within magnetic materials. Figure 1.7 presents a standard representation of the susceptibility-temperature product plotted against temperature, showcasing various magnetic materials, including paramagnets, ferromagnets, antiferromagnets, and ferrimagnets.

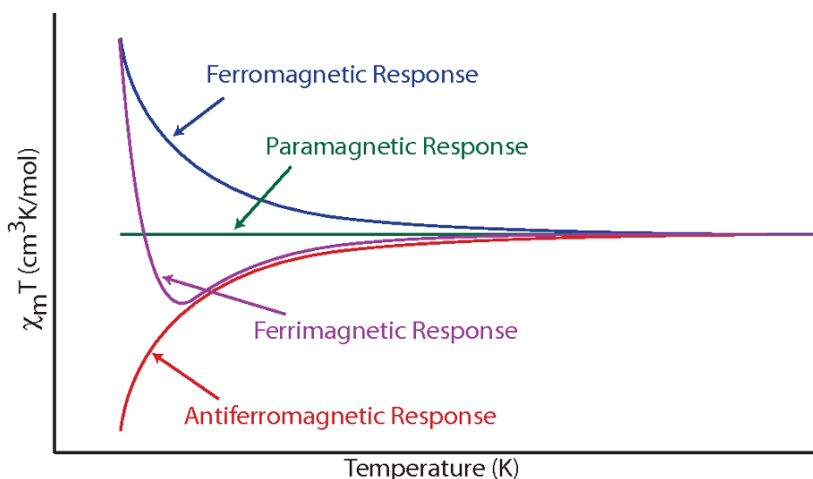


Figure 1.7 A typical plot depicting the χT vs T is presented for various magnetic materials, encompassing paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic substances. Adopted from [16]

The χT product of an ideal paramagnetic substance remains constant and is independent of temperature, unlike other forms of magnetism where variations occur. The magnetic materials exhibit a consistent segment of the χT product at higher temperatures due to their effective paramagnetic behavior above their T_c . In ferromagnetic materials, there's an upward deviation from the ideal paramagnetic curve, signifying that the energy from ferromagnetic interactions dominates over thermal energy. Conversely, antiferromagnetic interactions exhibit a decreasing trend as temperature drops, leading the magnetic moment towards zero. Ferrimagnetic materials initially show a slight downward trend owing to interactions among adjacent magnetic moments, followed by an upward trend due to the increasing correlation

length within the system (see Figure.1.7).

Curie law states that an ideal paramagnet's show a linear trend crossing at zero in its inverse susceptibility as a function of temperature. Deviation from this linear pattern and the Curie law become apparent in materials exhibiting cooperative magnetic phenomena. Figure 1.8 demonstrates that ferromagnetic substances exhibit downward deviations, whereas antiferromagnetic ones display upward deviations towards higher temperatures. In each case, data points at elevated temperatures adhere to a linear trajectory, indicating the prevalence of thermal energy over magnetic forces.

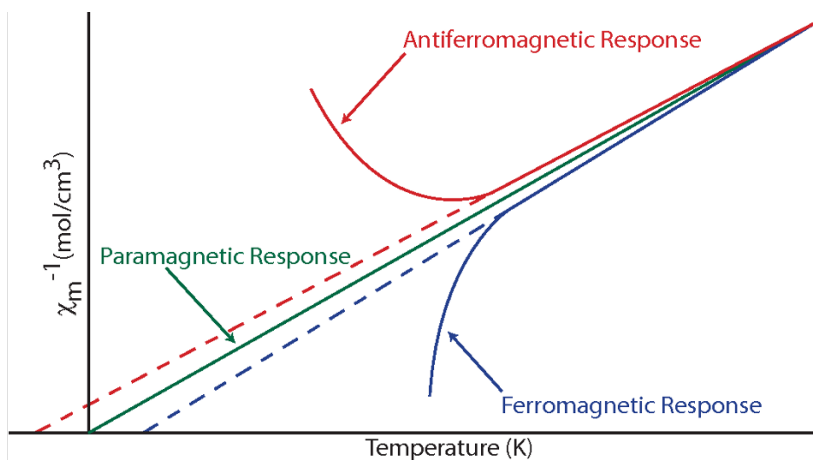


Figure 1.8 *Schematic plot demonstrating the inverse susceptibility as a function of temperature for a paramagnet, a ferromagnet, and an antiferromagnet. The dotted lines highlight deviations of the high-temperature data from the paramagnetic scenario [16].*

These deviations in their respective inverse susceptibility can be traced by Curie-Weiss law (1.9), which is an adaptation of the Curie law (1.5). The Weiss constant (Θ) is correlated to the intensity of observed magnetic interactions. A positive Weiss constant signifies ferromagnetic interactions, while a negative one suggests antiferromagnetic interactions. Curie-Weiss law is expressed as:

$$\chi_m = C/(T - \Theta). \quad (1.9)$$

Hysteresis, a distinctive feature found in materials exhibiting bulk magnetism, and this feature is seen both in the ferromagnetic and ferrimagnetic materials below their respective T_c . The hysteresis of a sample is evaluated by studying its magnetization in relation to an applied magnetic field. Figure 1.9 illustrates a typical hysteresis

curve for a bulk magnetic material. Further hysteresis loop can be characterised by two significant points which are remnant magnetization (M_r) and coercive field (H_c). Remnant magnetization indicates the level of inherent magnetism in a bulk magnetic substance, achieved by subjecting it to and then removing an external magnetic field. The coercive field represents the magnetic field required to nullify the magnetization of a sample.

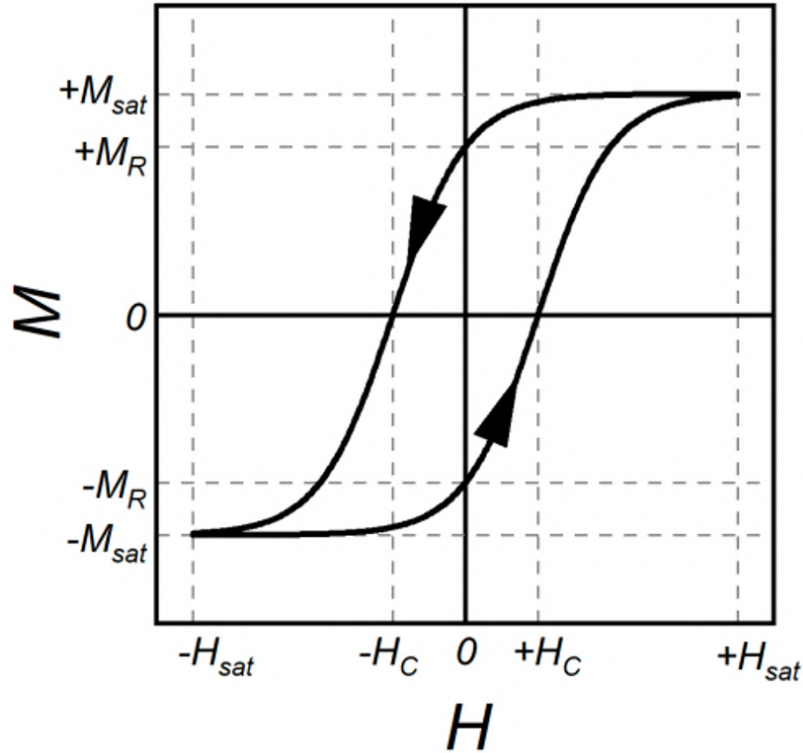


Figure 1.9 *A hysteresis curve illustrating the behavior of a material with a bulk magnetic moment is shown. M_R and M_{sat} represent remanent magnetization and saturated magnetization respectively. adapted from [17]*

There exist another group of magnetic materials known as high-spin materials, which contribute to the complexity of bulk magnetism by demonstrating diverse magnetic interactions. Within systems containing paramagnetic elements, there is a spectrum of responses to both temperature changes and applied magnetic fields. Investigating these responses will yield insights into the interactions between adjacent magnetic spins.

1.2.5 Theory of single molecular magnets

Molecular magnetism primarily focuses on investigating substances based on paramagnetic molecules. These materials are highly attractive because their magnetism can be tuned through chemical methods, allowing for a vast range of structural and physical property modifications. Moreover, the localized nature of molecular magnetic moments allows for the replication of magnetic states using finite-dimensional Hamiltonians, enabling precise control of quantum magnetic characteristics [18]. This combination of features facilitates the precise design of magnetic configurations, making it ideal for exploring fundamental physics.

Single Molecule Magnets - (SMM)

The discovery of significant magnetic anisotropy in $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO}_{16})(\text{H}_2\text{O})_4]$ [19], that in turn showed molecular magnetic hysteresis at low temperatures paved the way for the introduction of Single Molecule Magnets (SMMs) [20], [21]. SMMs are molecules displaying memory effects solely due to intra-molecular interactions, unlike bulk magnetic materials characterized by long-range order. Consequently, these zero-dimensional magnetic materials lack phase transitions and are referred as superparamagnets. This breakthrough ignited extensive research over the following three decades to explore SMMs that offer slower magnetic dynamics, aiming to achieve high-density magnetic memory based on molecules [22].

The essential prerequisites for SMMs are:

1. Large magnetic moment,
2. a bistable ground state
3. easy-axis magnetic anisotropy

The presence of a large magnetic moment and a bistable ground state is crucial for a molecule to exhibit strong magnetism, allowing it to function as a molecular magnet. This requires the molecule to possess two degenerate states, enabling the transition

between them akin to conventional binary memory. Another essential condition is magnetic anisotropy, which establishes a relationship between the physical structure of the molecule and its magnetic properties. Specifically, uniaxial easy-axis anisotropy dictates that a particular spatial orientation should exhibit the highest magnetic susceptibility [23]. These characteristics give rise to a distinct array of magnetic states with unique features.

Within this array, there exists an inherent energy barrier known as the anisotropy energy barrier, which separates the doubly degenerate ground state. Each molecule must overcome this barrier to reverse its magnetization. This barrier is fundamental to the slow magnetic dynamics observed in Single-Molecule Magnets (SMMs), ultimately leading to memory effects. The energy barrier for magnetic reversal, denoted as U_{eff} , induces an exponential temperature dependency in the magnetic relaxation rate, also known as the spin-lattice relaxation rate (τ_1), as illustrated in Equation 1.10.[24].

$$\tau^{-1} = \tau_0^{-1} e^{-U_{eff}/k_B T} \quad (1.10)$$

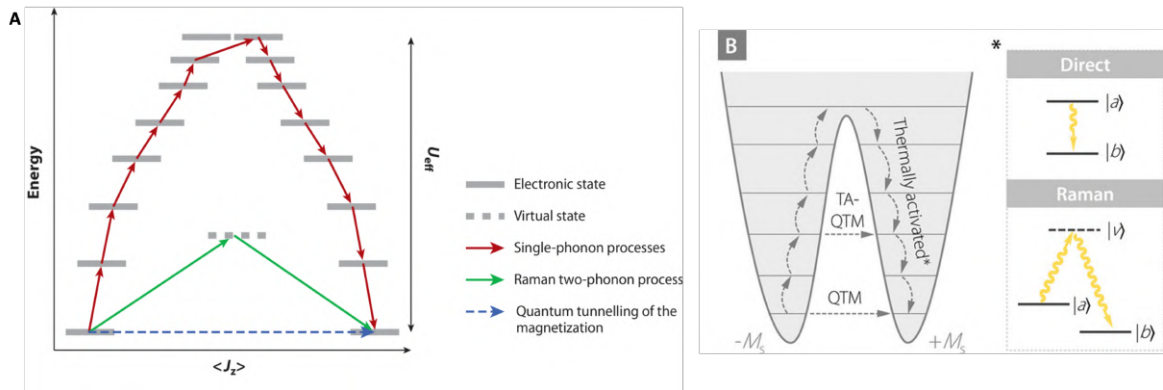


Figure 1.10 The diagram portrays the magnetic relaxation (U_{eff}) energy barrier observed in single-molecule magnets (adapted from [18]). B) The double-well energy potential illustrates the most efficient pathway for magnetization reversal, involving multistep magnetic relaxation. This process occurs alongside various other temperature-dependent spin-lattice relaxation mechanisms.[25]

1.2.6 SMM Relaxation Mechanisms

Studying magnetic relaxation in relation to temperature and field can offer valuable insights into the dynamics of relaxation mechanisms experienced by a superparamagnetic material (SMM). Figure 1.11 illustrates the typical relaxation rates of an ideal SMM, which can be classified into two distinct formats: one depicting the natural logarithm of relaxation time plotted against inverse temperature, and the other presenting a $\log 10 - \log 10$ plot of relaxation rate versus temperature. An ideal Lanthanide (Ln) - based SMMs has the capacity to experience various relaxation mechanisms, yet the total relaxation rates will be the accumulation of each individual mechanism. Depending on specific temperature ranges, one particular relaxation mechanism may prevail over others..

Orbach relaxation

Orbach relaxation exhibits an exponential dependence in its relaxation rate concerning temperature. For example, materials such as Mn12 and $[N(nBu)_4][Tb(Pc)_2]$ SMMs typically demonstrate relaxation rates that adhere to the Arrhenius law. The effective energy barrier (U_{eff}) can be accurately determined from the slope and τ_0 of the y-intercept when a linear correlation between the exponential temperature dependency of relaxation and U_{eff} is presented in natural logarithm form. In the Orbach mechanism framework, the quantized lattice transitions or vibrations (phonons) between electron microstates induce distortions in molecular geometry, consequently altering the wavefunction of electronic states. The magnetic relaxation process across the U_{eff} barrier involves multiple excitations and de-excitations through emissions (refer to Figure 1.10).

Quantum Tunneling of Magnetisation

Quantum Tunneling of Magnetization (QTM) is a relaxation phenomenon observed at extremely low temperatures between degenerate ground states. Typically, this phenomenon is independent of temperature but exhibits a strong dependency on

magnetic field strength. The rate of QTM is described by the equation $\tau_{QTM}^{-1} = \frac{B_1}{1+B_2H^2}$. However, in certain scenarios, Thermally Assisted-Quantum Tunneling of Magnetization (TA-QTM) can occur between degenerate states following spin-phonon excitations. QTM processes are exceptionally rapid and can be suppressed by a static magnetic field, allowing the observation of any slow relaxation processes that may be present in the material (refer to Figure 1.10 B).

Raman relaxation

Raman relaxation is a two-phonon process often observed in the intermediate temperature ranges between Orbach and QTM regimes. This mechanism entails the simultaneous absorption and emission of a pair of phonons while crossing the U_{eff} barrier (see Figure 1.10). It exhibits a power-law temperature dependence, typically appearing linear when plotted on a log 10 – log 10 scale (see Figure 1.11).

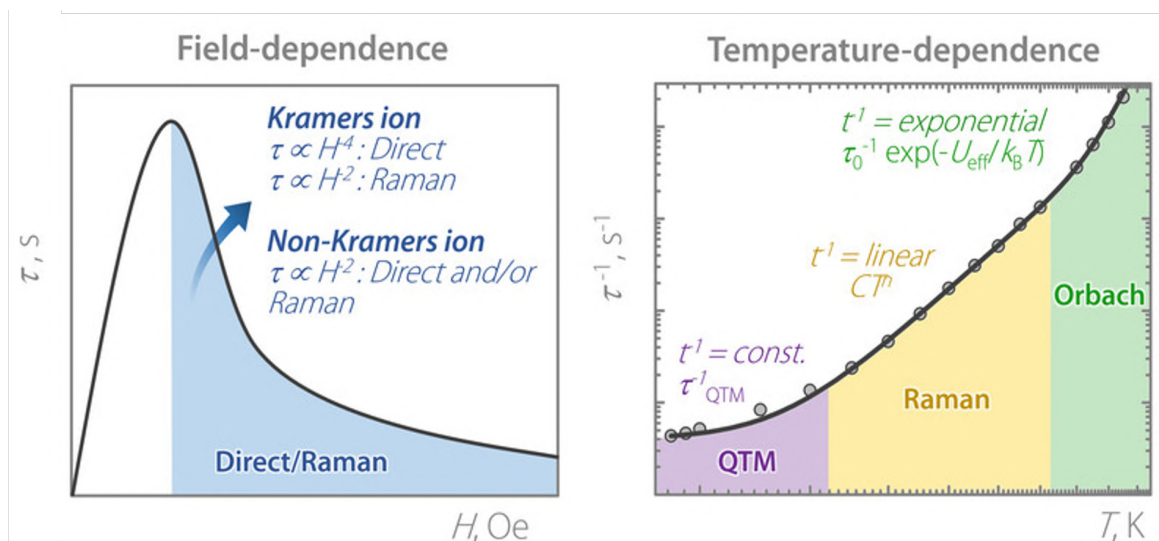


Figure 1.11 A diagrammatic depiction of the primary magnetic relaxation mechanisms commonly observed in lanthanide single-molecule magnets (SMMs), emphasizing their corresponding field and temperature dependencies. Adapted from [25]

Other relaxation mechanisms

An external magnetic field induces the superparamagnetic molecule (SMM) to undergo relaxation through additional pathways, such as direct relaxation. The magnetic field

their incomplete 4f shells, resulting in high intrinsic anisotropy. Furthermore, Rinehart et al. ([26]) suggested that by carefully selecting the coordination environment of the magnetic ions, the anisotropy barrier can be further enhanced.

1.3 Background: CVD diamond deposition

1.3.1 Synthetic diamond

Diamond exhibits exceptional electro-mechanical properties attributed to its unique packing arrangement, where each carbon atom forms covalent bonds with four neighboring carbon atoms. This tetrahedral sp^3 hybridized structure is responsible for diamond's exceptional tribological properties. With a bandgap of 5.47 eV, diamond is an insulator in its pure form. However, doping it with either *p*-type or *n*-type dopants transforms it into an excellent semiconductor, making it suitable for wide-band gap semiconductor electronics.

Graphite is the typical crystalline form of carbon observed under standard temperature and pressure (STP) conditions. It consists of interconnected hexagonal rings, where each carbon atom bonds with three others in a two-dimensional (2D) plane. However, under extreme pressure, carbon adopts a distinct allotrope known as diamond. These extreme conditions facilitate the formation of diamond as the thermodynamically favored form of carbon (see Figure 1.13).

Before the carbon phase diagram was fully understood, laboratory diamond deposition achieved success by replicating the natural process. This involved subjecting carbon to high pressure and high temperature. Bridgeman laid the foundation for understanding high-pressure high-temperature (HPHT) conditions. Subsequent efforts by H. Liander at Alleman Svenska Elektriska A.B. in Sweden, and F.P. Bundy and colleagues at GE, led to the successful synthesis of diamond in the 1950s [27].

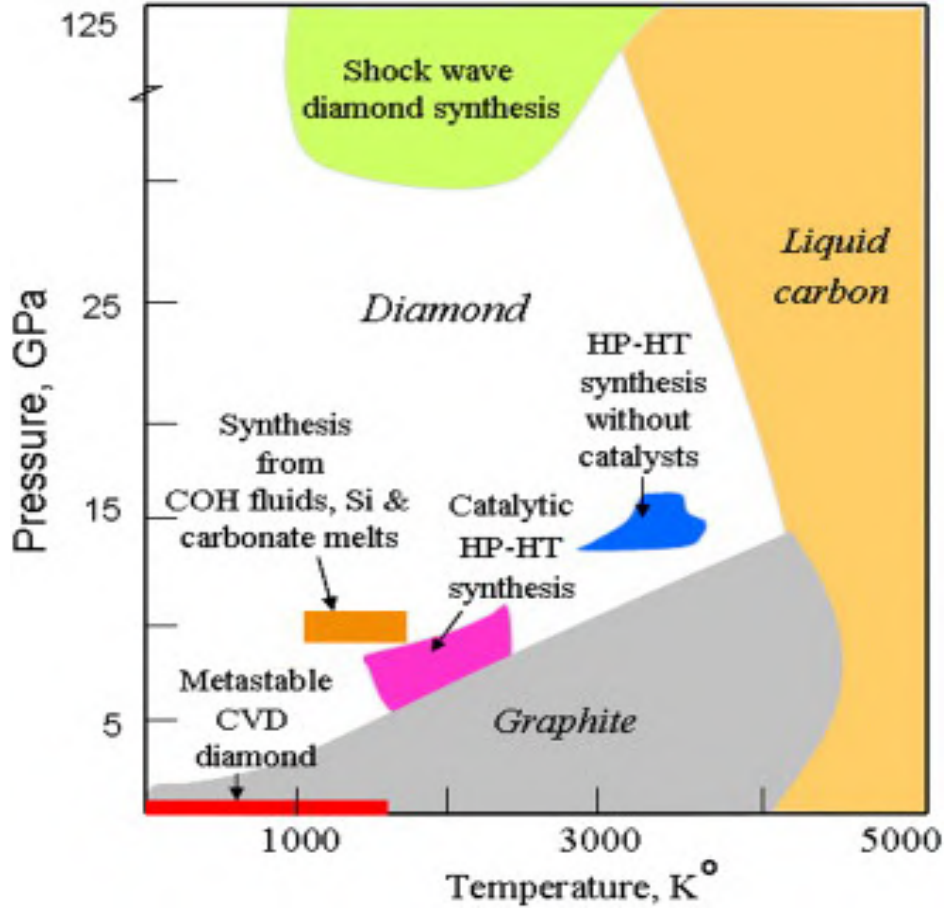


Figure 1.13 A phase diagram depicting pressure (p) and temperature (T) ranges where both high-pressure high-temperature (HPHT) and chemical vapor deposition (CVD) synthesis of carbon can occur. It should be noted that CVD is a non-equilibrium process. adapted from [28]

Diamond deposition using CVD at low pressures underwent nearly five decades of advancement following the understanding of the carbon phase diagram [29]–[34]. The CVD technique gained momentum in synthesizing diamond under laboratory conditions. Among various CVD techniques such as HFCVD, pulse DC CVD, Laser-induced plasma, Microwave (MW) CVD stands out as the most preferred method for synthesizing diamonds due to its capability to produce transparent single crystal diamonds. Additionally, MW-CVD has the potential to synthesize a wide range of polymorphs by adjusting the growth parameters. Presently, synthetic diamonds are produced in various morphologies and sizes, resulting in significant variations in their opto-electronic and mechanical properties. Consequently, synthetic diamonds find a wide range of applications including jewelry, semiconductor manufacturing, and the production of wear-resistant cutting tools.

Single Crystal Diamond

Single crystalline diamond (SCD) is grown homoepitaxially from small seed crystals, with one crystal size and ordering being characteristic features of SCD (see Figure 1.14a). SCD is primarily associated with the jewelry sector due to its higher production costs. The seeds used in SCD production are usually carefully selected, either with a (100) orientation using High-Pressure High-Temperature (HPHT) methods or sourced from natural diamonds. Employing homoepitaxial growth with such seeds results in fewer surface imperfections, provided that growth parameters are meticulously controlled throughout the growth period, which can extend over several days or even weeks. This method has successfully yielded gemstones measuring several millimeters, now commercially available through companies such as SCIO Diamond and Gemesis.

Microcrystalline diamond

Other variations of diamond, such as microcrystalline diamond (MCD), nanocrystalline diamond (NCD), and ultrananocrystalline diamond (UNCD), are grown through heteroepitaxy process, where a non-diamond substrate is utilized. This substrate requires either seeding or mechanical abrasion to initiate diamond growth. It must withstand the harsh conditions of chemical vapor deposition (CVD), including high temperatures around 800°C and exposure to a hydrogen atmosphere, while forming a thin carbide layer. If the substrate fails to develop this carbide layer (for instance, with materials like Germanium or Copper), the diamond film won't adhere and will simply detach when cooled. Conversely, substrates with a strong affinity towards carbon (like Nickel, Iron, or Cobalt) cause the growing diamond film to dissolve into the substrate, forming a thick carbide layer.

MCD also known as polycrystalline diamond (PCD) consists of small diamond crystallites surrounded by non- sp^3 carbon at the grain boundaries. MCD have grain sizes in the range of 100-10000 nm and shows a columnar structure due to packed continuum of different crystal sizes, when viewed through cross sectional SEM imaging.

Like most crystalline solids, diamond also has its crystals arranged in different planes

that exist periodically throughout the lattice. As the diamond crystal grows, the energetically favored plane propagates through the structure, leaving its surface exposed at the end of the deposition. Similar to most crystalline solids, diamond also have its crystals arranged in different planes that exist periodically throughout the lattice. As the diamond crystal grows, depending on the energetically favoured one of these planes propagates through the structure, leaving its surface exposed at the end of the deposition. $\langle 111 \rangle$ – diamond grains with pyramidal facets, $\langle 110 \rangle$ – diamond grains with triangular facets, and $\langle 100 \rangle$ – diamond grains with square facets are three dominant crystal planes commonly seen in a MCD material (see Figure 1.14b).

Nanocrystalline diamond

During the early 21st century, nanocrystalline diamond (NCD) films gained traction due to their smoother surfaces compared to microcrystalline diamond (MCD) films. This smoothness is attributed to the small size of the crystallites, typically ranging from 10 to 500 nanometers. This smoother surface enabled the production of transparent, freestanding polycrystalline diamond films through various polishing methods. There are two main methods for producing NCD films, each resulting in different properties.

In the first method, a high nucleation density is achieved by seeding with densely packed monolayers of detonation nanodiamonds (DND). Subsequent diamond growth using a mixture of 1% methane (CH_4) in hydrogen (H_2) yields a thin, continuous NCD film. If growth continues, the film thickens and transitions into an MCD film. However, stopping the growth when the film is less than 1 micrometer thick results in an NCD film composed of faceted nanocrystallites.

The second method involves depositing NCD films by increasing the methane content in the standard CVD gas mixture, typically ranging from 1% to 5%. Higher methane concentrations lead to a greater rate of renucleation. NCD films produced using this method often exhibit rounded grains with sizes around 100 nanometers, which tend to aggregate into ball-like or cauliflower structures.

Nanocrystalline diamond (NCD) have smoother surfaces with crystal sizes of few nm connected by non- sp^3 carbon network (see Fig 1.14c). It is obvious that NCD films

consists of greater proportion of sp^2 carbon when compared with MCD since the reduced grain size with increased surface area allows increased portion of non sp^3 content to grow during the deposition. Hence this material is often referred as poor quality diamond, although sometimes display a similar or better physical properties that of a MCD. Ultra-nanocrystalline diamond (UNCD) have grain sizes in the range of 3 – 10 nm and exhibits surface smoothness that are comparable with SCD films and most desirable for biological applications.

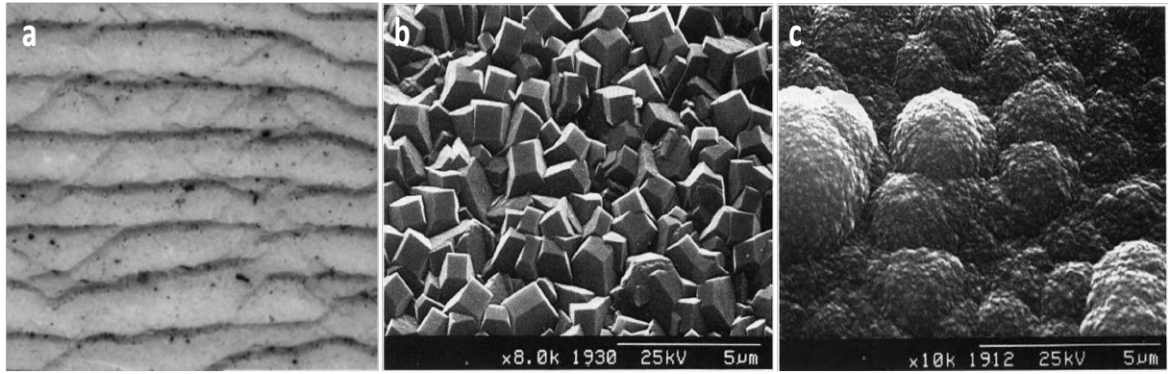


Figure 1.14 *Crystalline nature of diamond: a) Single crystal diamond. b) Microcrystalline diamond. c) Nanocrystalline diamond. Adapted from [35]*

1.3.2 Laboratory Based Synthesis of Diamond

High Pressure High Temperature (HPHT) Method

As the name suggests, synthetic diamonds are produced by subjecting graphite to high pressure and high temperature. By applying high pressure, graphite, an allotrope of carbon, can overcome an activation barrier to change its phase to a more thermodynamically stable carbon allotrope, namely diamond. The synthesis of diamond using the HPHT technique was initially demonstrated by a Swedish company ASEA in 1953 and later pioneered by General Electric in 1955 [27]. The HPHT method replicates growth conditions similar to those of naturally forming diamonds in the Earth's crust, at pressures around ~ 150 kbar and temperatures around $\sim 2000^\circ$ C. Utilising metal catalysts (Fe-Ni or Fe-Ni-Co alloy), which dissolve carbon and

facilitate the formation of diamond crystals, these growth parameter values can be slightly reduced, provided that the pressure and temperature satisfy the Berman-Simon boundary line on the carbon phase diagram (see Figure 1.13). In this method, both the metal catalyst/diamond seed and the carbon source are placed in large anvils within a carefully designed reaction chamber, and a temperature gradient is applied by slightly heating the carbon source at a higher temperature than that of the seed. This ensures the diffusion of carbon atoms through the catalyst and their deposition as diamond crystals on the seed.

Early HPHT produced diamonds were coloured due to the presence of impurities in the growth process, however with the advancements in the growth technique, nowadays, colourless jewellery quality are grown by greater control over the contamination levels in the HPHT process. At present vast number of HPHT diamond applications have spanned out due to commercialisation of these products by companies such as Element Six, DuPont, and Diamond Foundry. Furthermore, HPHT is also used for color enhancement of pre-grown diamonds through appropriate annealing. Although the commercial success of this method it is limited by the maximum size of the SCD can be grown which is off ~ 2 mm.

Diamond Growth: Chemical Vapor Deposition (CVD)

Despite the widespread applications of HPHT diamonds, chemical vapor deposition (CVD) is often preferred in various scenarios due to its versatility in producing diamond thin films over large areas and on different types of substrates. In the diamond CVD process, atomic hydrogen plays a pivotal role as the driving force behind all chemical reactions [30]. Hot filament or a microwave plasma can be employed to generate sufficient heat to dissociate hydrogen molecules into individual hydrogen radicals. These radicals then react with other hydrocarbon components in the gas mixture, leading to a complex mixture of atoms, radicals, ions, and clusters above the growing diamond surface. In an environment rich in atomic hydrogen, the etching rate for sp^2 carbon is considerably faster—ranging from 10 to 100 times faster—compared to sp^3 carbon [37]. Consequently, any graphitic carbon is etched away into the gas phase, while diamond-like sp^3 carbon remains bonded to the substrate, ensuring the kinetic

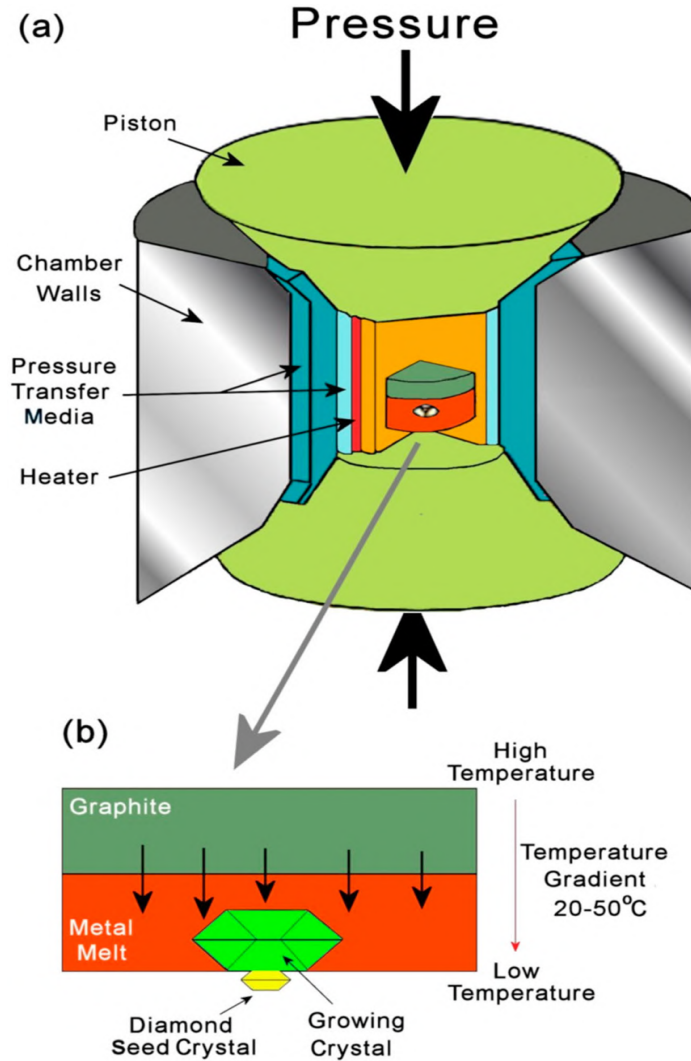


Figure 1.15 *A schematic illustration of an HPHT reactor is provided in (a), where a chamber holding graphite, a molten metal, and a diamond seed crystal is exposed to elevated pressures and temperatures. In such an environment, as depicted in (b), the graphite undergoes dissolution within the molten metal and subsequently precipitates onto the seed crystal, facilitating the growth of the diamond lattice.. adapted from [36]*

stability of the diamond structure [38].

Hot Filament CVD

In HFCVD reactors, a metallic filament, usually composed of Tantalum (Ta), Tungsten (W), or Rhenium (Re), undergoes resistive heating to reach temperatures ranging from 2300 to 2700 K. This process facilitates the activation of the hydrocarbon gas mixture through thermal means [39]. The diamond deposition process begins at elevated temperatures ranging from 2300 to 2700 K and low pressures of 20 Torr. This is

accomplished by placing the substrate relatively close to the filament, typically around 4 mm apart (refer to Figure 1.16), thereby exposing the substrate surface to a high flux of hydrogen and hydrocarbons.

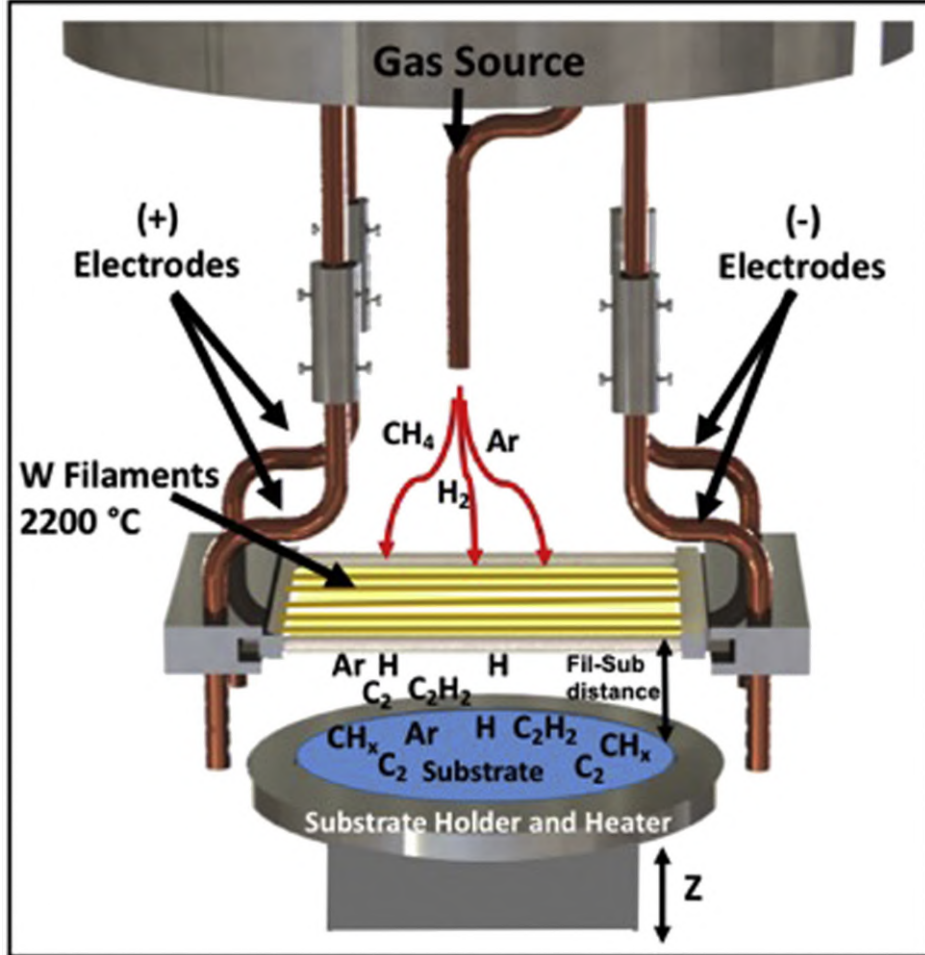


Figure 1.16 *Schematic illustration depicting the arrangement of the HFCVD-substrate setup, along with the flow of gases and the types of species involved in the growth process of UNCD films using the HFCVD system. adapted from [40]*

Although HFCVD systems offer the capability to deposit diamond over relatively large areas using arrays of filaments, they are slightly constrained by the susceptibility of certain reactant species to oxidize or corrode the filaments. Additionally, the filaments themselves can introduce contamination to the diamond films. As a result, HFCVD gas mixtures are restricted to those that do not contain oxygen.

Plasma assisted CVD diamond growth

At pressures ~ 20 Torr, gas molecules can undergo ionization when exposed to electromagnetic radiation. This process leads to the formation of a state called plasma, which contains charged species including electrons and ions, thereby creating a reactive medium. Hydrocarbon molecules become excited through collisions with free electrons, transforming into reactive species that move towards the substrate. Subsequently, these reactive species diffuse onto the substrate surface, forming a thin carbide layer (see Figure 1.17) [41]. The CVD plasma has two distinct attributes:

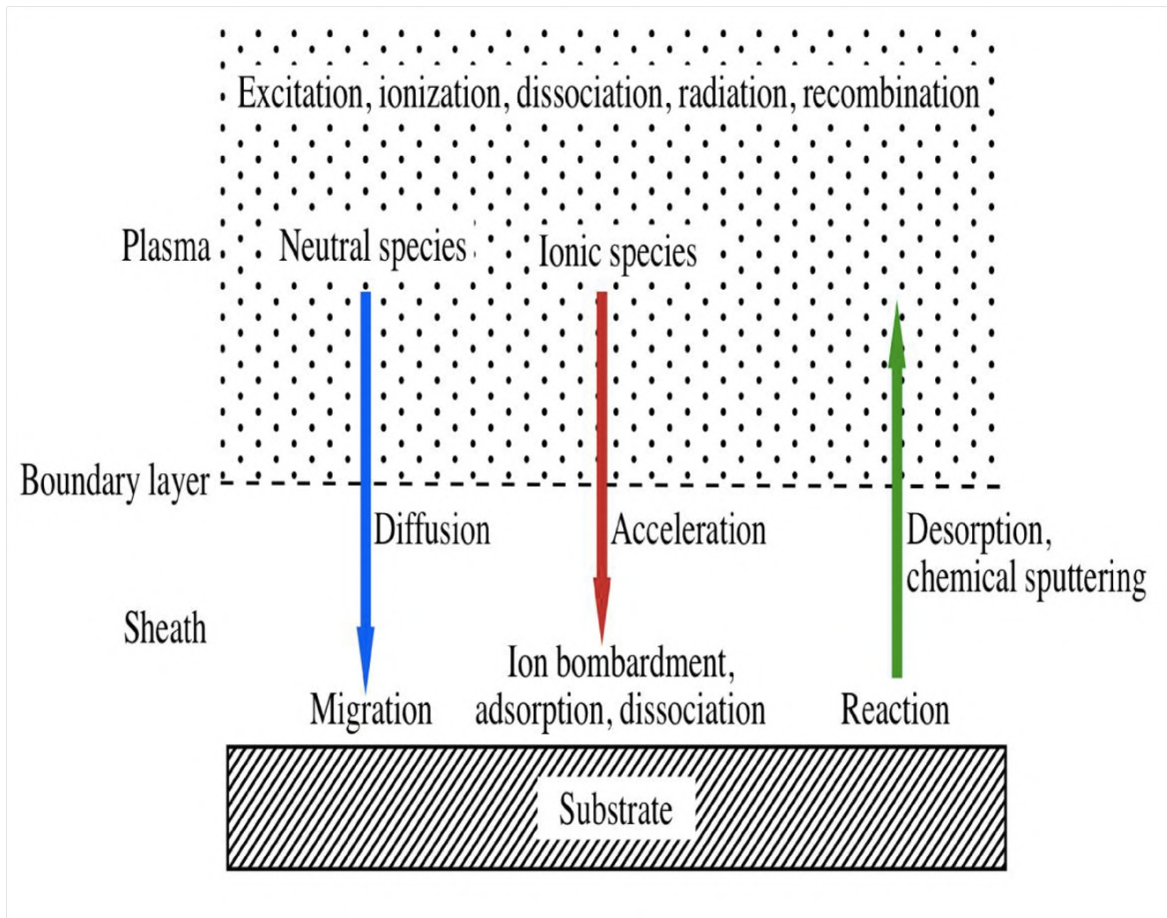


Figure 1.17 Occurrence of various events during the ionisation of gas molecules in the CVD diamond growth process. adapted from [41]

gas temperature (T_{gas}) and electron temperature (T_e). In PA CVD, plasma exhibits two distinct attributes: electron temperature (T_e) and gas temperature (T_{gas}). This differentiates the energy levels between free moving electrons and heavy charged ions.

Microwave Plasma Enhanced CVD diamond Growth

The MWCVD procedure involves depositing activated gas-phase carbon precursors containing methyl radicals onto a substrate gradually through either adsorption or surface diffusion (see Figure 1.17). Diamond synthesis via MWCVD involves

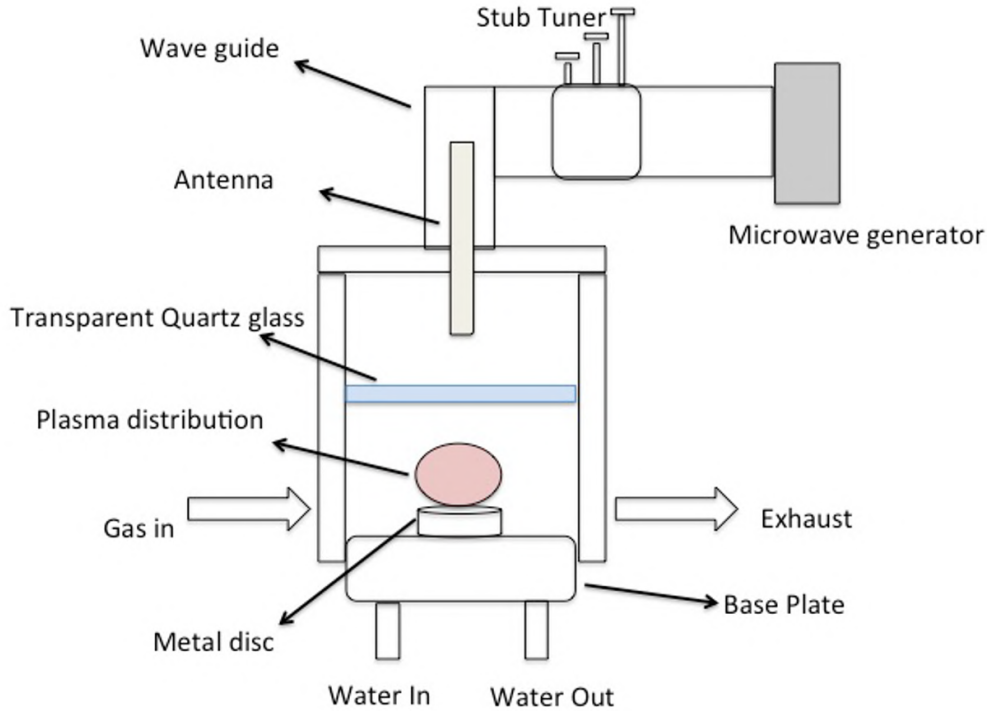


Figure 1.18 *A typical SEKI type MWCVD assembly model detailing variety of the instrumentation involved in the overall assembly.*

generating a plasma ball using microwaves with a frequency of approximately 2.4 GHz. The typical setup of an MWCVD reactor in this process is depicted in Figure 1.18. Microwaves enter the chamber through an applicator via a dielectric quartz window, allowing the creation of a plasma directly above the substrate. Temperatures within the plasma typically range from around 2000°C to 2500°C, resulting from collisions among electrons, molecules, atoms, and ions. Diamond growth rates achieved through MWCVD can vary from 0 to 100 $\mu\text{m/h}$, depending on the specific growth conditions.[31], [42]–[44].

CVD chemistry environment for diamond growth

Figure 1.19 presents the Bachmann diagram, which outlines the distribution of C/H/O species for both diamond and non-diamond growth. This diagram aids in understanding the necessary growth conditions for CVD diamond films [45]. It was formulated by analyzing the quality of diamond produced from over 70 different CVD processes and gas mixtures. The diagram underscores that whether diamond films are produced using C/H mixtures or C/H/O mixtures is not dictated by the original precursor gases employed. This implies that the combination of reactants above the growing diamond surface is uniformly mixed, with only the C:H:O ratio influencing growth. It also emphasizes the crucial role of hydrogen species in the diamond growth process, as higher concentrations of hydrogen assist in the transition from non-diamond to diamond growth. In HFCVD reactors, the presence of oxygen can rapidly degrade the metal filaments. As a result, much of the Bachmann diagram is not applicable to HFCVD. Consequently, there is a small region in the lower left side of the diagram (1-3% CH₄/H₂) that serves as the preferred CVD conditions in HFCVD.

CVD diamond growth model

Figure 1.20 illustrates a simplified diagram presenting the standard model for diamond growth on a diamond surface. Theoretical analysis indicates that the primary bottleneck in this growth process is the formation of a new layer of carbon atoms on the diamond surface. This crucial step involves the creation of a nucleus consisting of four carbon atoms on the 111 surface. This nucleus not only facilitates the growth of the subsequent diamond layer by adding another CH₃ group but also acts as a site for introducing impurities, thereby altering the properties of the diamond. For example, CN and NH₂ species can possibly be introduced during this phase to grow diamond films doped with nitrogen.

Diamond growth begins with the removal of a hydrogen atom from the diamond surface (abstraction), leading to the creation of a dangling bond or surface radical site. Subsequently, CH₃ molecules attach to these dangling bonds, forming new C-C bonds. This process continues until all available C-H bonds are utilized, resulting

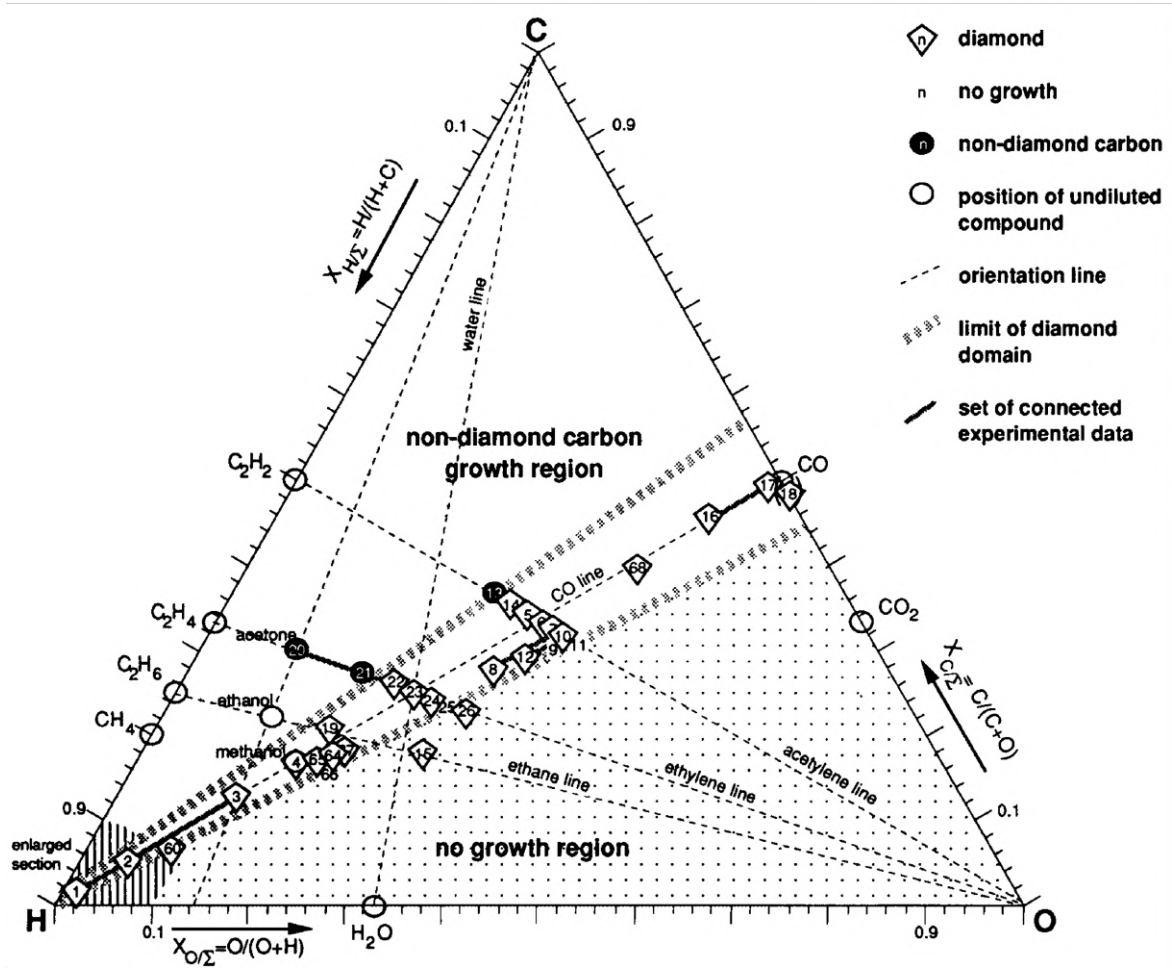


Figure 1.19 A phase diagram illustrating the relationships between carbon, hydrogen, and oxygen (C-H-O) summarizing findings from 70 experiments employing various gas combinations for diamond deposition via chemical vapor deposition (CVD). adapted from[45].

in the formation of a complete 6-membered ring and the establishment of the diamond structure. This description simplifies the surface mechanism of diamond growth, omitting factors like carbon atom migration, nucleation site formation, or the extraction of carbon atoms from the surface to produce gas phase hydrocarbon species.

In the growth process known as heteroepitaxial growth, where diamond films are deposited onto substrates other than diamond, the initial steps differ slightly. Here, a layer of either metal-carbide or silicon-carbide is first established. This carbide layer serves as the initial carbon layer for the subsequent hydrogen abstraction process and the formation of carbon-carbon bonds, as depicted in Figure 1.20. The thickness and sharpness of this carbide layer vary based on factors such as the substrate material and growth duration. For instance, it can vary from being precisely atomic on silicon

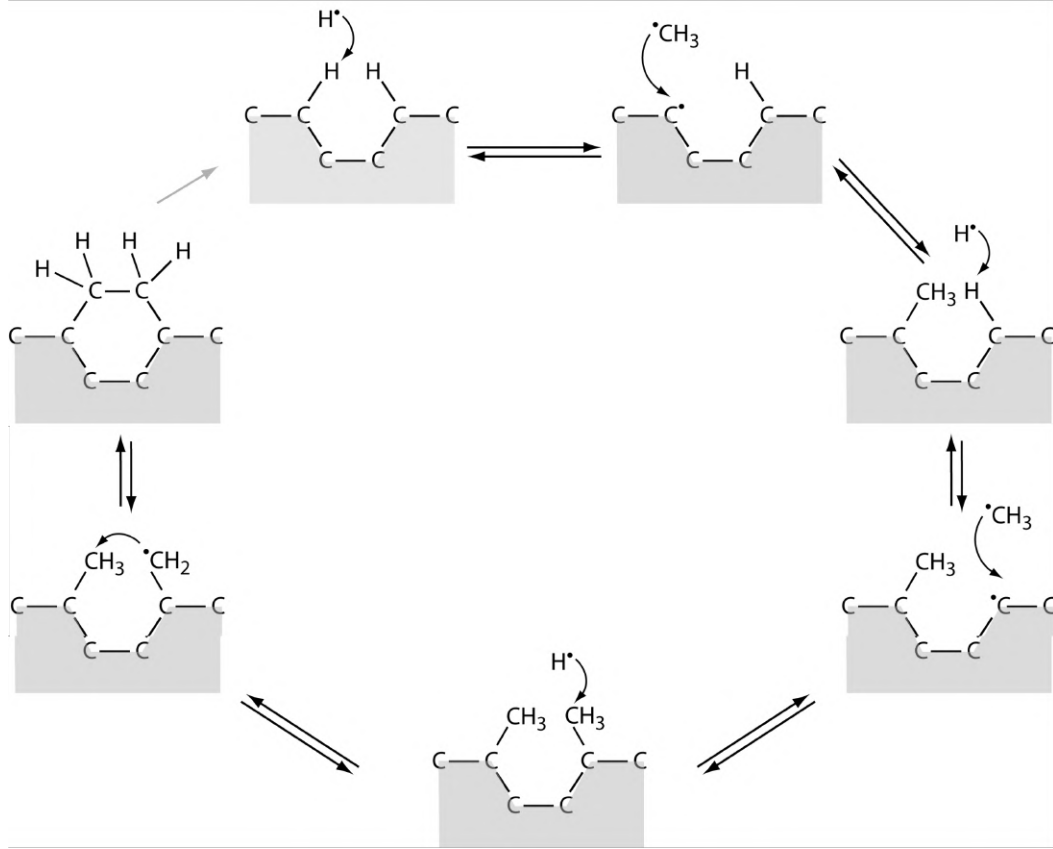


Figure 1.20 Basic schematic representation of the typical diamond-deposition model. adapted from [46], [47]

substrates to several micrometers thick on tungsten (W) substrates, or even ranging from tens to hundreds of micrometers thick on titanium substrates (Ti).

Gas phase chemistry modelling

In the diamond CVD system, chemical reactions primarily occur rapidly as hydrogen atoms abstract and add to C1 and C2 hydrocarbons. These reactions are influenced by the local gas temperature (T_{gas}) and the concentration of hydrogen $\chi(H)$, leading to a diverse distribution of hydrocarbon species according to thermodynamics. The gas-phase model suggests that hydrocarbon species with lower hydrogen content are favored in hotter plasma regions, while saturated species are more common in cooler peripheral areas. These conversions are facilitated by the abundant hydrogen concentration throughout the system [48]. In conjunction with surface chemistry at the substrate and chamber walls, this process presents a computationally challenging environment, which can benefit from advancements in in-situ plasma diagnostics.

Various spectroscopic techniques such as resonance-enhanced multi-photon ionization spectroscopy and IR laser absorption spectroscopy have enabled the accurate measurement of column densities of stable species, including CH_4 , C_2H_2 , and C_2H_6 , as well as the CH_3 radical within the CVD gas phase. In general, radical species are concentrated at the plasma center, correlating with hydrogen concentration and temperature determined.[49].

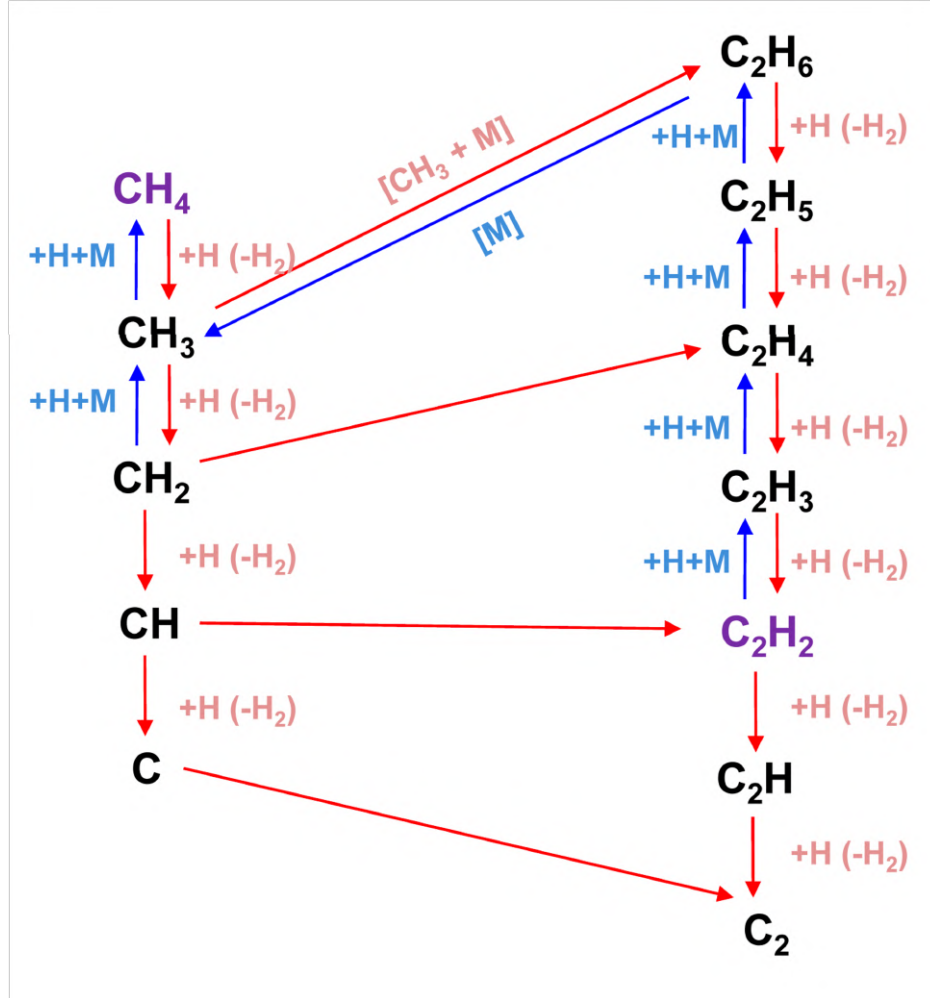


Figure 1.21 *CVD methyl radical formation: Conversion between C1 and C2 hydrocarbons through hydrogen-shifting reactions. ' $\rightarrow$ ' signifies high gas temperature (T_{gas}) and high hydrogen concentration $\chi(\text{H})$ at the plasma core. ' $\rightarrow$ ' indicates reactions occurring towards the periphery in areas characterized by lower (T_{gas}) but high $\chi(\text{H})$. adapted from [50]*

Dr. Yuri Mankelevich developed a self-consistent 2-D model that integrates electric-field propagation, gas-phase chemistry, and mass transport processes within the MWCVD reactor. This model enables computer-based predictions of gas and electron temperatures, as well as absolute hydrocarbon concentrations across diverse process

conditions. It proficiently describes various plasma environments, including those conducive to the growth of different types of diamond films [48], [51], [52].

The model encompasses around 290 forward and reverse reactions concerning neutral and charged species, driven by the non-equilibrium electron-energy distribution function, which is determined through solving the Boltzmann equation. To obtain meaningful outputs, the model employs numerical solutions for a set of non-stationary conservation equations pertaining to mass, momentum, energy, and mole fractions.

1.3.3 Diamond doping

Synthetic diamonds possess insulating characteristics due to their significant bandgap of 5.47 eV. However, through doping with either p-type or n-type impurities, we can transform them into semiconductor materials, expanding their utility in high-power electronics and wide-bandgap semiconductor industries. By introducing impurities with atomic numbers lower than carbon, acceptor levels are generated, supplying extra holes to aid electron removal from the valence band, thereby decreasing the effective bandgap. Conversely, the inclusion of atoms with higher atomic numbers than carbon results in additional electrons occupying delocalized states just below the conduction band. In both scenarios, the carrier density rises due to small binding energies relative to either the valence or conduction bands, leading to the creation of additional acceptor or donor levels and a narrowing of the material's bandgap [53].

Nitrogen doping

Although nitrogen is not typically included in the conventional Bachmann system which involves carbon, hydrogen, and oxygen chemistry in diamond growth, its presence in diamond-growing environments holds significance. Nitrogen can infiltrate these environments as an impurity in starting gases, due to insufficient vacuum conditions, or deliberately as an additive. Its influence extends across different aspects of diamond chemical vapor deposition, altering growth chemistry and rates, and affecting the properties and morphology of diamond films, including their electrical

and doping characteristics.

The addition of nitrogen into the source gases can significantly enhance the growth rate (G), with reports indicating an up to eightfold increase observed with just 100 ppm of N_2 added to MWCVD reactors [54]. However, nitrogen is not extensively integrated into the film [55]. Furthermore, even trace amounts of nitrogen (200 ppm) have been shown to promote the formation of 100 facets, which are perpendicular to the growth axis, thus aiding in the production of large, smooth diamond surfaces [56]. The impact of nitrogen on growth rate and morphology appears to be relatively dependent on the activation method, with Hot-Filament CVD being less affected compared to MWCVD.

One proposed mechanism for the enhanced deposition rate with nitrogen involves the creation of stable nuclei on the growing diamond surface through the CN group, which overcomes a rate-limiting step [57]. Although nitrogen isn't as potent a dopant as boron, its inclusion in ultra-nanocrystalline diamond (UNCD) films has demonstrated the ability to confer n-type conductivity, though conduction occurs along grain boundaries rather than true bulk doping [58], [59]. Additionally, a rise in sp^2 content has been observed with higher nitrogen content [60].

Extensive research has focused on defects induced by diamond doping, employing electron paramagnetic resonance (EPR) spectroscopy as the primary investigative tool, although photoluminescence (PL) studies are also utilized. Among the recognized defects, certain ones entail nitrogen substituting adjacent to a vacant diamond lattice site, creating NV pairs, typically introduced during diamond growth via chemical vapor deposition (CVD). Significantly, the NV^0 center (with an associated photoluminescence peak at 575 nm) and the NV^- defect (with a photoluminescence peak at 647 nm) are particularly intriguing for diamond-based quantum computing owing to their detectability within crystals and the possibility of manipulating their associated spin.

The existence of notable nitrogen levels in both natural and synthetic diamonds can affect optical transparency, potentially resulting in yellow or brown coloration in the crystal. Annealing procedures can occasionally alleviate undesired optical absorption in CVD single crystal diamonds.

Modeling diamond structures containing nitrogen atoms on or just below the surface

employs quantum mechanical (QM) calculations, revealing diverse behavior among different crystal surfaces. Introducing nitrogen-containing species into the lattice and as surface co-absorbates influences growth mechanisms, typically leading to higher deposition rates.

1.3.4 substrate pretreatment

A preparatory procedure is crucial in heteroepitaxial chemical vapor deposition (CVD) as it minimizes the time required for nucleation to generate uninterrupted diamond films. Various seeding methods are frequently employed, including basic manual abrasion with diamond powder, self-assembly of a polymer-diamond mixture, immersion in nanodiamond suspension followed by sonication, electrospray deposition of diamond particles, and the application of a negative substrate bias during diamond growth in the CVD reaction chamber.

Mechanical abrasion

A highly efficient method for nucleating a heterogeneous substrate surface involves inducing imperfections through mechanical scratching. This technique, demonstrated by [61], [62], particularly benefits materials like Si, where small embedded particles result from the scratching process. Achieving sufficient roughening for effective nucleation commonly employs mechanical abrasion with hard grit, such as SiC [42], c-BN, Al₂O₃, with diamond powder proving most successful [63], [64]. Nevertheless, this approach has limitations, including uneven surface damage that results in low-quality films, making it unsuitable for applications in tribological/MEMS technologies. Furthermore, it is restricted to treating planar substrates and is impractical for complex 3D shapes.

Ultrasonication

In the context of MCD deposition, while mechanical abrasion proves efficient for nucleating substrates, the smoother surfaces required for NCD and UNCD films

necessitate a gentler approach. An alternative method involves the application of nanodiamond (ND) seed particles onto the substrate surface, typically as a colloid or slurry suspension in a compatible liquid. These particles settle or embed themselves depending on the application method. Typically, nanodiamonds are dispersed in water due to their polarity aligning with the slightly charged nature of diamond surfaces. However, in less polar liquids, maintaining the stability of the ND colloid becomes a concern.

In the ultrasonication procedure, substrates undergo treatment by immersion in the ND suspension, followed by ultrasonic agitation to introduce or embed diamond seed particles into the surface, resulting in a high nucleation density [65]. This method also induces surface damage or scratching through cavitation or abrasion, which can beneficially facilitate diamond nucleation as long as it does not alter the film morphology [66]. Successful nucleation has been achieved using specific parameters, such as an ultrasonically-agitated suspension of 4-6 nm ND in alcohol for 15-30 minutes [67].

Spin Coating

The process involves generously applying the ND colloid onto a substrate and then subjecting it to rotation at around 2500 rpm for a specific period to achieve an even distribution of seed particles due to centrifugal force. Another approach is incorporating diamond seeds into a photoresist, enabling the creation of patterned substrates using photolithography techniques [68]. While extensively employed in the semiconductor industry, this method is only suitable for flat substrates, requiring different approaches for more intricate 3D shapes.

Self Assembly

The self-assembly method harnesses the zeta potential charge (ZPC) of the substrate in a liquid environment. ZPC signifies the difference in potential between the liquid medium and the surface species adhered to the substrate [69]. Typically, a Si wafer exhibits a negative ZPC due to its native oxide layer when in contact with water [70].

Scientists adjust the surface charge of nanodiamond particles, primarily by giving them a positive ZPC. This modification prompts a spontaneous self-assembly process on the substrate, resulting in a dense nucleation of nanodiamonds.

In an alternative technique, cathodic and anodic polymers are employed. Initially, the substrate is immersed in a solution of positively charged cathodic polymer to impart a positive charge. Subsequently, it is dipped into a mixture containing a negatively charged anodic polymer and a nanodiamond suspension. The negatively charged nanodiamond-PSS particles are attracted to the positively charged surface, forming a stable, self-assembled nanodiamond layer. Excess polymers and nanodiamonds are then removed from the substrate surface through subsequent washing and drying steps. Any residual polymer evaporates upon exposure to the reactive hydrogen atom atmosphere during the following CVD process.

Electrostatic spray deposition

The method of administering the seeding colloid onto the substrate includes ionizing droplets of the dispersion as they come out from a nozzle using a high voltage. These highly charged droplets repel each other, dispersing radially towards an earthed plate where the substrate is located. The distance from the nozzle to the substrate is adjusted in a manner allowing the liquid to evaporate before reaching the surface. This prevents splattering if too much liquid is dispensed or inadequate adhesion if too little liquid reaches the substrate. To ensure even deposition, the substrate is rotated at a few revolutions per second. This technique is widely used in various industries for depositing volatile suspensions of colloidal particles onto flat substrates.

Bias-enhanced nucleation

Bias-enhanced nucleation (BEN) is a method employed at the initial stages of diamond growth in a MW plasma CVD reactor. It involves applying a negative DC bias (-70 to -250 V) to the substrate to attract the positive hydrocarbon ions (CH_3^+ , CH_2^+ , etc.) from the gas plasma. This leads to the implantation of hydrocarbon ions into the sub-surface region of the substrate, termed 'sub-plantation', resulting in a thin carbon

layer. Subsequent ion collisions generate thermal spikes within this layer, assisting in annealing and alignment with the underlying Si lattice, leading to the formation of an almost epitaxial seed layer with a high nucleation density. However, this technique is constrained by the substrate type used and typically necessitates conductive substrates.

1.4 Fundamentals of electronic transport

Transport processes serve as the fundamental physical underpinning of modern electronic technology, encompassing various types such as energy, matter, charge, light, heat. Despite the diversity of transports, they are essentially governed by the same set of principles. The exploration of these principles originated more than 200 years ago with the descriptive understanding of electricity, pioneered by physicists like A.-M. Ampère, A. Volta, G. S. Ohm, C. A. de Coulomb, M. Faraday, and others.

As the conceptual foundation evolved, particularly with the adoption of atomistic models of matter, P. Drude introduced a microscopic theory of electron transport approximately a century later. This theory provided an intuitive explanation for the Ohmic resistance observed in metals [71], [72]. Subsequent integration of quantum theory further enhanced these classical models, with A. Sommerfeld refining them by integrating the accurate Fermi-Dirac statistics of electrons [73].

However, early quantum transport theory primarily focused on materials assumed to have macroscopic dimensions. It took several decades for technology to advance sufficiently to reliably produce and manipulate structures at a scale where quantum effects became prominent. In the 1980s, R. Landauer formulated the concept of coherent electron transport in quantum systems, establishing the foundational principles for the theory utilized in this field.[74], [75].

From a technological perspective, this theory becomes increasingly significant as the size of individual devices in integrated circuits decreases below the threshold where quantum effects start to play a crucial role in transport phenomena. The following section offers a brief overview of quantum transport concepts, closely adhering to the structure outlined by S. Datta in his work[76].

1.4.1 Electronic transport in low dimensions

Mesoscopic length scales

In the realm of mesoscopic physics, which bridges the microscopic world of single molecules requiring a comprehensive quantum mechanical description and the macroscopic scale where geometry and material properties are treated separately, quantum transport is influenced by the interplay of various length scales. The upcoming discussion will explore these characteristic length scales in detail.

Physical System Size

The fundamental aspect related to length scale lies in the size of the system, which is determined by the structure's geometry under investigation. Samples typically display notable variations in size across different dimensions. For example, in structures like two-dimensional electron gas (2DEG), the thickness might comprise just a few atomic layers, while lateral dimensions can extend over microns. Quantum wires are often confined within two dimensions, and their sizes vary accordingly. Single-walled carbon nanotubes (SWCNTs), for instance, typically exhibit dimensions of a few nanometers in both radial directions and length lengths extending > 100 nm. Multi-walled carbon nanotubes (MWCNTs), on the other hand, may have radial dimensions ranging from 10 to 20 nanometers and lengths comparable to SWCNTs. Graphene, having thickness of only a few Angstroms, its length can span up to several micrometers in two dimensions. More complex structures might require additional parameters to define system size.

electron mean free path

The electrical transport properties in low-dimensional systems are defined by various characteristic length parameters that indicate the predominant physical effects. One of the primary parameters for identifying the transport regime is the electronic mean free path (ℓ_e), which represents the distance an electron travels between scattering events. This distance is primarily influenced by the density of defects and the level of static

disorder that disturbs the regularity of the crystal lattice. These events can be either elastic or inelastic, based on whether energy is exchanged. Elastic scattering, such as scattering off impurities, alters the electron's momentum, whereas inelastic scattering, like electron-electron interactions, affects both momentum and energy. Despite the existence of distinct mean free paths for elastic (ℓ_{el}) and inelastic (ℓ_{in}) scattering, they are typically considered together.

phase coherence length

The phase coherence length (ℓ_φ) represents the average distance that an electron can move before its quantum phase gets disrupted by interactions with other electrons or dynamic scatterers like phonons or magnetic impurities possessing a net spin. Interference between different electron paths is only feasible if their phases stay coherent. Static impurities, devoid of an internal degree of freedom, do not definitively alter the phase of a scattered electron and therefore do not influence the coherence length.

The phase coherence length is determined by multiplying the phase coherence time (τ_φ) with the Fermi velocity (v_F), as shown by the equation: $\ell_\varphi = v_F \tau_\varphi$ (refer to Figure 1.22). Typically, the rate of phase decoherence corresponds to the rate of inelastic scattering events, as dephasing often involves energy transfer. The length ℓ_φ generally decreases with increasing temperature or higher density of states (DOS) at the Fermi energy, as both conditions result in more electron-electron collisions, effectively reducing the coherence length.

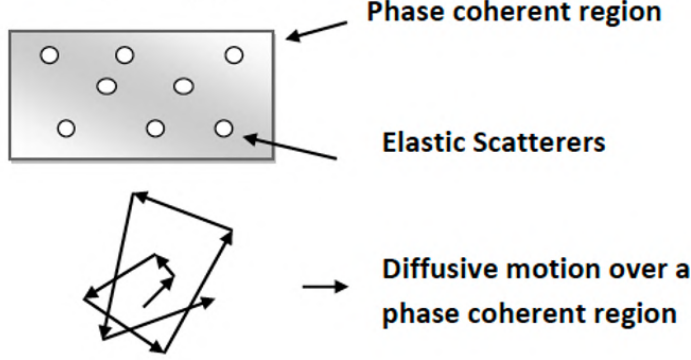
Fermi Wavelength

The electron distribution within any system at equilibrium follows Fermi-Dirac statistics. Electrons occupy electronic states ranging from the lowest energy level up to the Fermi energy (E_F). At moderate temperatures, most states are either fully occupied or completely empty. The electronic behavior of a system is predominantly determined by a narrow region near E_F , where quantum mechanical interferences play a significant role. This region corresponds to a specific wave vector k_F and its

Phase Relaxation Length

Mathematically defined as the product of the phase coherent time and Fermi velocity

$$\text{i.e. } L_\phi = V_f \tau_\phi$$



In a phase coherent region momentum is destroyed as a result of elastic scattering. The phase however, is preserved because elastic processes do not change the phase and hence multiple elastic scattering processes result.

Figure 1.22 *An illustration showing the phase relaxation length, which results from the product of the phase coherent time and Fermi velocity. In a phase coherent region, despite the elastic scattering mechanism and the diffusive pattern of electron momentum, the phase remains conserved. adapted from [76]*

associated wavelength $\lambda_F = \frac{2\pi}{k_F}$ in crystalline structures.

When the system size is comparable to or smaller than the Fermi wavelength, the electronic spectrum undergoes quantization into a discrete set of states. This quantization allows for selective adjustment of the system's dimensionality. The energy associated with a free electron moving in three dimensions can be represented by the equation $E(k) = \frac{\hbar^2 k^2}{2m}$, which in turn determines the density of states:

$$\begin{aligned}
 g_{3D}(E) &= 2 \frac{V}{(2\pi)^3} \int d^3k \delta(E - E(k)) \\
 &= 2 \frac{V}{(2\pi)^3} \int d^3k \delta\left(E - \frac{\hbar^2 k^2}{2m}\right) \\
 &= 2 \frac{V}{(2\pi)^3} \frac{d}{dE} \left(\frac{4}{3} \pi (k(E))^3 \right) \\
 &= \frac{\hbar^3 V}{\pi^2} \sqrt{2m^3 E}
 \end{aligned} \tag{1.11}$$

Here, $\delta(E - E(k))$ represents the Dirac delta function, and $k(E)$ is the wave vector corresponding to energy E . Including the initial factor of 2 to account for spin degeneracy. The volume V is considerably larger than the Fermi wavelength $\lambda_F = \frac{2\pi}{k_F} = \frac{2\pi\hbar}{\sqrt{2mE}}$ in all three dimensions.

Applying the restriction on height H of the system, the density of states in two dimensions can be expressed as:

$$\begin{aligned}
 g_{2D}(E) &= 2 \frac{WL}{2\pi^2} \int dk_x dk_y \sum_{n_z} \delta \left(E - \frac{\hbar^2}{2m} \left[k_x^2 k_y^2 + \left(\frac{\pi n_z}{H} \right)^2 \right] \right) \\
 &= \frac{WL}{2\pi^2} \sum_{n_z} \frac{d}{dE} \left(\pi [k(E - E_{n_z})]^2 \right) \\
 &= \frac{WLm}{\pi \hbar^2} \sum_{n_z} \Theta(E - E_{n_z}) \\
 E_{n_z} &= \frac{(\hbar \pi n_z)}{2mH^2}
 \end{aligned} \tag{1.12}$$

with the Heaviside step function $\Theta(x) = (|x| + x)/2x$. Applying the same restriction to the width W yields the characteristic van Hove singularities:

$$\begin{aligned}
 g_{1D}(E) &= \frac{2}{L^2} \int dk_x \sum_{n_y, n_z} \delta \left(E - \frac{\hbar^2}{2m} \left[k_x^2 + \left(\frac{n_y}{W} \right)^2 + \left(\frac{n_z}{H} \right)^2 \right] \right) \\
 &= \frac{L}{\pi} \sum_{n_y, n_z} \frac{d}{dE} \left(\frac{2k}{E - E_{n_y} - E_{n_z}} \right) \\
 &= \frac{L}{\pi} \sqrt{\frac{2m}{\hbar^2}} \sum_{n_y, n_z} (E - E_{n_y} - E_{n_z})^{-1/2}
 \end{aligned} \tag{1.13}$$

and finally, restricting the length L as well, the density of states in zero dimension can be expressed as:

$$\begin{aligned}
 g_{0D}(E) &= 2 \sum_{n_x, n_y, n_z} \delta \left(E - \frac{\hbar^2}{2m} \left[\left(\frac{n_x}{L} \right)^2 + \left(\frac{n_y}{W} \right)^2 + \left(\frac{n_z}{H} \right)^2 \right] \right) \\
 &= 2 \sum_{n_x, n_y, n_z} \delta(E - E_{n_x} - E_{n_y} - E_{n_z})
 \end{aligned} \tag{1.14}$$

In each case, if the extensions are of a similar magnitude as λ_F , the sum runs over a

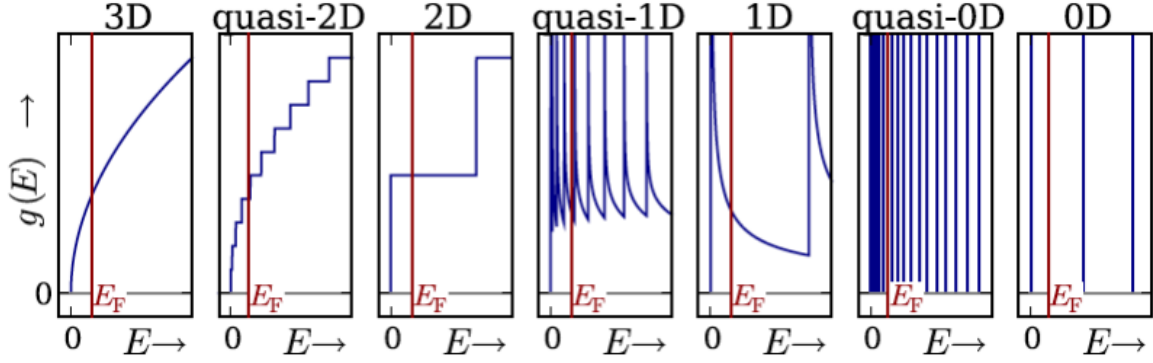


Figure 1.23 This sketch illustrates how the nature of the spectrum evolves with the dimensionality of the system, showcasing distinctive features at different band edges. 0D - QDs exhibit discrete energy levels in their spectra. 1D - In one dimension, there are $1/\sqrt{E}$ -shaped van Hove singularities at the band edges[77]. 2D - In two dimensions, the same band edges lead to the formation of steps in the spectrum. 3D (Three-Dimensional) For three-dimensional systems, the band edge yields a $\sqrt{E}$ -shaped spectrum.

Condition	dimensionality	example material
$\lambda_F \ll H, W, L$	3D	bulk crystals
$H \sim \lambda_F \ll W, L$	quasi-2D	thin films
$H \ll \lambda_F \ll W, L$	2D	2DEG, graphene
$H \ll W \sim \lambda_F \ll L$	quasi-1D	quantum wires, MWCNTs
$H, W \ll \lambda_F \ll L$	1D	atomic chains, SWCNTs
$H, W, L < \lambda_F$	0D	quantum dots, molecules

Table 1.1 Approximate classification of the dimensionality of systems according to Fermi wavelength λ_F and system sizes. The conditions $H, W, L < \lambda_F$ include the case that in certain directions the system is too small to define anything like a wavelength at all.

few energy levels (leading to the “quasi-nD” cases) while for extensions much smaller than λ_F , only the lowest level is relevant, resulting in truly reduced dimensions (See Tab. 1.1 and Fig. 1.23).

For systems without periodicity (like single molecules or CNTs in their lateral direction) the Fermi wavelength is undefined. Instead, the exact atomistic structure has to be considered to determine the number of discrete levels/bands.

The localisation length

The localization length (ℓ_{loc}) characterizes the average spatial range of quantum mechanical states. In a perfectly periodic system, Bloch states are infinitely extended (i.e., $\ell_{loc} = \infty$). However, in 1958, P.W. Anderson suggested that defects and disorder could lead to the complete localization of all quantum mechanical states within a system. This suggests that each state is confined to a finite spatial range, which depends on the system's dimensionality and potentially the magnitude of the disorder. The localization length can be represented through Green's function as follows:

$$\ell_{loc} = - \lim_{\ell \rightarrow \infty} \frac{\ell}{\langle \ln G(r, r + \ell)^2 \rangle} \quad (1.15)$$

In this context, the localization length takes on a finite value and can be mathematically defined using the spatial Green function. When the localization length ℓ_{loc} is notably smaller than the size of the system, it indicates strong localization regime. Conversely, if both the localization length and the system size are of comparable magnitude, the system is considered to be in the regime of weak localization.

The magnetic length

The length scale linked to the strength of an applied external magnetic field (B), referred as the magnetic length (ℓ_{mag}), typically is defined as: $\ell_{mag} = \sqrt{\frac{\hbar}{eB}}$

In this equation, $\hbar$ represents the reduced Planck constant, e denotes the elementary charge, and B stands for the external magnetic field strength. The magnetic length corresponds to the area that encompasses one magnetic flux quantum ($\Phi_0 = h/e$) within a given external magnetic field. It plays a critical role in determining the scale at which various mesoscopic effects involving magnetic fields occur, such as the Aharonov-Bohm effect, negative magnetoresistance due to weak localization, and others.

1.4.2 The Transport Regimes

The quantum transport regimes can be categorized according to the system's length L , discussed earlier in the section.

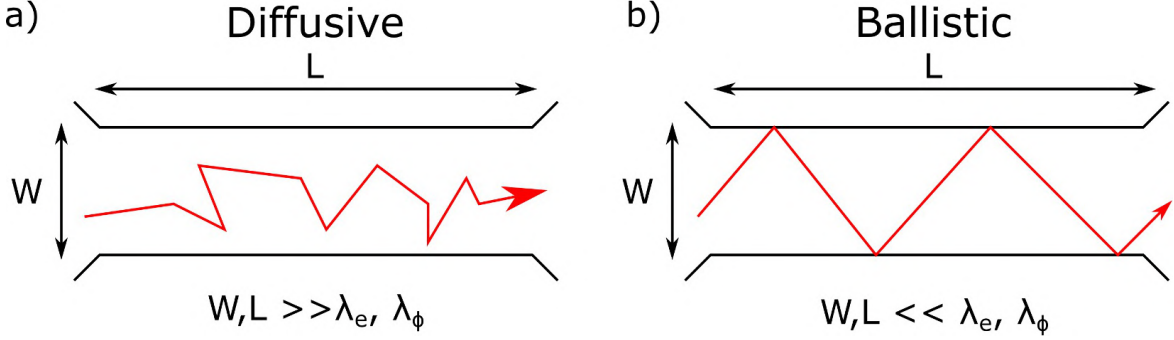


Figure 1.24 *Schematic illustrations of the diffusive (a) and ballistic (b) transport regimes. The electron trajectories are marked in red.*

For a system where its length is on the order of Fermi wavelength, i.e, $L \leq \lambda_F$, the system will have a **discrete energy spectrum**. Common in such instances are phenomena such as Coulomb blockade or resonant tunneling, which examine the individual states of the system. In a system where $L \geq \lambda_F$, the system will exhibit a **continuous energy spectrum**, and other length scales become pertinent.

In a system where $L \leq \ell_m$, it will demonstrate ballistic transport (1.24b). The resistance will become independent of L and will solely depend on the contacts. This transport regime can be explained by the Landauer formalism.

In a system where $L \geq \ell_m$, it will display diffusive transport (1.24a), where the transportation is predominantly affected by multiple scatterings. Consequently, the resistance increases with L . This transport regime can be described by the Drude-Sommerfeld model.

In coherent transport ($L \leq \ell_\varphi$), the resistance of the system increases exponentially with the length of the system. In this scenario, Ohm's law is only applicable when coherence is disrupted at a scale significantly smaller than the length of the conductor.

When the system's length satisfies $L \leq \ell_{loc}$, it enters a delocalized regime where the localization length competes with the phase coherence length. In this regime,

Conditions	Transport Regime
$\lambda_F \sim L \ll \ell_{el}, \ell_\varphi, \ell_{loc}$	discrete spectrum (resonant tunneling)
$\lambda_F \ll L \ll \ell_{el}, \ell_\varphi, \ell_{loc}$	ballistic transport
$\lambda_F, \ell_{el} \ll L \ll \ell_\varphi, \ell_{loc}$	diffusive transport
$\lambda_F, \ell_{el}, \ell_\varphi \ll L, \ell_{loc}$	Ohmic resistance
$\lambda_F, \ell_{el} \ll \ell_{loc} \sim L \ll \ell_\varphi$	weak localization
$\lambda_F, \ell_{el}, \ell_{loc} \ll L \ll \ell_\varphi$	strong localization (exponentially suppressed)
$\lambda_F, \ell_{el}, \ell_{loc}, \ell_\varphi \ll L$	strong localization (thermally activated)

Table 1.2 Overview of various transport regimes based on their characteristic lengths.

individual electronic states extend from one contact to the other, facilitating coherent transport. Decoherence, which disrupts coherence, is detrimental to transport, resulting in an increase in resistance with escalating dephasing factors such as rising temperature.

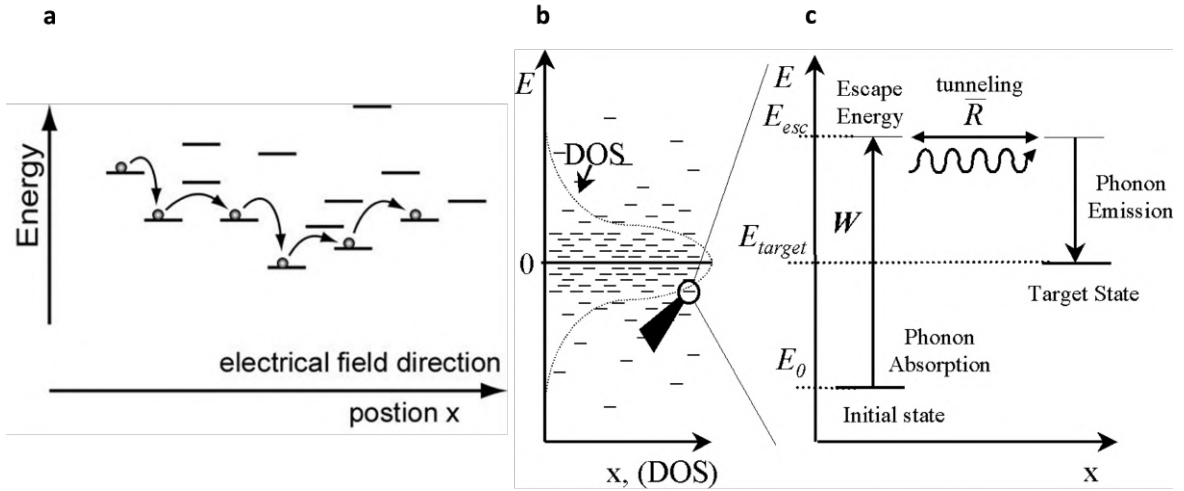


Figure 1.25 (a) A depiction of the hopping mechanism, where electrons can transition between different energy levels through tunneling, either within the same level or to a different level (a). The distribution of the DoS illustrates the availability of energy states (b). It demonstrates the excitation of electrons from a lower energy level to a higher one (W), and the potential tunneling route (R). adapted from [78]

When the system's length satisfies $L \geq \ell_{loc}$, it enters a strong localization regime. In this regime, coherent transport within a single state is exponentially suppressed. Conductance arises from thermally activated hopping between levels, leading to a decrease in resistance with increasing dephasing (see Figure. 1.25).

1.4.3 The Drude Model

In 1900, Paul Drude proposed a model aimed at elucidating the transport properties of materials. This model posits that freely moving electrons undergo continuous interactions with heavier, stationary positive ions. The kinetics of such electron is given by the following equation:

$$\frac{d}{dt}p(t) = qE - \frac{p(t)}{\tau} \quad (1.16)$$

where t denotes time, p -electron's momentum, q -charge, τ - mean free time between collisions and E stand for the electric field.

Drude illustrated a linear correlation between current density (J) and the applied electric field, as shown in equation (1.16), given by:

$$J = \left(\frac{nq^2\tau}{m} \right) E \quad (1.17)$$

where n and m denote the number density and mass of electrons, respectively.

The validity of Ohm's law is founded on this linear relationship. However, although the Drude model provides a reasonable approximation for electrical conduction on a macro-scale, it struggles to explain certain phenomena observed on micro and nano-scales, such as negative magnetoresistance. This limitation stems from certain assumptions inherent in the model, including:

- The model assumes the presence of numerous free electrons, i.e., delocalized electrons, which may not accurately represent the behavior of electrons in disordered systems.
- The model disregards long-range interactions between electrons and ions, however this interactions can be significant, especially in low-dimensional systems.
- The model neglects $e - e$ interactions.

- The model treats both electrons and ions as classical particles, but in quantum mechanics, this assumption is not entirely accurate. The wave-particle duality nature of electrons must be considered.

To overcome these shortcomings, revisions to the Drude model are required, incorporating changes to consider weak localization and electron-electron interactions in nanostructured materials. These are discussed in the chapter 7.

1.4.4 Localization

Localization refers to the restriction of wave propagation caused by scattering in disordered systems. This phenomenon can be categorized into weak and strong localization. When the distance between scatterers in an array exceeds the phase relaxation length, the resistance of the array increases linearly with its length, in accordance with Ohm's law. Anderson showed, that electrons can be localized by a random potential, suppressing diffusion even though classical particles would be delocalized [79]. The core principle of localization is the multiple interference of wave components, scattered by random scattering centers. Particles become localized when the disorder is strong enough. The envelope of the wave function decays exponentially from a point r_0 in space, expressed as

$$|\Psi(r)| \propto \exp\left(\frac{-|r - r_0|}{\xi}\right), \quad (1.18)$$

where ξ represents the localization length. In a random potential $V(r)$, electrons are scattered after an average time τ .

Anderson Localisation

The Anderson localization transition is influenced by a control parameter such as particle wave frequency, particle energy, or disorder strength. In regions where the random potential creates a deep well, localized orbitals form. Due to the varying energies of these orbitals, their overlap and admixture are minimal. Orbitals that are close in energy are spatially separated, resulting in an exponentially small overlap.

Consequently, electron wave functions are expected to be exponentially localized in strongly disordered systems. In one-dimensional systems, all states are localized regardless of the disorder's strength [80].

In three-dimensional systems, particles are delocalized when the disorder is weak. Localized and extended states cannot coexist because any perturbation would cause hybridization and subsequent delocalization. Localized and extended states with specific energies are spatially separated. As disorder increases, there is a sharp transition from delocalized to localized states at a critical disorder strength ν_c or energy. Ioffe and Regel proposed a qualitative criterion for predicting the Anderson transition in three-dimensional (3D) systems [81]. The transition occurs when the mean free path λ_e becomes smaller than the particle's Fermi wavelength λ_F :

$$\lambda_e < \lambda_F \quad (1.19)$$

The relevant mean free path in this context is associated with momentum transfer. With a fixed disorder strength and varying energy, a similar transition can be observed. The critical energy separating localized from delocalized states is known as the mobility edge [82], [83]. At zero temperature, the energy-dependent electron mobility is zero in the localized phase and increases continuously with energy in the delocalized phase.

1.4.5 Transition in 1, 2 and 3 dimensions

In a d -dimensional cube of length L , the dimensionless conductance g is considered in units of the quantum of conductance, defined as $g = \frac{G}{e^2/\hbar}$. In systems with strong disorder, all states are expected to be localized with an average localization length ξ . This implies that $g(L)$ decreases exponentially with increasing L :

$$g(L) \propto e^{-L/\xi} \quad (1.20)$$

Abrahams et al. [84] defined $\beta(g)$ as:

$$\beta(g) = \frac{d \ln g}{d \ln L} \quad (1.21)$$

which depends solely on g and can be calculated for both strong and weak disorder. For strong disorder, β is given by:

$$\beta(g) \propto \ln(g/g_c) < 0 \quad (1.22)$$

and is independent of dimensionality. In the regime of weak disorder, where the conductance behavior is ohmic:

$$g \propto L^{d-2} \quad (1.23)$$

this implies:

$$\beta(g) = d - 2 \quad (1.24)$$

To determine if the system is localized or delocalized, one integrates the equation from an initial point L_0 with known conductance. The conductance either vanishes or becomes infinite for L depending on whether β is negative or positive along the integration path.

In three dimensions ($d = 3$), both $\beta(g) > 0$ and $\beta(g) < 0$ occur for large and small g , respectively. There is a point where β equals zero, marking the boundary between localized and delocalized states. In one dimension, β is always negative, indicating all states are localized. In two dimensions, β approaches zero as g approaches infinity. To determine whether β is positive or negative for large g , scale-dependent corrections based on the Drude model are applied. With the addition of a correction factor, β is given by [84]:

$$\beta(g) = (d - 2) - \frac{a}{g}, \quad (1.25)$$

where $a = \frac{2}{\pi}$. This means $\beta(g) < 0$ for all g , indicating that all states are localized.

1.4.6 Temperature dependence and variable range hopping

The particle energy, and thus the temperature, is a key factor influencing Anderson localization. In a degenerate electron gas, the metal-insulator transition (MIT) occurs when the Fermi energy E_F crosses the critical energy or mobility edge E_c [85]. Analogous to conductivity considerations, conduction is ohmic if $E_F > E_c$. When $E_F < E_c$, states become localized. In localized systems, conductance decreases with decreasing temperature. At high temperatures, transport occurs via excitation to the mobility edge, and the conductance is given by:

$$\sigma = \sigma_0 e^{-(E_c - E_F)/k_B T} \quad (1.26)$$

At low temperatures, transport is expected to occur through variable-range hopping from one localized state to another. Neglecting electron-electron interactions, the conductivity follows [86]:

$$\sigma \propto e^{-(T_0/T)^{1/4}} \quad (1.27)$$

in the three-dimensional case and can be generalized to d dimensions as:

$$\sigma \propto e^{-(T_0/T)^{1/(d+1)}} \quad (1.28)$$

where T_0 is related to the localization length ξ and the density of states at the Fermi energy $D(E_F)$ as follows:

$$T_0(\xi) \approx 14 (\xi 2k_B D(E_F))^{-1} \quad (1.29)$$

where k_B is the Boltzmann constant [83], [86]. Ambegaokar et al. derived the same behavior as shown in the previous equation using the percolation method [87].

Chapter 2

Carbon Nanotube Functionalisation

2.1 Background

Molecular magnets attached to carbon nanotubes (CNTs) are being explored for their potential applications in spintronic and quantum technologies. However, the methods used to attach these molecules can significantly impact the physical and chemical properties of the resulting hybrid systems. The relationship between the degree of functionalization and the magnetic behavior of these systems has not been extensively studied due to their complexity. In this study, it is demonstrated that the level of chemical functionalization, particularly the loading of a molecular magnet like Gd-DTPA, can be used to finely tune the magnetic properties of CNT-lanthanide hybrid complexes.

2.1.1 CNT Functionalisation

Since their discovery in 1991[88], carbon nanotubes (CNTs) have been the subject of extensive research due to their exceptional physical properties. CNTs serve not only as fascinating subjects for understanding the fundamental physics of low-dimensional systems[89] but also exhibit material characteristics suitable for a wide range of applications[90]. Researchers are currently investigating the attachment of magnetic molecules to functionalized CNTs for potential applications in molecular

spintronics[91]. When metal ions are confined to carbon nanotubes, they display anisotropic spin behavior, leading to intriguing quantum phenomena like quantum tunneling magnetization (QTM) and spin blocking.

While CNTs are now widely studied, there is a pressing need to tailor and adjust their properties for specific applications. Chemical treatment is a primary method for introducing specific functional groups to CNTs[92], but the lack of reproducibility in these methods hinders the preparation of consistently homogeneous samples. This issue arises from the challenges in controlling the degree of functionalization and analyzing the conditions involved.

2.2 Raman evaluation of degree of CNT functionalisation

Raman spectroscopy, a spectroscopic technique, has proven useful in assessing the structural properties of carbon materials[93], [94]. Recent research has focused on deconvoluting Raman spectra to better understand the combined effects of functionalization and disruptions to the graphitic lattice. This approach, particularly emphasizing the relationship between first and second-order harmonics, has yielded valuable insights[95]. Minor bands and satellite modes located near the primary G and D bands provide a deeper understanding of structural modifications during chemical treatment. This analysis also addresses the limitations of the Koenig–Tuinstra relation when assessing the structural changes in multiwalled carbon nanotubes[96]. Figure 2.1 illustrates these deconvolution methods, which assess the contributions of minor modes adjacent to the G and D bands, denoted as $S + G_L$, D_R , D_L , and G_R .

Raman spectroscopy is a valuable tool that can detect both long-range and short-range order in carbon nanotubes (CNTs). The observed side bands in Raman spectra are believed to be connected to two specific aspects of nanotube surface modification.

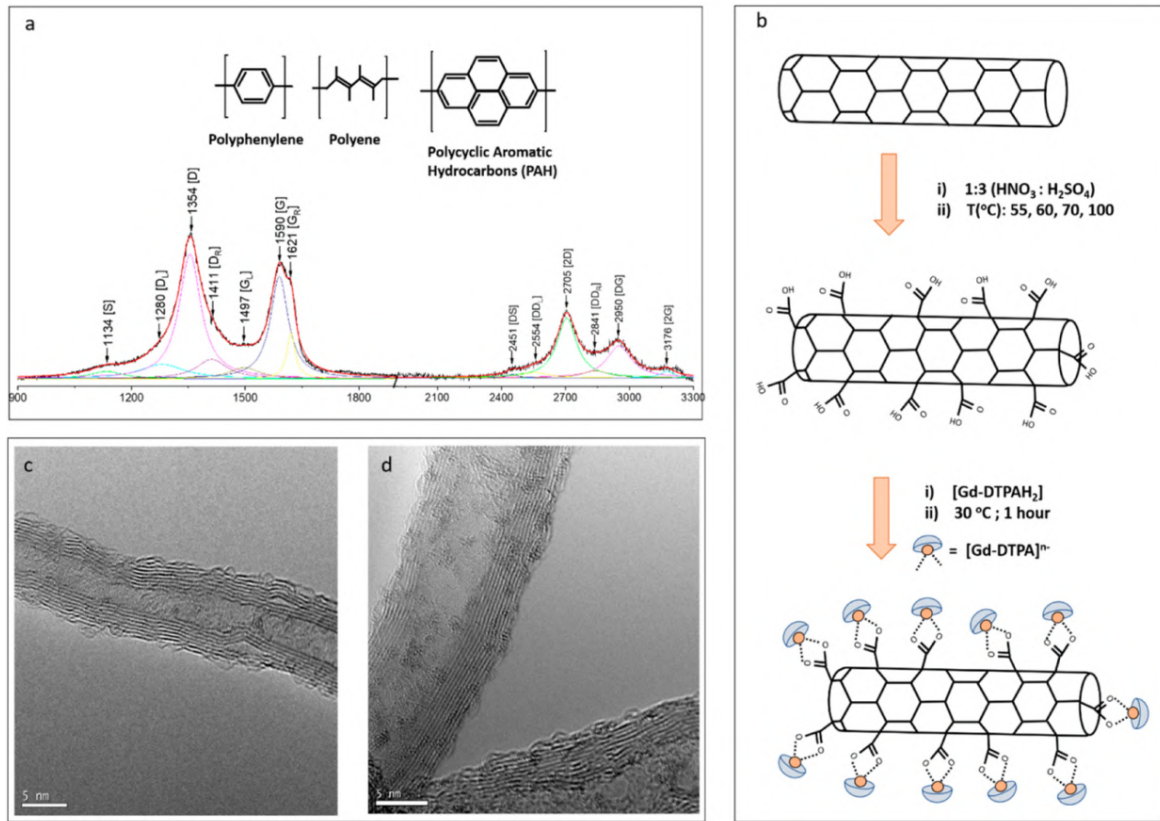


Figure 2.1 Raman spectroscopy is employed to assess the impact of a mild oxidative functionalization technique. The D and G bands are meticulously deconvoluted into seven distinct Lorentz curves, with their positions anchored by relevant second harmonic modes in the 2D region. **a)** Adhering to convention, further differentiation of minor modes is made based on their respective origins—either polycyclic aromatic hydrocarbon type (PAH) or out-of-plane vibrations akin to polyene and polyacrylic structures. This distinction facilitates the monitoring of functionalization evolution as influenced by experimental parameters such as oxidation time and reaction temperature. **b)** A schematic representation outlines the process of attaching a molecular magnet (Gd-DTPA) onto MWNTs through functional groups. **c, d)** High-resolution transmission electron microscopy (HR-TEM) images depict pristine MWNT and CNT (Gd-DTPA).

(i) The introduction of polycyclic aromatic hydrocarbon domains (PAH)[97], [98].
 (i) The presence of polyacetylene and polyacrylic-like regions[99]–[101]. This interpretation has been utilized in various subsequent studies[102]–[104], revealing that the balance between PAH domains and the Raman signatures of polyacetylene-like structures can serve as a more precise indicator of the extent of chemical functionalization than relying solely on the $I_{D/G}$ ratio[95].

Inspired by these intriguing findings, the present research aims to gain a deeper

understanding of how the functionalization process alters the nanotube surface and how these alterations affect the underlying physics, enabling the tuning of CNT properties. In this study, the previous research[95], [105] is extended by systematically investigating the degree of functionalization in multiwalled carbon nanotubes (MWCNTs). The functionalization of MWCNTs is carried out using a conventional oxidative reflux reaction. To assess the impact of the reflux reaction on nanotube quality, variations in reflux temperatures and reflux time are employed and monitored using Raman spectroscopy. This approach enables the tracking of the effects of increased functionalization.

In the final step, the functionalized MWCNTs are loaded with a molecular magnet (Gd-DTPA) through a two-step synthetic chemistry process, ensuring that Gd-DTPA attaches preferentially to functional groups along the MWCNT walls. As a result, the degree of functionalization is directly linked to the magnetic properties of the complex system. These modified MWCNTs are then assessed using Superconducting Quantum Interference Detector (SQUID) magnetometry, which can detect very subtle changes in magnetic behavior across the studied samples. This combined study provides insights into the precise tuning of magnetic properties through a controlled and monitored chemical treatment, which is expected to have significant implications for the advancement of CNT-based technologies, including novel spintronic devices[91], drug delivery systems[106], and nuclear magnetic resonance (NMR) contrast agents.

Raman spectroscopy has been widely employed to assess the level of structural disorder in sp^2 carbon. Typically, this is done by analyzing the ratio of I_D/I_G phonon peaks originating from the first-order spectrum[107]. However, in the case of multiwalled carbon nanotubes (MWNTs), the Raman spectrum is notably different from that of other carbon structures, such as graphite, graphene, double-walled, and single-walled nanotubes. The Raman spectrum of MWNTs more closely resembles that of chars and carbon blacks[96], [108], resulting in a prominent D band peak, even in pristine, unfunctionalized samples. Consequently, the conventional I_D/I_G ratio comparison is less effective in quantitatively assessing the level of disorder, and it

doesn't necessarily change significantly upon functionalization. Therefore, alternative methods are needed to determine variations in functionalization and disorder.

To address this issue, a deconvolution scheme has been developed to assess the chemical functionalization degree (CFD) of MWNTs[95]. This scheme evaluates changes in the minor bands concerning the primary D and G bands. The CFD is calculated as the area ratio of minor peaks (S, S_R , D_L , D_R , G_L , G_V) to the main D and G peaks and expressed:

$$\text{CFD} = \sum_{\text{area}} \frac{(S, S_R, D_L, D_R, G_L, G_V)}{(D, G)} \times 100 \quad (2.1)$$

This approach becomes possible because increased functionalization disrupts the aromaticity of the sp^2 lattice.

Inspired by this, the present research delves deeper into the evolution of the minor peaks and their connection to aromatic structures. The functionalization of MWNTs has a significant effect on the Raman spectra, particularly the broadening of the D and G bands due to the formation of shoulder peaks representing nanoscale Raman-active sites along the tube. This broadening is associated with polyacetylene/polyphenylene-type or polyaromatic hydrocarbon-like (PAH) structures [97]–[101]. In this context, the D and G peaks underwent further deconvolution, resulting in a cluster of approximately five to seven sub-peaks using Lorentz fitting[95], [102]–[104]. The D band is deconvoluted into two subpeaks, D_L (D left) and D_R (D right), located at $\sim 1250 \text{ cm}^{-1}$ and $\sim 1400 \text{ cm}^{-1}$, respectively. Similarly, the G band is deconvoluted into subpeaks, G_L (G left) and G_R (G right), at $\sim 1500 \text{ cm}^{-1}$ and $\sim 1610 \text{ cm}^{-1}$, respectively. Additionally, a side band (S) at approximately $\sim 1200 \text{ cm}^{-1}$ was observed on the left side of the spectrum. D_L , D_R , and G_L are associated with PAH domains, while S and G_V subpeaks are linked to polyacetylene-like structures. In the study, two fitting criteria are used: anchoring the bands in the $1100\text{--}1800 \text{ cm}^{-1}$ range to corresponding bands in the second overtone region (2D) (see Figure 2.1a) i.e., DS (D + S), DD_L (D + D_L), 2D (D + D), DD_R (D + D_R), DG_L (D + G_L), DG (D + G), and 2G (G + G), and utilizing only deconvolution analysis with R-squared values lower than 0.996. These criteria ensure accurate fitting to the data, consistent with previous reports[95].

2.2.1 Time dependent CNT functionalisation

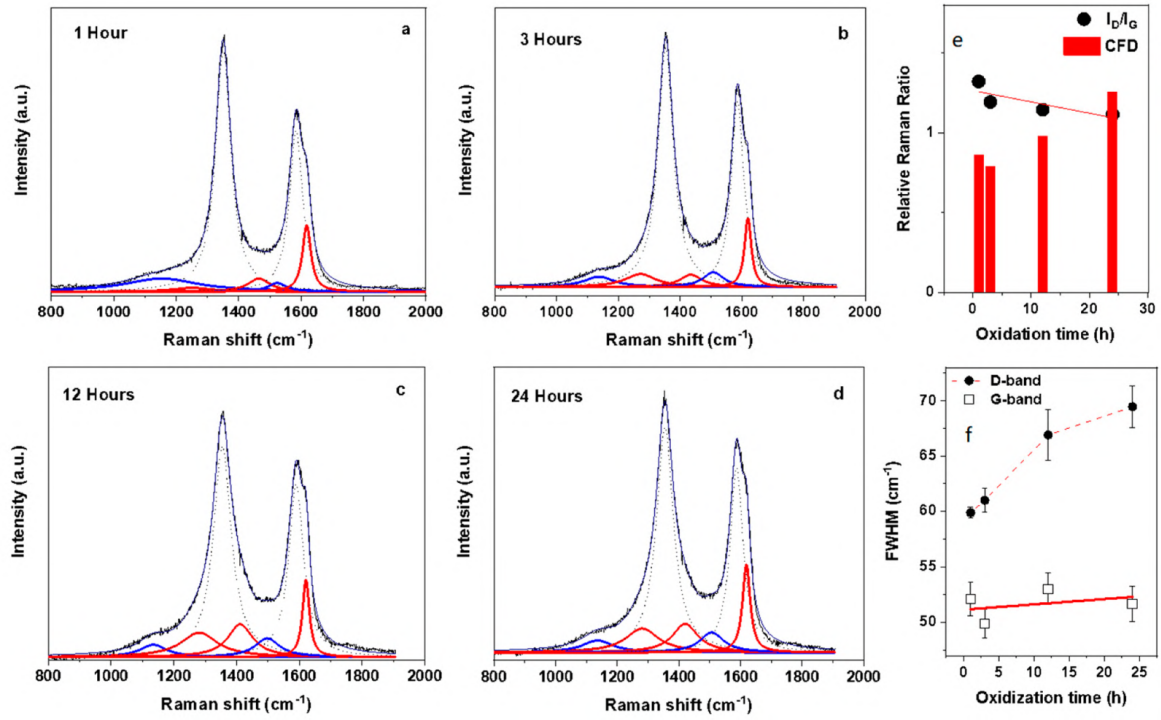


Figure 2.2 Raman spectroscopy was employed to assess the impact of an extended oxidation time on functionalizing MWNTs. **a–d)** The influence of oxidation time is evident in the significant modification of the Raman spectrum; as oxidation time is extended, satellite peaks relative to the main D and G modes are amplified. **e)** The conventionally used I_D/I_G ratio, employed to assess disorder in graphitic materials, exhibits a linear decrease with increasing oxidation time. However, this ratio does not fully capture the expanding effect of increasing functionalization. In contrast, the evaluation of the effective area of deconvoluted peaks proves more sensitive to variations in oxidation times, displaying a more pronounced rate of change compared to the I_D/I_G ratio. **f)** The increase in the effective area of satellite peaks coincides with a rise in the full width at half maximum (FWHM) of both the G and D bands.

The initial experiments focus on the effect of oxidation time on Raman modes (see Figure 2.2a-d). Extended oxidation treatment results in an increase in the full width at half maximum (FWHM) of the G band and changes in the effective percentage area of the subpeaks. As oxidation time increases, the minor bands show a substantial increase in area and weighting in the deconvolution process. The I_D/I_G ratio remains relatively constant across different oxidation times (see Figure 2.2e), while the ratio of minor bands to the main band (indicated by red bars) changes significantly. This highlights that using peak area rather than intensity is a more sensitive metric for

evaluating functionalization. Additionally, broadening of the FWHM of the G and D bands is observed (see Figure 2.2f), which is related to an increase in disorder and physical disruption of the graphitic lattice[105]. The study suggests that prolonged oxidation times (up to 24 hours) do not necessarily lead to increased destruction of the nanotubes due to functional group attachment, but rather due to pitting effects and tube cutting associated with an abundance of PAH domains. This insight is valuable in understanding the effects of functionalization on MWNTs.

2.2.2 Temperature dependent CNT Functionalisation

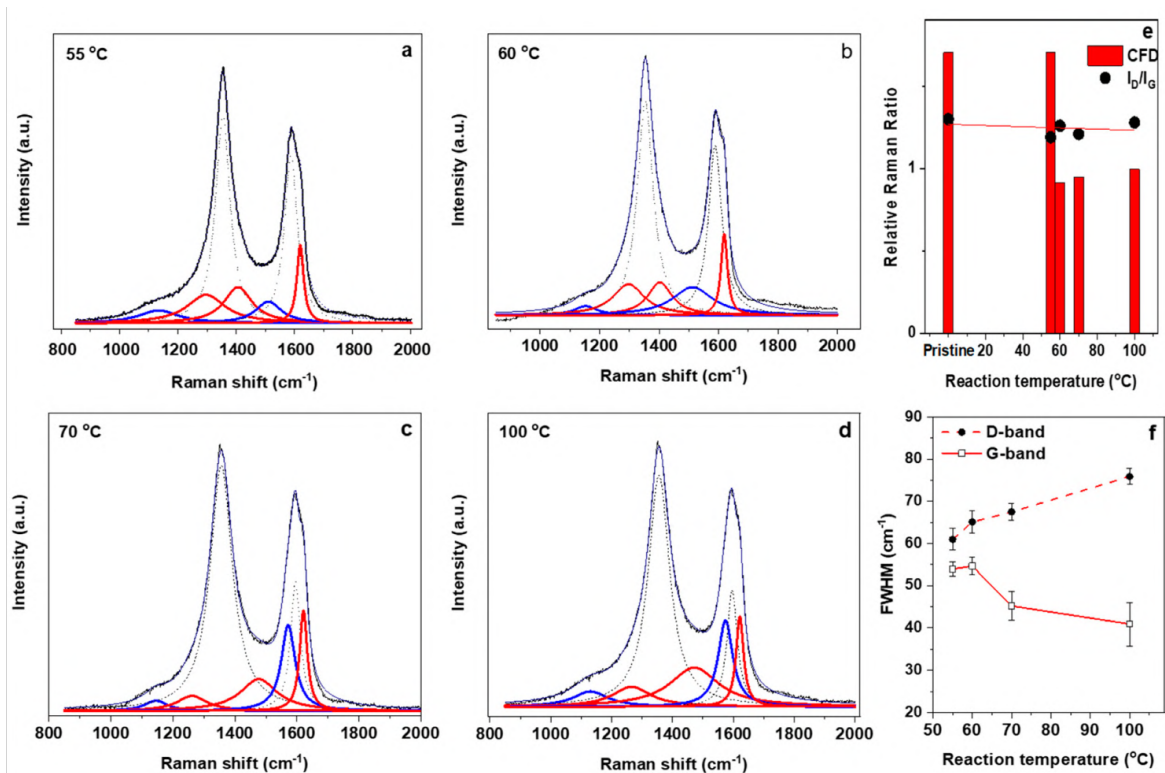


Figure 2.3 Raman spectroscopy is utilized to assess the impact of temperature on the mild oxidative reflux functionalization technique. As illustrated in Figure a–d), the deconvolution method reveals a distinct spectral shift, particularly in the shoulder bands closest to the D and G overlap. With increasing temperature, the D_R and G_L peaks exhibit the most significant increase. This shift in dominance concerning relative area serves as a metric for monitoring the rise in out-of-plane vibrational modes associated with functional group attachments. e) Similar to previous observations, the change in the effective area of the satellite peaks proves more sensitive to structural changes than the I_D/I_G ratio. f) The primary reason for the alteration in the chemical functionalization degree (CFD) is attributed to a change in the weighting of the D_R and G_L modes.

To further explore the impacts of reflux conditions on the functionalization of nanotubes, a temperature dependence study is conducted. In this investigation, the oxidization reaction temperature is the experimental parameter, with a fixed reaction time of 24 hours. As illustrated in Figure 2.3a–d, a noticeable difference is once again observed in the deconvoluted spectra. In Figure 2.3e, the I_D/I_G ratio exhibits a decrease with increasing reaction temperature, while an assessment of the ratio of minor to major bands (relative Raman ratio) demonstrates a more pronounced and sensitive change, notably decreasing sharply after 60 °C. In contrast to the time-dependent study, a significant spectral weight shifting is observed between minor bands. This shift is most notable in the overlapping regions of the D and G bands, likely due to the small energy difference in such modes. The spectral shift indicates that higher wavenumber bands are enhanced (in both intensity and percentage area) as the reaction temperature increases. This observation is crucial as it suggests an overall change in the type of functionalization occurring at higher temperatures.

In the temperature-dependent study, there is identified a substantial increase in the widening (area) of the G_L minor band (mirrored by an initial increase in the D_R band) and eventual total broadening of the D_R band. Since the G_L band is more closely associated with polyacetylene and polyphenylene-like formation, this observation implies that elevated reaction temperatures may lead to an increase in out-of-plane functionalization group attachment and degradation of the polyaromatic hydrocarbon (PAH) domains. This degradation is reflected in the broadening of the PAH-related bands, with the DR band being the most notably affected.

2.2.3 Evaluation of degree of CNT functionalisation

Figure 2.3f illustrates that changes in the effective area of the minor bands, indicative of functionalization, appear to be more pronounced at higher temperatures. This observation introduces a new metric for assessing the degree of functionalization, specifically focusing on the degradation of polycyclic aromatic hydrocarbon (PAH) domains in favor of polyacetylene-like networks, representing a higher degree of functional group attachment. To quantify this change in functionalization more

precisely, the ratio of $(S + G_L)/(D_L + D_R + G_R)$ is employed, providing a more refined assessment of the degree of functionalization and allowing for differentiation between the effects of various chemical treatments used for structural modification of MWNTs, as depicted in Figure 2.4b.

To support these findings, high-resolution transmission electron microscopy (HR-TEM) is used (Figure 2.4c and 2.4d). Prolonged oxidation durations result in the formation of graphitic pits on the nanotube wall (as observed in Figure 2.4c), while high-temperature oxidation promotes the creation of localized defects and nucleation sites (seen in Figure 2.4d). These defects enhance the non-covalent attachment of metal complexes to the nanotube. Therefore, it is determined that temperature-dependent acid reflux reactions generate more active oxygen functional moieties on MWNTs, which can subsequently be utilized for linking Gd-DTPA chelates. This finding provides valuable insights into the effects of temperature and reaction conditions on MWNT functionalization and its potential applications.

A more detailed analysis of the G band position has revealed that multiwalled carbon nanotubes (MWNTs) treated at higher temperatures exhibit a shifting of the G peak towards higher frequencies. This shift can be explained by the formation of a higher percentage of oxygen functional groups and their corresponding electronegative effects on the CNT structure, which influence the G band position, as depicted in Figure S2a and S2b.

This observation aligns with the fact that samples treated at higher temperatures show a greater percentage of Gd molecule attachment on the CNT surface. This further supports the argument that a deeper analysis of the area of minor Raman bands can serve as a new metric for evaluating the degree of functionalization. In this case, the shift in the G band position is an indicator of the increased functionalization of MWNTs, and this analysis can be used to quantify the extent of functionalization more effectively.

For qualitative analysis of the Gd-DTPA metal ligand complex attached to carbon nanotubes, we employed the time-of-flight secondary ion mass spectrometry (ToF-

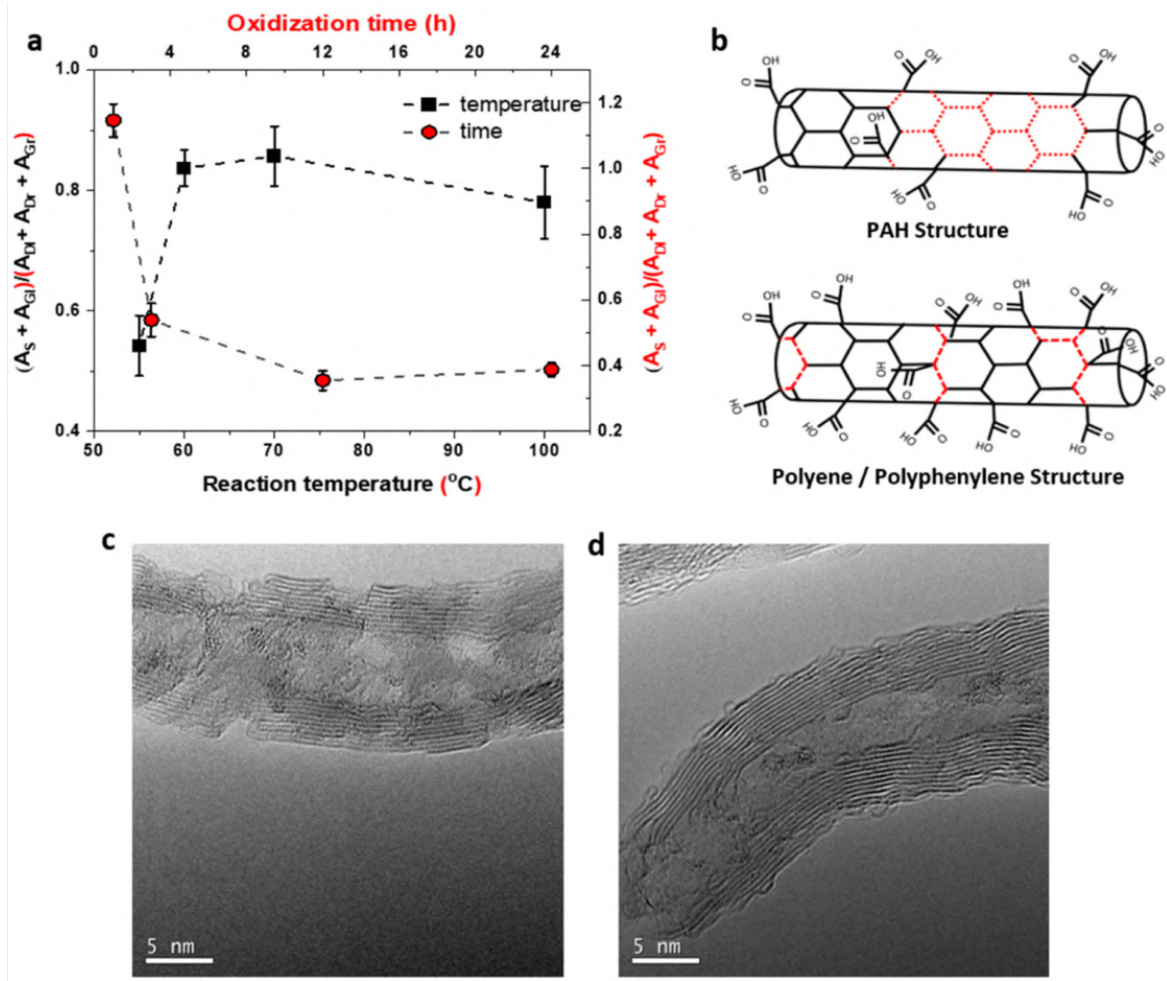


Figure 2.4 The evaluation of the ratio of minor bands, grouped by predicted structural origin (polyphenylene or PAH), provides insights into the impact of oxidation time and reaction temperatures. **a)** Noticeable differences between oxidation time and reaction temperatures indicate that these two distinct experiments favor the formation of different functionalities. The relative Raman ratio exhibits a sharp decrease, followed by saturation, as oxidation time increases. This is linked to a decrease in the area of the S and G_L bands relative to the D_L , D_R , and G_R bands. Conversely, when varying the reaction temperature, higher oxidation temperatures lead to an increase in the relative Raman ratio (increase in S and G_L over the D_L , D_R , and G_R bands). **b)** This information can be correlated with the quality of functionalization of the tubes, as the S and G_L bands are more closely associated with polyphenylene-like structures, whereas the D_L , D_R , and G_R are related to PAH clusters (schematically shown on the right). Raman spectroscopy findings are supported by high-resolution transmission electron microscopy (HR-TEM) studies, as depicted in **(c)**. Longer oxidation times lead to pitting effects and the formation of graphitic segments that give rise to the PAH Raman signatures, as opposed to the temperature-dependent study in **(d)**, where polyphenylene-like signatures dominate in the oxidized nanotube samples.

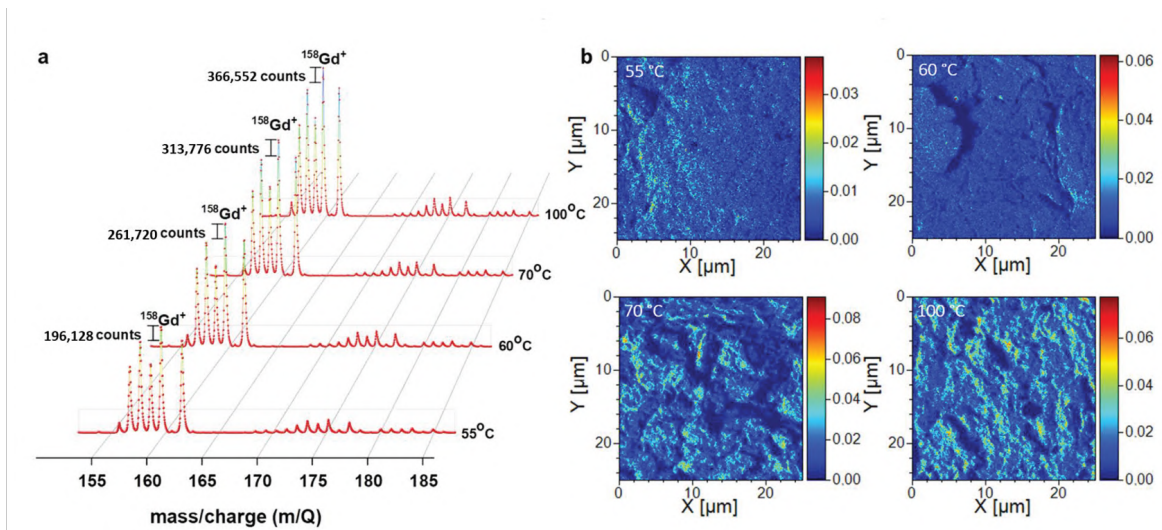


Figure 2.5 (a) ToF-SIMS spectra demonstrate elevated Gd counts for samples exhibiting a higher degree of functionalization, attributed to increased reaction temperatures. (b) ToF-SIMS element distribution maps reveal the uniform distribution of the Gd complex on the carbon nanotube (CNT) surface. Additionally, an incremental increase in the percentage of Gd in the CNTs is visually evident, indicated by a brighter contrast, corresponding to higher reaction temperatures.

(SIMS) surface characterization technique. Figure 2.5a illustrates the increase in Gd⁺ secondary ion counts concerning the reaction temperature. The Gd⁺ secondary ion fragment, expected at a mass-to-charge ratio (m/Q) of 158, is used as a marker. The sample treated at 55°C exhibited the lowest Gd⁺ ion counts (196,128), while the sample treated at 100°C showed the highest Gd⁺ ion counts (366,552). This finding further validates the newly adopted Raman analytic technique for evaluating the degree of chemical functionalization. It suggests that increased polyphenylene-like structures resulting from higher-temperature reflux conditions promote the successful non-covalent attachment of the Gd³⁺ metal ion complex to the nanotube surface. It's worth noting that although Boehm titration revealed more carboxylic groups on the CNTs treated at 55°C compared to those treated at 100°C, the Gd⁺ ion concentration is low in the 55°C sample and high in the 100°C sample (Figure S1b). This discrepancy indicates that the attachment of the metal ion complex to CNTs is favored via carboxylic dimerization, specifically oxalic functional groups ($-\text{C}_2\text{H}_2\text{O}_4$) formed at higher reaction temperatures.

At higher temperatures, the formation of polyene and polyphenylene-like aromatic structures on the nanotube surface acts as active sites for successful metal ion

attachment. Oxalic functional groups are known to function as excellent chelating agents, forming stable complexes with metal ions. In the case of the samples, a high percentage of Gd_2O_3 was used for the 55°C sample, but it resulted in a poor attachment of the Gd^{3+} ion complex to the nanotube, as most of the Gd^{3+} ions were removed during the sample washing process. In contrast, the 100°C sample showed that most of the Gd^{3+} ion complex formed a stable non-covalent bond with the oxalic functional groups and remained intact on the nanotube surface even after multiple washing cycles. This highlights the role of oxalic functional groups and their ability to form stable complexes with metal ions, contributing to the success of the non-covalent attachment of the Gd^{3+} ion complex to carbon nanotubes.

In addition to the analysis described earlier, time-of-flight secondary ion mass spectrometry (ToF-SIMS) elemental mapping of Gd^+ secondary ions was conducted to examine the distribution of Gd^+ metal ions on the carbon nanotubes (CNTs), as depicted in Figure 2.5b. The elemental mapping reveals an even distribution of Gd^+ metal ions on the CNTs. Notably, the brightness contrast of Gd^+ ions increases as the temperature of oxidative treatment rises from 55°C to 100°C . This observation suggests that temperature-based oxidative conditions can be effectively employed to create controlled chemical functionalization across the nanotubes. It also indicates that varying the temperature during treatment can result in different percentages of magnetic metal ion complex loading on the nanotubes. Consequently, a highly correlated spin system with desirable magnetic properties can be developed, where the CNT serves as a bridging material to access nanoscopic quantum properties. This research holds promise for advancing the development of novel technologies in the field of spintronics and quantum applications.

2.3 Magnetism of Gd-DTPA MWCNTs

The analysis of the Raman data reveals that an increase in reaction temperature results in the disruption of the delocalized π -electron framework and an increase in polyene-like structures dominating over polyaromatic hydrocarbon (PAH)-like structures. This is significant because the magnetic properties of Multi-Walled Carbon Nanotubes

(MWNTs) are closely tied to the conduction π -electrons of the graphitic lattice. Therefore, any structural changes induced by chemical treatment are expected to influence the magnetic properties of MWNTs [109]. The diamagnetism of nanotubes, utilized to determine the interaction between inner tubes in MWNTs [110], is anisotropic [111] and has been linked to an Aharonov-Bohm effect [112]. Residual catalysts such as Fe, Ni, or Co are known to enhance the paramagnetic signature in opposition to the diamagnetic framework [113].

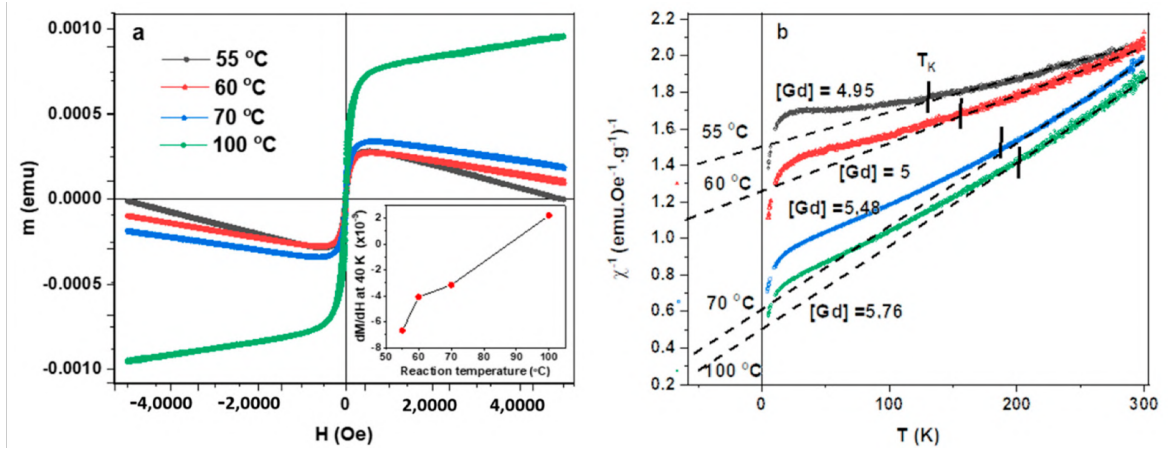


Figure 2.6 (a) The intrinsic diamagnetic response of the nanotubes diminishes with increasing temperature, indicating the disruption of the conduction π -electron network as more Gd-DTPA is attached to the nanotubes. This is evident through the increase in slope of the high-field data. Inset—The slope increases with rising reaction temperature at higher fields. (b) The temperature dependence of the magnetic susceptibility suggests an interactive magnetic system with dominant antiferromagnetic interaction. The Weiss temperature, extracted by fitting the Curie–Weiss law, exhibits a pronounced increase with higher reaction temperatures. The breakdown of linear behavior at low temperatures signifies a modification in spin-interactions due to the functionalization process and can be linked to the onset of a Kondo effect, with the Kondo temperature denoted by T_K .

To accurately assess the magnetic signatures of functionalized nanotubes, it is essential to evaluate both high-field and low-field properties. At higher fields, paramagnetic contributions are saturated, enabling the establishment of the magnetic properties of MWNTs. As shown in Figure 2.6a, distinct differences in magnetic moment with applied field are observed for samples prepared at different reaction temperatures, along with cohesive and remnant fields. The most notable observation is the change in the diamagnetic slope at higher fields. The transition from a negative (diamagnetic) to a positive slope indicates a shift to a dominant paramagnetic response in highly functionalized samples. As reaction temperature increases, structural degradation of

the graphitic lattice occurs, leading to a decrease in the π -electron framework and, subsequently, the diamagnetic character, aligning with Raman analysis findings. These features suggest a dilute or mixed magnetic material, with the interaction between delocalized electrons and the strong magnetic moment of Gd-DTPA ligands likely resulting from an *RKKY* interaction [28]. As structural disruption increases at higher temperatures, the material becomes more resistive, reducing the likelihood of interaction via conduction electrons and thereby decreasing the coercive field. This behavior, observed in magnetically decorated nanotubes, is indicative of a transition to a superparamagnetic state when interactions between magnetic centers are completely prevented [114].

However, our system does not exhibit the hallmark features of superparamagnetism [30] but rather resembles a strongly spin-interacting system. In Figure 2.6b, the temperature dependence of the magnetic moment for field-cooled measurements (FC) reveals no clear blocking temperature, ruling out a purely superparamagnetic scenario. The Curie–Weiss law, expressed as $\chi = C/(T - \theta)$, is consistent with a pronounced linear region, indicating the presence of antiferromagnetic coupling in the sample, with lower Weiss temperatures corresponding to higher degrees of functionalization. This suggests that surface functionalization affects the conduction electrons mediating magnetic interaction. As the reaction temperature increases, so does the degree of functionalization, suppressing the intrinsic diamagnetism of the nanotubes and increasing the overall paramagnetic character. The magnetic character is not solely dictated by the Gd-DTPA complex; instead, it results from the coupling between diamagnetic CNTs and the Gd complex. This deviation from the Curie–Weiss law at low temperatures is indicative of a highly correlated spin system and suggests the presence of the Kondo effect, with the point of deviation serving as an indication of the Kondo temperature [115], [116]. In Figure 2.6b, we determine Kondo onset temperatures (T_K) [116], [117] of 132, 155, 188, and 202 K with increasing Gd concentration, in agreement with the Raman deconvolution study. These findings shed light on how structural degradation and magnetic loading can lead to enhanced spin correlations in functionalized carbon systems, as demonstrated by the observation of the impurity Kondo effect [118]–[120]. Furthermore, these results are significant as they help explain the role of itinerant electrons in mediating the interaction between

spatially separated spin centers and may provide a mechanism for tuning the system from a superparamagnetic material to a highly correlated system with a definite spin texture. This is crucial for applications that require specific magnetic characteristics, such as NMR contrast agents relying on a superparamagnetic system and novel spintronic devices relying on highly correlated spin interactions [121]–[123].

2.3.1 Modification of Magnetic Properties of Functionalized MWNTs Loaded with Gd-DTPA

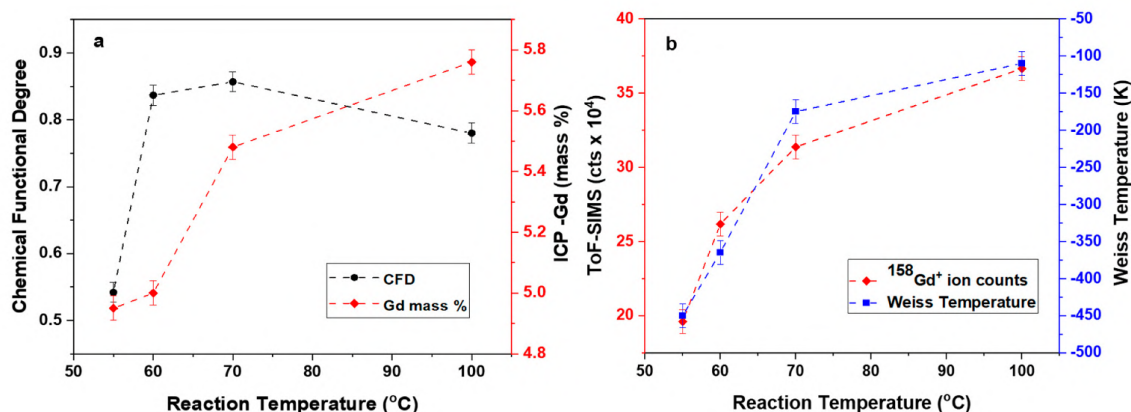


Figure 2.7 Controlling the magnetic properties of Multi-Walled Carbon Nanotubes (MWNTs) in conjunction with the Weiss temperature by varying the degree of functionalization and the corresponding loading percentage of magnetic molecules. The alteration in the oxidation reaction temperature of CNTs has a direct impact on (a) the chemical functionalization degree, (b) the loading percentage of magnetic molecules (Gd-DTPA) as determined by ICP-OES and ToF-SIMS counts, and the Weiss temperature.

A combination of Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-AES) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) is employed to validate and quantify the successful attachment of the Gd-containing chelate to the Carbon Nanotube (CNT) surface. According to ICP-AES, the weight percentage of loaded Gd increases from 4.95% to 5.8% (Figure 2.7a), corresponding to an elevated chemical functional degree. The Gd ion weight percentages align with the respective ^{158}Gd counts measured from ToF-SIMS. The integration of Raman spectroscopy and magnetic property analysis facilitates a direct assessment of modified Multi-Walled Carbon Nanotube (MWNT) properties resulting from chemical treatment

and magnetic impurity loading. Figure 2.7a,b demonstrates that secondary analyses from all measurements exhibit an increasing trend in the chemical functionalization degree, magnetic impurity loading percentage, and Weiss temperature concerning the heightened acid reaction temperature. This upward trend in Weiss temperature indicates a shift in magnetic ordering from antiferromagnetic to ferromagnetic with increased Gd^{3+} ion loading, achievable through an augmented MWNT chemical functionalization degree. A direct correlation is observed between the CNT Chemical Functionalization Degree (CFD) and the Weiss temperature in the CNT(Gd-DTPA) hybrid complex. In future theoretical analyses, efforts will be directed toward quantifying the relationship between CFD and Weiss temperature.

2.4 Conclusion

We have demonstrated that the oxidative functionalization of Multi-Walled Carbon Nanotubes (MWNTs) under mild conditions offers a refined and controllable approach to tailor the physical properties of the MWNTs. Our study also highlights the significance of recent advancements in interpreting the deconvoluted Raman spectrum of MWNTs in determining the extent of functional group attachment to the MWNTs. Employing the conventional seven-peak deconvolution scheme of the G and D band regions, we establish that the ratio of minor bands $(S + G_L)/(D_L + D_R + G_R)$, associated with two distinct types of Raman active structural components (chain-like polyacetylene/phenylene-type or PAH-type clusters), serves as a novel and valuable metric for assessing structural modifications during oxidative functionalization. This is crucial, as previous studies have indicated that the well-known Koenig–Tuinstra relation, suitable for other nanostructured carbon systems, does not adequately explain the Raman spectra of MWNTs.

Furthermore, we establish a connection between the functionalization of the tube surface, the subsequent attachment of magnetic Gd-DTPA, and the resulting changes in the magnetic character of the system. The magnetic properties are intricately linked to the concentration of Gd-DTPA and the quality of the nanotube lattice (and hence the degree of functionalization). As the use of MWNTs in various applications requires

the functionalization of the outer walls, it becomes essential to ensure a controlled functionalization process and systematically analyze such modifications. In this study, we propose that the combination of SQUID magnetometry and Raman spectroscopy analysis provides a sensitive and systematic approach to engineering a highly correlated spin-interactive system with MWNTs as a host material, holding potential applications in spintronics and quantum information processing.

Supplementary Information

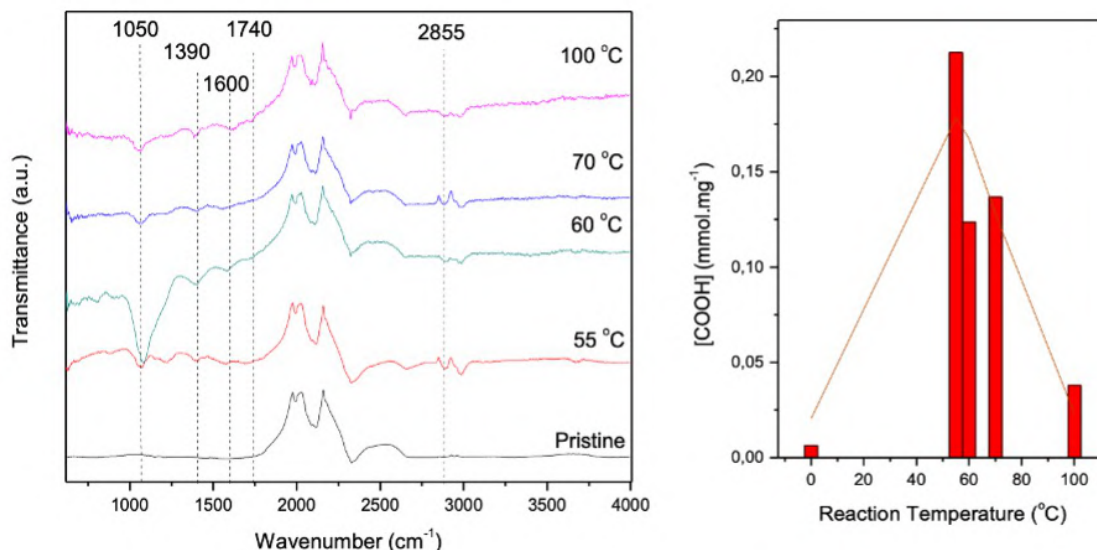


Figure 2.8 *CNT Functionalisation analysis: a) FT-IR spectra of MWNTs treated at varied oxidative temperatures showing characteristic -COOH peak at $\sim 1700\text{ cm}^{-1}$ wavenumber . b) Boehm Titration results of carboxylic groups present on acid treated carbon nanotubes with varied temperature conditions*

Fourier-transform infrared spectroscopy (FT-IR) is a complementary technique in evaluating the functional groups (-COOH) on the nanotube. FT-IR spectra of pristine and functionalized MWNTs treated at various temperatures (55 °C, 60 °C, 70 °C, and 100 °C) were collected and find the appearance of additional peak at 1720 cm^{-1} in the absorbance spectrum associated with C=O stretching frequency [124] for the functionalized MWNTs (figure 2.8 a). This additional peak can be attributed to carboxyl groups (-COOH) formed during the oxidation of MWNTs.

Further to quantify the number of carboxyl groups present on the nanotube, Boehm

titration was performed on the functionalized MWNTs. The titration results reveal that high number of carboxylic group present in the CNT sample treated at 55 °C (0.237 mmol COOH/mg CNT) and low number of carboxylic groups in the sample treated at 100 °C (0.038 mmol COOH/mg CNT). However, from the literature it is envisioned that acid treatment at higher temperatures would result -COOH dimer formation ($-C_2H_2O_4$ - Oxalic functional groups)[125].

Figure 2.9 provides information on the shift of G peak position in the MWNTs treated with functionalized conditions temperature and time respectively, excited with 514.5 nm wavelength line source. G peak position has shifted to higher wave number for both the functionalization conditions used in this study. It's well established in the literature that the G peak shift to higher frequencies in the case of p-type doping [126] and shifts to lower frequencies in the case of n-type doping [127]. During the creation of oxygen functional groups an π -electron transfer from the MWNT to the oxygen atoms happens and this in turn can influence the G band shift towards higher frequencies [128]. In our study we have noticed that MWNTs treated with varied temperatures showed G band position at higher frequencies (1595 cm^{-1}) than that of MWNTs treated with extended oxidation times (1589 cm^{-1}). This further supports our new CFD analysis that more oxygen functional groups are formed on the CNTs treated with higher temperatures and this can be used to add more Gd ions on to the nanotube surface.

By comparing the results of SQUID magnetometry for the various samples we are able to establish the origin and type of magnetic interaction. As can be seen in figure 2.10b, the pristine MWNTs show a very small paramagnetic response this has been observed before and is attributed to ferromagnetic particles remaining from synthesis. The effect of these particles are however small when compared to the magnetic response of the Gd functionalized nanotubes. In this study the molar susceptibility was used along with the Curie-Weiss law to determine the properties such as the Curie constant and Weiss temperature presented in the paper. This was done to allow for calculation of the effective moment which requires knowledge of molar concentration of the magnetic species. Figure 2.10(a) , the Gd-DTPA complex clearly

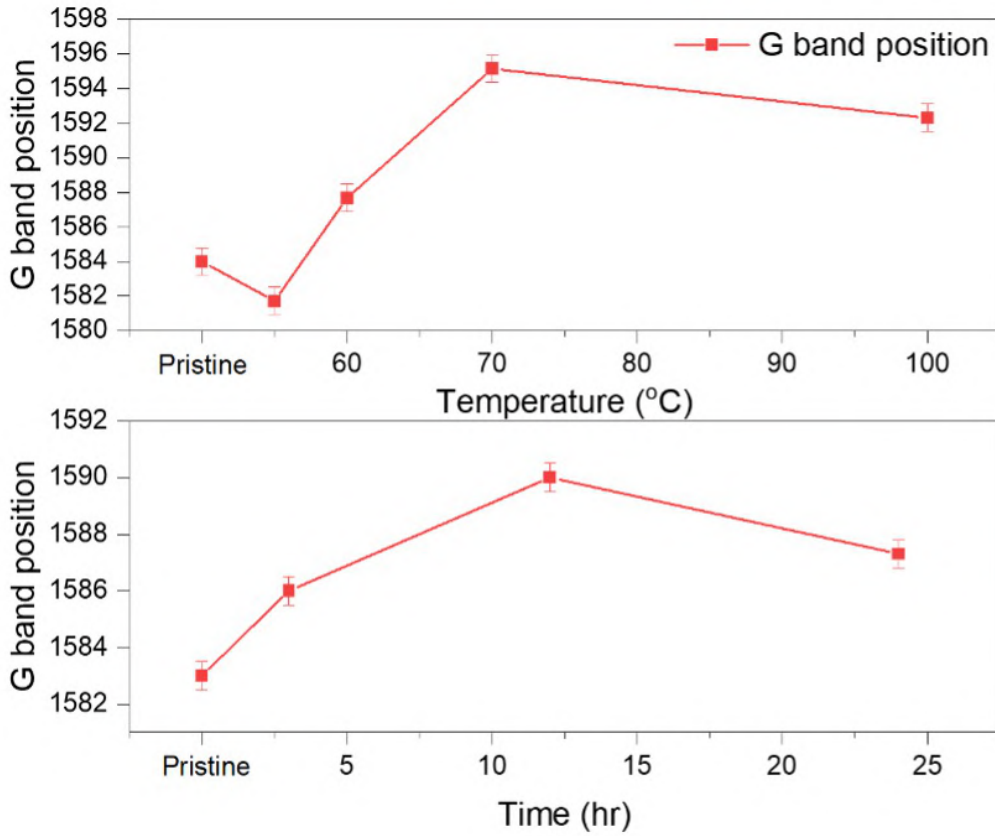


Figure 2.9 Change in G band position with respect to a) extended oxidation times and b) varied temperatures.

showed paramagnetic susceptibility. The effective moment calculated from the inverse susceptibility of the Gd-DTPA was found to be 8.7 μ_B which is roughly 10% larger than that of the bare Gd³⁺ ion theoretical value [129]. But smaller than the typical experimental values. Modification of the Gd effective moment, both enhancement and reduction, has been observed in Gd-carbon systems and is generally attributed to correlation effects [130] between Gd ion and carbon lattice or molecule. The Increase in moment here indicates a ferromagnetic coupling between Gd and DTPA molecule [130]–[133]. The Gd-DTPA (Figure 2.10 a) which is paramagnetic differs significantly from the functionalized Gd-DTP-MWNT complex as presented in the paper, this is a strong indication that the resultant interaction observed is due to MWNT-Gd correlations and not dominated exclusively by the Gd-DTPA. This does present some difficulty in determining the effective moment of the respective samples as the susceptibility is presented in terms of number of moles of only the Gd found in each sample. The concentration was determined from the elemental analysis. This

means, as stated in the manuscript, that the effective moment calculated in this way will lead to an over estimation as it does not take into account the carbon nanotube contribution.

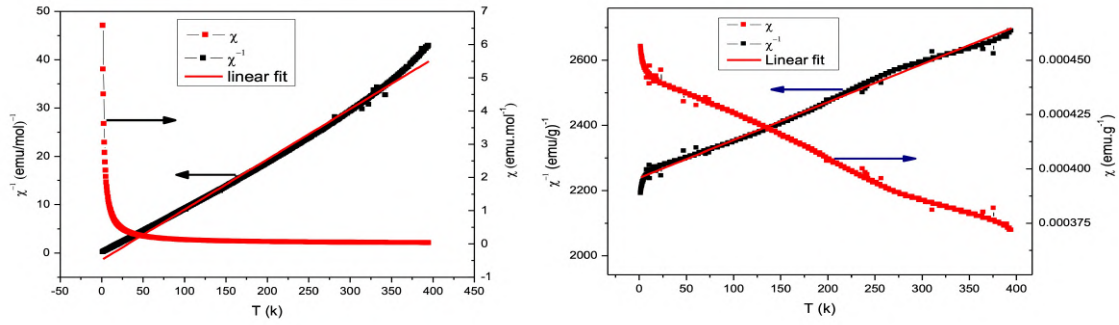


Figure 2.10 The plot of temperature dependence on susceptibility and inverse susceptibility for a) Gd-DTPA molecular complex and b) pristine MWNTs.

Chapter 3

Magnetism of LnEDTA-CNT Molecular Hybrids

3.1 Magnetic bistability

Magnetic bistability is a distinctive magnetic property observed in low-dimensional materials, particularly in single molecule magnets (SMMs). In these materials, the spin state can exist in two distinct configurations, showcasing the ability of these molecules to maintain two stable magnetic states. The two stable magnetic states exhibited by single molecule magnets (SMMs) can be effectively utilized for information storage in binary units of 0 and 1. However, this magnetic bistability characteristic, typically observed in individual SMMs, tends to diminish in hybrid molecular systems. This occurs when SMMs interface with conducting surfaces, as the local environment influences the spin state through factors such as exchange interactions, dimensionality (resulting in a reduction of the anisotropy barrier), and chemical stability, impacting the coordination of the SMM complex. Recent research efforts have been directed towards addressing this challenge, specifically focusing on preserving magnetic bistability even after grafting SMMs onto conducting surfaces. This preservation is essential for enabling the integration of SMMs into electronic devices. Researchers aim to overcome the perturbing effects of the local environment, ensuring the stability of the magnetic states and facilitating the practical implementation of SMMs in electronic applications.

3.2 Slow Magnetic relaxation in SMMs

Magnetic bistability, extensively explored in magnetic complexes known as single-molecule magnets (SMMs), has been observed and studied in various crystal structures. This behavior stems from distinct molecular attributes, particularly a high-spin ground state and a easy axis of magnetization for the individual molecules organized within the crystal. When attempting to develop information storage devices utilizing single magnetic molecules, even under extremely low temperatures, a notable challenge involves confirming the presence of magnetic bistability at the individual molecule level.

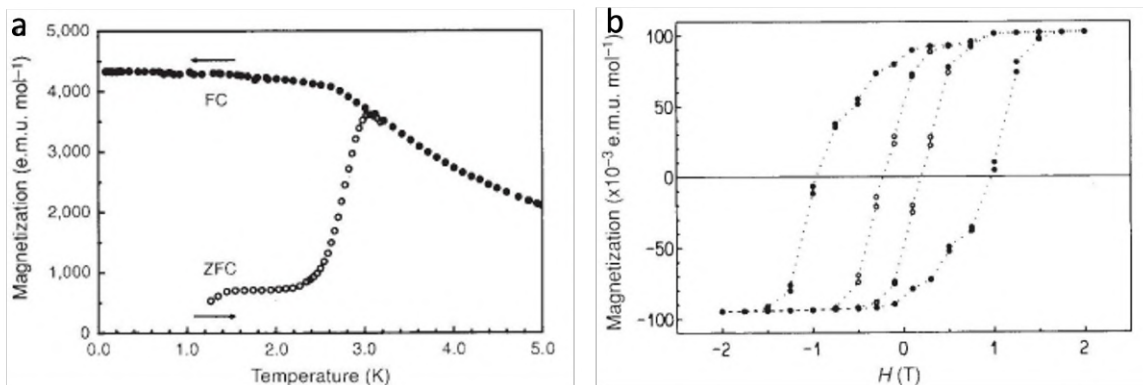


Figure 3.1 *Magnetic Bistability in Mn₁₂-ac complex. a: Temperature dependence of the magnetization of Mn₁₂ measured in zero field cooling (ZFC), and field cooling (FC) by applying an external field. b: Hysteresis loops measured at 2.2 K and 2.8 K showing magnetic bistability of Mn₁₂ metal ion cluster. adapted from [20]*

Early investigations focused on Mn₁₂ SMMs [20]. The single molecule magnet (SMM), known as a Mn₁₂Ac-complex [Mn₁₂O₁₂(OAc)₁₆(H₂O)₄], was discovered in the early 90s, with a blocking temperature (T_B) of 3.1 K (see Figure 3.1(a)) [20], [21]. When the molecular magnet's relaxation time is briefer than the experiment's timescale, it leads to the occurrence of open magnetic hysteresis. This arises because the molecules do not have sufficient time to relax as the magnetic field approaches zero, resulting in the persistence of a non-zero magnetization. This phenomenon is termed magnetic

bistability, stemming from the presence of two stable magnetization states at zero field (see Figure 3.1(b)). The significant zero-field splitting can be traced back to the single-ion anisotropy of the Jahn-Teller distorted manganese (III) ions. This Mn_{12} complex comprises a magnetic center formed by multiple exchange-coupled metal ions, coordinated by organic ligands. Specifically, eight Mn^{IV} ions with a spin of $s = 2$ exhibit antiferromagnetic coupling with four Mn^{III} ions having a spin of $s = 3/2$. This arrangement results in a substantial spin state of $S = 10$, generating a strong uniaxial magnetic anisotropy.

Later a detailed study was done on this complex to understand the quantum tunneling of magnetization (QTM) at low temperatures [134]. Magnetic assessments were carried out on a singular crystal of the Mn_{12} complex across 12 different temperatures, ranging from 1.55 K to 3.2 K, utilizing applied magnetic fields of up to 5 T. An identifiable 'staircase' hysteresis loop manifested when the magnetic field direction opposed the magnetization, as illustrated in Figure 3.2(a). In the flat segments of the hysteresis loop, the times for magnetization relaxation significantly surpassed the measurement time window, estimated to be approximately 600 s. Conversely, in the steep regions, the relaxation times were comparable to the measurement time window. Plotting $\frac{\partial M}{\partial H}$ against H enables us to precisely determine the critical fields H_n , at which the relaxation times reach a minimum (see Figure 3.2(b)). Additionally, it allows us to define the width ΔH_n of the transitions from long to short relaxation times.

The primary objective in enhancing magnetic bistability is to establish a high magnetic anisotropy barrier when crafting a molecular magnet. The magnetic anisotropy can be described using the spin Hamiltonian: $H = DS_z^2$, where $D < 0$. This expression is often conceptualized as a double-well potential, as depicted in the figure 3.3. In scenarios where the sample is magnetized at low temperatures, indicating occupancy in only one of the two wells, the subsequent return to equilibrium, referred to as the demagnetization process, occurs by traversing the energy levels within that specific well. This process results in a relaxation time that experiences exponential growth at

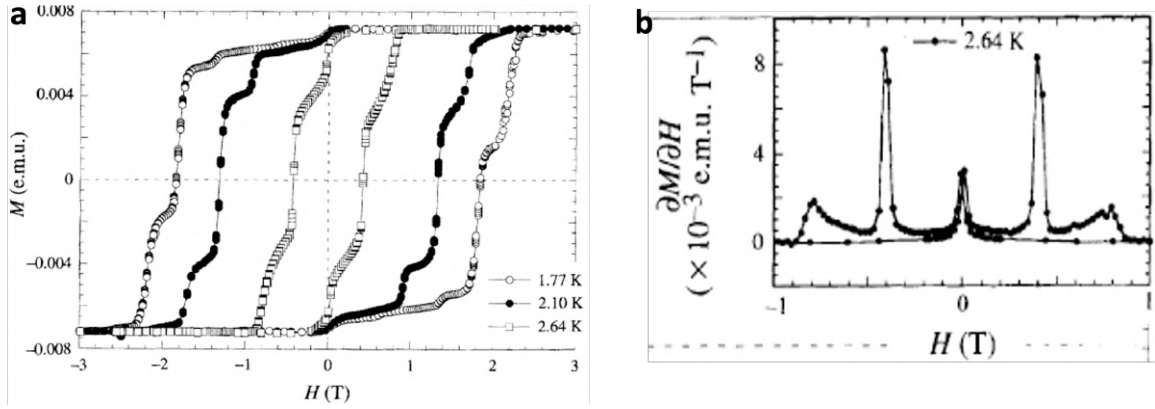


Figure 3.2 *Magnetic Bistability and derivative magnetisation. a: Magnetisation hysteresis loops of Mn_{12} single crystal showing quantum tunnelling of magnetization feature. b: Quantum Tunneling Magnetization associated with resonant energy levels of spin-up and spin-down units in the Mn_{12} crystal is observed through derivative magnetization as a function of field. adapted from [134]*

low temperatures, adhering to the Arrhenius law.

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{k_B T}\right) \quad (3.1)$$

where $\Delta E = DS^2$ represents the height of the barrier, while stands τ_0 for a pre-exponential factor primarily indicative of the effectiveness of spin-phonon coupling. Therefore creating a large spin ground state and a uniaxial co-ordination would effectively improve the magnetic bistability of the molecule. In this regard the evolution of Single-Molecule Magnets (SMMs) is an ongoing and dynamic process. Due to the intricate interplay between classical and quantum mechanical principles that govern SMM behavior, scientists in this field have consistently adapted their approaches to create optimal system (see Fig.3.4).

Initially, molecular magnetism research centered on large polynuclear clusters of transition metals, driven by the discovery of the Mn_{12} complex with traditional magnet-like properties. The goal was to achieve substantial energetic barriers for magnetic moment reversal by emphasizing the exponential dependence of the energy barrier (U) on the total spin of the complex. However, despite attaining high spin ground states in molecules like Mn_{19} , Mn_{25} , and Fe_{42} , there was limited improvement in Single-Molecule Magnet (SMM) behavior.

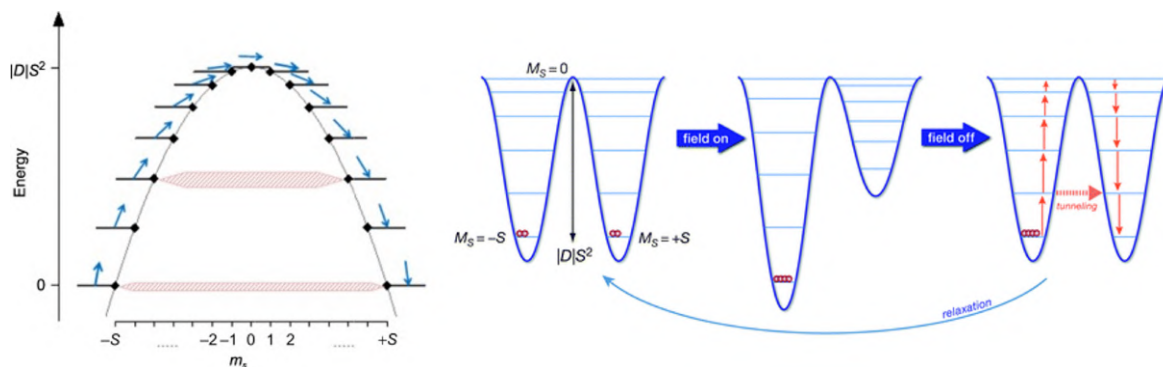


Figure 3.3 *Anisotropy barrier that magnetic ion must overcome to relax its magnetic orientation. b) Illustrative depiction outlining the magnetization and magnetic relaxation mechanisms in a single molecule magnet. adopted from*

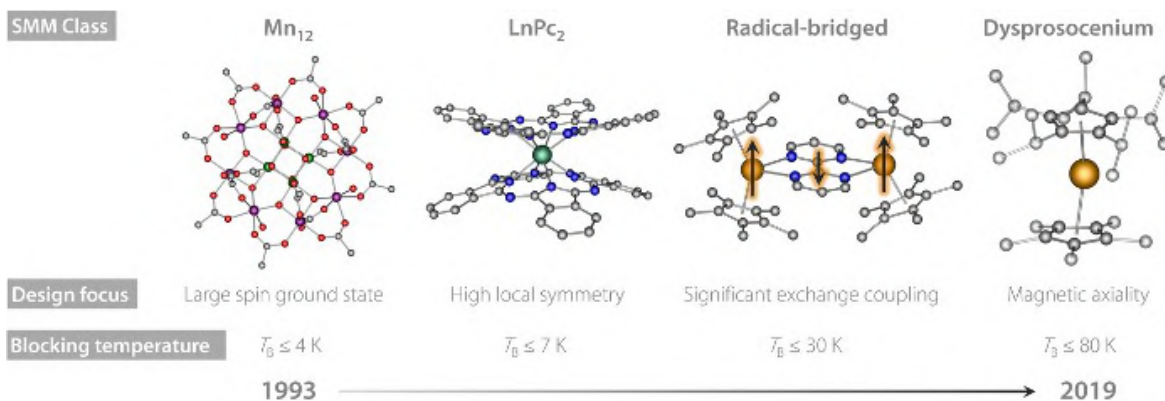


Figure 3.4 *Schematic illustration showing the progression in the design and advancement of high-performance SMMs. adapted from [25]*

A significant milestone was reached when Ishikawa and colleagues showed that a single lanthanide center in an $LnPc_2$ complex could function as a magnet at the single-molecule level, outperforming polynuclear clusters in terms of effective energy barrier (U_{eff}). This breakthrough led to a redirection of attention towards regulating the magnetic anisotropy of metal complexes. Lanthanide ions, known for their substantial orbital contribution to the ground state, emerged as optimal candidates for creating bistable magnetic ground states, which are essential for observing single molecule magnet (SMM)-type behavior (see Figure.3.4).

Unlike transition metals, lanthanides exhibited significant inherent magnetic anisotropy, leading to some of the highest blocking temperatures and energy barriers. This discovery highlighted the potential of single molecule magnets (SMMs) in applications such as molecular spintronics and quantum computing devices, marking a significant revolution in the field.

3.2.1 Slow magnetic relaxation in Ln-EDTA

The phenomenon of slow magnetic relaxation in Ln-EDTA (where Ln represents Gd, Tb, and Dy) molecules has been observed within the low-temperature range. The subsequent discussion delves into the dynamics of magnetic property alterations concerning the substitution of the central metal ion in Ln-EDTA molecules. The magnetization versus magnetic field (M vs. H) data below 7 K reveals a swift rise in magnetization at low magnetic fields, reaching a plateau of $6.77\mu_B$ at 1.8 K after a gradual increase) Fig.3.5. The plot depicting M vs. H/T for the diluted Gd-EDTA complex revealed that a saturation point was not attained, and the curves did not align on a single master curve (refer to Fig.S8 of [135]). This observation is typically associated with anisotropic behavior, indicating that the ionic anisotropy of Gd^{III} in this instance is notably stronger than in the crystalline sample. Additionally, investigations into the magnetization of the 1-D network of Eu-EDTA, Tb-EDTA, and Dy-EDTA have revealed a slower magnetic relaxation at lower temperatures. The direct current (dc) magnetic properties of the compounds Eu-EDTA, Tb-EDTA, and Dy-EDTA were examined under a 1000 Oe field within the temperature range of 1.8–300 K (see Fig.3.5b).

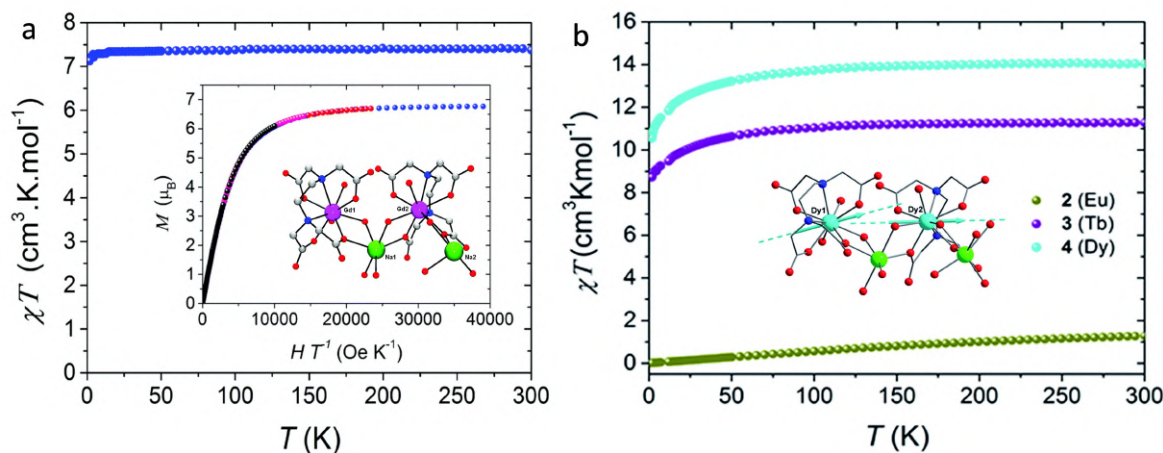


Figure 3.5 *Ln-EDTA molecule magnetisation. adapted from [135]*

The slow magnetic relaxation observed in Gd-EDTA is ascribed to spin-phonon transitions between different energy levels, both direct and Raman-type, occurring on each Gd site. The magnetic interactions within and between Gd sites mainly

arise from dipolar forces [135]. However their studies revealed dipolar coupling cannot be accounted the magnetic relaxation slowdown at temperatures as low as 1.8 K. Instead, the dipolar interaction contributes to accelerating magnetic relaxation on Gd sites. The absence of magnetic relaxation in zero dc field aligns with expectations for nearly isotropic magnetic sites, where fast quantum tunnelling of magnetization occurs. When a dc field of 0.45 T is applied, quantum tunnelling is significantly suppressed. Therefore, the slow magnetic relaxation is accounted for weaker spin-phonon coupling in the Gd-EDTA. Unlike other lanthanides, Gd complexes exhibit complex magnetization relaxation involving transitions between numerous levels, particularly at low temperatures. Simulation of the temperature dependence of relaxation time further highlights the unconventional nature of magnetization dynamics in Gd complexes.

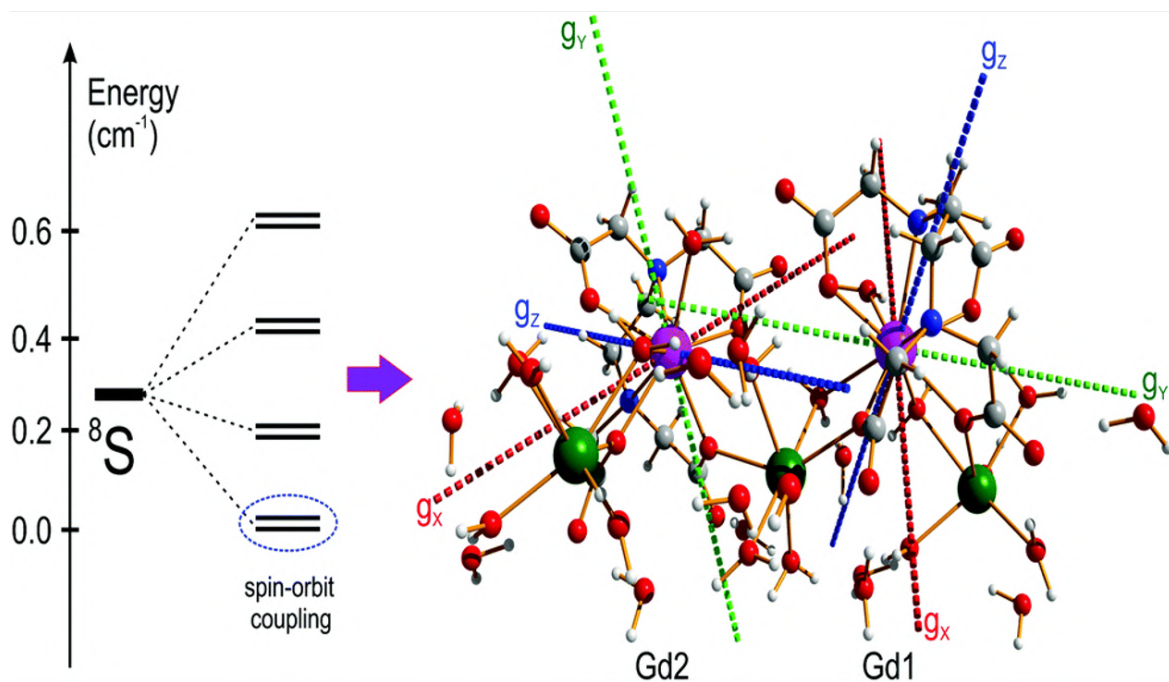


Figure 3.6 *Magnetic Anisotropy of Gd-EDTA* The magnetic orientation of the Kramers doublets on Gd sites in relation to the molecular frame is influenced by spin-orbit coupling on metal sites. It is important to observe that at temperatures exceeding the separation of the ground 8S term, the Gd^{III} ion exhibits magnetic isotropy. adapted from [135]

3.3 Magnetic Bistability in Adhered Surfaces

In order to leverage the quantum properties of individual SMMs, it is imperative to affix them onto conducting surfaces. This would facilitate the construction of molecular devices, allowing access to the quantum state through the conducting surface that connects the nanoworld. Nevertheless, when coupled with conducting surfaces, the pristine magnetic properties of Single Molecule Magnets (SMMs) undergo alterations or diminishment due to external environmental factors. Notably, no magnetic hysteresis was observed when these molecules were anchored on surfaces. This underscores the critical importance of retaining the magnetic bistability of SMMs absorbed on conducting surfaces to enable their utilization in quantum computation and memory storage devices. An additional crucial aspect involves exploring the interplay between electron transport and the magnetic characteristics of SMMs, potentially offering avenues for manipulating individual molecules [10], [136], [137]. Despite the presence of high-temperature single-molecule magnets (SMMs) [138], the magnetic characteristics of SMMs attached to surfaces are typically constrained by relaxation mechanisms related to the substrate, which are not well-understood in most cases.

In previous instances where a magnetic hysteresis opening resembling a butterfly shape was achieved in sub-monolayer LnPc_2 SMMs, the molecules were either adsorbed onto substrates with weak interactions, such as gold[139], graphite[140], [141], or graphene[142], [143], or molecular functionalization was employed to diminish interaction by creating spatial separation from the substrate. Therefore, the ability to access and manipulate the quantum state of a molecular spin system largely depends on how we align it with the easy axis of magnetization. This alignment is further influenced by the interactions of SMMs with the adsorbed surface. However, in the context of molecules, this configuration can be controlled through the intentional design of ligands. One of the most promising approaches to retain the magnetic bistability at the molecular level is the assembly of SMMs through a ligand on carbon nanotubes (CNTs).

3.3.1 Magnetic Bistability in SMM grafted carbon systems

In the field of electron transport, molecules play a role as pristine quantum dots formed through bottom-up techniques. SMMs as zero-dimensional structures with quantized energy levels. [144]. When establishing an interface between the molecule and metallic surfaces, an energy barrier emerges that affects the flow of electrons into and out of the molecule. The height of this energy barrier depends on the degree to which molecular orbitals blend with the wave functions of the charge reservoir. Three distinct coupling configurations are outlined:

Strongly Coupled: In this scenario, the energy barrier is minimal, facilitating electron delocalization between the molecule and leads. While the molecule readily accepts charge from reservoir electrons, its molecular orbitals undergo substantial hybridization, leading to a loss of distinctive features.

Weakly Coupled: Molecular states in this setting exhibit weak hybridization with those of the leads, resulting in a substantial energy barrier. Charging the molecule requires more energy from lead electrons, yet the molecule retains its characteristic features.

Intermediate Coupling: In this context, the molecule is effectively influenced by the leads but still preserves most of its distinctive traits. The coupling is neither overly strong nor weak, striking a balance between efficient charge transfer and the preservation of molecular characteristics.

The extensive literature on CNTs offers us multiple approaches for engineering and investigating interactions between SMMs and these extended conducting channels. The presence of magnetic spin can influence the flow of current within a 1D conductor in diverse ways, contingent upon the coupling facilitated by the binding ligand. In the weak-coupling regime, non-covalent binding proves suitable because the dipolar interactions of SMMs can alter localized charge density states, thereby creating

scattering centers that diminish the conductance of the device (see Fig. 3.7). Another approach involves influencing the charge flow of a one-dimensional CNT. Another alternate approach involves changes in the Zeeman energy, which influence the charge carriers of Carbon Nanotubes (CNTs) through the capacitive gating effect (see Fig.3.7).

A third interaction scheme involves utilizing discrete levels of the CNTs themselves by biasing and observing the corresponding effect on the magnetization of the SMM molecule (see Fig.3.7). This configuration device know as double-dot device, has enabled the detection of single or a few SMMs and the flipping of their magnetization. Understanding the operation of these devices is crucial, as it could pave the way for genuine control of spintronic devices and the underlying physical mechanisms.

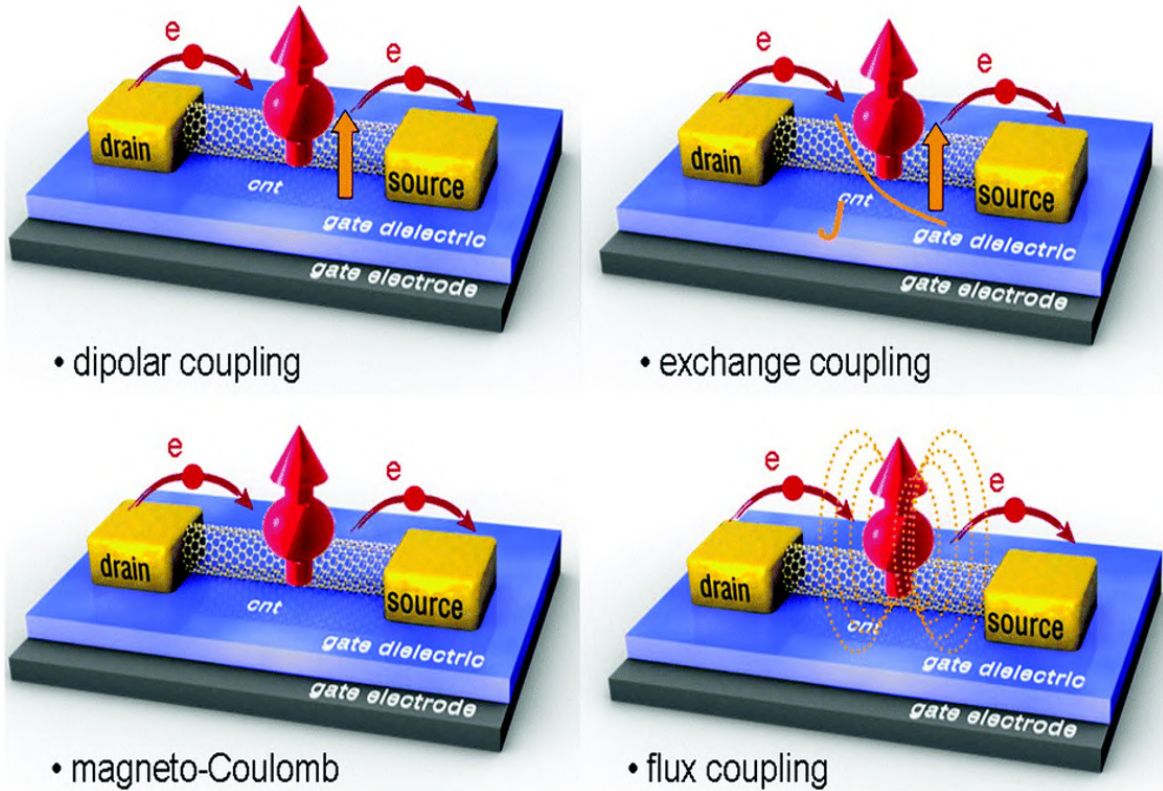


Figure 3.7 Various coupling mechanisms exist between the single molecule magnet (SMM) and the carbon nanotube (CNT). The quantum dot (QD), represented by the CNT here, may interact with the SMM through. a) dipolar interactions, b) exchange interactions, c) magneto-Coulomb interactions or d) via flux interactions. adapted from [144]

Currently, researchers are exploring the synthesis of hybrid molecular complexes by grafting SMMs onto carbon nanotubes (CNTs) to access quantized magnetic states through CNTs' electrical conduction properties. Carbon nanotubes have excellent

electronic properties with low spin-orbit coupling, hyperfine couplings, and quantized phonon modes. Their diamagnetic properties make them suitable for accessing the quantum features of SMMs without disturbing the magnetic properties of SMMs. This approach has been demonstrated with porphyrin dimeric rings grafted onto CNTs, showing well-preserved spin geometry and quantum coherence times. Various lanthanide ion-based molecules, such as Gd, Tb, and Dy grafted onto CNTs, are being explored for applications in molecular spintronics, spin valves, FET transistors, and quantum information processing.

These hybrid complexes are often referred to as "molecular double quantum dots" and offer advantages for building novel electronic devices by tailoring desired magnetic properties through specific magnetic molecule grafting onto CNTs. This approach introduces new energy scales, such as spin-spin exchange energy (J), spin-dependent correlations (Kondo peak at zero bias voltage), and spin-phonon coupling, which can be used for building novel spin-based molecular electronics. Recently, the introduction of spin degree of freedom through sp^3 defects on single-walled CNTs has shown long coherence times, making quantum control operations feasible through one-dimensional molecular platforms. While there has been progress in rare earth element-based SMMs, many aspects of this supramolecular complex system, such as their magnetic bistability upon attachment to CNTs, magnetic property tunability through magnetic anisotropy, and large ground state splitting through coordination chemistry, are yet to be extensively explored.

In recent studies, terbium stabilized with phthalocyanine anchored onto single-walled CNTs has demonstrated improved magnetic properties (see Fig. 3.9), and spin-valve devices made from this hybrid material have shown giant magnetoresistance at low temperatures. Researchers have also reported the Kondo effect with enhanced magnetic properties in the Gd-MWCNT system and explored how the magnetic properties can be tuned through chemical functionalization of multi-walled CNTs. Additionally, the relaxation of spin through spin-phonon coupling with the discrete phonon spectrum of CNTs has been investigated.

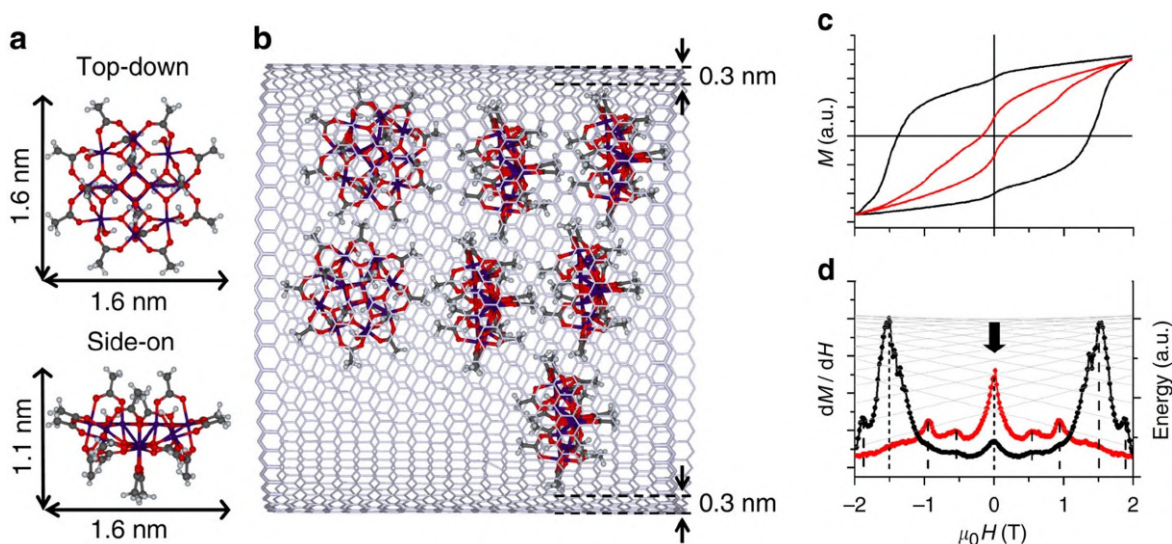


Figure 3.8 Diagram illustrating the innermost layer of a graphene-modified carbon nanotube (GMWNT) hosting $Mn_{12}Ac$ molecules. adapted from [145]

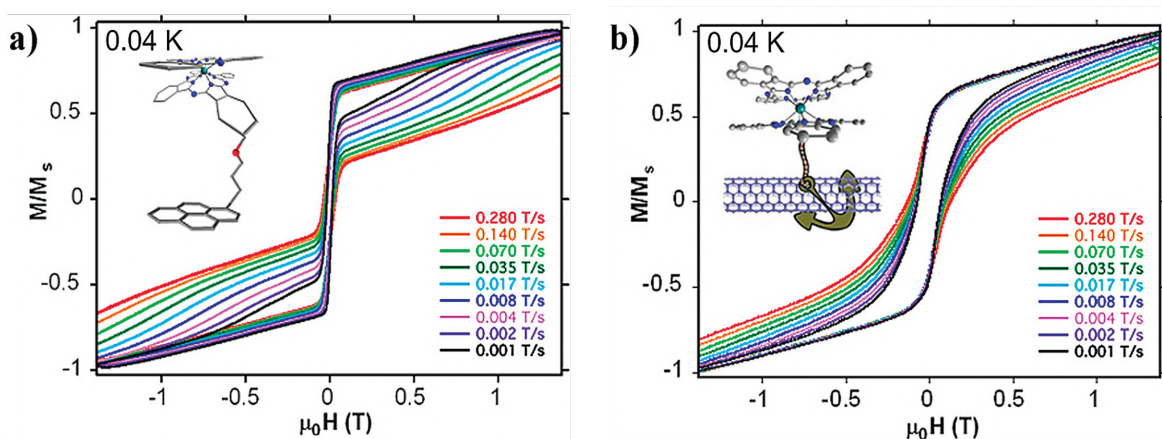


Figure 3.9 Comparison of the hysteresis cycles between $TbPC_2$ and $TbPC_2$ grafted CNT reveals that the hysteresis loops appear more open at zero field for $TbPC_2$ grafted CNT, attributed to reduced intermolecular interactions. adapted from [146]

3.4 Ln-EDTA complex (Ln = Gd³⁺, Tb³⁺, Dy³⁺)

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent commonly used to sequester metal ions for a wide range of industrial applications. EDTA has a strong affinity for metal ions, particularly those with an exophilic nature, such as lanthanide ions, making it an effective metal-trapping agent (see Fig.3.10). The magnetic

properties of Gd-EDTA chelate have been extensively studied, especially when used as a contrasting agent in Magnetic Resonance Imaging (MRI). It has been reported that this chelate exhibits unusually slow relaxation of magnetization at low temperatures.

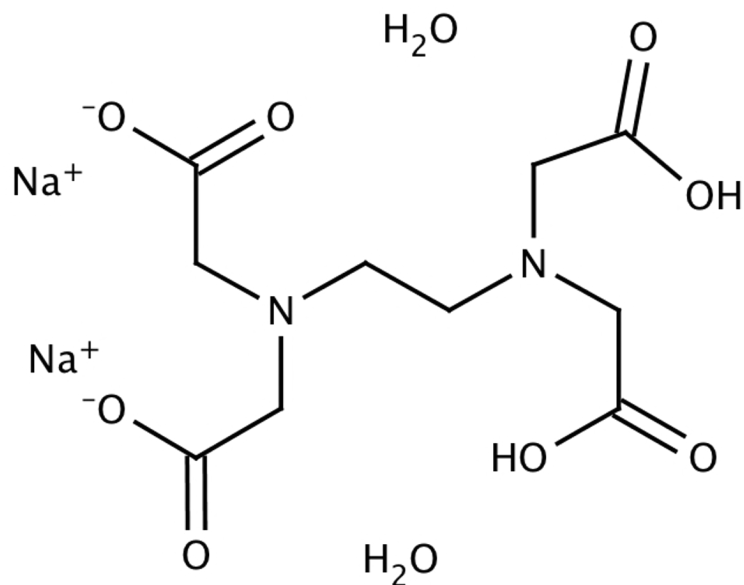


Figure 3.10 *EDTA Complex:*

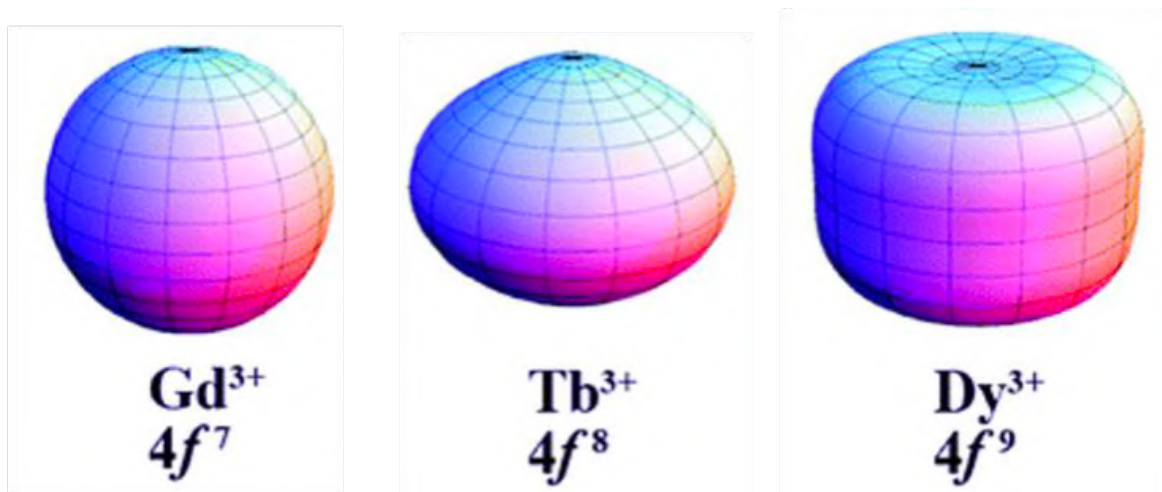


Figure 3.11 *4f element electron distribution*

3.4.1 Crystal Structure Description

The Ln-EDTA chelate is prepared using the solvothermal synthesis method, followed by a gradual evaporation of the solvent under ambient conditions to yield high-quality

single crystals. The crystal structure of the Ln-EDTA complexes depicted in Figure 3.12 (a and b) exhibits a one-dimensional chain structure in the chiral space group $Fdd2$, with consistent cell parameters a , b , and c . For detailed crystallographic information, please refer to Table 3.1.

In this structure, the Ln atom is coordinated by two EDTA molecules through both Ln-O bonds (involving atoms O1, O3, O5, and O7) and Ln-N bonds (involving atoms N1 and N2), as illustrated in Figure 3.12a. These bonds are formed through the carboxylate and amine groups of EDTA, respectively. Additionally, the Ln atom is further coordinated by two oxygen atoms, O10 and O11, which are bonded to sodium atoms Na3 and Na4, with O3 forming a bond with Na4. The Ln atom also has one coordinated water molecule, and the sodium atoms each have a water molecule bonded to them. Furthermore, Na4 is bonded to O9, and Na1 and Na3 are bonded to Na2. This connectivity pattern is observed within the asymmetric unit. Overall, these bonding arrangements result in a one-dimensional chain network within a three-dimensional packing arrangement, as depicted in Figure 3.14a and b.

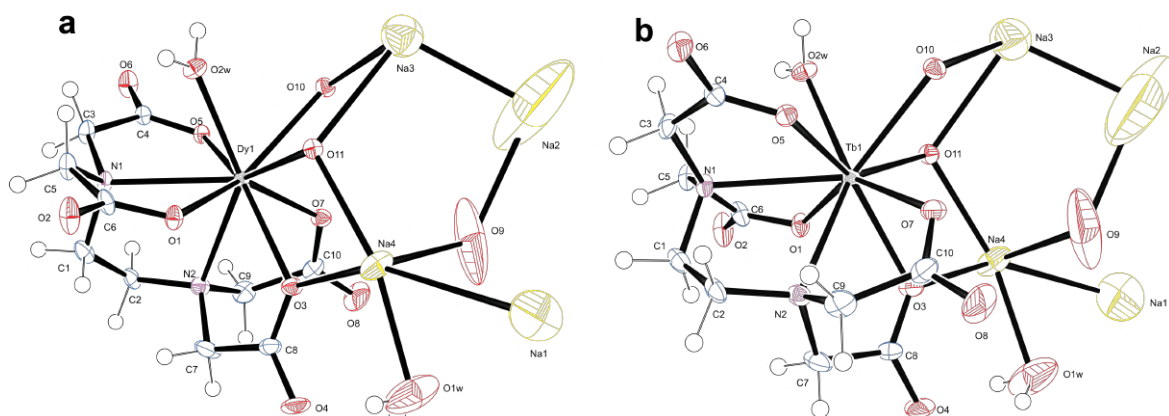


Figure 3.12 *Ln-EDTA crystal structure:*

The distances between lanthanide (Ln) atoms, both within the same molecule and between different molecules, are crucial factors influencing the magnetic relaxation dynamics. In this context, the intramolecular distances between Ln atoms are of particular significance. For instance, in this case, the Tb...Tb distance is measured at 6.071 Å. These intramolecular distances likely have a substantial impact on the interactions between the spin carriers within the same molecule.

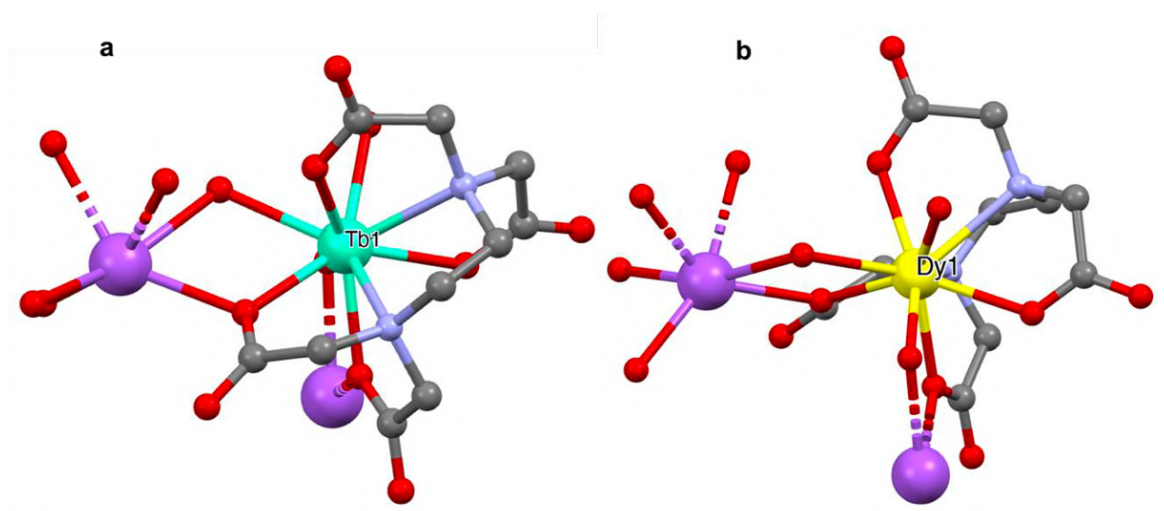


Figure 3.13 *Ln-EDTA crystal structure:*

In contrast, interactions between the chains of Ln atoms involve intermolecular distances. In this study, the Tb...Tb distance for intermolecular interactions is measured at 9.437 Å. As shown in Figure 3.20 and 3.21, these intermolecular distances play a role in determining the interactions between the Ln atoms across different molecules.

The packing diagram presented in Figure 3.14a-b illustrates that the Tb- and Dy-EDTA complexes form an overall three-dimensional (3-D) packaging arrangement. However, it is important to note that there can be variations and distortions within the individual Ln metal chain networks. These variations can significantly affect the overall magnetic anisotropy of the complexes, highlighting the intricate relationship between the molecular structure and magnetic properties.

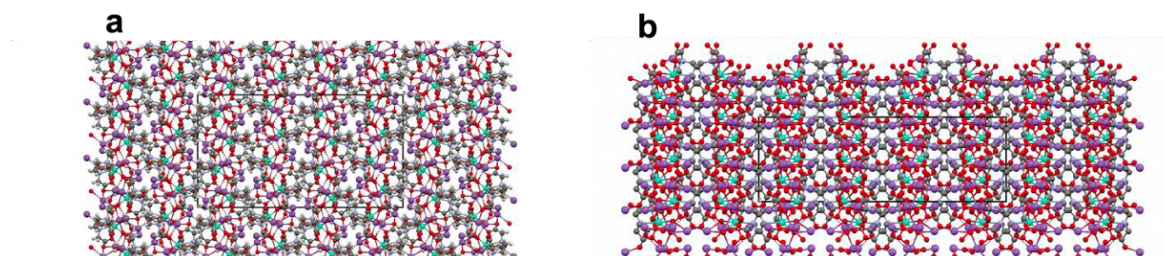


Figure 3.14 *Ln-EDTA Packing arrangement*

Table 3.1 *Crystal data for Tb-EDTA and Dy-EDTA magnetic molecules*

Parameter	Tb-EDTA	Dy-EDTA
Formula	$\text{C}_{10}\text{H}_{16}\text{TbN}_2\text{Na}_4\text{O}_{13}$	$\text{C}_{10}\text{H}_{16}\text{DyN}_2\text{Na}_4\text{O}_{13}$
Mr	623.13 g mol ⁻¹	626.71 g mol ⁻¹
Temperature/°C	−100	−100
Crystal size/mm	$0.684 \times 0.502 \times 0.487$	$0.549 \times 0.393 \times 0.188$
Crystal system	Orthorhombic	Orthorhombic
Space group (no.)	Fdd2	Fdd2
a/Å	19.3067 (11)	19.3107 (18)
b/Å	35.1670 (19)	35.216 (3)
c/Å	12.0522 (6)	12.0558 (11)
V/Å ³	8182.9 (8)	8198.6 (13)
Z	16	16
Dc/g cm ⁻³	2.028	2.031
μ (Mo-K α)/mm ⁻¹	3.608	3.796
Theta range/°	3.134 to 29.999	2.641 to 29.996
Total reflections	55,841	44,545
No. unique data	5936	5946
R (int)	0.0194	0.0194
No. data with I > 2 σ (I)	5930	5933
final R (I > 2 σ (I))	0.0230	0.0282
final wR2 (all data)	0.0591	0.0677
Restraints/parameters	1/274	1/274

3.5 Anchoring Ln-EDTA on CNTs

Prior to grafting Ln-based single-molecule magnets (SMMs), multi-walled carbon nanotubes (MWCNTs) underwent pretreatment in an acid mixture of concentrated sulfuric and nitric acid ($\text{H}_2\text{SO}_4/\text{HNO}_3$ —3:1 ratio). This step ensured the removal of catalytic metal particles (Fe) and the introduction of carboxylic groups onto the nanotube surface. Traditionally, two chemical routes were employed to attach SMMs

to the CNT surface: covalent bonding between functionalized CNTs and the molecular complex, and non-covalent attachment through electrostatic interactions and/or π - π stacking of the molecular complex on the CNTs. The non-covalent attachment was chosen to preserve the integrity and electronic character of the carbon nanotubes. However, studies have reported successful covalent attachment without hindering CNT electronic properties through careful acid treatment during CNT functionalization [147].

Additionally, the study aimed to explore surface interactions between CNTs and metal ions stabilized with EDTA ligand. A covalent attachment of Ln-EDTA molecules involved treating -COOH-terminated MWCNTs with Ln-EDTA molecules dissolved in deionized water under continuous magnetic stirring. Figure 3.15(a) illustrates the attachment of Ln^{3+} -EDTA molecules onto the CNTs, while Figures 3.15(b), (c), and (d) depict high-resolution transmission electron microscopy (HR-TEM) images of Gd^{3+} , Tb^{3+} , and Dy^{3+} ions attached to the nanotube surface, respectively.

While both covalent and non-covalent approaches can yield numerous nanoparticles per unit volume of CNT, a controlled number of SMM attachments is crucial for spintronic applications, resulting in a diluted magnetic system. The study utilized a careful acidic pre-treatment of MWCNTs for a shorter duration, producing carboxylic group-terminated MWCNTs without damaging structural integrity (see Figure 3.15b). This approach allowed the grafting of a controlled number of Ln-EDTA molecules onto the MWCNTs, as indicated by respective energy-dispersive X-ray spectroscopy (EDAX) profiles in Figure 3.15(e)–(g), showing Ln^{3+} ion concentration. The EDAX results revealed that 0.5 wt%, 0.8 wt%, and 1 wt% of Gd, Tb, and Dy, respectively, were doped onto the MWCNTs, enabling the study of the single-molecule magnetic behavior of the respective lanthanide molecules.

The report discusses the magnetic anisotropy and magnetization dynamics observed by replacing the central ion in the Ln-EDTA (lanthanide ethylenediaminetetraacetate) grafted multi-walled CNT molecular system. The chosen lanthanide ions include Gd, Tb, and Dy, as they exhibit isotropic and oblate-shaped electronic distribution systems, providing large magnetic anisotropies in strong axial ligand fields and enabling slow magnetic relaxation. These lanthanide EDTA complexes have shown

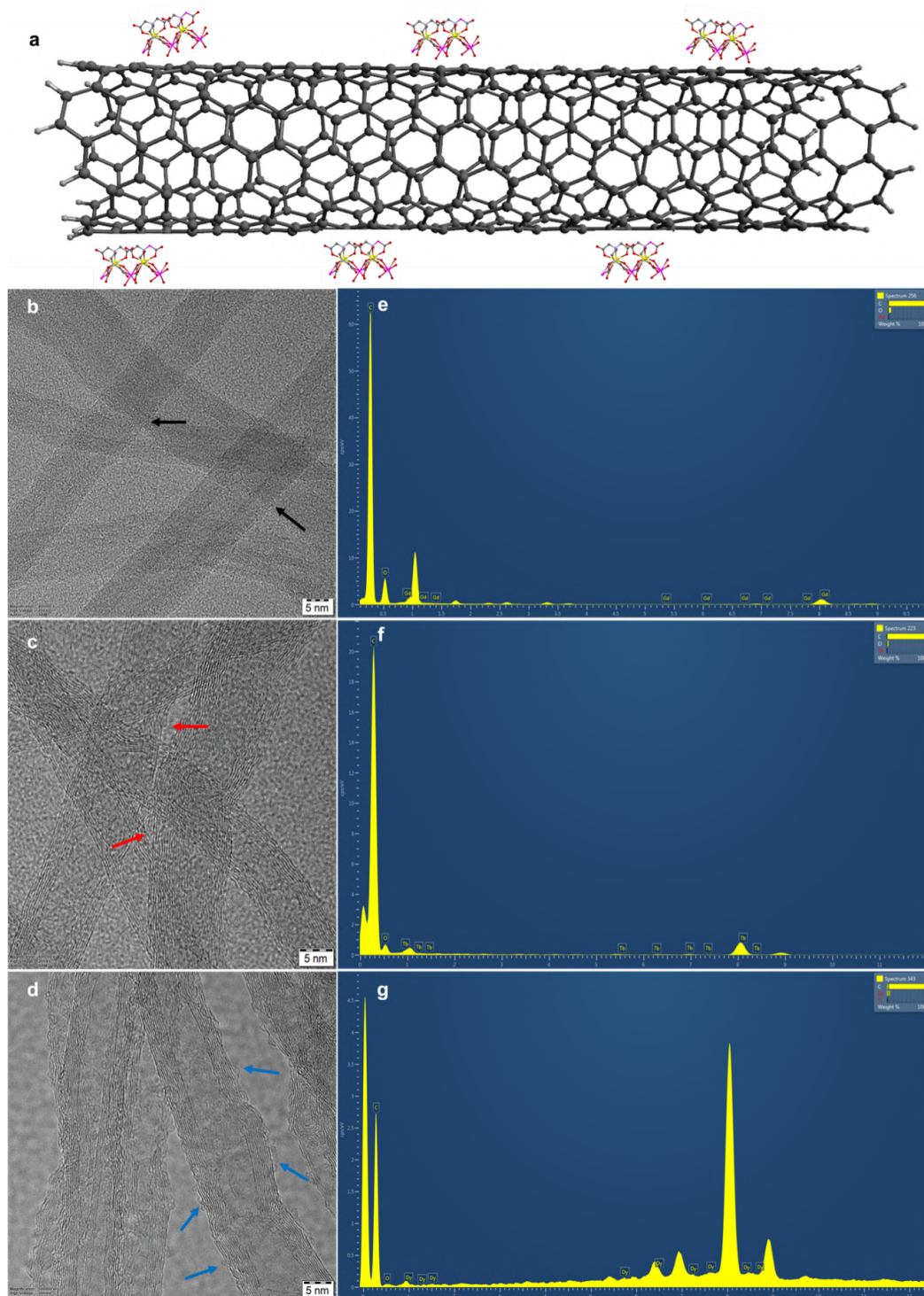


Figure 3.15 (a) Depiction of single-molecule magnets (SMMs) attached to carbon nanotubes. (b–d) HR-TEM images showcasing Gd-, Tb-, and Dy-EDTA magnetic molecules affixed onto multi-walled carbon nanotubes (MWCNTs); arrows are employed to emphasize the magnetic molecules grafted onto the nanotube. (e–g) Energy-dispersive X-ray spectroscopy (EDAX) graphs illustrating the concentration of respective Ln^{3+} magnetic ions in the functionalized MWCNT samples.

slow magnetic relaxation in one-dimensional (1D) networks. When these molecules are grafted onto conducting surfaces, they typically exhibit reduced or nullified magnetism due to screening from the surrounding environment. However, effective grafting onto multi-walled CNTs and arranging metal SMMs into a 1D network can significantly improve magnetic behavior through dipolar and superexchange interactions mediated via π electrons of CNTs. This study focuses on the magnetic bistability retained after grafting Gd, Tb, and Dy-EDTA as magnetic core ions onto CNTs. Structural characterization, including high-resolution transmission electron microscopy (HR-TEM) and single-crystal X-ray diffraction, has been conducted on all three Ln-EDTA complexes to understand the magneto-structural correlations and the origin of magnetic interactions.

Additionally, controlling the assembly of discrete one-dimensional lanthanide (Ln) complexes on carbon nanotubes (CNTs) offers significant advantages for the development of molecular magnetic materials. Inspired by these considerations, researchers have synthesized Ln-EDTA chelates, with Ln representing Gd, Tb, and Dy, and have grafted them onto multi-walled carbon nanotubes (MWCNTs) through a one-step chemical process. Single crystal X-ray diffraction measurements have been performed to understand the molecular structure and establish correlations between the magnetic properties of the resulting Ln³⁺-MWCNTs, as determined from DC-VSM (Direct Current Vibrating Sample Magnetometry) measurements. This research aims to explore the relationship between the molecular structure and magnetic behavior of these Ln³⁺-MWCNT complexes.

3.6 Magnetism of LnEDTA-MWNT system

Temperature-dependent direct current (dc) magnetic susceptibility measurements were conducted in the temperature range of 2 K–300 K with an applied dc field of 200 Oe to investigate the static magnetic behavior of Ln-EDTA grafted multi-walled carbon nanotubes (MWCNTs). Zero-field cooled (ZFC) magnetic measurements

revealed a one-dimensional hybrid molecular system with high magnetic anisotropies (see Figure 3.16a and Figure 3.17a,b).

The molar magnetic susceptibility (χ_m) of the 1-molecular system (Figure 3.16a) exhibited a gradual decrease in the temperature range from 300 K to 70(4) K, followed by a transition to negative values of χ_m below 70 K, reaching 2 K. This behavior indicated a quasi-antiferromagnetic interaction between the unpaired spins of Gd^{3+} and the conduction electrons of the CNTs. In contrast, the 3-molecular system (Figure 3.16b) displayed a linear increase in χ_m with temperature from 300 K to 20(3) K, followed by a sharp upturn as the temperature decreased to 2 K. Meanwhile, the 2-molecular system (Figure 3.16a) maintained a constant χ_m from room temperature to 40(3) K, with a slight downturn to 2 K upon further temperature reduction.

The low-temperature declines in χ_m for both the 1- and 2-molecular systems may be attributed to various factors, including anti-ferromagnetic ordering, Kondo screening of itinerant conduction electrons, and thermal depopulation of the Stark sublevels. The replacement of central metal ions in the Ln-MWCNT hybrid molecular system led to changes in bonding configurations and subsequently altered magnetic properties. The substantial magnetic anisotropies originated from exchange interactions between the metal ion and the π -electronic systems of the MWCNTs. The local spins (molecular magnets) in proximity to the itinerant conduction electrons developed either ferromagnetic or anti-ferromagnetic ordering through a range of exchange interactions, including Coulomb, spin-exchange[148], and weak intra- or inter-molecular interactions[149]. The competition between these interactions was mediated by the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, with the effective RKKY exchange interaction (J_{RKKY}) determining the magnetic ordering in the one-dimensional molecular system.

To gain further insights into the magnetic behavior of these molecular systems, the inverse susceptibility as a function of temperature (χ^{-1} vs T) was examined (refer to Figure 3.16b and Figure 3.17a,b). An intriguing magnetic reversal feature

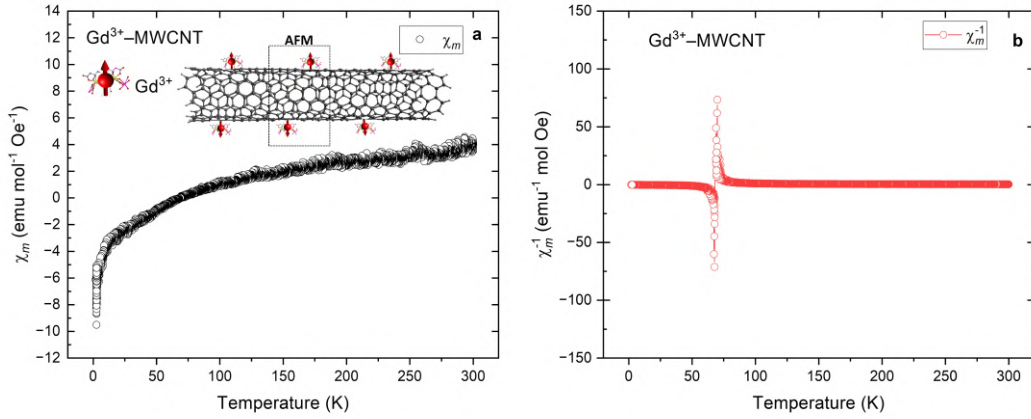


Figure 3.16 (a) The molar magnetization of the Gd-Multi-Walled Carbon Nanotube (MWCNT) hybrid molecular system exhibits negative susceptibility at low temperatures (< 70 K). (b) The Gd-MWCNT molecular system displays a noteworthy magnetic phase change, as evidenced by a crossover feature from positive to negative values in inverse susceptibility (χ^{-1}) at a temperature $T \approx 70 \pm 4$ K.

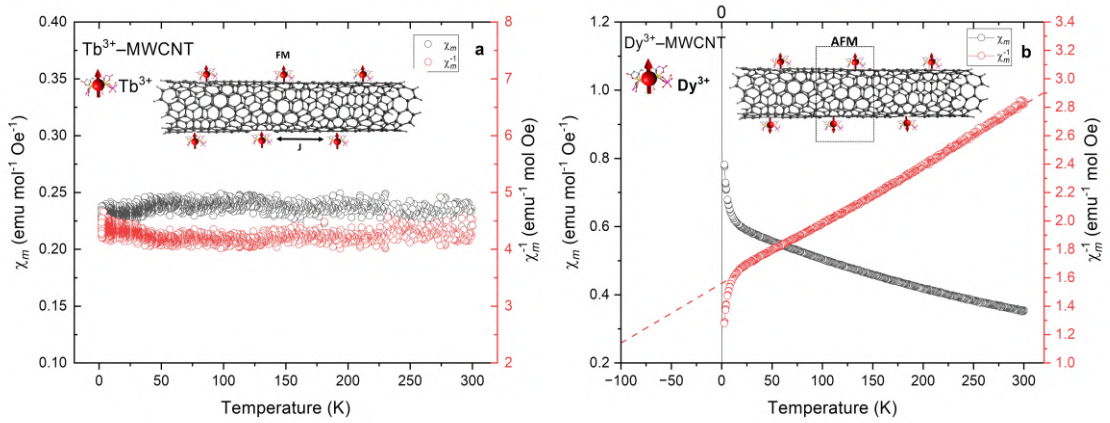


Figure 3.17 Molar magnetic susceptibilities at Zero Field Cooling (ZFC) of Carbon Nanotube (CNT) molecular systems **2** and **3** are presented: (a) χ^{-1} vs. T plot of Tb^{3+} -MWCNT, revealing a quasi-ferromagnetic behavior. (b) Dy^{3+} -MWCNT supramolecular system exhibiting an anti-ferromagnetic ordering as the temperature is decreased.

is evident for the 1-molecular system, indicating a magnetic phase transition from diamagnetic to quasi-anti-ferromagnetic behavior around the transition temperature $T \cong 70 \pm 4$ K. Notably, χ^{-1} undergoes a crossover from positive to negative magnetic moments as the temperature decreases. A similar observation of magnetization reversal was previously reported in rare-earth ion-modified carbon nanotubes[150]. The plausible explanation for this phenomenon lies in the competition and balance

between thermal activation relaxation and macroscopic quantum tunneling. As the temperature decreases, thermally activated relaxation slows down, and macroscopic quantum tunneling-based relaxation becomes predominant[151]. Additionally, the shape anisotropy of CNTs (length/diameter ratio) influences the interactions between the grafted magnetic ions. Given the tubular geometry of CNTs, shape anisotropy can impact magnetization reversal through coherent rotations, transverse rotation of unpaired electron spins, and the nucleation and propagation of vortex domain walls, all influencing spin rotations[152], [153].

The inverse magnetic susceptibility (χ^{-1} vs T) of the 2-molecular system remains constant up to 35 ± 2 K, followed by a subtle increase in χ^{-1} with decreasing temperature, indicative of typical quasi-ferromagnetic behavior. Thus, the Tb-MWCNT system undergoes a symmetry-breaking transition from a disordered to a magnetically ordered state. At higher temperatures, thermal fluctuations are relatively stronger than the magnetic ion (local spin) interactions. However, upon lowering the temperature, at around $T \cong 35 \pm 2$ K, the interaction between neighboring ions strengthens, leading to the development of magnetic ordering. In contrast, the 3-molecular system exhibits a linear decreasing trend in χ^{-1} vs T and undergoes a sharp decrement in χ^{-1} at $20 \pm$ K upon lowering the temperature, characteristic of anti-ferromagnetic ordering. Here, extensive screening of electrons from a diamagnetic carbon nanotube results in a net reduced magnetic moment, thus developing an effective anti-ferromagnetic ordering. A Curie-Weiss law fitting is performed for the 3-molecular system to calculate the effective magnetic moment using the equation:

$$\chi_M = \frac{C}{T - \theta} \quad (3.2)$$

The Weiss constant (θ) and Curie constant (C) are found to be -150 ± 4 K. It is noteworthy that χ^{-1} vs T for both the 1- and 2-molecular systems did not fit well with the Curie-Weiss law, likely due to factors such as low one-dimensionality and core diamagnetism from the CNTs.

3.7 Magnetic bistability of Ln-EDTA grafted CNT molecular system

Figures 3.18a, c, and e present isotherm plots illustrating the variation of magnetization with applied magnetic field (M vs. H) for the Gd^{3+} -, Tb^{3+} -, and Dy^{3+} -MWCNT molecular systems, respectively. Magnetization hysteresis measurements were conducted over the temperature range of 2–300 K. Interestingly, all three molecular systems exhibited characteristic "S"-shaped hysteresis with an open loop at zero field, indicating a slow magnetic relaxation. This hysteresis loop and the area enclosed within it increased as the temperature decreased to 2 K, suggesting the presence of a quantum-tunneling mechanism at low temperatures, a typical behavior of single-molecule magnets (SMMs).

Table 3.2 provides the values of coercivity (H_c), remnant magnetization (M_r), and saturation magnetization (M_s) for each molecular system at temperatures 2 K and 300 K. Notably, significant remnant magnetization and coercive field were observed at 2 K for all three molecular systems, indicating the retention of magnetic bistability post-grafting onto MWCNTs. Magnetic bistability is a crucial characteristic of SMMs and depends on the ground state spin (S) and zero-field splitting parameter (D) with a negative value. Superexchange interactions between magnetic ions, combined with magnetic anisotropy, often result in a large energy barrier for magnetization reversal between the two magnetically polarized states (negative and positive moment). The slow relaxation in magnetization, stemming from the formation of this large energy barrier, can be exploited for high-density data storage applications. Notably, in our study, all three compounds exhibited a hysteresis loop at low temperatures, with the **2** and **3** molecular hybrids displaying particularly large hysteresis loops, respectively (see Table 3.2).

To further assess the hysteresis loops observed in the Ln^{3+} ion-doped MWCNTs, the derivative of magnetization with respect to field (dM/dH) for all three molecular

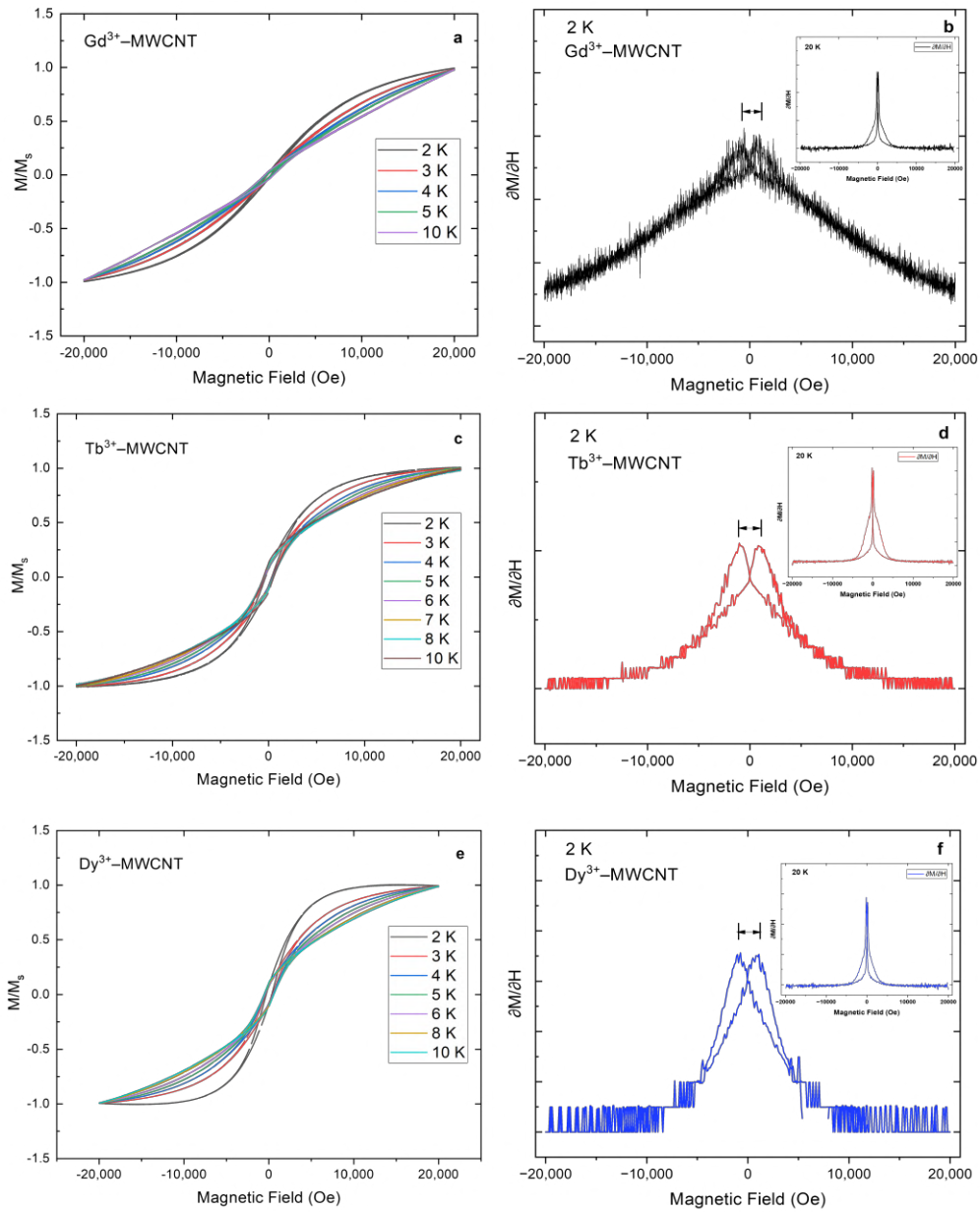


Figure 3.18 The field dependence of normalized magnetization (M/M_s vs. H) is depicted for Ln^{3+} ($\text{Ln} = \text{Gd}$ (a), Tb (c), Dy (e)) -grafted Multi-Walled Carbon Nanotube (MWCNT) hybrid molecular systems, illustrating characteristic "S"-shaped hysteresis loops. To further understand their behavior, the respective dM/dH vs. H plots are provided ($\text{Ln} = \text{Gd}$ (b), Tb (d), Dy (f)).

hybrids was analyzed (refer to Figure 3.18b–f). Initially, the field is ramped to 20 k Oe, where all the doped molecules' magnetic moments align parallel to the external field, achieving magnetization saturation. When the field is subsequently swept back to zero from 20 k Oe, the magnetization should ideally be zero if there are equal

Table 3.2 *Coercivity (H_c), remnant magnetization (M_r), saturation magnetization (M_s) of the Ln^{3+} -MWCNT ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$) molecular system at 2 K and 300 K.*

Molecular System	$H_c(2 \text{ K})$	$H_c(300 \text{ K})$	$M_r(2 \text{ K})$	$M_r(300 \text{ K})$	$M_s(2 \text{ K})$	$M_s(300 \text{ K})$
Gd^{3+} -MWCNT	250	145	0.026	0.010	1.307	0.022
Tb^{3+} -MWCNT	320	58	0.073	0.012	0.44	0.054
Dy^{3+} -MWCNT	322	65	0.084	0.011	0.27	0.025

numbers of "spin up" and "spin down" molecules. However, in all three MWCNT hybrid molecular systems, step-like features in the hysteresis are observed at 600 Oe for **1**, 1040 Oe for **2**, and 1090 Oe for **3**, respectively, on both sides (positive and negative) of the applied field at 2 K. This indicates the presence of an energy barrier for the molecules to reverse magnetization when the external field is cycled between positive and negative fields. Additionally, it is evident that these step-like positions concerning the magnetic field vary for **1**, **2**, and **3**, correlating with the varied relaxation energy barrier due to different magnetic anisotropy resulting from the replacement of the central metal ion in the Ln-EDTA and effective exchange interactions with the π electrons of the MWCNTs.

The dM/dH plots also reveal that slow relaxation is absent at higher temperatures. The step-like sharp peaks are absent and merge into a single sharp peak at zero field, indicating faster relaxation of magnetization at temperatures $> 20 \text{ K}$ (see Inset Figure 3.18b–f).

In the field-dependent magnetization (M vs. H) plots shown in Figure 3.18a,b for molecular systems **1** and **2**, the magnetization curve saturates at 19 k Oe and 10 k Oe, respectively, remaining constant at low temperature and high field. Conversely, for molecular system **3** (Figure 3.18c), the magnetization curve at 2 K increases until 6 k Oe, remains constant up to 15 k Oe, and then shows a decreasing trend at higher fields, likely due to a large diamagnetic influence from the MWCNTs. Diamagnetic materials, such as graphite/graphene, have no unpaired electrons and hence no net magnetic moment per atom, resulting in a large diamagnetic susceptibility[154]. Electrons within the graphitic layers of the MWCNTs can rearrange their orbits,

creating small eddy currents that oppose the external magnetic field[110]. The slight decrease in magnetization at 2 K at higher fields in Figure 3.18c can be attributed to the disruption of these eddy currents. However, the diamagnetic contribution is significantly reduced at higher temperatures, likely due to Van Vleck's paramagnetic contributions from localized defects in the MWCNTs [155], [156]. As mentioned earlier, a single Ln-MWCNT molecular system with a replaced central metal ion exhibits significant magnetic anisotropic behavior.

The plots of M vs HT^{-1} for the Gd, Tb, and Dy-MWCNT systems are presented in Figure 3.19a,c,e, respectively. It is noteworthy that the M vs HT^{-1} curves for all three molecular systems do not superimpose onto a single master curve, confirming the presence of magnetic anisotropy. To obtain additional complementary information on the Ln-MWCNT hybrid molecular complex, we performed M/M_s plot fitting with theoretical Brillouin curves for different values, respectively (see Figure 3.19b,d,f). Magnetization concerning the field can be fitted using the following equation:

$$M = ngJ\mu_B B_J(x) \quad (3.3)$$

where n is the number of Ln^{3+} ions in the sample, g is the electron spin factor, J is the total angular momentum, μ_B is the Bohr magneton and the Brillouin function is

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right) \quad (3.4)$$

and

$$x = \frac{gJ\mu_B H}{k_B T} \quad (3.5)$$

where k_B is the Boltzmann constant.

Finally, an effective magnetic moment can be determined by substituting the J value into Equation 3.6 as follows:

$$\mu_{eff} = g[J(J+1)]^{1/2}\mu_B \quad (3.6)$$

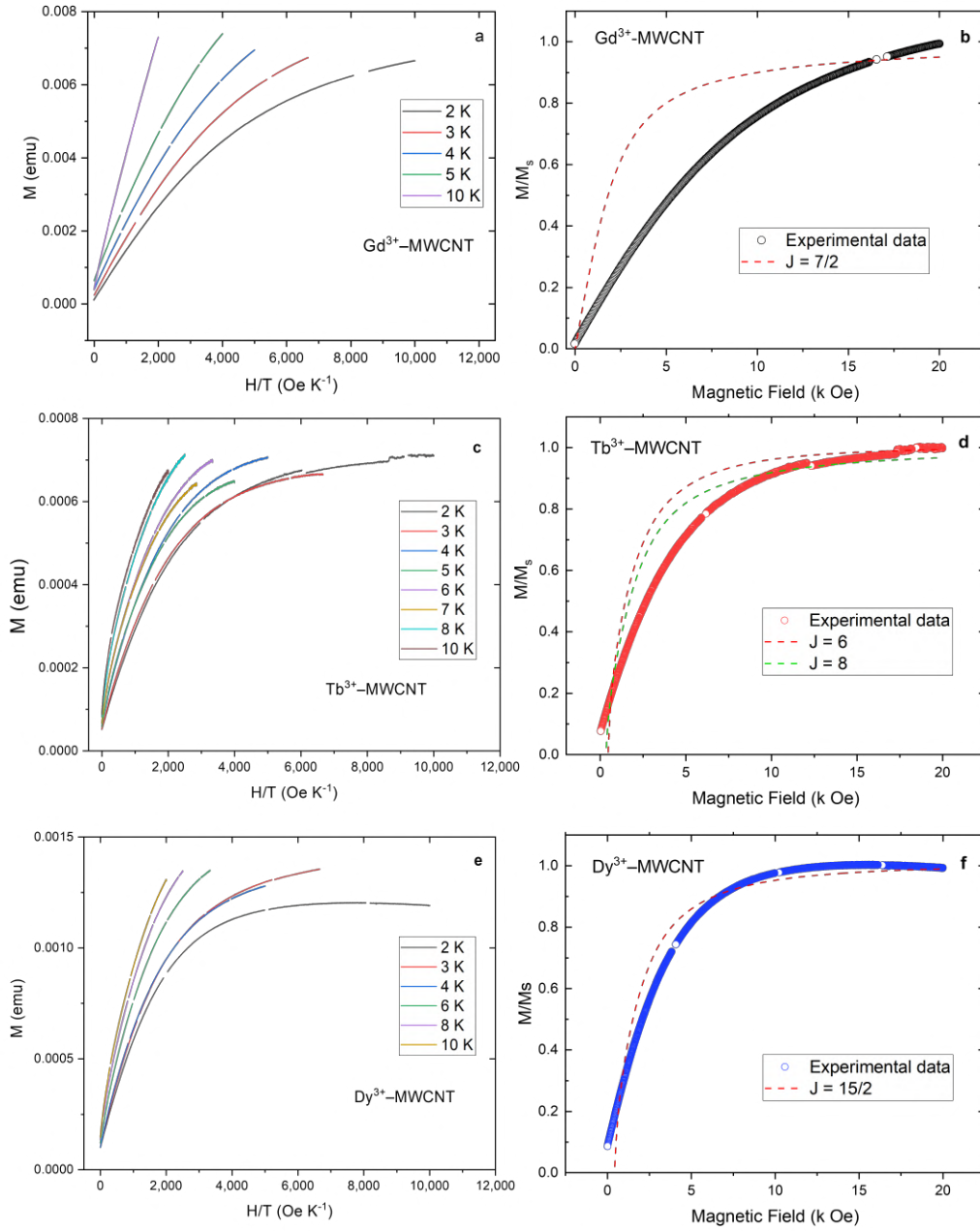


Figure 3.19 (a, c, e) Displayed are the plots of magnetization vs. the ratio of field and temperature (M vs. H/T) for Gd-, Tb-, and Dy-grafted Multi-Walled Carbon Nanotube (MWCNT) systems, respectively. (b, d, f) Brillouin function fitting for the corresponding molecular systems has been performed to assess the exchange interaction parameter J .

We considered the best-fitting values and found $J=8$ and $J=7.4$ for molecular systems **2** and **3**, respectively. However, we could not fit molecular system **1**, and this might be attributed to the presence of metal impurities or defective sites opened on the CNT surface during acid treatment. Substituting these values into Equation 3.6, we find the experimentally derived effective magnetic moments (μ_{eff}) to be $12.7279\mu_B$ and

$10.4859\mu_B$ for systems **2** and **3**, respectively. These values were then compared with the theoretical values $\mu_{eff} = 9.72\mu_B$ and $10.65\mu_B$. We observed that the Tb-MWCNT system showed a higher value, while the Dy-MWCNT system showed a lower value (refer to Table 3.3). This further confirms the evaluation of inverse susceptibility, where **2** displays ferromagnetic ordering and **3** shows anti-ferromagnetic ordering.

Table 3.3 Comparison of theoretical and experimental effective energy barrier (μ_{eff}).

Rare Earth	S	L	J	g	$\mu_{eff} = g\sqrt{J(J+1)}$	μ_{eff} Experimental
Gd ³⁺ 4f ⁷ ; n = 7	7/2	0	7/2	2.00	7.94	NA
Tb ³⁺ 4f ⁸ ; n = 8	3	3	6	1.50	9.72	12.7279 μ_B
Dy ³⁺ 4f ⁹ ; n = 9	5/2	5	15/2	1.33	10.65	10.4859 μ_B

Discussion

The introduction of magnetic molecules onto a conducting surface, such as a CNT, provides access to spin degrees of freedom, enabling the realization of condensed matter phenomena interactions like spin-spin exchange, spin-phonon coupling, and spin correlations for building various molecular electronic devices. By carefully controlling the chemical functionalization of CNTs with magnetic molecules, enhanced magnetic properties can be achieved in the compound molecule. Magnetic ions 1, 2, and 3 were each grafted onto the CNTs via EDTA ligand, and controlled attachment resulted in the grafting of 0.5–1 wt% of magnetic metal ions onto the CNT surface, as confirmed by EDAX results.

Since the concentrations of Ln³⁺ ions on the CNT surface are low, it can be inferred that the CNT hybrid molecular system is grafted with isolated Ln³⁺ ions rather than a bulk chain of molecular magnets. Therefore, the observed enhanced magnetic properties are attributed to superexchange interactions. Furthermore, the steps seen in Figure 3.18b, d, f indicate these interactions occurring only at low temperatures (<10 K). A similar magnetization phenomenon is observed in diluted Dy(III) SMMs [157] and Tb(III)-encapsulated SWCNTs [158]. It is interpreted that grafting affects

the magnetic dipole interactions between neighboring Ln^{3+} ions, effectively reducing QTM-type relaxation and leading to slow relaxation.

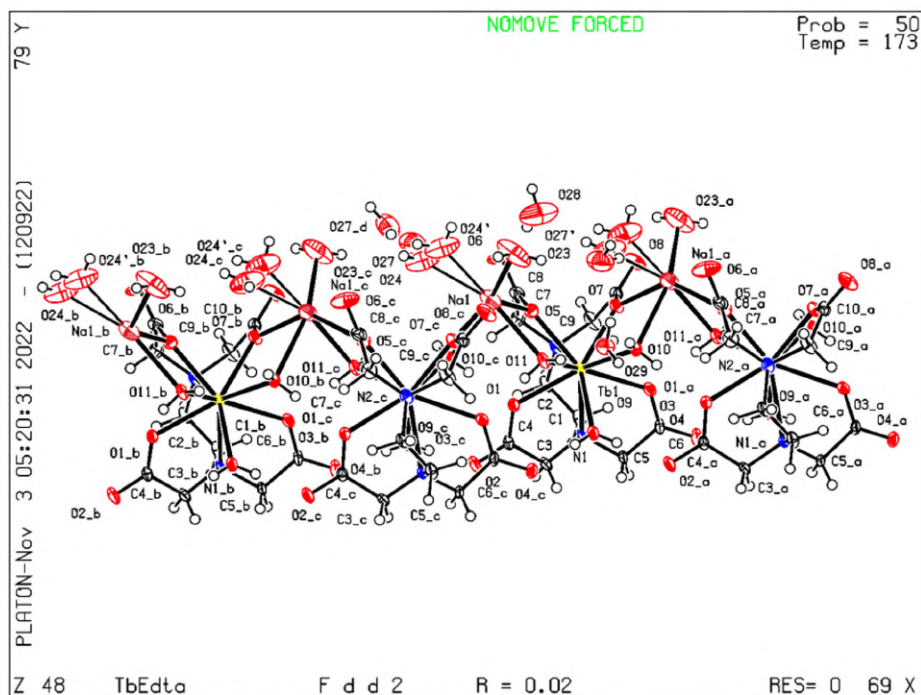
Table 3.3 displays the effective energy barrier of the respective magnetic molecule-coupled CNT hybrid molecular systems. Significant magnetic anisotropy is evident in the Ln-EDTA-coupled CNT molecular hybrid by replacing the central metal ion. The enhanced and varied magnetic properties are plausibly due to complex magnetic interactions between the itinerant conduction electrons of the CNTs and rare earth ions. Systems **2** and **3**, in particular, exhibit a magnetization reversal energy barrier (μ_{eff}) of $12.7279\mu_B$ $10.4859\mu_B$, respectively, resulting from slow magnetic relaxation via the Orbach mechanism (suppressed QTM). In contrast, for system 1, the experimental data could not be fitted with the Brillouin function (using Equation 3.4), suggesting that QTM-type relaxation dominates. A theoretical model has been developed to understand the different dominant relaxation mechanisms involved when an SMM is attached to a conducting surface[159]. Particularly when a magnetic spin center is grafted onto a conducting surface, the manifestation of magnetization can be attributed to spin-flipping events assisted by the phonon spectrum of the CNT. Further understanding of the magnetic mechanism in this molecular hybrid will be studied through frequency-dependent AC magnetization and low-temperature transport studies.

Conclusion

Single-molecule magnets (SMMs) based on lanthanide ions exhibit high anisotropy due to their local geometry and symmetry. The magnetic properties of SMMs can be fine-tuned by varying the lanthanide centers while maintaining the same ligand environment. In this study, we have presented a one-step approach for synthesizing Ln-EDTA chelates and demonstrated the controlled attachment of SMMs based on 4*f*-electronic systems ($\text{Ln} = \text{Gd}, \text{Tb}, \text{Dy}$) onto multi-walled carbon nanotubes (MWCNTs), achieving a higher-order retention of magnetic bistability.

We have highlighted that intramolecular distances between Ln-Ln interactions play a crucial role in an SMM's one-dimensional chain network, influencing spin-spin interactions and thereby affecting magnetic properties. However, when introduced as isolated Ln³⁺ magnetic impurities onto a conduction channel like a CNT, superexchange interactions via the RKKY mechanism and extensive π -electron screening influence the final magnetic properties. Molecular system **1** (Gd³⁺-MWCNT) exhibited superparamagnetic behavior, while systems **2** and **3** (Tb³⁺- and Dy³⁺-MWCNT, respectively) displayed clear SMM behavior. Notably, system **1** changed its magnetization value from positive to negative as the temperature decreased. Furthermore, our study demonstrated that the characteristic properties of individual SMMs can be effectively transferred to the CNT hybrid molecular system through a carefully designed grafting approach.

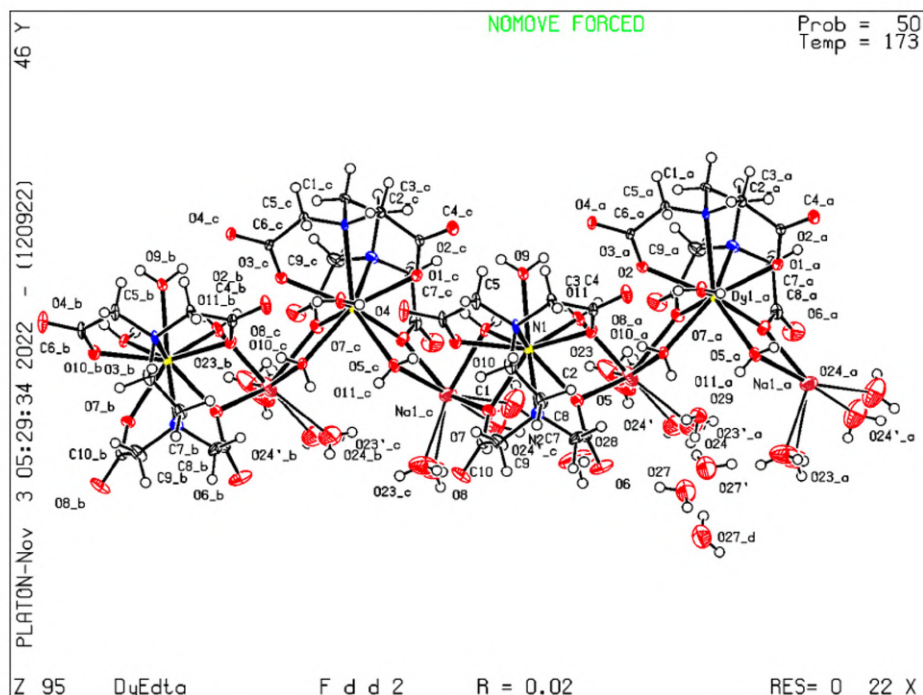
Low-dimensional nanoparticles are expected to exhibit enhanced magnetic properties, and this was confirmed for all Ln³⁺-grafted CNT hybrid molecular systems: **1** ($H_c = 250$ Oe), **2** ($H_c = 320$ Oe), and **3** ($H_c = 322$ Oe). The work underscores the significance of central ions in the hybrid molecular complex and their impact on magnetic properties. Consequently, we envision the careful engineering of a molecular system that allows for the tuning of desired magnetic properties. Designing an SMM molecular system where individual spin centers can be easily accessed and regulated is crucial. In this context, our work provides insights into developing a simple approach for effectively grafting spin centers onto a diamagnetic material and accessing them through the semiconducting nature of CNTs.



Datablock: TbEdta

Bond precision:	C-C = 0.0072 Å	Wavelength=0.71073	
Cell:	a=35.306(3)	b=19.2934(15)	c=12.0542(10)
	alpha=90	beta=90	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	8211.0(12)	8211.0(12)	
Space group	F d d 2	F d d 2	
Hall group	F 2 -2d	F 2 -2d	
Moiety formula	C10 H22 N2 Na O13 Tb, 1.5(H	C10 H22 N2 Na O13 Tb, 2(H	
	O0.50), 2(H2 O)	O0.50), 2(H2 O)	
Sum formula	C10 H28 N2 Na O16 Tb	C10 H28 N2 Na O16 Tb	
Mr	614.26	614.25	
Dx, g cm-3	1.988	1.988	
Z	16	16	
Mu (mm-1)	3.548	3.548	
F000	4896.0	4896.0	
F000'	4896.66		
h,k,lmax	46,25,15	46,25,15	
Nref	4943[2588]	4919	
Tmin,Tmax	0.136,0.178	0.655,0.747	
Tmin'	0.077		
Correction method= # Reported T Limits: Tmin=0.655 Tmax=0.747			
AbsCorr = MULTI-SCAN			
Data completeness=	1.90/1.00	Theta(max)= 27.998	
R(reflections)=	0.0166(4919)	wR2(reflections)=	
		0.0436(4919)	
S =	1.491	Npar= 282	

Figure 3.20 Single crystal structure of Tb-EDTA molecule.



Datablock: DyEdta

Bond precision:	C-C = 0.0098 Å	Wavelength=0.71073
Cell:	a=19.3107 (18) alpha=90	b=35.216 (3) beta=90
Temperature:	173 K	c=12.0558 (11) gamma=90
Volume	Calculated 8198.5 (13)	Reported 8198.6 (13)
Space group	F d d 2	F d d 2
Hall group	F 2 -2d	F 2 -2d
Moiety formula	C10 H16 Dy N2 Na4 O13	C10 H16 Dy N2 Na4 O13
Sum formula	C10 H16 Dy N2 Na4 O13	C10 H16 Dy N2 Na4 O13
Mr	626.71	626.71
Dx, g cm ⁻³	2.031	2.031
Z	16	16
Mu (mm ⁻¹)	3.796	3.796
F000	4864.0	4864.0
F000'	4865.34	
h, k, lmax	27, 49, 16	27, 49, 16
Nref	5965 [3115]	5946
Tmin, Tmax	0.182, 0.490	0.596, 0.746
Tmin'	0.114	
Correction method=	# Reported T Limits: Tmin=0.596 Tmax=0.746	
AbsCorr =	MULTI-SCAN	
Data completeness=	1.91/1.00	Theta(max)= 29.996
R(reflections)=	0.0261 (5933)	wR2(reflections)= 0.0677 (5946)
S =	1.305	Npar= 274

Figure 3.21 Single crystal structure of Dy-EDTA molecule.

Chapter 4

Spintronics with LnEDTA-CNT molecular hybrid

4.1 Interfacing molecular magnets with CNT-Molecular Spintronics

Carbon nanotubes (CNTs) find a wide range of applications, including serving as single-photon emitters, contributing to the field of spintronics, and enabling flexible electronics. CNTs offer an exciting platform for quantum bits (qubits) due to their exceptional electron mobility within the one-dimensional π -network, making them a promising candidate for quantum computing. While CNTs are inherently diamagnetic, when they are functionalized with magnetic materials, particularly rare earth metal ions, they exhibit exotic phenomena such as Kondo screening of conduction electrons and spin-valve features. These phenomena can be harnessed for the development of molecular spintronic devices. By adjusting the doping concentration of magnetic molecules on CNTs, it becomes possible to fine-tune the magnetic properties of the molecular complex, creating highly spin-correlated systems.

Moreover, the confinement of various molecules within CNTs has proven to be an interesting avenue for exploring fundamental physical and functional properties. One-dimensional CNT systems functionalized with magnetic molecules provide an

ideal platform for exploring unique and non-standard physics while exploiting specific properties that are of interest for building electronic applications. Notably, carbon nanotubes doped with single-molecule magnet terbium (III) bis(phthalocyaninato) neutral complex (TbPc2) have demonstrated their suitability for conducting quantum bit operations. The fundamental operation in this molecular system is based on the spin-phonon coupling mechanism, where the electron spin of a magnetic ion interacts with the discrete vibrational (phonon) modes of a carbon nanotube, eventually returning to its equilibrium state by exchanging quanta of phonon energy. Given the high magnetic anisotropy of $4f$ elements, changes in the magnetization enable the magnetic ion spin to alter the direction of the local CNT lattice's vibrational vector through phonon emission. Furthermore, the spin-boson model has been widely applied in recent research for quantum information processing, highlighting the ongoing exploration of CNT-based systems for various quantum applications.

Consequently, research focused on the physics of spin-phonon coupled systems and the Kondo effect has gained significant importance. Building upon these intriguing findings, we have employed double-walled nanotubes (DWNTs) filled with the rare earth ion Gd^{3+} (with a net spin of $S = 7/2$) to explore spin-phonon coupling properties that could potentially be applied for multi-qubit operations. In this communication, we specifically emphasize our findings related to magnetic studies and the features of spin-phonon coupling observed through low-temperature Raman spectroscopy.

Raman spectroscopy, which involves the optical observation of inelastic scattering events, is a valuable technique for studying the electronic structures and phonon modes of nanotubes. While previous studies have predominantly focused on DWNTs to distinguish their semiconducting and metallic behavior, observe trends in the phonon frequency changes induced by various filling materials inside the tubes, and investigate the polarization dependence of phonon modes with respect to the polarized angle, investigations into phonon renormalization related to spin ordering at low temperatures in one-dimensional materials (such as DWNTs) have been limited.

Raman spectroscopy measurements on single-walled carbon nanotubes typically reveal two components of the G band: one component is associated with the C-C bond vibrations along the axis of the SWCNT, while the other is related to the C-C bond vibrations tangential to the circumference of the SWCNT. The lower wavenumber radial breathing modes (RBMs) are linked to the radially symmetric expansion and contraction of the SWCNT. Changes in peak position $\Delta\omega$, peak width $\Delta\Gamma$, and intensity vary with temperature, and these variations are attributed to the anharmonicity in the vibrational potential. These changes can be explained using the Balkanski model.

In the case of a magnetic material, variations in phonon mode frequency with temperature occur due to anharmonicity ($\Delta\omega_{anh}$) arising from effective lattice interactions in the disordered structure and a spin-phonon coupling contribution $\Delta\omega_{s-ph}$ resulting from the spin ordering of magnetic ions. Therefore, by conducting low-temperature Raman spectroscopy on DWNTs filled with magnetic molecules, we can analyze the individual contributions and, in turn, determine the spin-phonon coupling constant. This can be achieved by employing Heisenberg's exchange spin-spin correlation function $\langle S_i \cdot S_j \rangle$ in conjunction with magnetization studies.

4.2 Spin-Phonon Coupling

Raman spectra were obtained for both untreated and Gd filled Double Walled Carbon Nanotubes (DWNTs) across various temperatures (80 K–300 K), utilizing a green laser with energy (E_{laser}) of 2.41 eV. The first-order Raman spectra of DWNTs encompassed low-frequency radial breathing modes ranging from $\sim 100 \text{ cm}^{-1}$ to 300 cm^{-1} [Fig. 4.2(a)], attributable to radially symmetric vibrations. Additionally, high-frequency tangential G band modes from $\sim 1500 \text{ cm}^{-1}$ to 1650 cm^{-1} [Fig. 4.2(b)] were observed, arising from C-C bond vibrations along and tangential to the axis of the inner and outer nanotubes.

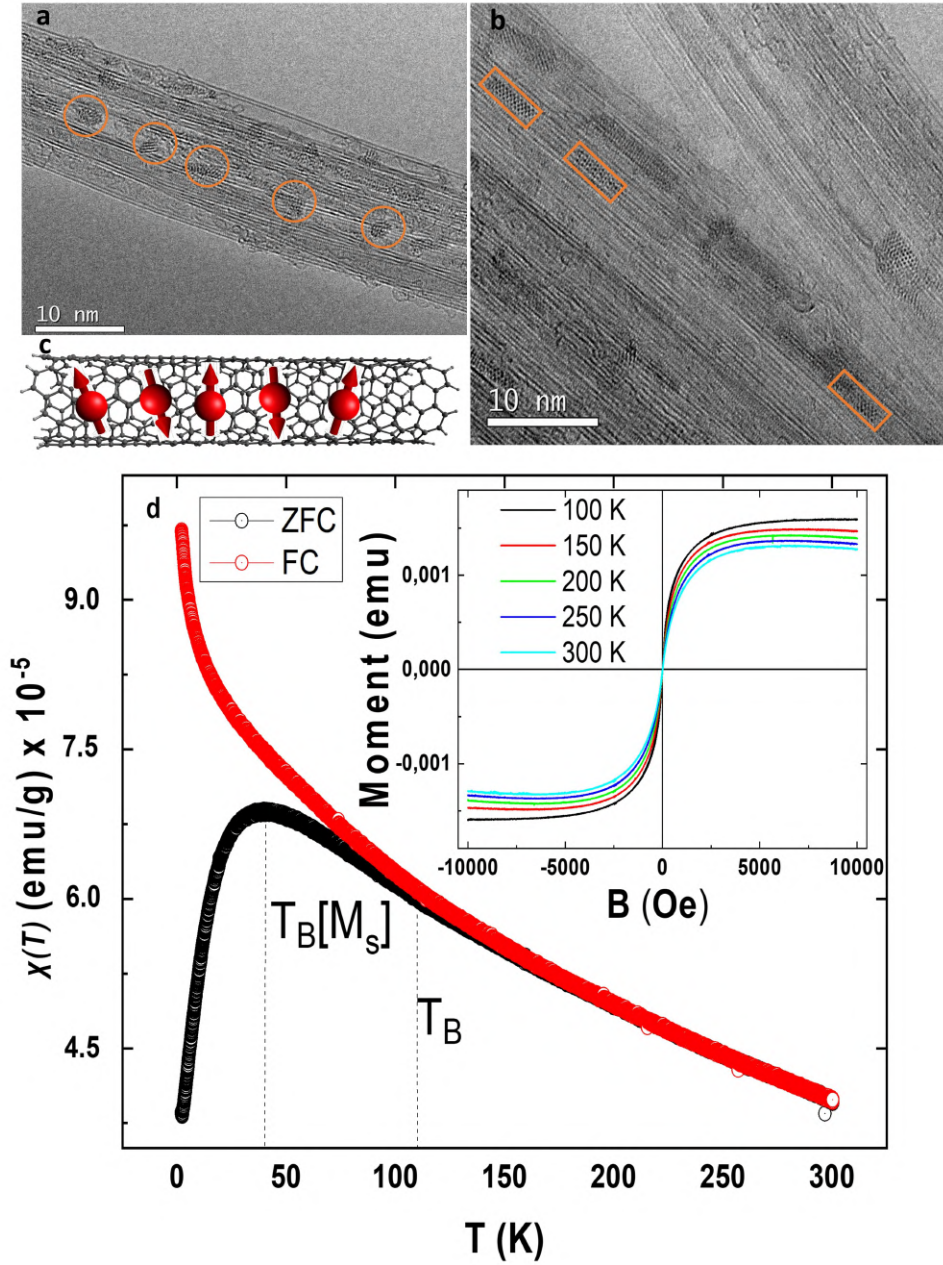


Figure 4.1 (a) and (b) HRTEM images of Gadolinium (Gd) filled double-walled carbon nanotubes (DWNTs) displaying various shapes of Gd ions trapped within the nanotube. (c) Visualization of the molecular system of Gd-filled DWNTs. (d) SQUID measurements of Gd DWNTs with respect to temperature, conducted using Zero Field Cooling (ZFC) and Field Cooling (FC) at an applied magnetic field of 0.01 T. The disparity in the rate of magnetization between FC (red curve) and ZFC (black curve) becomes evident at a critical temperature of T_C (~ 110 K) and achieves magnetization saturation at 45 K for ZFC. Inset in figure (d): M vs H curves depict the superparamagnetic behavior of Gd-filled DWNTs.

Radial Breathing Modes (RBMs) originate from the cylindrical structure of the nanotube. In our sample, Double Walled Carbon Nanotubes (DWNTs) exhibited

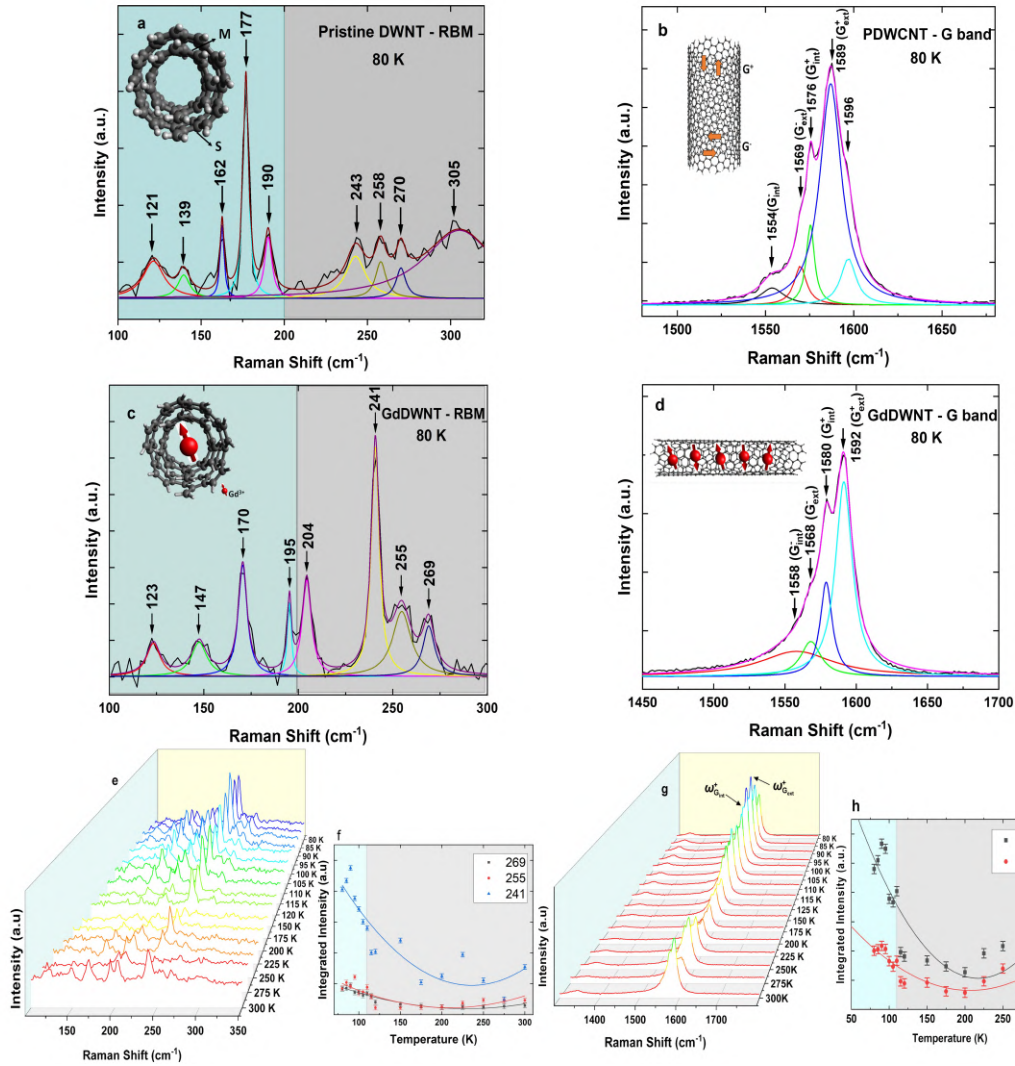


Figure 4.2 Raman spectra were obtained using a 514.5 nm excitation wavelength, illustrating both the RBM and G band characteristics of Pristine and Gd filled double-walled carbon nanotubes (DWNTs) at various temperatures: (a) RBMs spanning from 100 cm^{-1} to 300 cm^{-1} wavenumber are depicted, with the blue highlighted region corresponding to the outer tube (Lorentzian peak approximately from 121 cm^{-1} to 190 cm^{-1}) and the gray highlighted region corresponding to the inner tube (Lorentzian peak approximately from 243 cm^{-1} to 270 cm^{-1}). (b) The G band, ranging from 1450 cm^{-1} to 1650 cm^{-1} , is deconvoluted into five distinct peaks originating from four symmetry modes and one asymmetric (BWF) mode of the DWNT. (c) The RBM mode of Gd-filled DWNTs reveals additional peaks associated with filled impurities, along with indications of the inner and outer diameter of the tube. (d) Alterations in the G band induced by Gd^{3+} ion filling are presented. (e)-(h) Integrated intensities plot of RBM and G bands of Gd-filled DWNTs are displayed as a function of temperature, showcasing a sharp increase in their respective intensities below the critical temperature (T_c) of approximately 110 K.

Lorentzian peaks corresponding to outer ($\sim 121\text{--}190\text{ cm}^{-1}$) and inner diameters ($\sim 243\text{--}270\text{ cm}^{-1}$) [Fig. 4.2(a)]. Since we are examining bundles, there is a variety of DWNTs with different diameter distributions, leading to four possible configurations of inner and outer nanotubes: S@S, S@M, M@M, and M@S. Based on a comparison with the literature [160] and information from the theoretical Kataura plot [161], our experimental results indicate that our DWNTs are of M@S configuration. In this configuration, the inner tube shows a metallic ($E^{M_{11}}$ transition), and the outer tube shows a semiconducting ($E^{S_{33}}$ transition) nature when a 2.41 eV excitation laser is used. Additionally, we used the relation 4.1 to calculate the RBM frequency of inner and outer tubes, respectively [162].

$$\omega_{RBM} = \frac{227}{d_t} \sqrt{1 + C_{env} d_t^2} \quad (4.1)$$

where d_t represents the diameter of the nanotube, and C_{env} accounts for the environmental impact on the Radial Breathing Mode (RBM) frequency, where $C_{env} = 0.056\text{ nm}^2$ is considered in this context. Environmental effects on RBM frequency encompass intratube interactions, such as those in alcoholic or functionalized environments, and inter-tube interactions, including mechanical coupling between inner and outer tube layers [163]. The inner tube diameter (d_{in}) ranges from 0.84 to 0.93 nm, and the outer tube diameter (d_{out}) ranges from 1.30 to 1.87 nm. These values are in good agreement with earlier reports [164].

The electronic properties of a nanotube are well-known to be chiral angle (θ) specific and dependent on the nanotube diameter [162]. The chiral angle represents the degree of twisting of the nanotube, governed by a chiral vector defined by two integers (n , m) [165]. Therefore, when applying carbon nanotubes in engineering applications, it is crucial to have precisely defined electronic properties. The unique vibrational signature of the Radial Breathing Mode (RBM) in carbon nanotubes allows for understanding doping effects by examining its relative intensity [162]. In Figure 4.2(c), the Lorentzian peaks at $\sim 177\text{ cm}^{-1}$ and $\sim 243\text{ cm}^{-1}$, associated with the outer and inner diameters of DWNTs, respectively, are downshifted to $\sim 170\text{ cm}^{-1}$ and

$\sim 241 \text{ cm}^{-1}$, respectively, due to strain induced by Gd^{3+} ion filling. A significant change in intensity is observed in the higher frequency region of RBM related to the inner diameter, where the intensity of $\sim 241 \text{ cm}^{-1}$, 255 cm^{-1} , and $\sim 269 \text{ cm}^{-1}$ phonon modes sharply increases below the critical temperature ($T_c \sim 110 \text{ K}$) [Figs. 4.2(e) and 4.2(f)]. This behavior is attributed to Gd^{3+} ion spin ordering through exchange interaction (paramagnetic behavior), altering the local vibronic potential and inducing strain on both the inner and outer tubes. Supporting this, the respective intensities as a function of temperature were plotted, reaching a maximum at $\sim 90 \text{ K}$ corresponding to the onset superparamagnetic phase at $\sim 110 \text{ K}$.

Now, let's discuss the G-band and how it characterizes local C—C bonds, specifically examining how doping with impurities influences C—C bond lengths in a nanotube through Raman spectra measurements. In semiconducting Single-Walled Nanotubes (SWNTs), five Lorentzian components were reported [166], [167], while in metallic SWNTs, a Lorentzian component and a Breit-Wigner-Fano (BWF) line shape components were observed [166]. Therefore, the position and line shape of the G-band components differ for metallic and semiconducting Carbon Nanotubes (CNTs). In a M@S configured Double-Walled Carbon Nanotube (DWNT), a mixture of these G-band components would be observed.

In Figure 4.2(b), the G-band of the original double-walled nanotube (DWNT) is analyzed by deconvoluting it into five Lorentzian peaks with frequencies at 1554 cm^{-1} , 1569 cm^{-1} , 1576 cm^{-1} , 1589 cm^{-1} , and 1596 cm^{-1} . The G-band's lower frequency peak $\omega_{G_{\text{int}}}^-$ at 1554 cm^{-1} is identified as the asymmetric line shape of the inner metallic nanotube transition ($E^{M_{11}}$ transition), specifically characterized by a BWF line shape. This BWF line shape can be further described as

$$I_{\omega} = I_o \frac{\left[1 + \frac{\omega - \omega_o}{q\Gamma}\right]^2}{\left[1 + \frac{\omega - \omega_o}{\Gamma}\right]^2} \quad (4.2)$$

where ω_o and Γ represent the peak position and full width at half maximum (FWHM)

at maximum intensity (I_o), respectively. The $1/q$ value is directly linked to the strength of electron–phonon coupling. As $1/q$ approaches zero, the BWF line shape transforms into a Lorentzian function, indicating a semiconducting nature of the tube. Conversely, when $1/q$ reaches unity or exceeds 1, the tube exhibits a metallic nature [168]. The peaks at 1589 cm^{-1} and 1576 cm^{-1} are attributed to the $\omega_{G_{\text{ext}}}^+$ (S) longitudinal optical (LO) and $\omega_{G_{\text{int}}}^+$ (M) transverse optical (TO) modes, corresponding to the C—C bond stretching parallel and perpendicular to the nanotube axis, respectively. The peak at 1569 cm^{-1} is designated as the $\omega_{G_{\text{ext}}}^-$ (S) mode.

The assignment of LO and TO phonon modes for the G^+ band of outer (S) and inner (M) nanotubes, respectively, is considered due to electron–phonon coupling (also known as the Kohn anomaly effect) softening the LO mode in the case of a metallic nanotube. It becomes challenging to assign respective modes for both outer semiconducting and inner metallic nanotubes of a double-walled nanotube (DWNT) since both are in resonance with the same excitation laser, $E = 2.41\text{ eV}$. The G^+ frequency values of the outer nanotube (S) at room temperature closely align with previously reported values [169], [170], indicating consistency in our evaluation.

Following the introduction of Gd^{3+} ions into the double-walled nanotube (DWNT) (Figure 4.2(d)), the deconvoluted Raman spectra reveal notable changes in the G-band. Specifically, the $\omega_{G_{\text{ext}}}^+$ and $\omega_{G_{\text{int}}}^+$ symmetry modes associated with the G-band exhibit an upward shift, while other modes such as the $\omega_{G_{\text{ext}}}^-$ mode ($\sim 1568\text{ cm}^{-1}$) remain unchanged, the $\omega_{G_{\text{int}}}^-$ mode (BWF line shape $\sim 1554\text{ cm}^{-1}$) broadens, and the highest tangential mode ($\sim 1596\text{ cm}^{-1}$) disappears entirely. This phenomenon arises due to the selective screening of conduction electrons in the π -network of the nanotube by the magnetic Gd^{3+} ion, leading to a change in the local deformation potential. As discussed in the introduction, a decrease in temperature results in an upshift of the G-band ($\omega_{G_{\text{ext}}}^+$) and ($\omega_{G_{\text{int}}}^+$) peak positions (Figure 4.2(d)), an increase in their intensities (Figures 4.2(g) and 4.2(h)), and a reduction in peak widths ($\Delta\Gamma$) [Figure S1 in the supplementary material]. A significant observation in Gd-filled DWNTs is the frequency shift of both ($\omega_{G_{\text{ext}}}^+$) and ($\omega_{G_{\text{int}}}^+$) positions to higher wavenumbers. Additionally, their respective integrated intensities exhibit a sharp increase below the

critical temperature ($T_c \sim 110$ K), indicating that the Gd spin undergoes a change in its local magnetic moment (spin–spin exchange interaction). This change influences the π -network electrons of both the inner and outer tubes, thereby altering the local vibronic potential in strong resonance with the excited laser (Figures 4.2(g) and 4.2(h)). In our study, we rely on peak position variation to explain the spin–phonon coupling interaction, as uncertainties are lower compared to peak width.

In Raman spectra, the observed shift in the frequency of phonon modes to lower or higher wavenumbers at low temperatures can be attributed to various factors, including pure thermal effects (lattice expansion/contraction), lattice anharmonicity, electro-phonon coupling, and spin–phonon coupling interaction, expressed as:

$$\omega(T) = \omega_o + \Delta\omega_{latt}(T) + \Delta\omega_{anh}(T) + \Delta\omega_{e-ph}(T) + \Delta\omega_{s-ph}(T) \quad (4.3)$$

where ω_o is the frequency of the phonon at $T=0$, $\Delta\omega_{latt}$ is the phonon frequency change due to lattice expansion/contraction, $\Delta\omega_{anh}$ is the intrinsic anharmonic contribution due to effective lattice interactions, $\Delta\omega_{e-ph}$ is the phonon frequency change due to electron–phonon coupling, and $\Delta\omega_{s-ph}$ is the spin–phonon coupling due to the modulation of the exchange integral by lattice vibrations. The thermal lattice expansion coefficient and lattice constant values of a single-walled nanotube (SWNT) were determined to be very small[171], and therefore, the contribution of $\Delta\omega_{latt}$ to the phonon frequency at low temperatures is minimal.

Generally, the strength of electron–phonon coupling $\Delta\omega_{e-ph}$ is more pronounced in metallic nanotubes, primarily attributed to the Kohn anomaly effect, which softens the LO mode. This coupling factor exhibits strong sample dependence, indicating that the deformational potential, resulting from local area variations, is low or negligible for the lowest LO mode when electrons and phonons are confined to the same region of the carbon nanotube (CNT). The $\Delta\omega_{e-ph}$ coupling factor reaches its maximum (>1) when the electronic wavefunction is sharply localized around a region of maximum strain, as observed in doped double-walled nanotubes (DWNTs) where filled metal

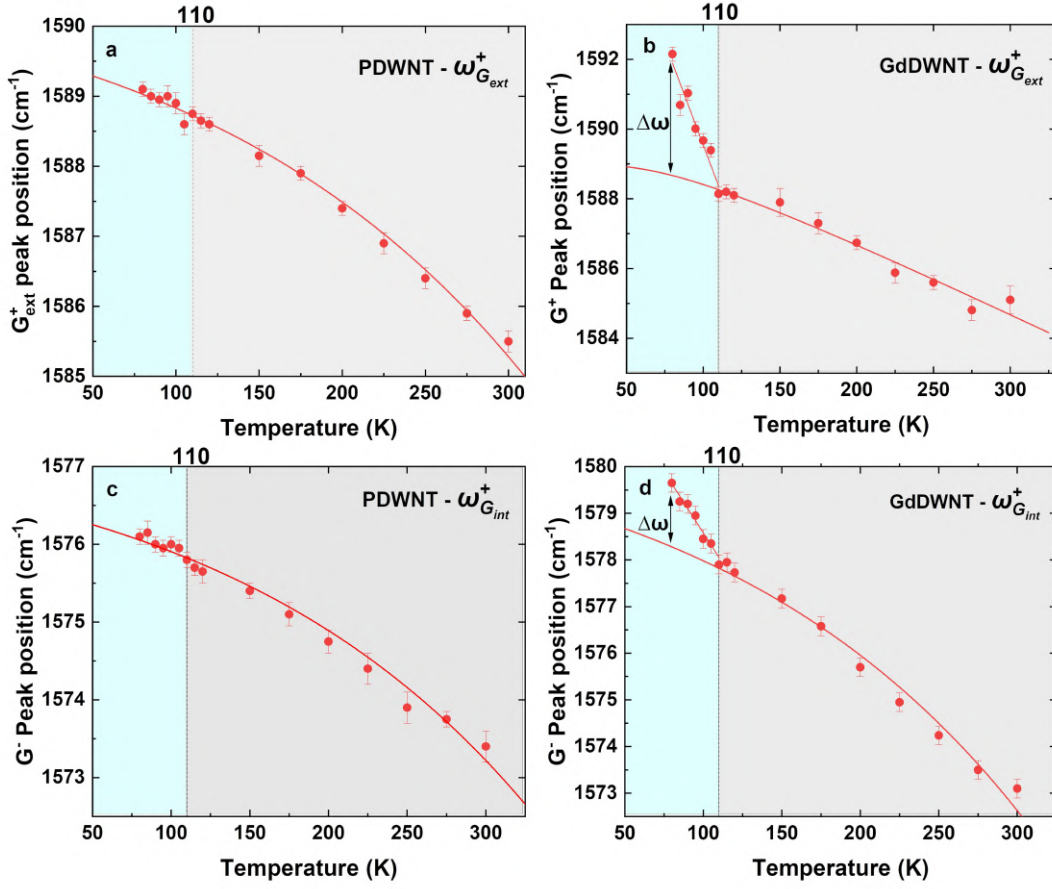


Figure 4.3 The change in the frequency of phonon modes with respect to temperature is presented, and a nonlinear fitting approach is employed using cubic anharmonicity 4.4. (a) and (c): The temperature-dependent variation in the phonon mode frequency ($\omega_{G_{ext}}^+$ and $\omega_{G_{int}}^+$) for pristine double-walled carbon nanotubes (DWNTs) is demonstrated, showing a cubic anharmonic decay. (b) and (d): The phonon modes $\omega_{G_{ext}}^+$ and $\omega_{G_{int}}^+$ of Gd-filled DWNTs exhibit a departure in their phonon frequency at a critical temperature of 110 K.

impurities induce strain on the inner tube. The concentration of metal impurities is also pivotal in determining this factor and, consequently, its impact on the Raman frequency shift. Existing literature suggests that this $\Delta\omega_{e-ph}$ coupling is more pronounced at room temperature due to higher-order ground-state-to-excited-state vibronic transitions [172], [173]. However, at lower temperatures, where thermal energy for vibronic transitions is limited, it is assumed that the $\Delta\omega_{e-ph}$ coupling becomes low or negligible. Consequently, these two terms ($\Delta\omega_{latt}$ and $\Delta\omega_{e-ph}$) are disregarded during further analysis.

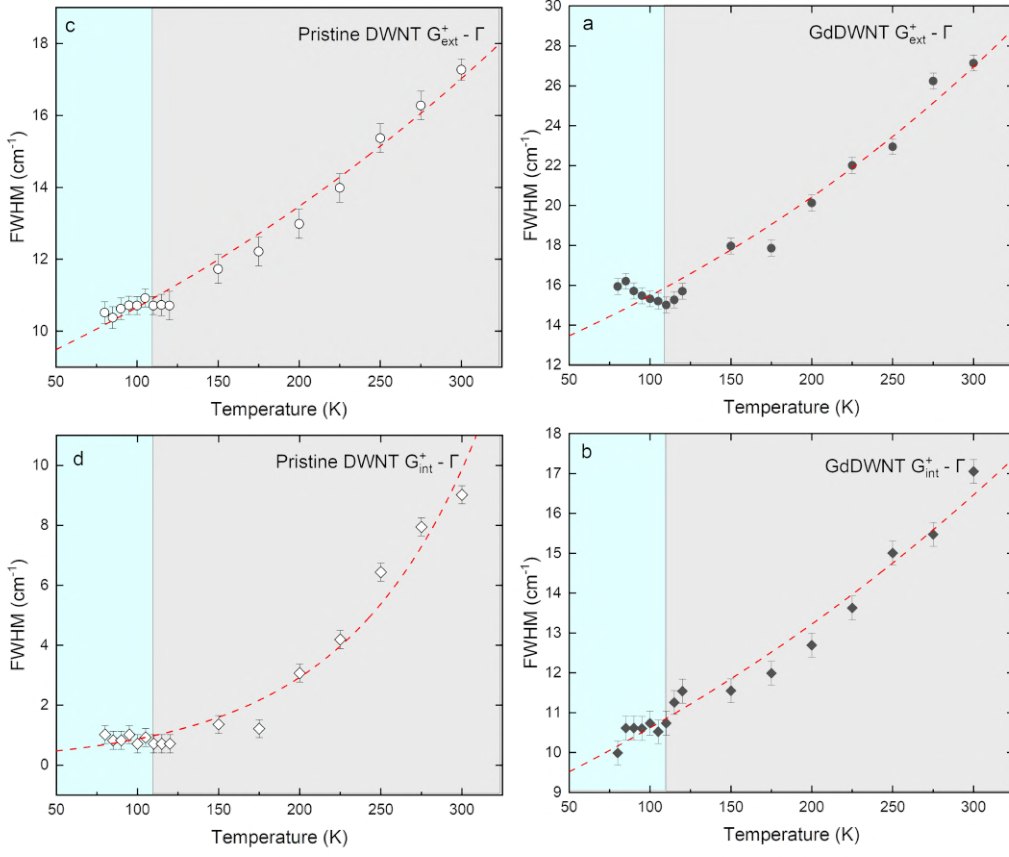


Figure 4.4 Peak width for the G mode: (a) & (c) FWHM of pristine $\omega_{G_{ext}}^+$ and $\omega_{G_{int}}^+$ phonon modes follow cubic anharmonicity due to pure thermal effects. b) FWHM of G^+ phonon showing anomalous behavior at low temperatures T_C (110 K) coinciding with onset super magnetic behavior. Whereas d) $\omega_{G_{ext}}^+$ phonon follows the cubic anharmonicity.

Charge transfer between the shells of a nanotube induced by functionalization might induce a frequency shift of the G-band[174], [175]. However, its influence on the G-band frequency shift as a function of temperature is deemed minimal[176]. In particular, changes in the frequency of a phonon mode in a magnetic compound with temperature can be attributed to intrinsic anharmonicity ($\Delta\omega_{anh}$) and spin-phonon coupling ($\Delta\omega_{anh}$) due to magnetic spin ordering at the critical temperature. This behavior has been reported in various magnetic compounds such as GaFeO_3 [177], SrRuO_3 [178], $\text{BaFe}_{12}\text{O}_{19}$ [179], $\text{Al}_{0.5}\text{Ga}_{0.5}\text{FeO}_3$ [180], and others.

The anharmonic contribution to the phonon frequency in the first-order Raman spectrum of a one-dimensional carbon nanotube is modeled by cubic anharmonicity,

expressed by the equation:[181]

$$\Delta\omega_{anh}(T) = \omega_o + C \left[1 + \frac{2}{e^x - 1} \right] \quad (4.4)$$

Here, $x = \hbar\omega_o/2k_BT$, $\hbar$ is Planck's constant, k_B is the Boltzmann constant, and C is an anharmonic constant. This model accounts for the three-phonon decay process due to potential anharmonicity in the nanotube structure, with the exclusion of the four-phonon process, which becomes significant only well above room temperature.

Figures 4.3(a)–(d) depict the variation of phonon frequencies of $(\omega_{G_{ext}}^+)$ and $(\omega_{G_{int}}^+)$ modes as a function of temperature for both pristine and Gd-filled double-walled nanotubes (DWNTs). A nonlinear fit using Eq. 4.5, considering the cubic anharmonicity contribution, is applied to both the pristine and Gd-filled DWNT samples (shown as a solid line in Fig. 4.3). The good fit observed between the data and the solid curve over most of the temperature range indicates that cubic anharmonicity provides an accurate description of the phonon frequency variation, justifying the omission of contributions from other processes. At lower temperatures, a decrease in slope suggests a weaker contribution from phonon decay processes [182]. However, in the Gd-filled DWNT sample, both $(\omega_{G_{ext}}^+)$ and $(\omega_{G_{int}}^+)$ phonon modes exhibit a clear deviation of the data from the values expected due to anharmonic contribution alone at low temperatures [Figs. 4.3(b) and 4.3(d)]. This observation indicates a significant phonon hardening upon introducing Gd ions inside the DWNT, attributed to spin ordering occurring at the critical temperature ($T_c = 110$ K), as evidenced in magnetization measurements [Fig. 4.1(d)]. This anomalous hardening, due to the spin–phonon interaction ($\Delta\omega_{s-ph}$), can be quantified, as discussed below.

The deviation in the phonon mode frequency below the critical temperature (T_c), i.e., the observed phonon hardening, is attributed to the spin–phonon coupling effect and can be described by the equation:

$$\Delta\omega = \omega - \omega_o = \lambda_{s-ph} \times \langle S_i.S_j \rangle \quad (4.5)$$

Here, ω is the renormalized phonon frequency due to spin-phonon interaction at finite low temperature, ω_o is the phonon frequency in the absence of this interaction, λ is the spin-phonon coupling strength, and $\langle S_i.S_j \rangle$ is a spin-spin correlation function. The spin-spin correlation function is approximated using the molecular field approximation and can be obtained from the ensemble average of nearest-neighbor spins:

$$\langle S_i.S_j \rangle = 2 \left[\frac{M(T)}{M_s} \right]^2 \quad (4.6)$$

Here, $M(T)$ is the magnetization per Gd-site magnetic ion, and M_s is the saturation magnetization. The spin correlations develop as the temperature is decreased, and the spin-phonon coupling strength becomes significant when the system exhibits superparamagnetic behavior below T_c (~ 110 K). The spin-phonon coupling strength is found to be larger for the $\omega_{G_{ext}}^+$ mode, suggesting a direct coupling of Gd^{3+} electron spin with the phonon mode of the double-walled nanotube (DWNT) (see Fig. 4.5). A larger λ value implies that this mode is more sensitive to magnetic interaction. Although the magnetic interaction of Gd^{3+} spin with the $\omega_{G_{int}}^+$ mode is weaker for the tangential DWNT phonon mode compared to $\omega_{G_{ext}}^+$, it is still significant when compared to multiferroic compounds reported earlier [177]–[179]. Notably, the spin-phonon coupling values are approximately three times higher than those of the referenced magnetic compounds. This observation of spin-phonon coupling strength in an optical manner in a magnetic molecule-filled one-dimensional system is intriguing, and further investigations of this system have implications for developing reliable spin qubits through a controlled spin-phonon coupling interface between a magnetic ion and DWNT.

The microscopic origin of spin-phonon coupling has been the subject of study for nearly 90 years, tracing back to the original suggestion by Waller and Van Vleck, demonstrating how spin dipolar interactions could influence spin relaxation pathways [183], [184]. Despite the Gd-carbon nanotube (CNT) system being more

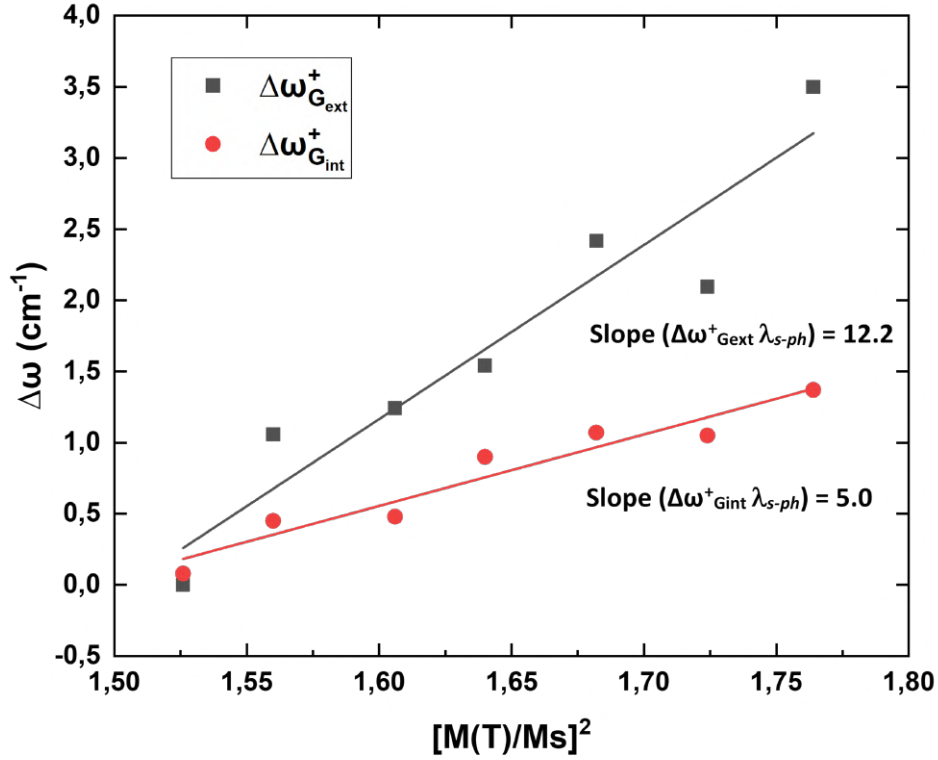


Figure 4.5 Graphs depicting the spin-phonon frequency component (ω_{s-ph}) versus magnetization (M) are presented for both $\omega_{G_{ext}}^+$ and $\omega_{G_{int}}^+$ phonon modes. A linear least squares fitting method was applied to determine the spin-phonon coupling strength (λ_{s-ph}), with the slope of this line representing the coupling strength.

complex than some molecular systems, a notable similarity between these materials has been observed by treating CNTs as one-dimensional (1D) molecules with distinct Raman features [Fig. 4.2(d)]. The modulation of d-electron crystal field effects observed in molecular systems can be extended to f-electron systems in the case of CNTs. The modulation of an electric field (Stark effect), resulting from spin-spin interactions, can generate random magnetic fields that function analogously to the well-known spin-orbit interactions. This, in turn, leads to phonon renormalization, where spin relaxes by coupling to discrete phonon modes in double-walled nanotubes (DWNTs), as evidenced in our low-temperature Raman data. This observation is further supported by the angle dependence of Raman intensity (Fig. 4.6), where both $\omega_{G_{ext}}^+$ and $\omega_{G_{int}}^+$ phonon modes exhibit a significant increase in intensity for Gd-filled DWNTs.

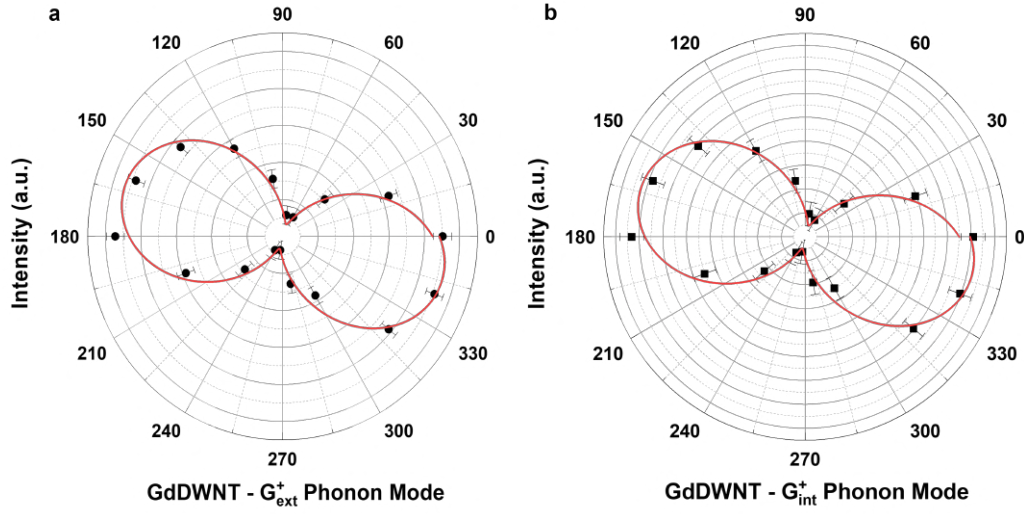


Figure 4.6 (a) and (b) The angle-dependent Raman intensity for Gd-filled double-walled carbon nanotubes (DWNTs) of $\omega_{G_{ext}}^+$ and $\omega_{G_{int}}^+$ phonons conforms to a $\sin \theta$ function.

The angle dependence of Raman intensity further reveals that the G mode exhibits maximum intensity at $\theta = 0^\circ$ and minimum at $\theta = 90^\circ$ due to the relaxation of depolarization effects[185]. This observation is consistent with the relaxation of depolarization effects influencing the Raman scattering characteristics. The spin-phonon mechanism has been interpreted as a three-level system by associating one level with the spin-flip process, which can be elucidated more generally by the Kondo resonance state. Below the Kondo temperature, a spin-flip from the impurity atoms occurs, manifesting itself in both the increased resistivity of the sample and the shift of the Raman frequency[118]. Considering Gd atoms connected to the carbon nanotubes (CNTs) as quantum dots, the Gd-CNT system can be described as a Kondo lattice. A detailed discussion of this interpretation will be presented in a future publication.

Conclusion

One-dimensional carbon nanotubes (CNTs) filled with a magnetic molecule present a promising platform for the development of molecular spin qubits. A spin system based on double-walled nanotubes (DWNTs) filled with rare-earth metal (Gd^{3+}) offers advantages over those based on single-walled nanotubes (SWNTs). In our experimental investigation of temperature-dependent Raman spectra for Gd_{3+} -filled

DWNTs, we have demonstrated that the phonon hardening coincides with the onset of superparamagnetic behavior at the critical temperature ($T_C = 110$ K). We attribute this anomalous phonon hardening behavior of both $\omega_{\text{G}_{\text{ext}}}^+$ and $\omega_{\text{G}_{\text{int}}}^+$ phonon frequencies to the spin–phonon coupling interaction induced by Gd^{3+} ions inside the DWNTs. Moreover, our findings reveal that the spin–phonon coupling strength (λ_{s-ph}) in a one-dimensional DWNT molecular system is approximately three times higher than that observed in other reported multiferroic compounds. This underscores the potential for engineering a spin-qubit network through a one-dimensional DWNT phonon waveguide. In such a system, Gd^{3+} spins, carrying quantum bit information, can be effectively coupled with discrete phonon modes, offering a promising platform for the development of efficient quantum computation.

4.3 Kondo Lattice

Magnetically fictionalised carbon nanotubes hold great promise as bases for custom quantum material configurations. Here, we demonstrate experimental evidence of a highly correlated material formed using a precise synthesis method, where a Gd-based molecular system is covalently linked to multiwalled carbon nanotubes. The magnetic characteristics, including susceptibility and hysteresis, suggest departure from behaviors seen in non-interacting superparamagnetic systems. Key indicators of a Kondo lattice, such as susceptibility deviating from the Curie-Weiss law at a temperature identified as the Kondo point via temperature-dependent resistance, are evident. Furthermore, peculiar transitions in low-temperature resistance among higher concentration samples provide additional support for emergent coherence. These findings strongly suggest the realization of a one-dimensional Kondo lattice, offering a platform for investigating various rare and unusual phenomena.

Magnetic molecules constitute a diverse and expanding array of functional components with the potential to revolutionize conventional electronics, provided their intricate properties can be seamlessly integrated into electronic or spintronic circuits and nanodevices. Recent attention has been notably directed towards chemically

synthesized spin systems, such as those based on magnetic modifications of carbon nanotubes or graphene, diverging from the traditional spin-crossover (SCO) molecules. These systems have attracted considerable interest due to their ability to function as spin switches, undergoing alterations in their spin states in response to external stimuli like light, pressure, or temperature. This spin modification, facilitated by an electro-structural transition within the molecule, leads to observable changes at the macroscopic level, including shifts in luminescence, magnetism, volume, and electron properties. Such adaptability grants chemically synthesized spin systems functionalities like spin switching, spin memory, or sensing capabilities, opening up new avenues for exploration in electronic and spintronic applications.

Such hybrid spin systems offer insights into fundamental aspects of highly correlated systems. For instance, when a localized spin impurity interacts with conduction electrons in a metallic host, it leads to the formation of a many-body singlet state known as the Kondo resonance or Kondo cloud [186]. This phenomenon, termed the Kondo effect, has been extensively studied and observed across a wide range of materials and systems [187]–[189]. However, our understanding is less developed for systems where dense concentrations of spin impurities enable interactions between spin centers. In such scenarios, the localized spin centers indirectly couple due to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [190], [191], resulting in a coherent superposition of screening clouds across the material and exhibiting Heavy Fermion (HF) behavior [192]. Kondo lattice systems are thus intriguing subjects of study as they provide access to exciting physical phenomena such as correlated disorder [193], macroscopic entanglement [194], and notably, Quantum Criticality [195]–[197]. Quantum criticality has garnered significant attention both theoretically and experimentally. The fundamental physics underlying these phenomena is encapsulated in the Kondo lattice Model (KLM):

$$H_{KLM} = -t \sum_{\langle i,j \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} + J_K \sum_i \mathbf{S}_i^c \cdot \mathbf{S}_i^f + J_H \sum_i \mathbf{S}_i^f \cdot \mathbf{S}_{i+1}^f \quad (4.7)$$

Where t , $c_{i,\sigma}^\dagger$, and $c_{j,\sigma}$ represent the hopping integral and creation/annihilation operators describing the conduction electrons. S_i^f and S_i^c denote the spin operators of

the localized f and conduction electrons at site i , respectively, coupled by the Kondo interaction J_K . The coupling, J_H , between neighboring localized spins is considered in the last term. This model is crucial for examining Quantum Critical Points (QCPs) and enables investigations into the global phase diagram of a system. The Doniach parameter [198], $x = \frac{TK}{J_H}$, serves as a direct probe of the competing energy scales of the Kondo effect and RKKY interaction. Variations in the density of spin impurities can alter the interaction strength, facilitating investigations into exotic phase changes as the magnetic impurity concentration varies [199]. Much of this research aims to determine the point at which global coherence is established (or broken), indicating the occurrence of a QCP [200]–[202].

Such diverse physical phenomena have been observed across a range of systems, including heavy fermionic materials [203], [204], artificial Kondo lattice systems [205], [206], and more recently, quantum-engineered molecular nanosystems [202], [207], [208]. Despite Carbon Nanotubes (CNTs) exhibiting numerous Kondo-related phenomena, little exploration has been conducted to investigate lattice behavior in CNTs. This is surprising given that CNTs have enabled studies of the Orbital Kondo effect in CNT-based charge qubits [209] and have recently demonstrated the impurity Kondo effect when functionalized [118] or filled with magnetic materials [210]. Additionally, owing to their reduced dimensionality, CNTs provide access to quasi-one-dimensionality, which represents an interesting limiting case of a Kondo lattice system [211]. Furthermore, CNTs can be easily integrated into nanoelectronic devices for high-resolution quantum transport studies.

In this study, we investigate Carbon Nanotubes (CNTs) as a potential quasi-one-dimensional Kondo lattice system. Through a precisely controlled synthetic chemistry process, we attach a Gd molecular magnet to CNTs, varying the concentration of the Gd spin impurity across different samples. Our findings reveal thermodynamic properties, such as temperature-dependent susceptibility and resistance, suggesting not only the presence of a Kondo effect (previously reported in [118]) but also potential characteristics of a Kondo lattice, including a coherent phase at low temperatures in samples with higher Gd content. To further explore these properties, we conduct low-temperature conductivity measurements on devices fabricated from bundles of

the functionalized CNTs. These measurements reveal a zero-field splitting manifested as finite energy resonance peaks, consistent with theoretical predictions for a low-dimensional Kondo lattice system [212].

4.3.1 Kondo signatures in temperature dependent magnetic susceptibility and resistance.

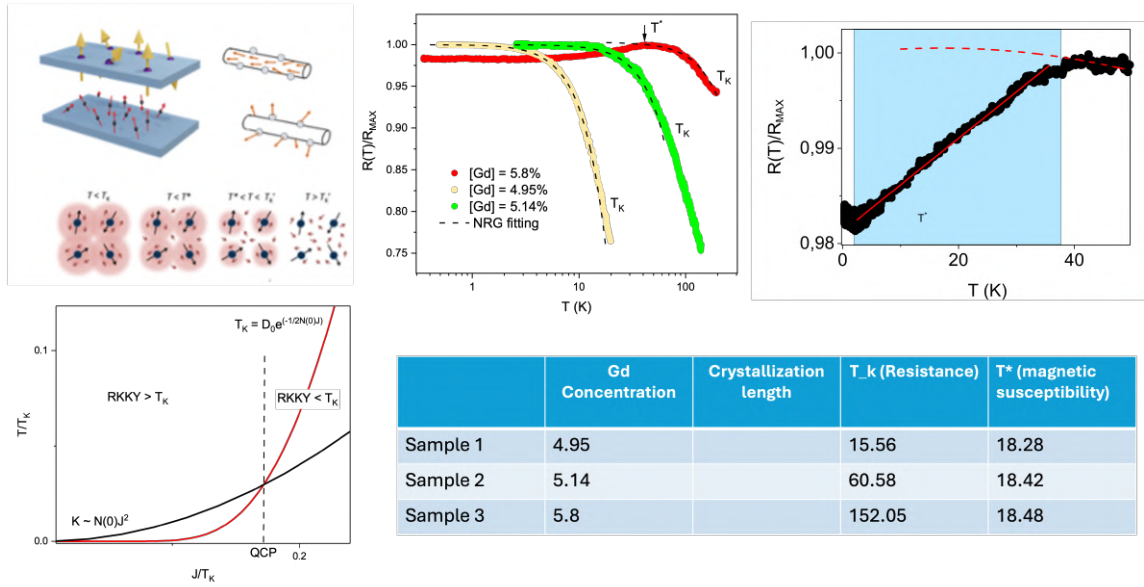


Figure 4.7 *Multiwalled CNTs possess intrinsic metallic properties due to their delocalized π -electron framework. When these nanotubes are functionalized by attaching magnetic centers, they exhibit a Kondo effect. Consequently, by adjusting the concentration of impurity spins, these systems can display lattice effects, making them ideal for studying quasi-one-dimensional Kondo lattice characteristics. In panel b, the transition from Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions to the Kondo effect is denoted by a Quantum Critical Point. Panel c demonstrates how the Kondo effect and RKKY interactions typically manifest in temperature-dependent resistance. In panel d, in samples with the highest concentration of Gd and consequently the strongest spin interaction, additional resistance transitions resembling a one-dimensional Kondo lattice can be observed. The table documents the progression of sample properties as the Gd concentration increases across samples.*

The presence of the impurity Kondo effect is evident in the temperature-dependent resistance. As depicted in Figure 4.7 (c and d), as the temperature decreases, the resistance increases in all samples. At the lowest temperatures, fitting to Wilson's Numerical Renormalization Group (NRG) formula is possible, which describes the

logarithmic rise in resistance attributed to spin-flip scattering from the magnetic impurities.

$$\rho(T) = \rho(0)[1 - c(T/T_K)^2] \quad (4.8)$$

Higher concentrations of Gd result in a higher Kondo temperature (T_K), similar to observations in magnetic susceptibility (Figure 4.8). In the case of the highest concentration of Gd (sample c), an additional decrease in resistance occurs after reaching a maximum resistance. This anomaly suggests the presence of a Kondo lattice system, where resistance decreases due to coherence effects between the spin centers. Such behavior typically indicates a crossover in the competition between the Ruderman-Kittel-Kasuya-Yosida interaction (J_H) and the Kondo interaction (J_K) [211].

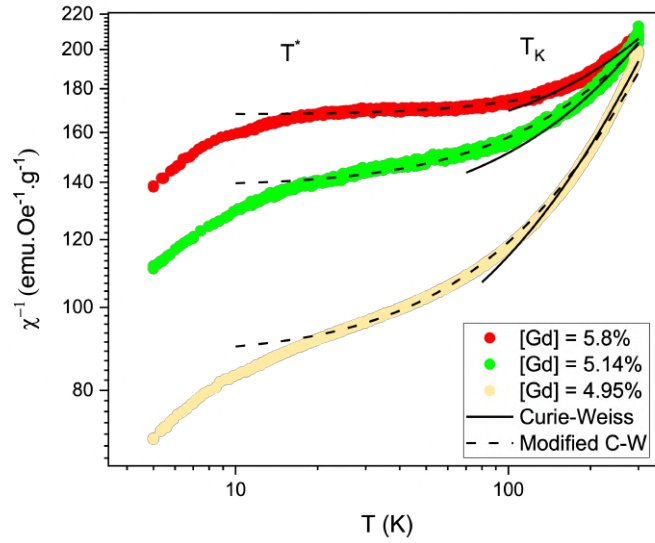


Figure 4.8 *a) The inverse susceptibility closely adheres to the Curie-Weiss law at elevated temperatures but diverges from the linear fit at lower temperatures, suggesting a transition to Pauli susceptibility and consequently entering a Kondo regime. Notably, the low-temperature rise in inverse susceptibility is more pronounced in samples with higher Gd concentration.*

As depicted in Figure 4.8, the inverse susceptibility of the material displays intricate behavior, characterized by a deviation from the Curie-Weiss law. This departure can only be adequately fitted to the data at elevated temperatures, eventually reaching a plateau and saturating with increasing Gd concentration. To model the data, a

modified Curie-Weiss law is employed:

$$\chi = \frac{C}{T - \theta - \ln(T_K)} \quad (4.9)$$

Here C represents the Curie constant and θ stands for the Weiss temperature, a modified term is introduced to account for the Kondo effect at lower temperatures. This modification incorporates a logarithmic dependence on the Kondo temperature (T_K), which is anticipated for a nanoscale system demonstrating the Kondo effect. By applying this modified Curie-Weiss fitting, it becomes possible to extract T_K as a variable dependent on the material's Gd concentration, revealing that higher concentrations correspond to higher T_K [213].

4.3.2 High spin concentration and 1D kondo lattice physics

As previously mentioned and emphasized in Figure 4.7d, the sample containing the highest Gd concentration displays an intriguing phenomenon: a further decrease in resistance following the attainment of maximum resistance. This observation suggests the potential for achieving magnetic phase transitions and quantum critical points via a chemical synthesis approach. However, it is crucial to subject the introduction of disorder through the chemical process to careful examination. On one hand, the additional attachment of Gd spins elevates the spin concentration, thereby decreasing the distance between spin centers along the lengths of the CNT tubes and enabling spin interactions. However, increased functionalization also leads to a greater disruption of the sp^2 framework of the CNT, consequently reducing conductivity.

As previously demonstrated [211], it is feasible to estimate the exchange interaction between the Gd spin centers and the conduction electrons utilizing the Kondo expression:

$$T_K = \frac{1}{n} \exp\left(-\frac{1}{J_K n}\right) \quad (4.10)$$

Where $n = 29 \text{ dos/eV}$ represents the density of states, employing $K_F = 11 \times 10^8 \text{ cm}^{-1}$. we derive an estimate of $J_K = 0.0069 \text{ meV}$. Considering the observation of the

RKKY regime, which suggests a breakdown or crossover from the Kondo regime, J_H is anticipated to be comparable or equal in magnitude to the calculated J_K above. For the sample with a higher concentration of Gd, we adhere to previous findings [214] to determine the characteristic RKKY temperature of K.

$$T_{RKKY} = J_H^2 n \sim 16K \quad (4.11)$$

Which is near to the final saturation of the temperature resistance in sample 3, i.e. approximately 10 K as seen in figure 4.7 d.

4.3.3 Conclusion

In this study, we have explored the potential of creating a spin-correlated system based on carbon nanotubes. Our findings demonstrate that by adjusting the concentration of Gd-ligands, we can not only observe the impurity Kondo effect but also detect characteristics of Kondo lattice behavior, including additional transitions in resistance at low temperatures associated with the coherence of the Kondo lattice. This research holds significance as it showcases how precise synthetic methods can be employed to fabricate a highly correlated spin system, providing insights into heavy fermion behavior. From a fundamental perspective, this work addresses several unresolved questions concerning the transition from impurity to lattice Kondo systems. These include inquiries into the nature of the Kondo breakdown, the interplay between RKKY and Kondo interactions, and their role in the emergence of quantum critical points and the potential measurement of the Kondo screening cloud, which determines the entanglement length of the system. Moreover, this research holds promise for the development of innovative nanoscale spin-textured materials, which are increasingly relevant for emerging spintronic applications such as spin-circuits and SWD nanowire elements. While this report represents only the initial exploration of this field, we anticipate that further investigations, including studies on heat capacity and transport in single nanotube devices, will offer deeper insights into the realization of a true one-dimensional Kondo lattice, a milestone that has yet to be achieved in a molecular system.

Chapter 5

CVD diamond synthesis

5.1 MPECVD diamond Reactor optimisation

The present chapter delves into enhancing the functionalities of the Microwave Assisted Plasma Chemical Vapor Deposition (CVD) reactor situated at NSTPL, University of the Witwatersrand, alongside discussing the parameters for diamond growth within it. The expansion of operational capabilities involves several upgrades, such as enhancing the waveguide by integrating an applicator to concentrate the electric field within specified regions of the reaction chamber, adjusting the substrate holder assembly to resonate with the microwave frequency for stable plasma ignition near the sample, and so forth. By modifying the original design of the microwave plasma CVD reactor, including the replacement and adjustment of aforementioned components, as well as refining the gas flow design and operational parameters, it enables maximum forward power transfer with minimal reflection, thereby facilitating the generation of stable plasma over a 1-inch area. Consequently, this advancement allows for the growth of continuous diamond thin films on various substrates like silicon, fused quartz, and single crystal diamond.

5.1.1 Original MPECVD Reactor Assembly

The MWCVD system installed at NSTPL consists of a microwave power generator paired with a rectangular waveguide for transmitting microwaves. These microwaves

are conveyed through a dielectric quartz window attached to the end of the rectangular waveguide port. The reactor, or cavity, is constructed from stainless steel (SS) material and has a long cylindrical shape with two side port windows for observing the plasma. The substrate stage holder comprises a round SS plate connected to an adjustable Z-axis rod, positioned 200mm below the rectangular shaped dielectric window within the vacuum zone of the microwave reactor cavity (See Figure 5.1). A multi-chambered

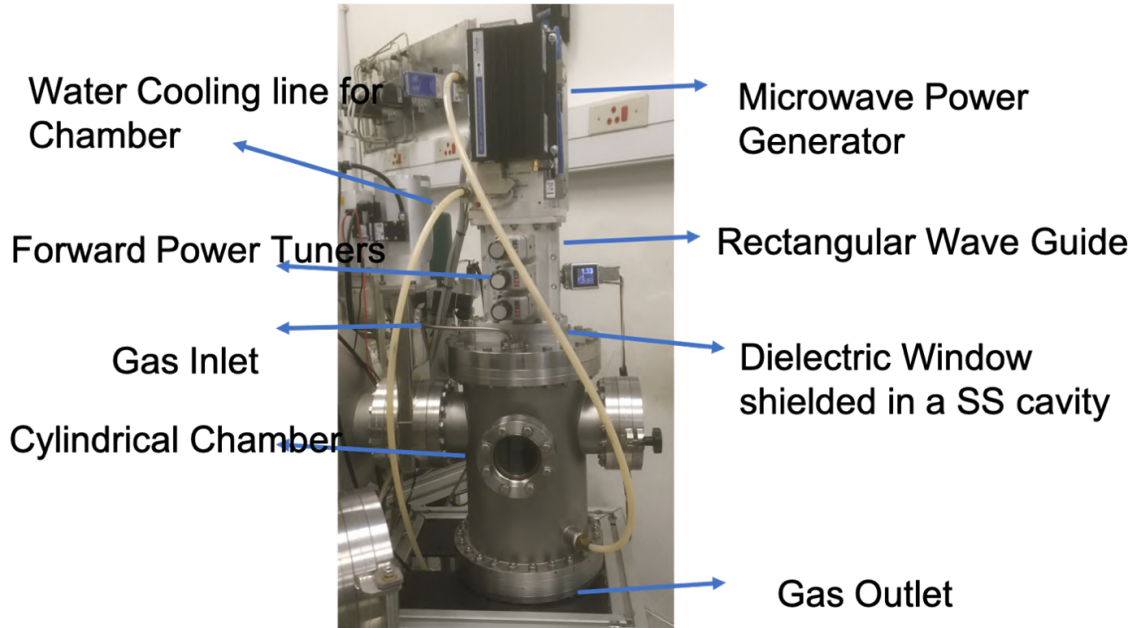


Figure 5.1 *Original MPECVD reactor assembly at NSTPL:*

deposition system, developed by Vacutec, was designed for in-situ sample transfer for metal film deposition and etching after diamond deposition in the MWCVD. Initially, a movable arm was intended to serve as the substrate holder, but this configuration disrupted the gas flow pattern between the two chambers, resulting in a failure to generate plasma. This issue was resolved by introducing an independent movable substrate stage, enabling plasma ignition within the MW CVD chamber.

Numerous experiments were conducted to optimize the CVD reactor system, aligning the microwave frequency with the cavity length by adjusting the Z-axis (height) of the substrate holder. This optimization resulted in a consistent capability to initiate plasma in the CVD reactor system (refer to Fig 5.1). However, plasma instability and significant thermal gradients across the small area led to substrate etching, particularly along the edges of the copper stub (Fig 5.2). During operation with CH_4/H_2 at a gas flow ratio of 2%:98%, amorphous carbon deposition was observed predominantly at

the bottom of the copper stub.

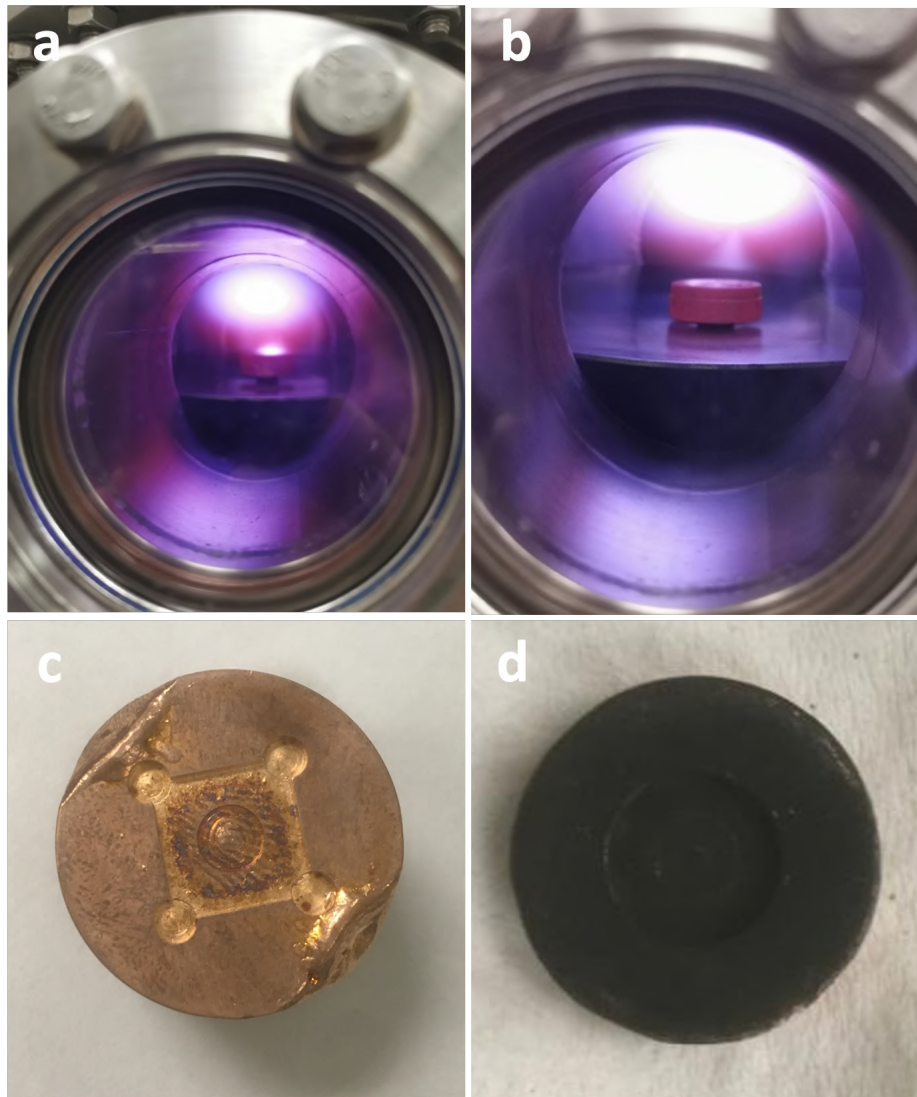


Figure 5.2 *Plasma and substrate:*

Summary of the operational issues:

- Inadequate microwave cavity coupling configuration, including the transition from waveguide to coaxial transmission and tuning antenna setup.
- Plasma instability, requiring sustained positioning for prolonged periods, necessitating alignment of cavity geometry with microwave frequency (2.45GHz).
- Lack of capability to determine Plasma Power density (T_e and T_{gas}), crucial for assessing diamond deposition quality, with the suggestion of incorporating a two-color pyrometer.

- Absence of a cooling stage for extended growth runs.

Recommendations:

- Introduce a Microwave Guide to Coaxial Transition Unit alongside tuning probe/antenna adjustments for improved cavity coupling.
- Implement modifications in substrate holder and cavity design to enhance gas flow pattern and achieve better microwave frequency matching.
- Integrate a cooling system for the substrate holder to regulate temperature during high-power microwave usage, considering the use of a two-color pyrometer for temperature measurement.
- Install an electronically controlled pressure gate valve to maintain stable gas flow conditions within the cavity.
- Incorporate a microwave leak detector for safety and system integrity.

5.1.2 CVD Diamond Reactor Engineering

The MPECVD process stands out as the predominant technique for producing high-quality diamond thin films. Unlike HF CVD reactors, it offers advantages such as the ability to apply high pressure and high power to generate top-notch diamond thin films. Additionally, it eliminates the need for a separate substrate heater since the plasma provides adequate thermal energy transfer. The evolution of CVD technique in successfully depositing diamonds has already been discussed earlier.

To facilitate diamond deposition within a CVD reactor, it's essential to create plasma, a region with high electric field strength, near the substrate where diamond deposition occurs. Successful plasma ignition and focusing it near the substrate involves exciting an electromagnetic cavity at its resonant frequency. This frequency is dependent on the geometry and dielectric properties of the cavity. The primary consideration in the design of microwave plasma reactors is cavity matching, ensuring the electric field

structure aligns to locally amplify the field strength in front of the substrate, promoting enhanced and uniform field distribution.

There are two types of resonance modes: TE and TM, depending on whether the electric or magnetic field, respectively, is perpendicular to the cavity axis (see Figure 5.3). These modes become significant in designing the dimensions of the CVD reactor chamber, as the boundary conditions on the cavity's metal walls require zero tangential components for the electric field, thereby enforcing the field to be normal to the surface. Transverse magnetic modes, especially TM_{0mn} modes, are often favored in plasma reactor design over transverse electric modes. This preference arises because in transverse electric modes, high electric field regions in contact with the metallic walls might not effectively ignite plasma near the substrate holder.

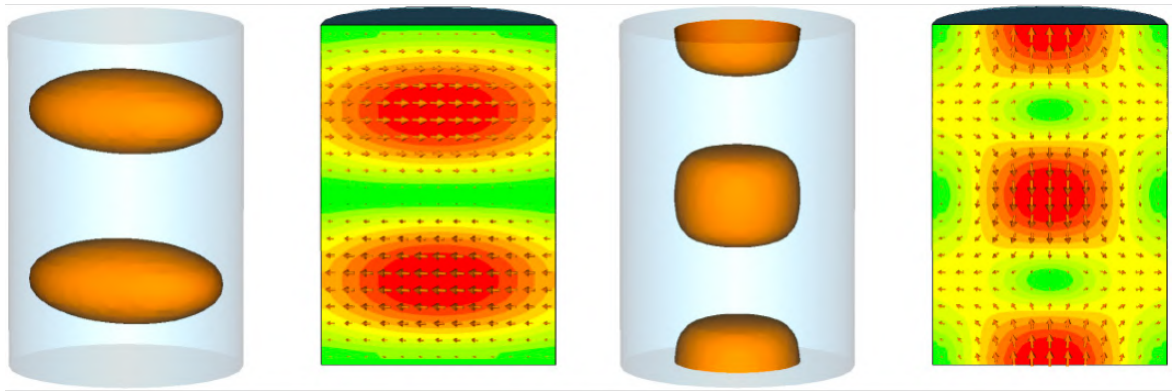


Figure 5.3 *Electric field distribution in TE and TM modes. here, TE₁₁₂ on the left and TM₀₁₂ on the right. adapted from [215]*

The quality of diamond thin films produced through this technique hinges on the characteristics of the plasma discharge. Power density, measured as the ratio of maximum absorbed power to plasma volume, directly impacts the plasma discharge, subsequently affecting electron temperature (T_e) and gas temperature (T_{gas}). A typical microwave plasma chamber comprises a plasma chamber, a substrate holder within the plasma chamber to support the substrate for diamond material deposition, a microwave coupling setup to transmit microwaves from a generator into the plasma chamber, and a gas flow system to introduce and remove process gases. The microwave coupling setup typically includes an annular dielectric window, a coaxial waveguide with inner and outer conductors to transmit microwaves to the annular dielectric window, and a waveguide plate featuring multiple apertures arranged in an annular

pattern with arms extending between the apertures, each forming a waveguide to direct microwaves towards the plasma chamber.

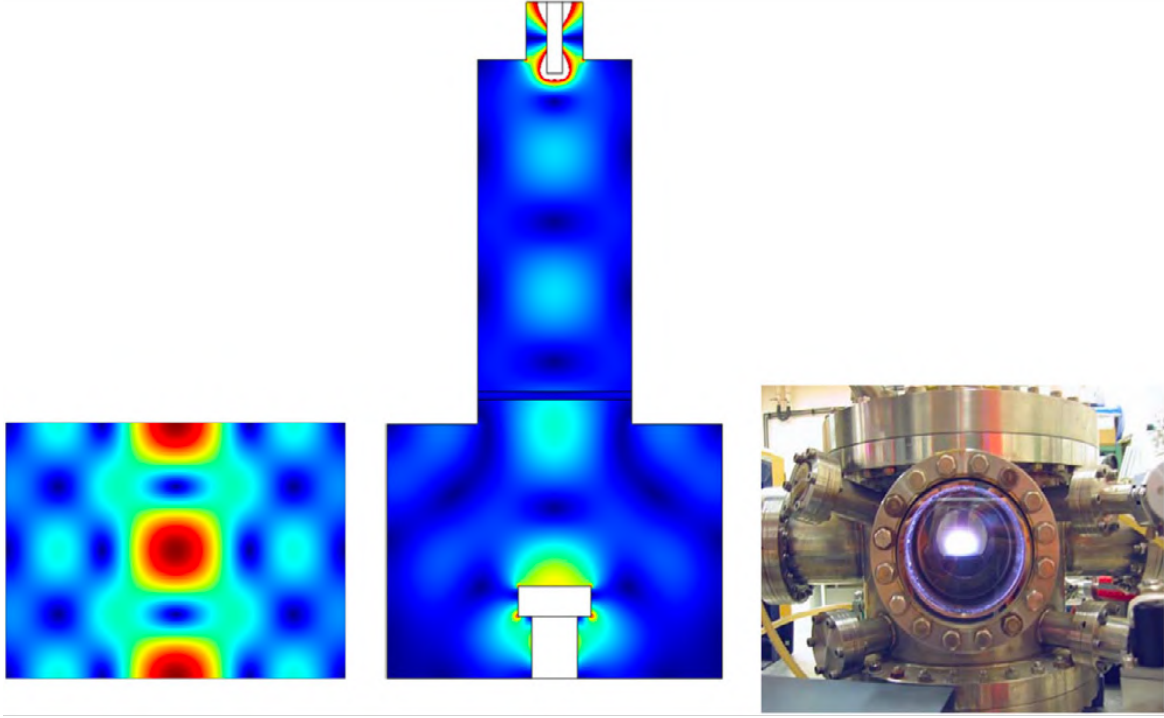


Figure 5.4 *Electric field distribution in SEKI model: adapted from [215]*

The growth of CVD diamond is intricate, making it challenging to fully explain. It entails understanding the gas composition surrounding the growing surface and detailing surface kinetics, including adsorption-desorption, abstraction, and migration phenomena. The model presented by Harris and Goodwin simplifies the growth process considerably. According to this model, diamond growth occurs through two species, H and CH₃, engaging in five distinct reactions.

Figure 5.5 illustrates the evolution of distribution of the key growth parameters across a pressure range of 50 to 300 mbar. The microwave (MW) power has been adjusted accordingly at each pressure to maintain a consistent plasma volume. Notably, the power deposition within the plasma is uneven, with a notable concentration near the substrate surface. In essence, the use of MW for generating atomic hydrogen offers several advantages. Firstly, MW plasmas facilitate high gas temperatures (>3200 K), crucial for efficient H production through the thermal dissociation of H_2 , in contrast to hot filament sources limited to approximately 2500 K. Secondly, MW reactors provide design flexibility, enabling improved plasma uniformity over extensive surfaces while

simultaneously achieving high growth rates.

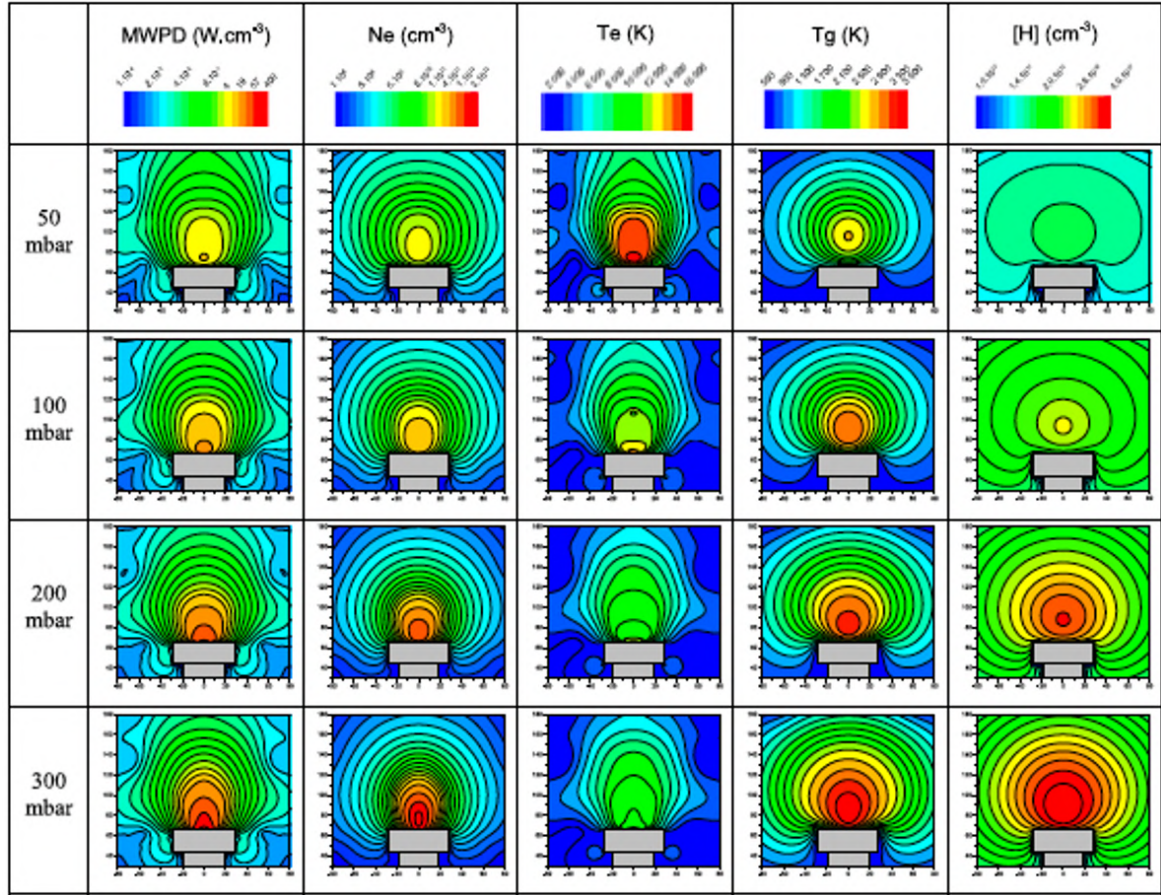


Figure 5.5 CVD diamond key growth parameters: adapted from [215]

5.1.3 Upgraded MPECVD reactor

The enhanced MPECVD reactor now incorporates a coaxial transmission/applicator for efficient microwave coupling to the cavity (AsteX), along with a circular dielectric window isolating the chamber from the atmosphere. It features a gas diffuser integrated with the gas inlet pipe, as well as a circular stage holder with a flat surface for positioning 1-inch tungsten/molybdenum metal discs. Additionally, an optical pyrometer is installed to accurately measure the substrate temperature 5.6. The upgraded MPECVD setup enables the ignition of plasma focused on the substrate. Additionally, the plasma remains stable, facilitating the growth of uniform diamond films on the surface.

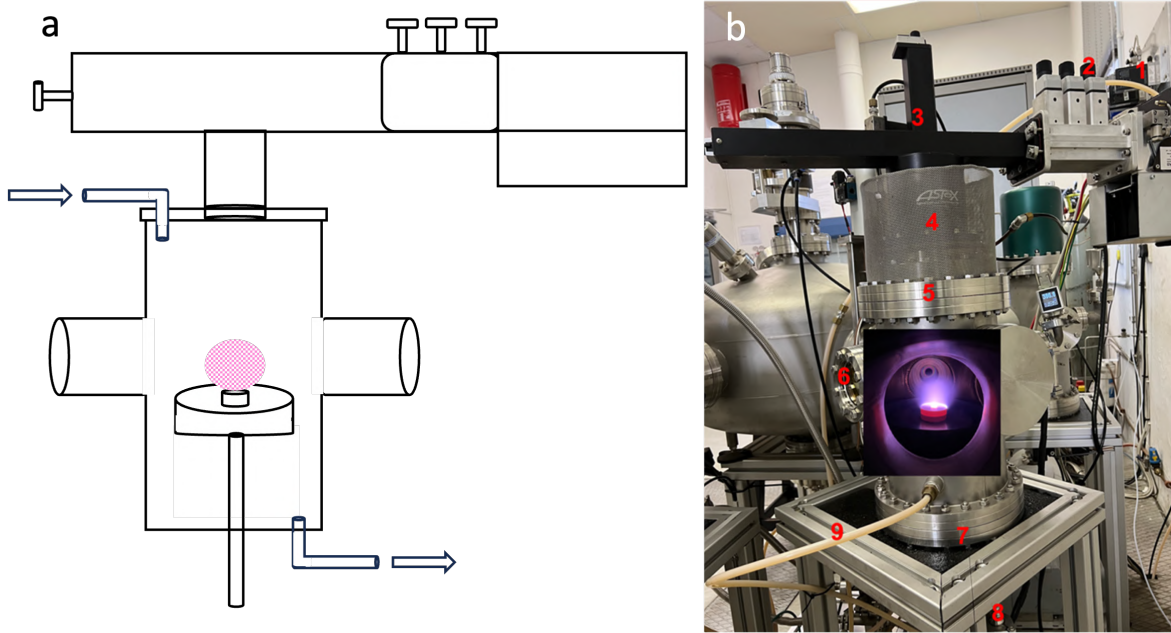


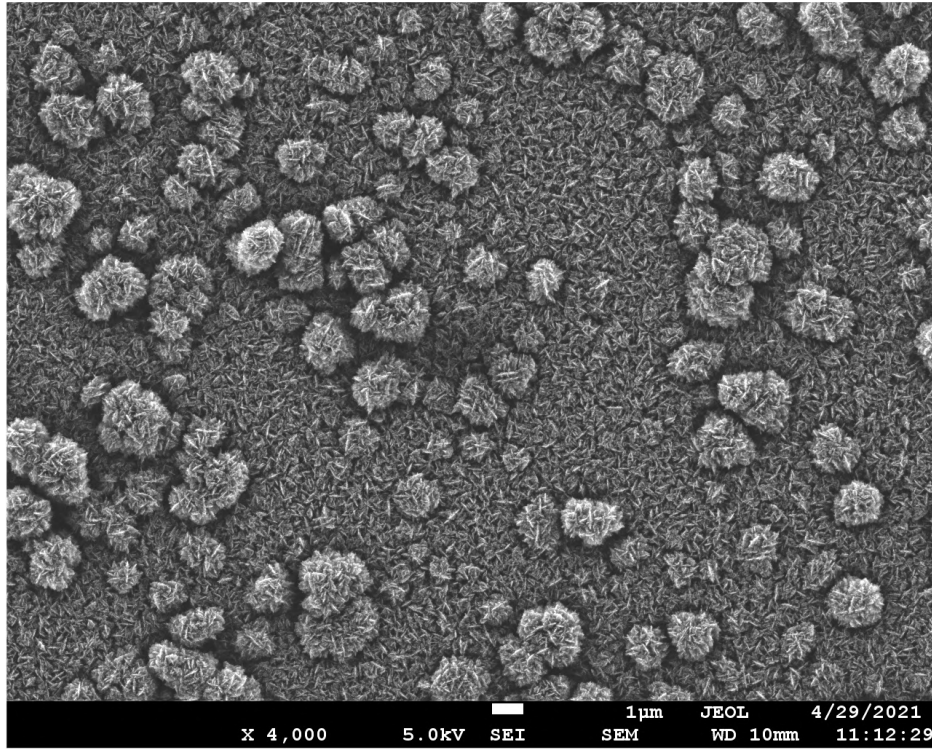
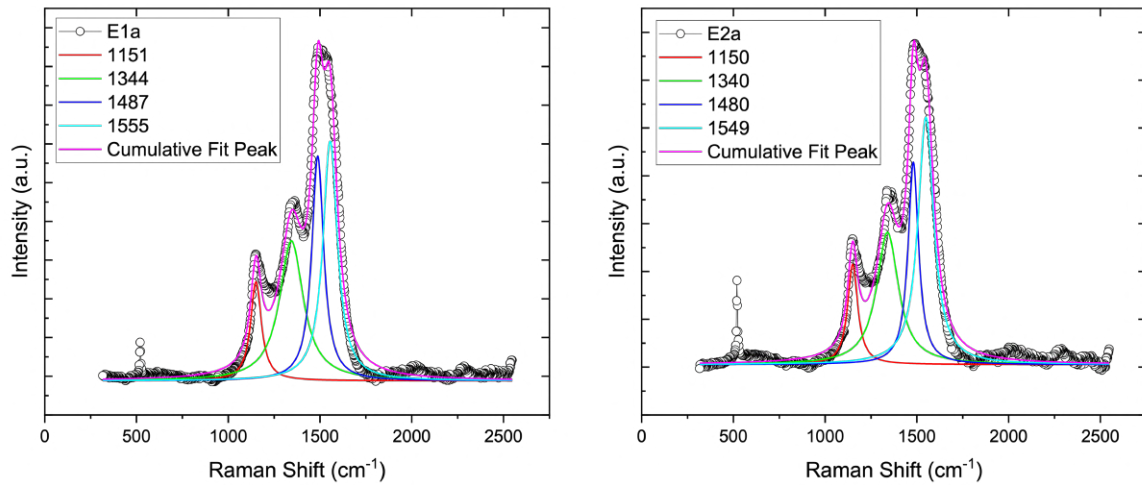
Figure 5.6 *Custom-built MPECVD reactor at NSTPL: a) Schematic picture of self-assembled MPECVD system. b) MPECVD with different parts including a (1) MKS solid state Microwave generator, (2) Sub tuner, (3) Waveguide with applicator, (4) antenna connecting the waveguide and CVD chamber, (5) a transparent quartz window is placed between the antenna and the CVD chamber, (6) CVD main chamber with substrate stage and holder, (7) Stage height adjustor, (8) Vacuum line, and (9) Water circulation line.*

5.2 UNCD films growth Optimisation

Growth trails with Original MWCVD assembly

Figure 5.7 illustrates the standard morphology of carbon films grown on a silicon substrate utilizing the original MPECVD assembly. Due to the uneven distribution of the plasma region, the majority of the deposited material appeared as amorphous carbon, a finding confirmed through Raman spectra measurements (see Fig 5.8 and 5.9). The deposition process occurred on a silicon substrate under conditions of 40 mbar pressure, a substrate temperature of 800°C, MW power 800 W and utilizing a gas mixture comprising 1% CH₄/H₂ at 200 SCCM flow rate.

Figures 5.8 and 5.9 display the deconvoluted Raman spectrum of carbon films grown using the original MPECVD assembly, excluding the MW applicator. Raman peaks centered at 1150 cm⁻¹ and 1480 cm⁻¹ are attributed to t-PA carbon, while the D peak

Figure 5.7 *Original CVD:*Figure 5.8 *Carbon films grown using original MWPECVD assembly*

centered at 1340 cm^{-1} is associated with disordered carbon. Additionally, the G peak centered at 1550 cm^{-1} is indicative of graphitic carbon. It is noteworthy that diamond peak at 1332 cm^{-1} is not seen and therefore the film grown is considered as amorphous carbon.

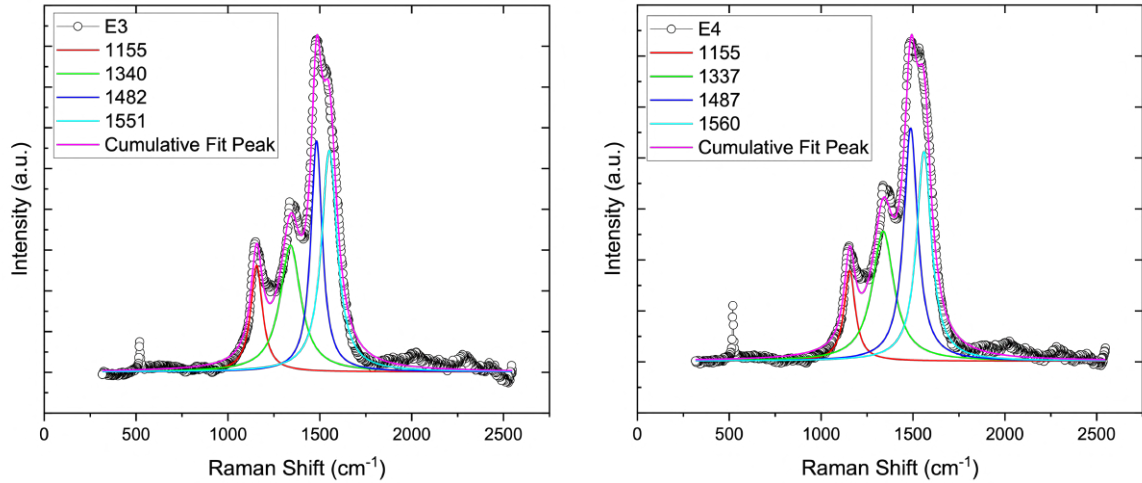


Figure 5.9 Raman spectra of carbon films grown using original MWPECVD assembly: a) E3 and b) E4.

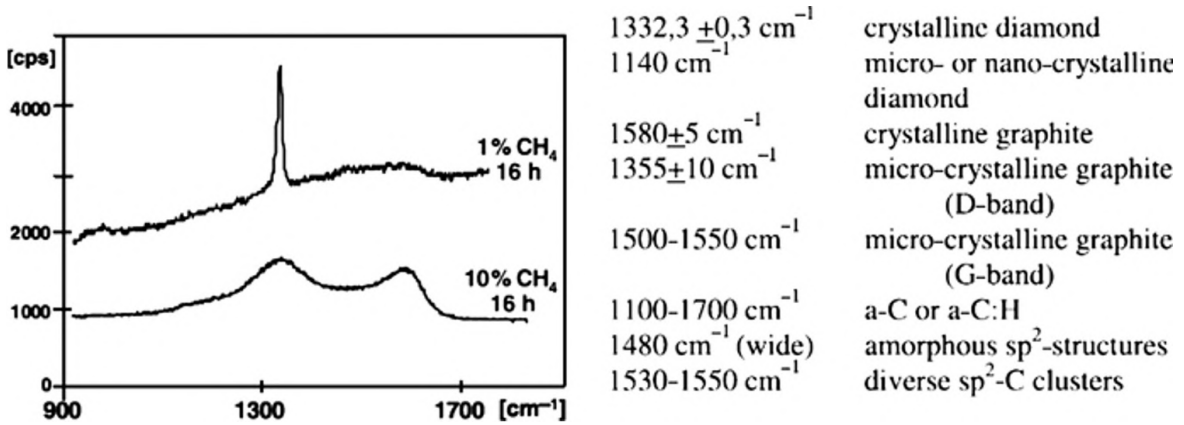


Figure 5.10 Analysis of Raman spectra and assigning peaks to different carbon microstructures. adopted from [216]

5.2.1 Growth Optimisation with upgraded MPECVD reactor

CVD diamond synthesis has historically aimed at creating faceted diamond layers, but certain growth conditions have led to the observation of polycrystalline diamonds, often in half-spherical shapes referred to as ballases. Various methods for depositing diamond are now available, allowing for faceted diamond growth under diverse parameters, mainly relying on CH_4/H_2 gas mixtures to produce atomic hydrogen and carbon radicals [217]. These faceted CVD diamond layers are utilized in industrial settings for abrasives, optics, and heat sinks. However, under deteriorating growth conditions resulting in heightened carbon saturation, twin and stacking faults can increase significantly [218], leading to the radial growth of unfaceted, polycrystalline

diamonds resembling ballas [219], which possess enhanced abrasive properties due to their high density of twin defects [220]. Raman spectroscopy is commonly used to analyze carbon bonding in diamond films, distinguishing between diamond, graphite, and amorphous carbon based on their spectral characteristics (see Fig 5.10). Crystalline diamond displays a sharp peak at 1332 cm^{-1} , while graphite exhibits a peak between $1550\text{--}1585\text{ cm}^{-1}$. Additionally, Raman spectroscopy can detect micro- or nano- crystalline forms, with micro-/nano- crystalline diamond featuring a peak at $1140\text{--}1180\text{ cm}^{-1}$ and micro/nanocrystalline graphite at approximately $1333\text{--}1340\text{ cm}^{-1}$ (D-band) [221].

In this research, I have investigated the parameters necessary for the growth of ballas-type layers using a microwave CVD method and CH_4/H_2 gas mixtures at substrate temperatures ranging from 800 to $1200\text{ }^\circ\text{C}$. By increasing the concentration of CH_4 , we observed the transformation from faceted diamond layers to ballas structures, and subsequently, the shift from ballas layers to depositions containing graphitic elements. The characterization of these changes was conducted through SEM imaging and Raman spectroscopy.

Faceted crystals (both (111) and (100)) typically exhibit a distinct resonant peak at 1332 cm^{-1} . However, the presence of defects like twinning and carbon supersaturation, achieved by increasing methane concentration, can result in the formation of ballas and ballas-graphite-type nanodiamond structures showing a broader peak centered at $1333 - 1340\text{ cm}^{-1}$ (see Fig.5.11).

Fig 5.12 depicts ballas-shaped nanodiamond structures formed following upgrades to the MWPECVD assembly. The Raman spectroscopy data (see Fig. 5.13 and 5.14) reveals the vibrational modes of different carbon structures as follows:

- A peak in the range of $1150\text{--}1155\text{ cm}^{-1}$ represents trans-polyacetylene (t-PA) carbon.
- A peak centred at 1132 cm^{-1} signifies diamond.
- A peak at 1482 cm^{-1} corresponds to second order resonant peak of t-PA carbon.
- Lastly, a G-band centered at 1551 cm^{-1} indicates the presence of graphitic carbon.

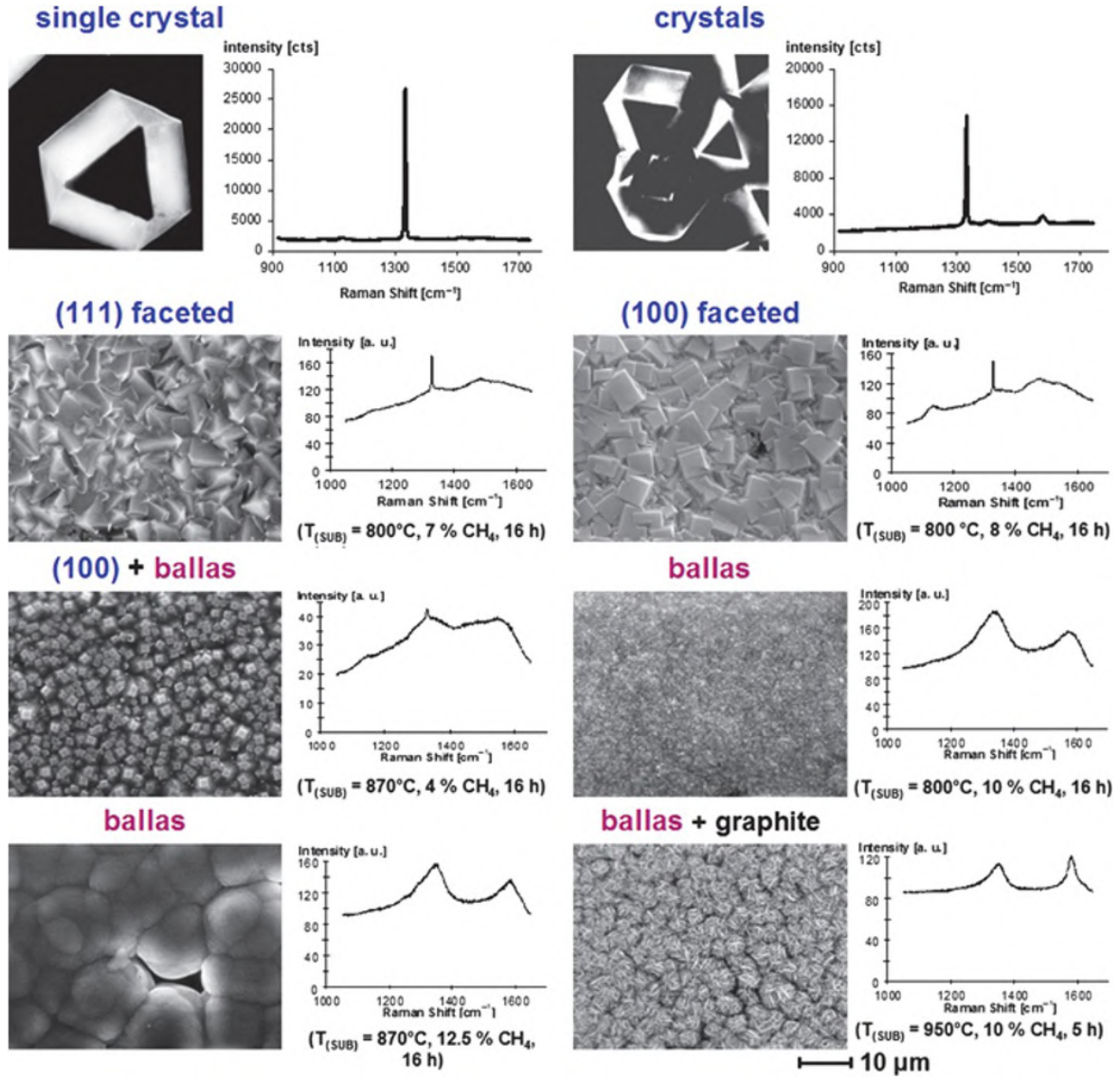


Figure 5.11 Raman spectra of various diamond morphologies. adopted from [216]

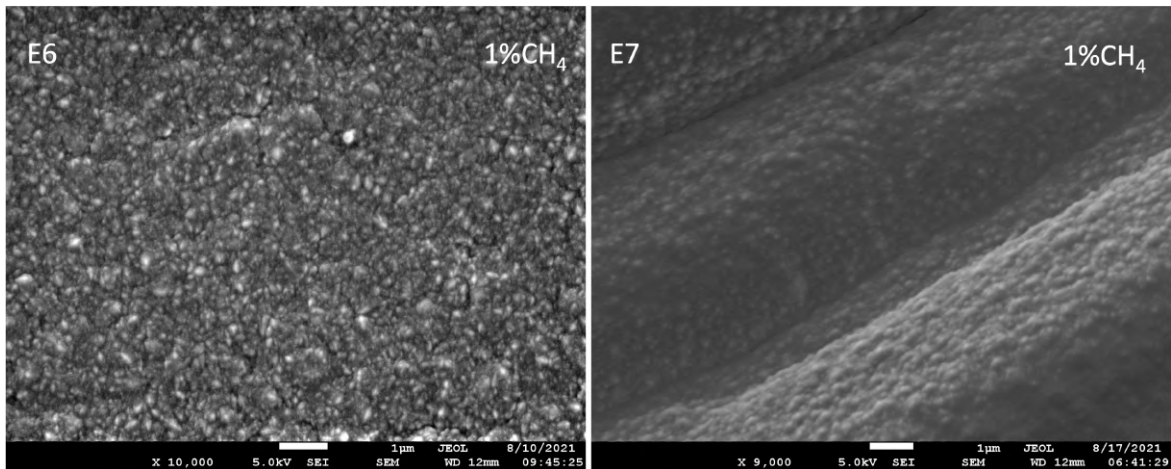


Figure 5.12 SEM images of ballas shaped nanodiamond structures grown on Si substrate.

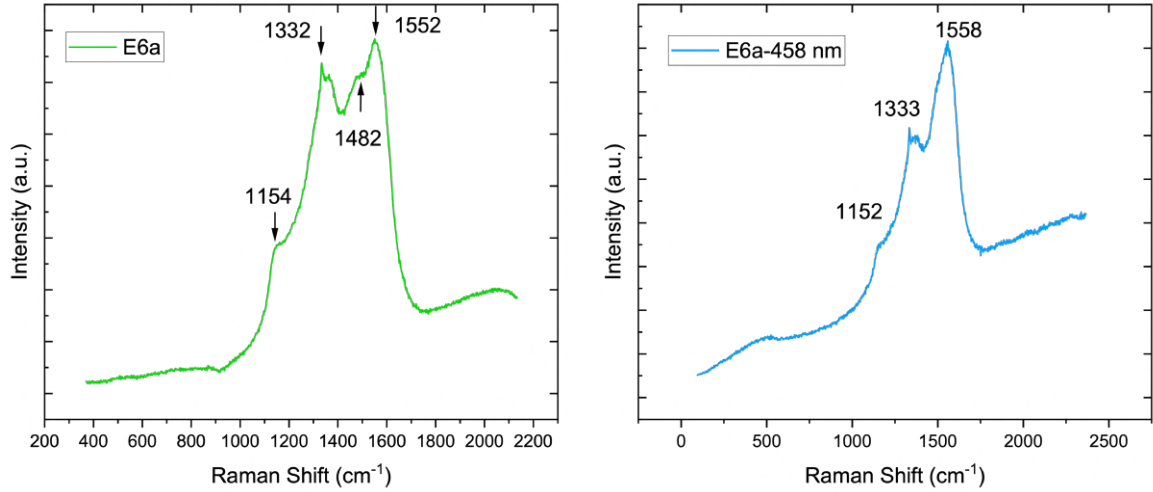


Figure 5.13 Raman spectrum obtained on nanodiamond structures using 514 nm (Green) and 458 nm (Blue) wavelength lasers. a)

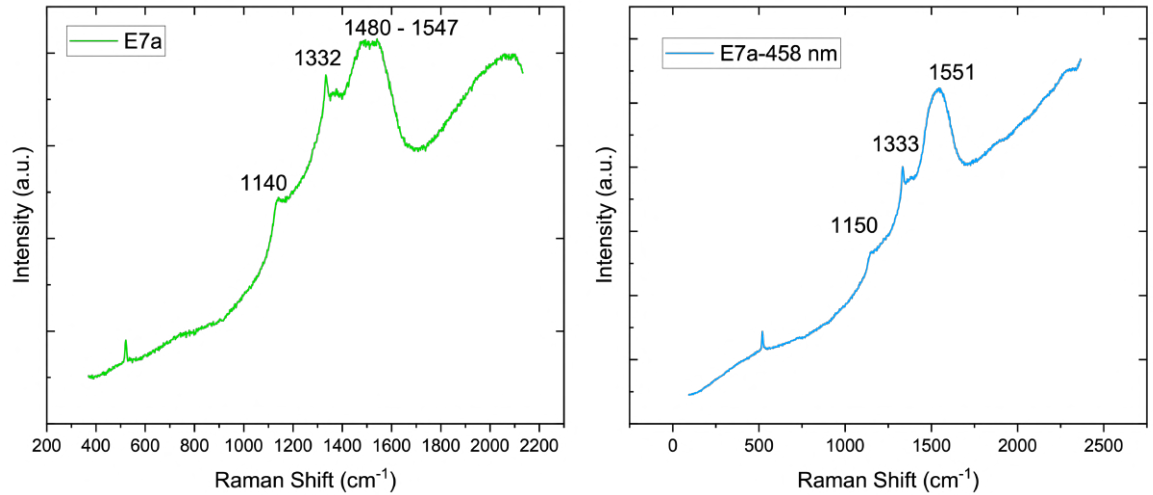


Figure 5.14 Raman spectrum obtained on nanodiamond structures using 514 nm (Green) and 458 nm (Blue) wavelength lasers.

5.2.2 Faceted nanodiamond thin films growth

The process of chemical vapor deposition for diamond film formation progresses through four distinct stages over time: nucleation, growth of nuclei, coalescence (or coagulation), and the formation of continuous layers. The kinetics of this CVD process are primarily influenced by the substrate temperature. However, other factors such as pressure and the concentration of methane in hydrogen also play a significant role. During the initial stage of growth, diamond particles exhibit nearly ideal shapes such as octahedrons, cubooctahedrons, or pseudopentagons when the substrate temperature (T_s) exceeds 750°C . At lower temperatures, they tend to form globular

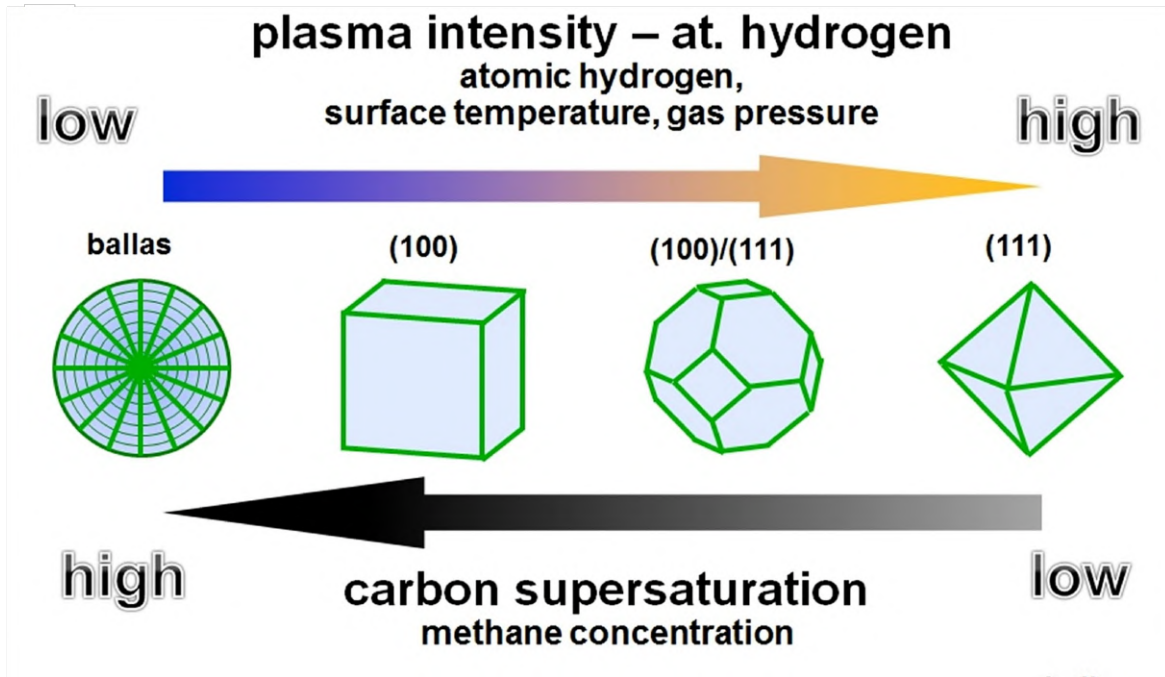


Figure 5.15 *Schematic representation of morphological changes with respect to change in the methane concentration and plasma intensity. adapted from [222]*

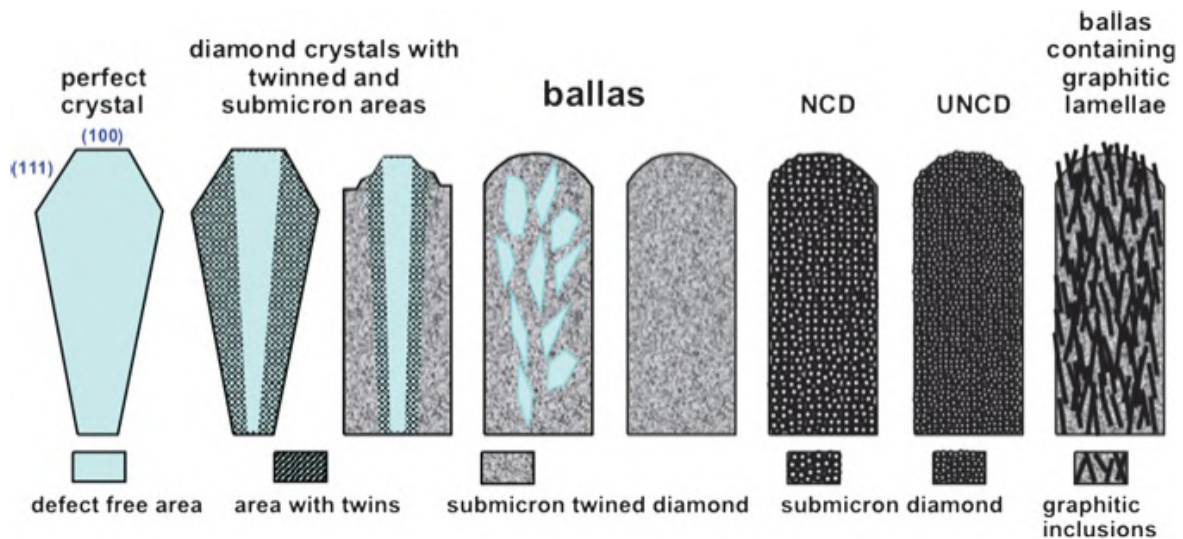


Figure 5.16 *Scheme diagram illustrating different defect distributions seen in diamond layers with varying morphologies. a-f) shows the transition of diamond microstructure from well faceted over ballas to graphitic carbon. adapted from [216]*

shapes. Once coagulation occurs, continuous films are established. The quality of diamond crystallinity improves with lower pressure and methane concentration. The spherical shape is altered due to the development of triple joints in continuous films, resulting in distortion without porosity. By introducing the lower concentration of methane and substrate temperature at 800 C, faceted nanodiamond structure can be

grown. The structured diamond (Fig. 5.11) has been extensively documented, yet in contrast to naturally occurring diamond, which is primarily characterized by high crystallinity, CVD diamond may harbor numerous imperfections. Micro-twins are predominantly visible in the growth sectors aligned with the (111) orientation, while dislocations tend to occur more frequently in the growth sectors aligned with the (100) orientation. As depicted in Fig. 5.16, the areas exhibiting micro-twins expand until the facets vanish, resulting in the formation of a ballas morphology (refer to Fig. 5.16 - submicron twinned diamond). An interim phase of (100) facets amidst an unfaceted surrounding can also be observed (Fig. 5.16 - area with twins).

Figure 5.17 depicts the growth process of a faceted diamond structure on a quartz substrate within a gas mixture comprising 1% CH₄, 5% N₂, and H₂. Notably, despite an increase in N₂ concentration, the faceted diamond structures persist, indicating the sustenance of carbon supersaturation. It's been observed that heightened carbon supersaturation typically induces a shift in diamond morphology from faceted to unfaceted, leading to the formation of radially grown polycrystalline nanodiamond structures. However, it's noteworthy that at lower temperatures, this transition between morphologies extends to higher methane concentrations.

Figure 5.18 displays the Raman spectra of faceted nanodiamond structures grown on quartz substrates with 5% and 10% N₂ doping, respectively. The Raman spectra reveal peaks centred at 1159 cm⁻¹, 1332 cm⁻¹, 1480 cm⁻¹, and 1575 cm⁻¹, which are commonly recognized as characteristic signatures for confirming UNCD. The full width at half maximum (FWHM) of the diamond peak (FWHM_D), representing the diamond area, is measured at 181.6, whereas the FWHM of the graphitic carbon peak (FWHM_G) is 80. This further verifies that a larger portion of the thin film is covered with sp³ hybridized carbon even though up to 10% N₂ doping is introduced.

5.2.3 Ballas nanodiamond thin films growth

The transition from faceted nanodiamond to ballas-shaped nanodiamond layers with the increase in methane concentration from 1% to 4% in the total gas mixture is

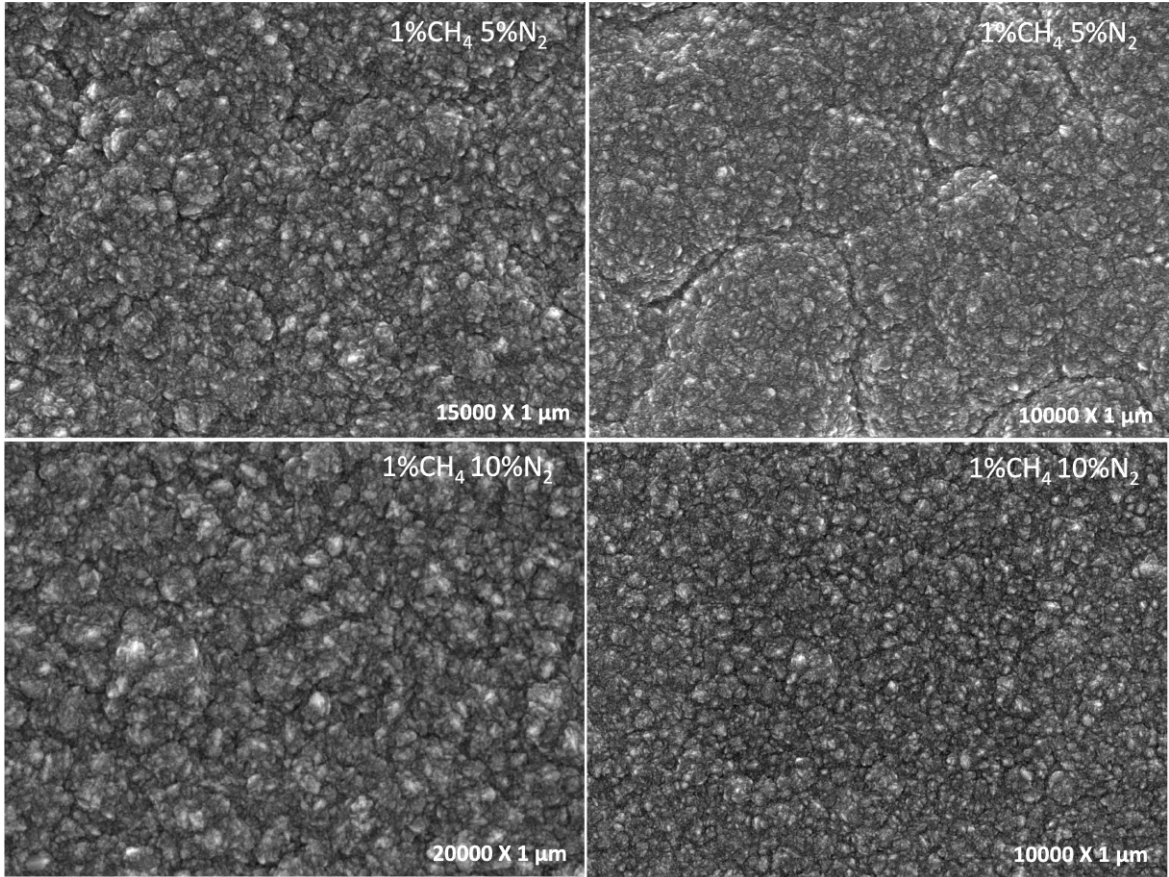


Figure 5.17 *Faceted nanodiamond structure grown on a quartz at substrate temperature 800 C and MW power of 900W with 1%CH₄/5% - 10%N₂/H₂ gas mixture.*

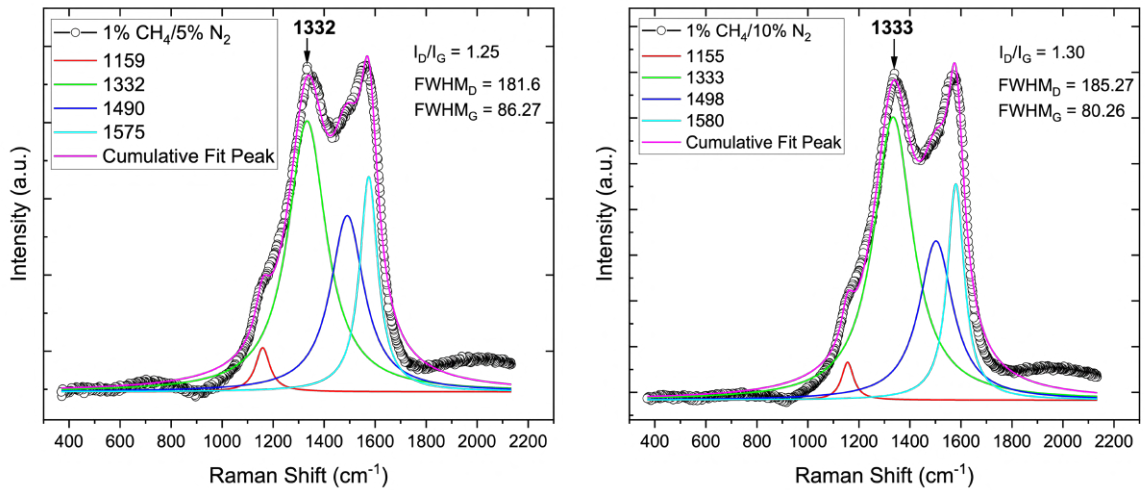


Figure 5.18 *Raman Spectra of faceted nanodiamond structures grown on a quartz substrate with 5% N₂ and 10% N₂ doping.*

discussed below. Nano-crystalline materials are highly intriguing due to their distinct mechanical and physical attributes compared to coarse-grained varieties. In the realm of diamond, the CVD ballas type stands out as a nano-crystalline material. Ballas, also

known by various names such as ball-shaped diamond or cauliflower-like, is essentially a non-faceted, polycrystalline diamond grown in a spherical manner with a radial structure. The deposition conditions can lead to different morphological structures of ballas, including faceted regions, flat formations, and those with graphitic inclusions. In recent years, advancements in nano-crystalline diamond coatings have been made by incorporating fullerene into the deposition gas or by using Ar/CH mixtures with reduced hydrogen content.

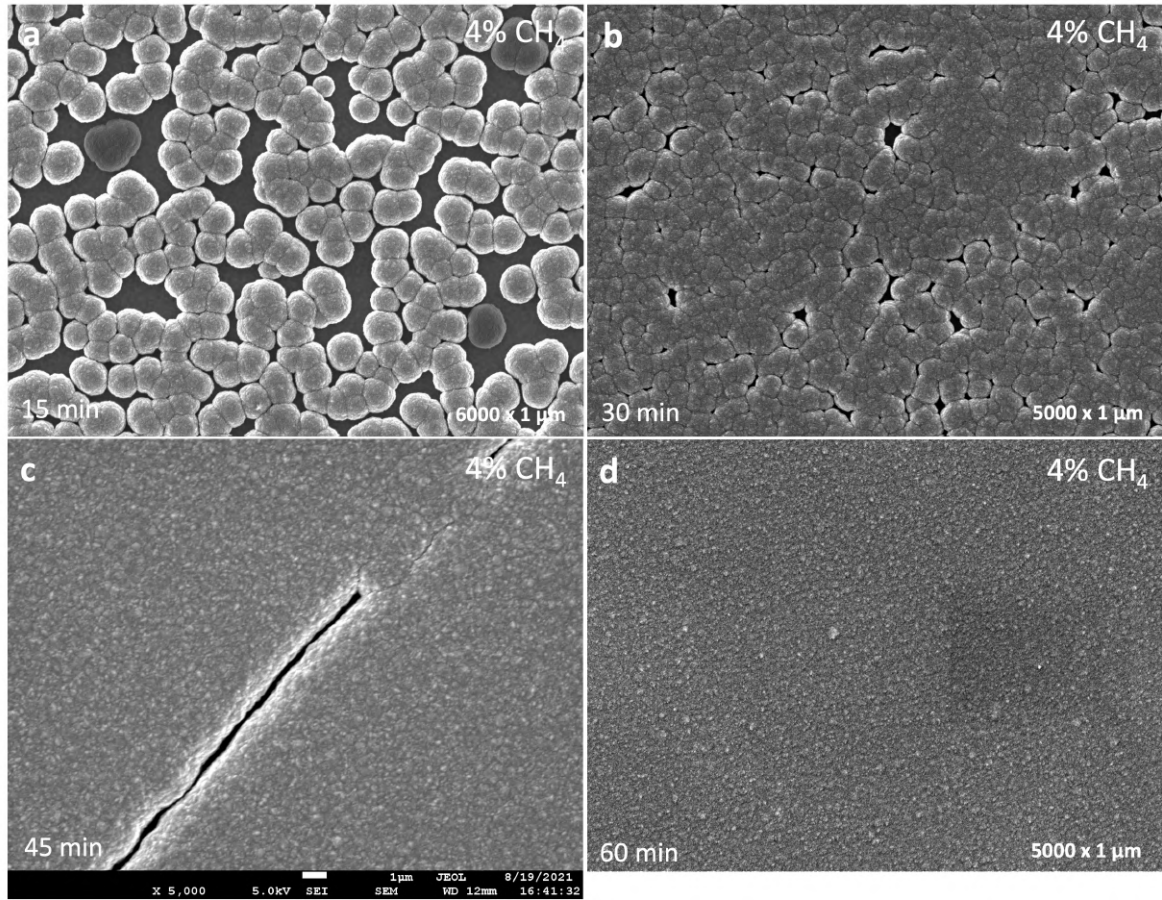


Figure 5.19 *Thin film evolution as a function of time: FE-SEM micrographs showing the UNCD thin films grown on a fused quartz substrate as a function of growth duration. a) 15 minutes, b) 30 minutes, c) 45 minutes and d) 60 minutes*

Various techniques enable the growth of faceted diamonds [223], with diamond formation achievable under a wide range of conditions (e.g., temperatures spanning from 300 to 1000°C). These methods primarily rely on generating significant quantities of atomic hydrogen and carbon radicals [217]. As the carbon oversaturation increases (for example, the amount of CH present in the gas phase), the prevalence of faceted

diamonds diminishes, while an elevated occurrence of twins and stacking faults emerges in the deposited diamond ([218], [220]). Ultimately, this leads to the radial expansion of polycrystalline, non-faceted diamonds, showcasing the distinctive "ballas-type morphology".

Figure 5.19 illustrates the growth process of ballas nanodiamond structures, depicting their deposition and subsequent radial expansion, resulting in the formation of a continuous and uniform thin film with respect to prolonged growth duration. Moreover, it is noteworthy that the methane concentration was elevated from 1% to 4%, leading to an augmentation in CH radicals within the plasma. This escalation facilitates the incorporation of sp^2 carbon into the diamond matrix at accelerated rates.

5.2.4 Transition from ballas nanodiamond to ballas + graphite

As aforementioned, the evolution from pure ballas nanodiamond to ballas containing graphitic elements becomes evident at elevated substrate temperatures (refer to Figure 5.16 - showing graphitic inclusions). Likewise, we observed the emergence of ballas nanodiamond with graphitic elements with higher nitrogen concentration ($>10\%$ N_2), leading to an increase in substrate temperature (see Figure 5.20).

Figure 5.21 shows the Raman spectra of ballas nanodiamond with varying degrees of nitrogen doping. One notable finding is that as the nitrogen concentration rises from 5% to 20%, the vibrational peak corresponding to diamond, originally centered at 1332 cm^{-1} , shifts to a higher wavenumber of 1337 cm^{-1} . Concurrently, the G-peak associated with graphitic carbon shifts to a higher wavenumber, transitioning from 1565 cm^{-1} to 1580 cm^{-1} . Additionally, the t-PA peak experiences a downshift from 1162 cm^{-1} to 1155 cm^{-1} .

5.2.5 N_2 doped UNCD growth on Si substrate

Ultrananocrystalline diamond films doped with nitrogen were synthesized on silicon substrates with the aim of investigating how nitrogen affects the electronic conductivity

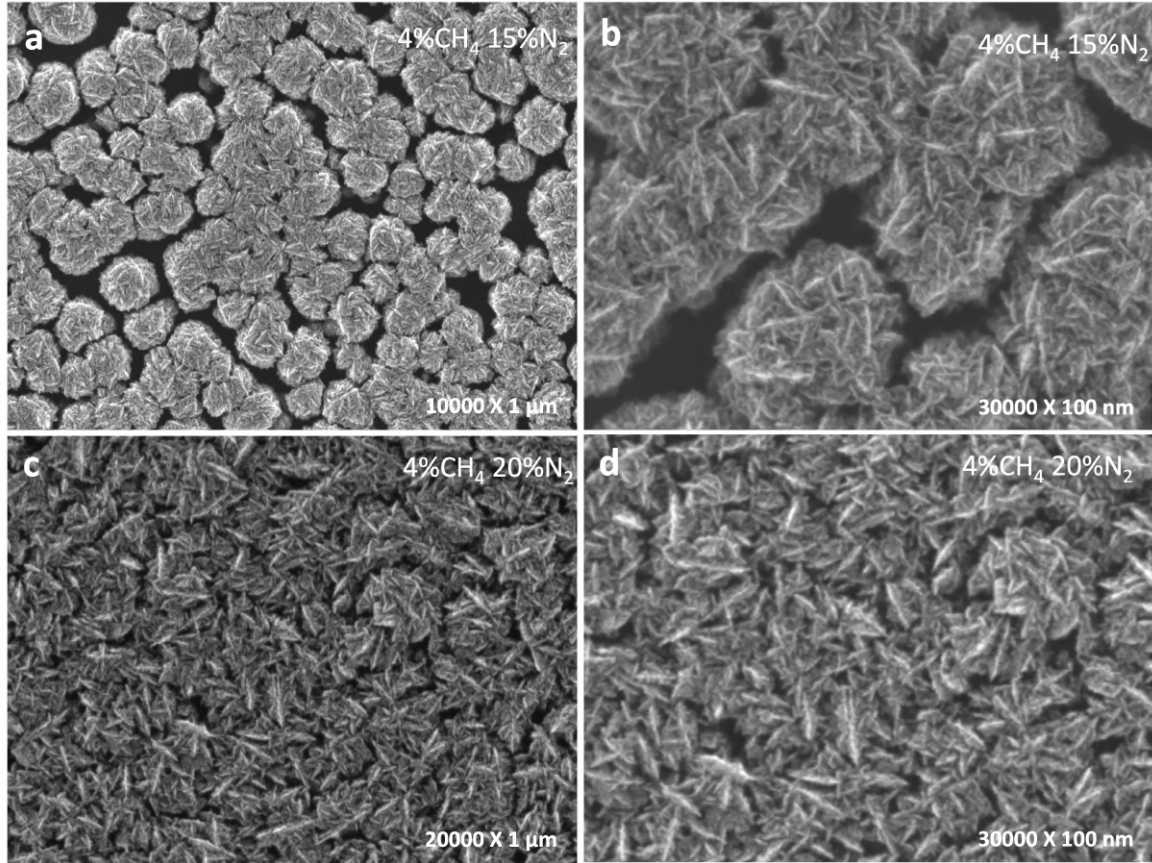


Figure 5.20 *N₂ doped UNCD on quartz substrate: a and b) 15% N₂ doped UNCD sample at 10,000 and 30,000 magnification. c and d) 20% N₂ doped UNCD sample at 20,000 and 30,000 magnification.*

of these films. To prevent current leakage through the silicon substrate, which could disrupt the accuracy of transport measurements, a dielectric layer consisting of ultrananocrystalline diamond (UNCD) was initially deposited onto the silicon substrate. Subsequently, the nitrogen-doped UNCD layer was grown on top of this dielectric layer (see Fig 5.26).

The dielectric layer comprises faceted nanodiamond structures, as illustrated in Figure 5.22. It's evident that the thin film developed on the silicon substrate exhibits uniformity throughout the substrate. The growth of these nanodiamond structures occurs under specific conditions: 900 W microwave forward power, substrate temperature of 800 degrees Celsius, utilizing a gas mixture of 1% CH₄/H₂, and maintaining a pressure of 40 mbar. Figure 5.22 illustrates the morphology of UNCD at various levels of magnification.

Following the growth of a dielectric layer on a silicon substrate, nitrogen-doped

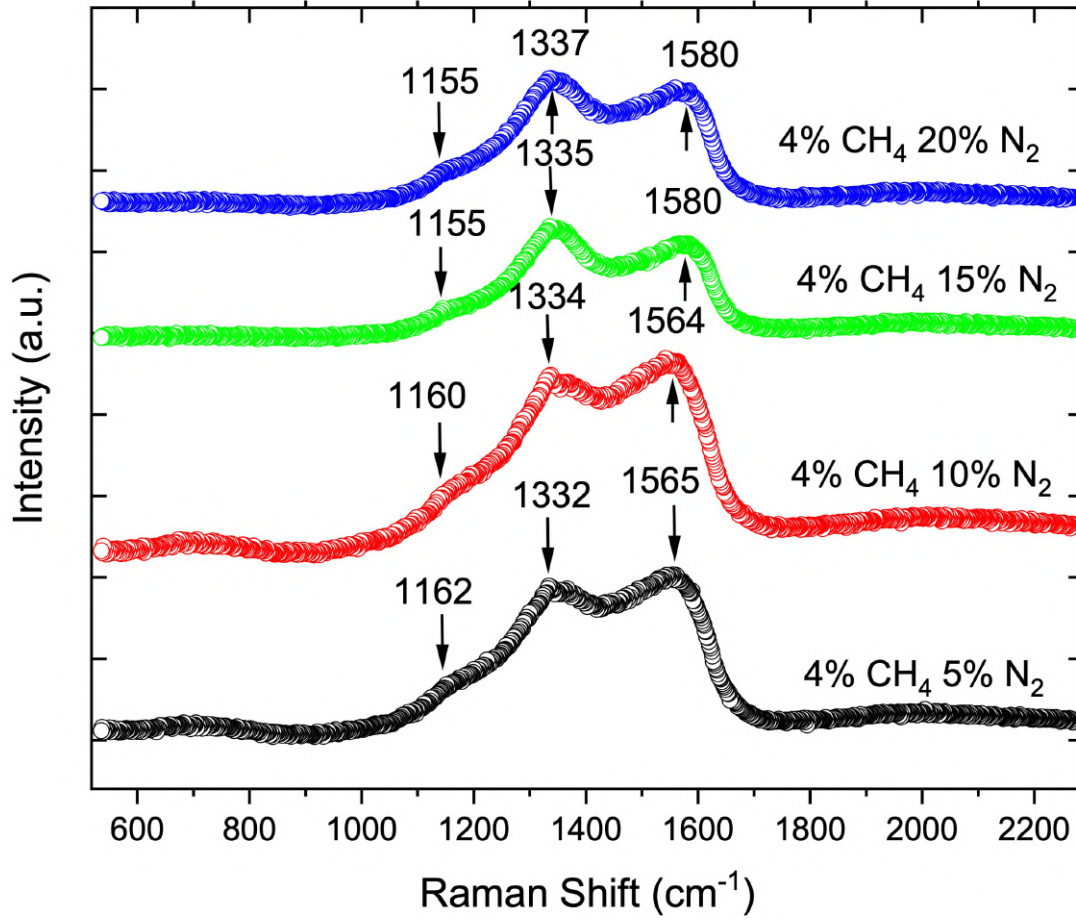


Figure 5.21 *Raman Spectra of ballas nanodiamond relative to the nitrogen doping*

ultrananocrystalline diamond (UNCD) films are deposited atop the dielectric layer 5.23. Unlike the faceted diamond dielectric layer, the nitrogen-doped film is comprised of ballas nanodiamond with graphitic elements forming lamellar structures embedded within the UNCD layer.

Figure 5.24 depicts the scanning electron microscope (SEM) image showcasing the deposition of nanodiamonds along both the width and edges of the silicon substrate. The primary goal behind the growth of nitrogen-doped UNCD films is to investigate their electronic properties at low temperatures. However, during the growth process, carbon deposition occurs on the sides of the silicon substrate, creating a connection between the conductive layer and the substrate. This inadvertently leads to electrical short circuits when the film is placed on a chip carrier. To circumvent this issue, the films undergo laser cutting to precise dimensions, thereby preventing unwanted electrical connections and ensuring proper functionality when integrated into chip

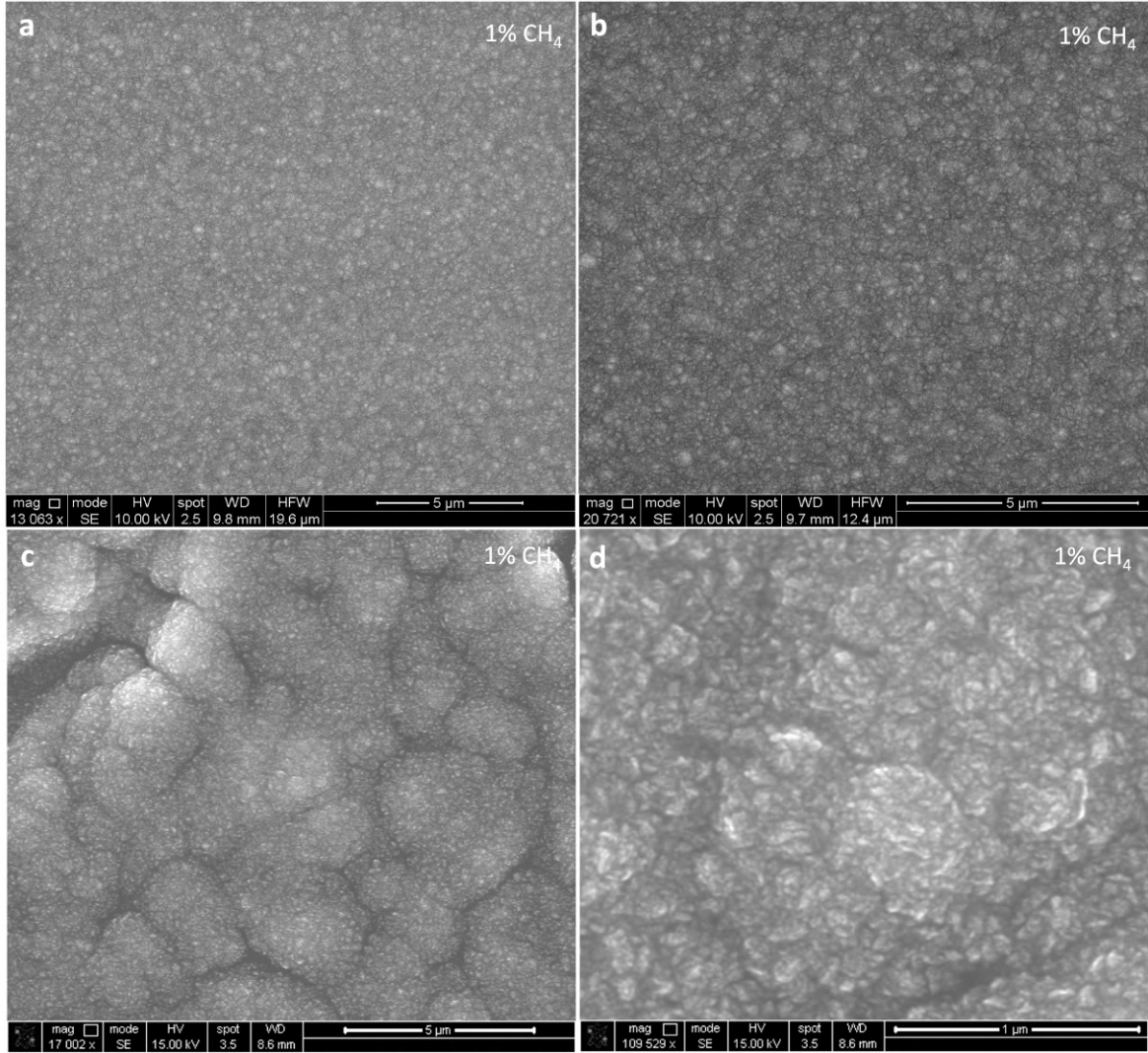


Figure 5.22 *UNCD growth on Si: a and b) SEM image showing a uniform diamond layer grown on Si substrate. c and d) Typical faceted nanodiamond structures that are seen at lower methane concentration.*

carriers. Figure 5.25 displays the cross-sectional imaging conducted on the laser-cut samples.

Laser Cutting

The image depicted in Figure 5.26 illustrates the cross-sectional view of a laser-cleaved film of nitrogen-doped ultrananocrystalline diamond (N₂-UNCD). A clear differentiation is observable between the dielectric layer, constituted of UNCD grown using a 1% CH₄/H₂ gas mixture, and the conductive layer, consisting of N₂-doped UNCD grown with a 4% CH₄/N₂/H₂ gas mixture. The dielectric layer measures

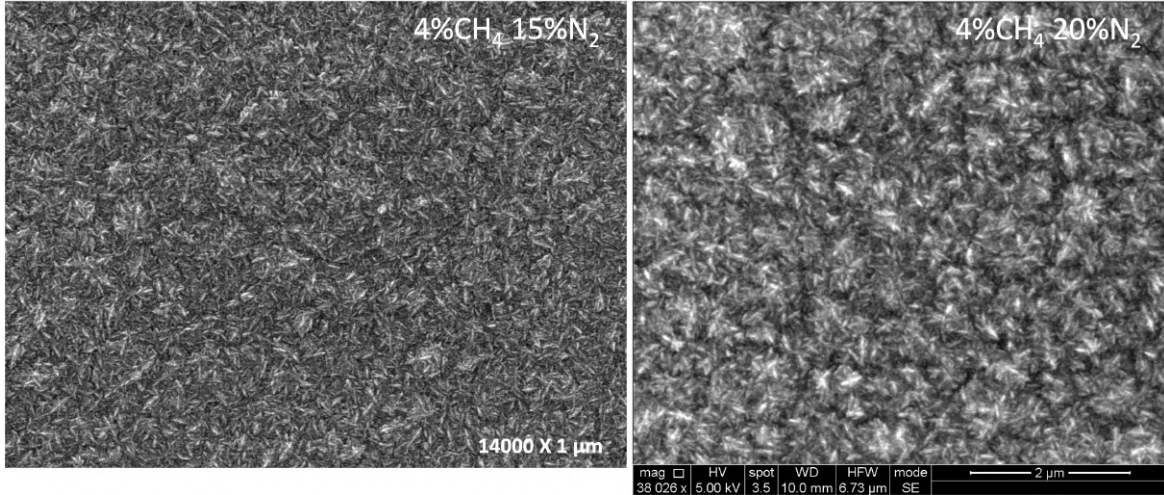


Figure 5.23 *Nitrogen doped UNCD growth on UNCD/Si substrate. Heavily nitrogen doped thin films consists of graphitic lamellar structures embedded with in the UNCD film.*

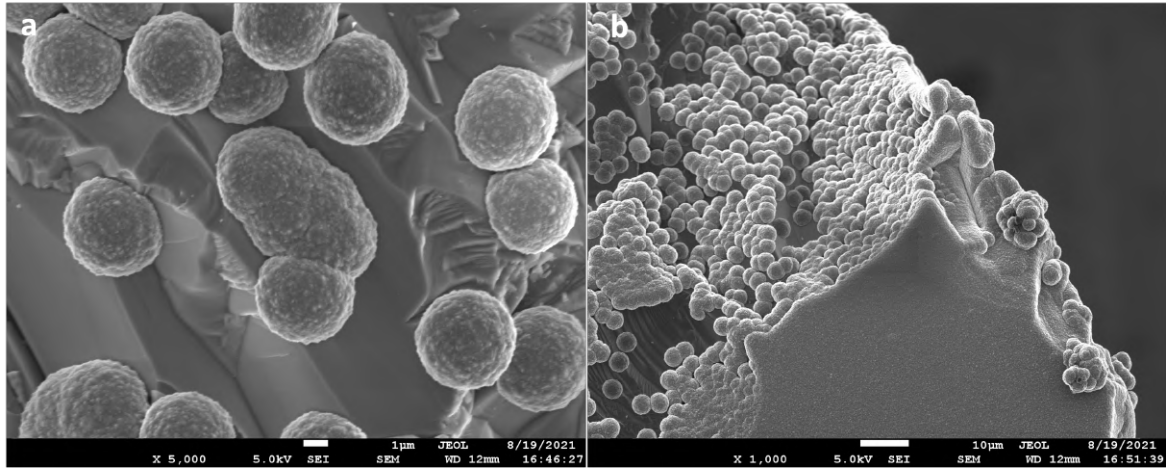


Figure 5.24 *UNCD growth on edge of the substrate: SEM image of nanodiamond structures grown on the periphery of the substrate, establishing a direct connection to the conductive silicon substrate.*

approximately $1.5 \pm 0.2 \mu\text{m}$ in thickness, while the thickness of the conductive layer ranges from 3 to 7 μm , contingent upon the concentration of nitrogen doping. Furthermore, upon closer examination at the base of the silicon substrate, it was determined that the thickness measures 0.5 μm , and the insulating layer of SiO_2 is approximately 280 nm thick. The thickness values of the substrate measured using FE-SEM correspond with the specified dimensions provided by the silicon wafer supplier.

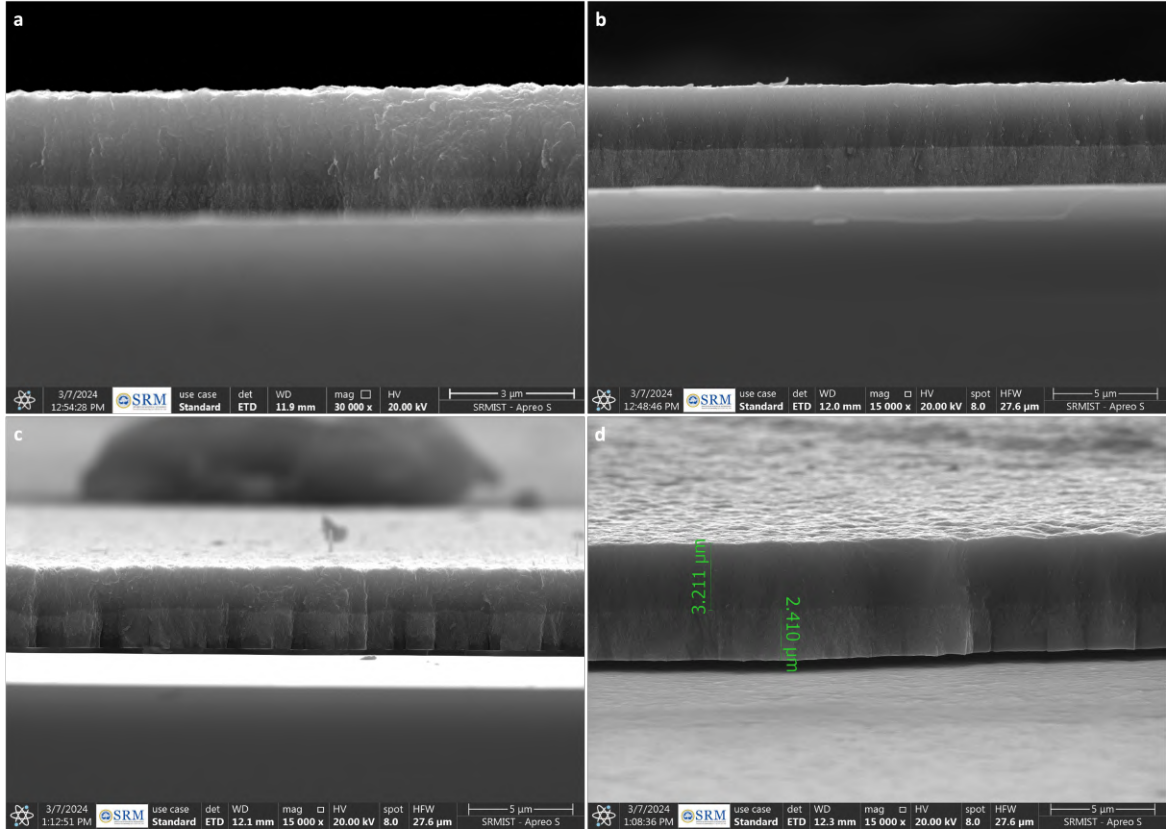


Figure 5.25 *Cross sectional image of N_2 doped UNCD thin films: a) 5% N_2 , b) 10% N_2 , c) 15% N_2 , d) 20% N_2 .*

5.3 Conclusion

As we conclude this chapter concerning the MPECVD reactor and the optimization of the diamond growth process, it is appropriate to reflect on the principal observations gleaned thus far. Initiating plasma near the substrate surface necessitates an applicator coupling to a wave-guide and the CVD chamber. Additionally, tungsten or molybdenum materials are utilized as substrate holder materials for plasma ignition due to their resonant frequency matching with the 2.4 GHz frequency of microwaves. Furthermore, auxiliary instruments such as optical pyrometers and optical emission spectrometers are necessary to monitor the quality of the diamond growth process. A water cooling stage is essential for controlling the substrate temperature, as the kinetics of carbon radical addition near the surface are influenced by the local temperature.

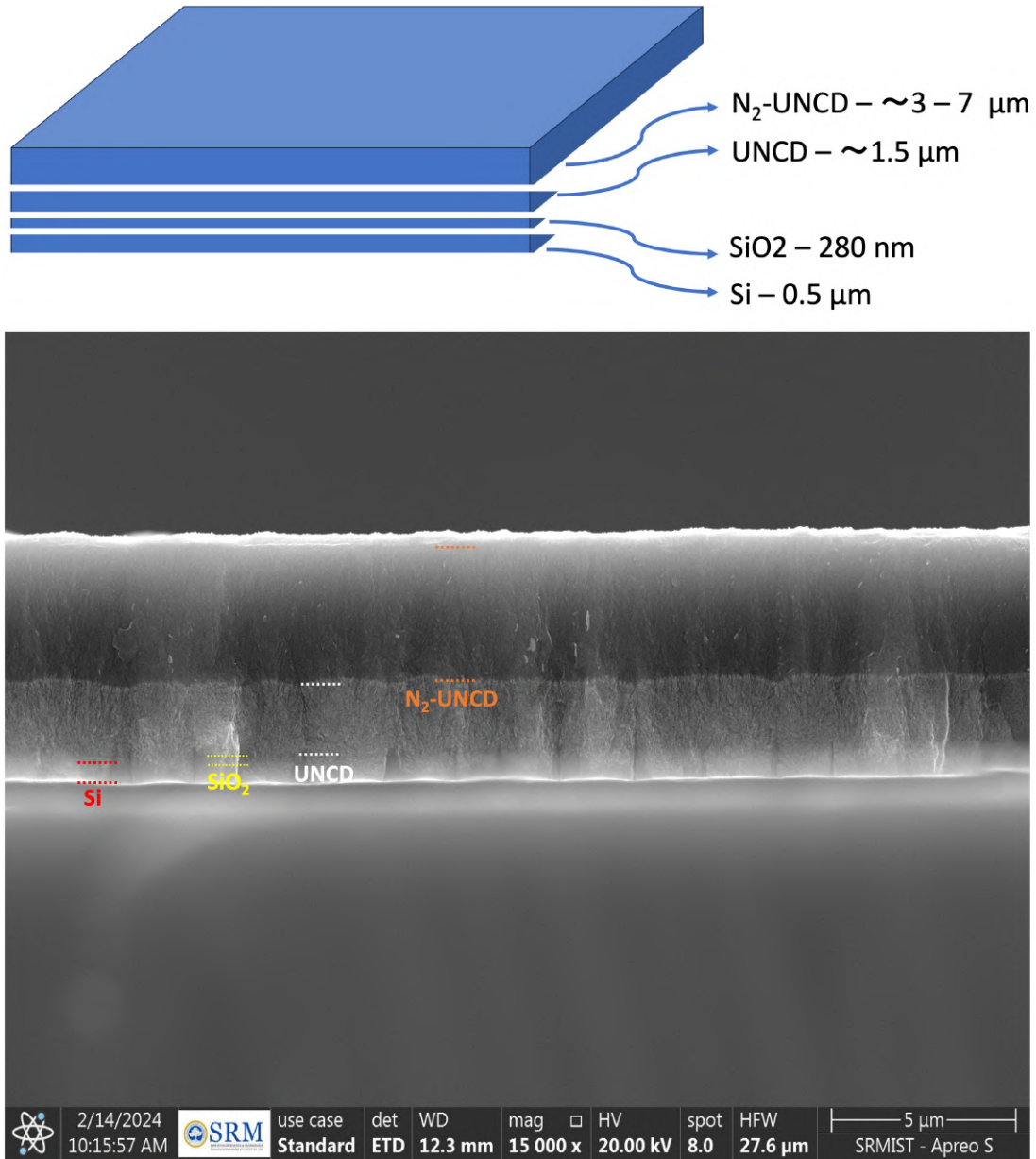


Figure 5.26 *UNCD cross sectional image of N₂-UNCD: a) Schematic depiction of a 20% nitrogen-doped UNCD film grown on a UNCD/silicon substrate. b) SEM image illustrating the nitrogen-doped film, highlighting the distinction between various layers.*

At low methane concentrations (1% - 2%) and substrate temperatures, faceted nanodiamond growth is favored, whereas increased methane concentrations (3% - 4%) facilitate the formation of ballas nanodiamond structures. Additionally, introducing nitrogen dopant into the gas mixture of 4% CH₄/H₂ results in the formation of ballas nanodiamond layers containing graphitic elements.

A layer of undoped nanodiamond dielectric should be established before N₂ doping

to prevent current leakage through the conductive Si substrate. It's crucial to acknowledge that growth on the substrate edges poses a significant concern for electronic studies. Laser cutting should be employed to trim the sample, ensuring it is free from short contacts during electronic measurements.

Chapter 6

Diaphite-Deposition of novel sp^3-sp^2 nanostructures

6.1 N₂ doping in diamond

Ultra-nanocrystalline diamond (UNCD) films, characterized by grain sizes below 10 nm, originated at Argonne National Laboratory in the USA and are now commonly referred to by this name, though initially a proprietary term. Typically grown in microwave chemical vapor deposition (MWCVD) systems with low hydrogen content, the usual gas mixture consists of 99% argon (Ar) and 1% methane (CH₄), occasionally with 1% to 3% hydrogen (H₂) added. This process encourages frequent renucleation, resulting in diamond films with remarkably small grain sizes. Despite an increase in grain numbers and boundaries, UNCD exhibits inferior electronic and mechanical properties compared to single crystal diamond (SCD). However, owing to their smooth nanometer-scale surfaces, UNCD films find utility in various electronic applications such as microelectromechanical systems (MEMS) devices, biosensors, and nanolithography. The tiny grain size of UNCD poses challenges for doping; while reports suggest n-type doping, it occurs differently from the conventional method. In these films, nitrogen (N) atoms introduced during CVD do not substitute carbon (C) atoms within the diamond lattice but rather aggregate along the grain boundaries, enhancing the electrical conductivity of UNCD films.

6.2 Diaphite

The ability to produce synthetic diamonds through chemical vapor deposition (CVD) has opened up numerous opportunities for using diamonds in various applications. Diamond, with its wide bandgap property, can have its electronic characteristics diversified by adjusting the band gap through the process of doping. For example, adding boron can create a p-type semiconductor material, while doping with nitrogen or phosphorus can produce an n-type semiconductor material within a diamond structure. Ultra-nanocrystalline diamond, a specific type of diamond with smaller grains typically measuring less than 10 nm, has found practical applications in areas such as electron emitters, bionics, bio implants, acoustics, and optics.

UNCD material is a mixed-phase composite that includes both sp^3 (diamond grains) and sp^2 (graphitic) carbon, resulting in a combination of varied structural and electrical properties. While diamond is typically an insulator, in UNCD films, electrical current primarily flows through the network of graphitic grain boundaries. By controlling the concentration of dopants during the CVD growth process, it's possible to influence the formation of these grain boundaries, which are composed of sp^2 grains with a typical size of about 1 nm. The introduction of nitrogen (N_2) as a precursor in the gas mixtures is often used to alter the material's morphology, increasing the presence of sp^2 grain boundaries within the diamond matrix. This, in turn, leads to significant enhancements in electrical conductivity, often by several orders of magnitude[224].

Recent attention has been focused on the structural variations within the diamond grains embedded in the nanocrystalline diamond matrix. UNCD films consist of different phases, including sp^3 (diamond) and sp^2 grains, leading to the creation of unique nanodiamond structures known as "polymorphs," each with exceptional physical properties. These polymorphs include hexagonal (h)-diamond, i-diamond, m-diamond, and n-diamond. Researchers are particularly interested in harnessing the outstanding properties of these nanodiamond polymorphs for practical applications. For example, h-diamond, previously known as lonsdaleite [225] and currently recognized as twinned cubic diamond[226], boasts superior compressive strength,

hardness, and rigidity compared to the more commonly encountered cubic (c)-diamond [227]. The i-diamond [228] is denser than c-diamond, while m-diamond is harder. n-diamond is used for shielding against external electromagnetic interference in wireless communication equipment [229]. The main limitation of these polymorphs is that they are typically only found in meteoritic nanodiamonds formed under extreme conditions due to extraterrestrial impacts.

The quest for new carbon materials with unique nanostructural characteristics that offer unique electro-mechanical properties, along with an exploration of their structural changes under extreme conditions during laboratory synthesis as compared to extraterrestrial impact events, has been a driving force for researchers. One such material, diaphite [230], [231] is of significant interest due to its nanostructured composition comprising a mix of sp^3 and sp^2 hybridized carbon, often referred to as a diamond-graphene hybrid [232]. Much effort has been dedicated to understanding the structural evolution of diaphite at the laboratory scale [233]. Early attempts involved generating diaphite domains by subjecting a graphite wafer to femtosecond (10^{-15}) laser pulses, leading to the conversion of localized sp^2 and sp^3 hybridized carbon [234]. However, maintaining the diaphitic structure required a vacuum environment. Another endeavor aimed to create an atomically thin h-diamond film by compressing tri-layer graphene under extreme pressure (20 GPa), but this structure could only be sustained at pressures exceeding 1 GPa [235]. In this context, we present a novel growth model for cultivating diaphite structures within the UNCD matrix by adjusting the N_2 doping concentration in an H_2 -rich plasma gas mixture. This method holds significant importance as it allows the modulation of electromechanical properties and the generation of novel nanodiamond structures at the laboratory level. Recent studies have also suggested that N_2 doping in diamond at concentrations of 100 – 200 ppm exhibits unconventional magnetization at temperatures below 25 K, attributed to the presence of mixed $sp^3 - sp^2$ phase defects. This finding hints at the potential for superconductivity and superparamagnetism [236]. Additionally, research has shown that an interfacial grain boundary network in boron-doped nanocrystalline diamond films induces strong localized spin-orbit coupling, which results in conduction occurring in a triplet state [237]. Overall, the precise regulation of doping and control over the

formation of mixed-phase defects in nanocrystalline diamond structures have garnered significant interest in recent years. Here, we report a novel growth technique where modulation of growth parameters including pressure, substrate temperature, and N₂ doping in the gas mixture can yield UNCD films primarily characterized by Diaphitic domains.

To facilitate understanding, we will use the following abbreviations for UNCD thin films grown with different nitrogen doping concentrations: UNCD₅, UNCD₁₀, UNCD₁₅, and UNCD₂₀, corresponding to doping concentrations of 5%, 10%, 15%, and 20%, respectively. The growth conditions for these UNCD samples on a quartz substrate are detailed in Table 6.1. Throughout the growth process, the microwave power, pressure, total flow rate, and growth duration remained constant, while the flow rate of N₂ was adjusted. It's important to note that the substrate temperature varies depending on the concentration of N₂ gas introduced. Figure 6.1a illustrates a spherical plasma ball focused on the seeded quartz substrate, which is generated using a 2-kW solid-state microwave generator. In Figure 6.1b, you can see a scanning electron microscope (SEM) image of a continuous UNCD film grown on quartz without any N₂ doping. In the conventional plasma-assisted chemical vapor deposition (CVD) growth of diamond, H₂ gas plays a crucial role in creating *sp*³ grains-rich diamond by continuously adding and removing methyl radicals on the surface of the seeded substrate. However, both the plasma gas temperature and the substrate temperature significantly impact the quality of the resulting diamond thin film. UNCD films with a typical grain size >10 nm are conventionally grown in Ar-rich plasma. In our case, the UNCD film is grown in a plasma rich in N₂ gas, as opposed to the more traditionally used Ar-rich plasma. It has been previously demonstrated that providing growth conditions that encourage re-nucleation favors the formation of nanocrystalline diamond over the columnar growth of microcrystalline diamond [238].

In our growth model, we have employed a microwave power (MW) of 900 W while maintaining a total chamber pressure of 40 mbar. This setup ensures the formation of continuous thin films on a quartz substrate. However, it's important to mention that an increase in MW power to 1 kW temporarily raised the substrate temperature and resulted in cracks in the thin film. These cracks were a consequence of increased

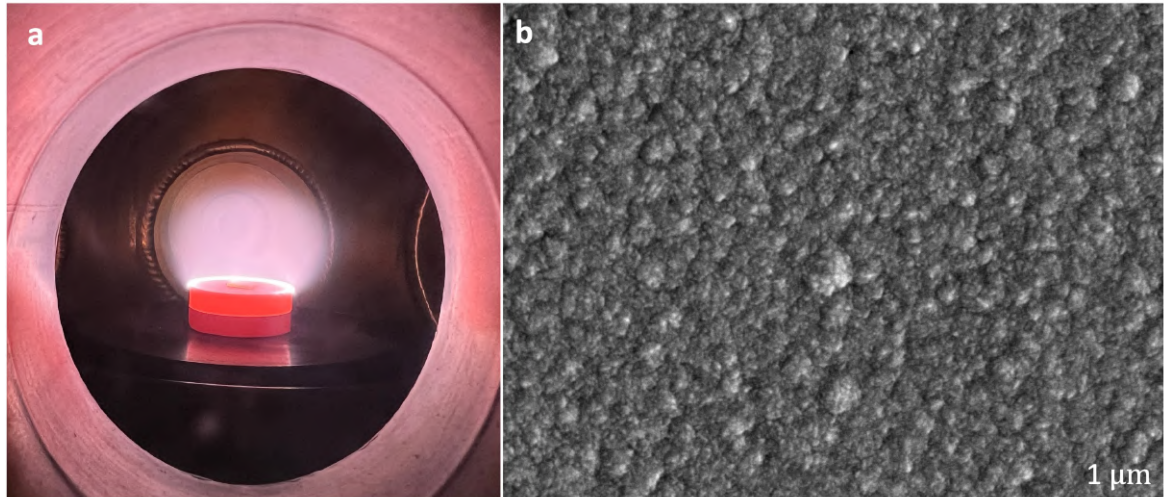


Figure 6.1 *MPECVD growth of diamond. a) A $5 \times 5 \times 0.5$ mm quartz nanodiamond-seeded substrate is positioned on a tungsten substrate holder. The setup is exposed to a CH_4/H_2 plasma, and an adjustable stage height provision is utilized during the process. b) A continuous Ultrananocrystalline Diamond (UNCD) film is grown on the quartz substrate.*

strain and thermal mismatch between the substrate and the diamond layer. As a result, we have chosen to maintain a total MW power of 900 W for the growth of all the UNCD samples to avoid such issues.

Table 6.1 *MPECVD growth parameters used for growing nitrogen-doped ultra-nanocrystalline diamond thin films.*

Type of sample	MW Power	Pressure (mbar)	T_{sub} (K)	CH ₄ SCCM	H ₂ SCCM	N ₂ SCCM	Growth duration (h)	Film Thickness (μm)
UNCD	900	40.0	1074	4	196	0	2	1.8 (± 0.1)
UNCD ₅ (5% N ₂)	900	40.0	1124	4	186	10	2	3.5 (± 0.1)
UNCD ₁₀ (10% N ₂)	900	40.0	1172	4	176	20	2	3.9 (± 0.1)
UNCD ₁₅ (15% N ₂)	900	40.0	1236	4	166	30	2	5.2 (± 0.2)
UNCD ₂₀ (20% N ₂)	900	40.0	1305	4	156	40	2	7.1 (± 0.2)

Structural Properties

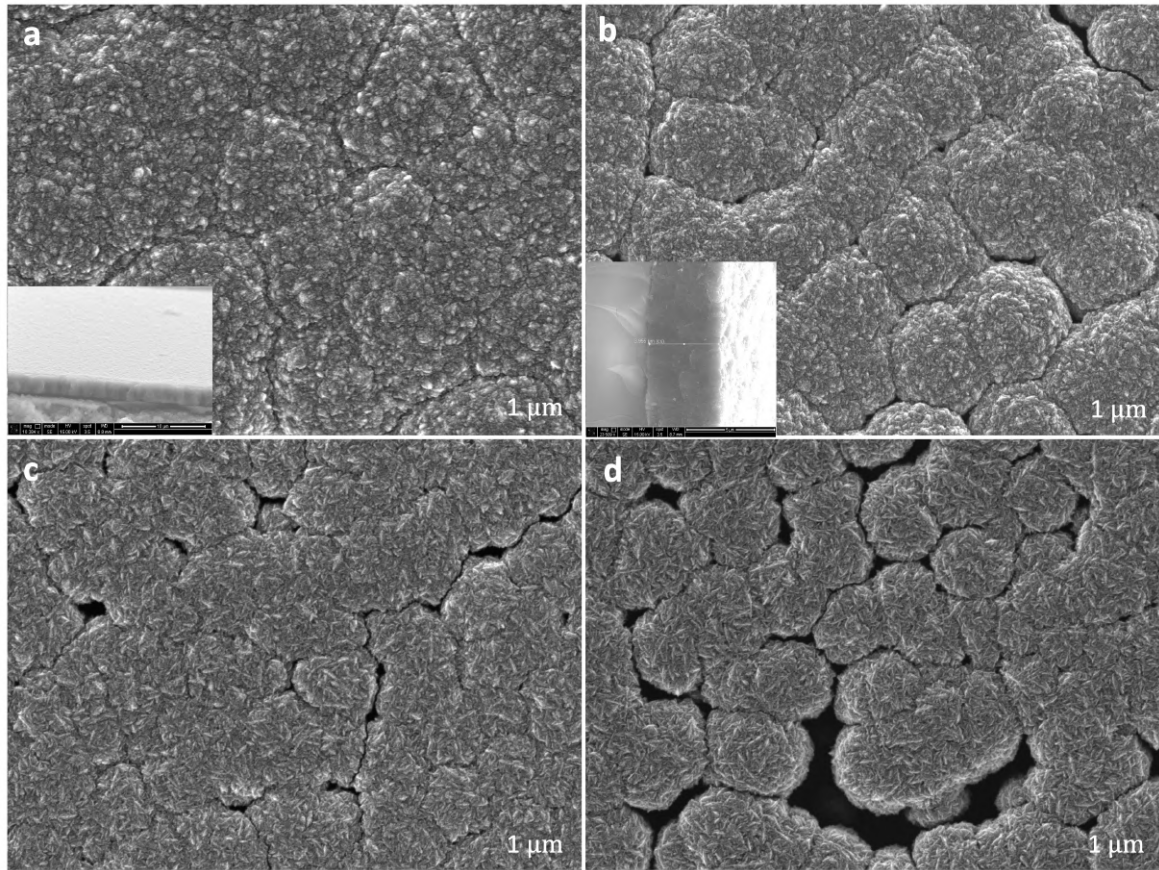


Figure 6.2 *FE-SEM images of Nitrogen doped Ultrananocrystalline Diamond (UNCD) samples: a) For 5% N₂ doping, the image reveals a robust and continuous nanodiamond morphology. The inset provides a cross-sectional view displaying a film thickness of 3.5 μm. b) In the case of 10% N₂ doping, the image shows sharp edges on the rigid morphology. The inset presents a cross-sectional image indicating a film thickness of 3.9 μm. c) With 15% N₂ doping, the image displays a rigid morphology with a few needle-shaped facets protruding outside the diamond matrix. d) For 20% N₂ doping, the image indicates a needle-shaped morphology with distinct void formations in the continuous film, suggesting significant graphitization of the sample.*

SEM images in Figures 6.2a-d showcase the morphological alterations in UNCD samples as nitrogen (N₂) concentration increases. For UNCD₅ and UNCD₁₀ (Fig. 6.2a-b), the films exhibit a continuous, smooth structure with small, densely packed nanometer-sized diamond grains. Conversely, the UNCD₁₅ sample (Fig. 6.2c) displays increased graphitization at the grain boundaries between nanodiamond grains, accompanied by the emergence of small voids. In the UNCD₂₀ sample (Fig. 6.2d), these voids enlarge, leading to the formation of pits within the film. Notably,

the transition from densely packed nanodiamond grains to needle-shaped, semi-void, ordered nanographitic platelets is attributed to the elevated concentration of N_2 doping in the gas mixture. This heightened N_2 concentration significantly impacts methyl radical formation, diminishing the role of hydrogen and enabling the growth of a graphitic carbon network between the diamond grains[239], [240]. Cross-sectional imaging indicates film thicknesses of $3.5 \pm 0.1 \mu\text{m}$, $3.9 \pm 0.1 \mu\text{m}$, $5.2 \pm 0.2 \mu\text{m}$, and $7.2 \pm 0.2 \mu\text{m}$ for UNCD₅, UNCD₁₀, UNCD₁₅, and UNCD₂₀, respectively (Fig. 6.12 a-d).

Figures 6.3a-d depict height sensor images, while e-h present 3D topographies of nitrogen-doped UNCD samples. UNCD₅ and UNCD₁₀ exhibit smooth surfaces with crystalline sizes ranging from 20 to 40 nm, whereas UNCD₁₅ and UNCD₂₀ display rough surfaces with needle-like carbon protrusions. The root mean square (RMS) values indicate an increase from 20.2 to 43.4 nm as nitrogen content rises from 5per to 20per, respectively. Specifically, UNCD₅ and UNCD₁₀ show lower RMS values of 20.2 nm and 26.1 nm, while UNCD₁₅ and UNCD₂₀ exhibit values of 29.4 nm and 43.4 nm, respectively. This suggests that the grain size of UNCD becomes coarser with higher nitrogen content, emphasizing the significant influence of N_2 on the growth of the sp_3 phase. These findings align with SEM observations and are consistent with previous reports noting changes in grain size with varying N_2 concentrations[241], [242].

The NanoScope Analysis V1.9 software was employed to analyze the grain size of the UNCD samples. For UNCD₅ and UNCD₁₀, the grain size ranged from 4 to 10 nm, with the highest median at 5 nm. In contrast, for UNCD₁₅ and UNCD₂₀, the grain size spanned from 8 to 20 nm. Figure 6.3d illustrates topography featuring well separated grains and prominent grain boundaries, providing additional evidence of the impact of N_2 on diamond growth.

Raman spectroscopy, a widely used optical technique for assessing the diamond-to-graphite ratio in UNCD samples, reveals distinctive features. In a single crystalline diamond, a sharp phonon band emerges at a wavenumber of 1332 cm^{-1} . Conversely, UNCD displays a spectrum of phonon bands, including trans-polyacetylene peaks (t-PA) at 1180 cm^{-1} and 1496 cm^{-1} , associated with sp^2 carbon formed between nanograin boundaries (often confirming UNCD[243]). The diamond peak (sp^3) appears

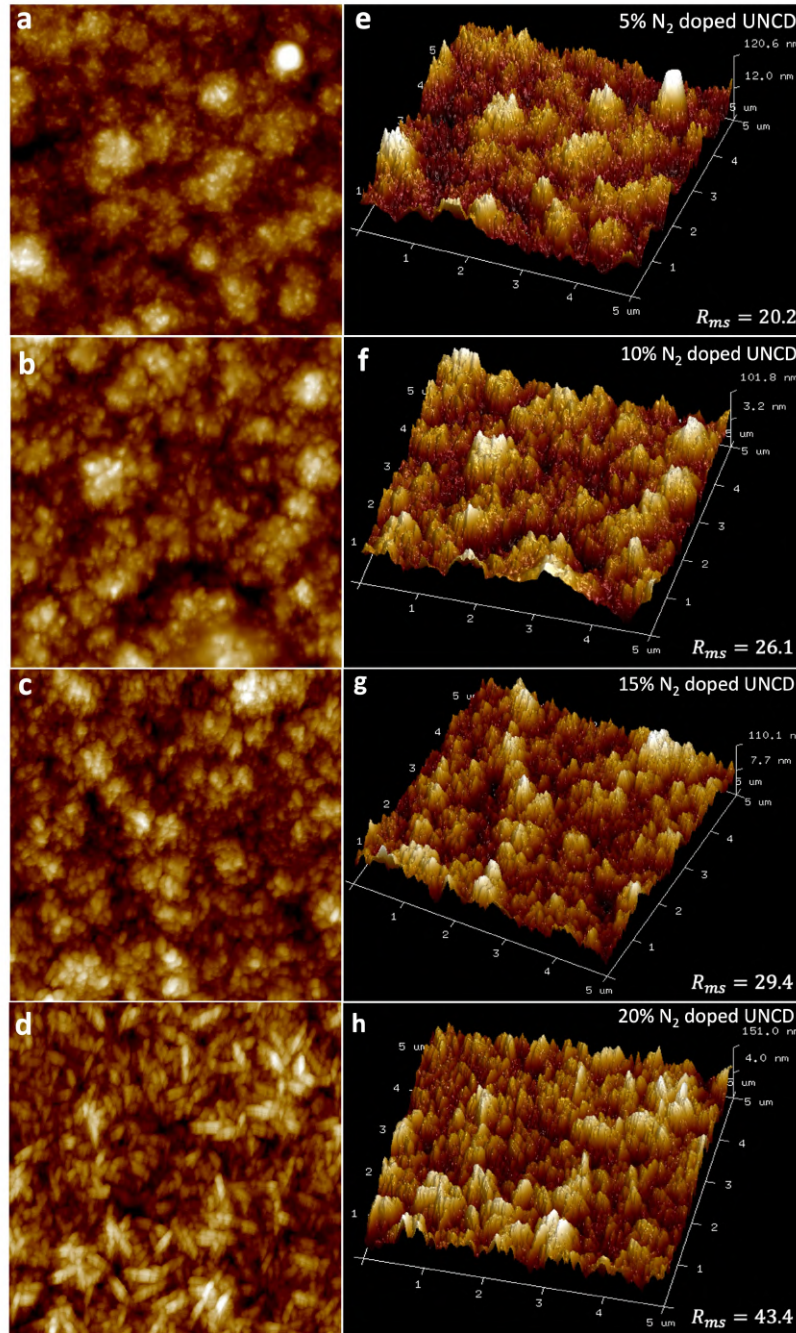


Figure 6.3 Atomic Force Microscopy (AFM) investigation of Ultrananocrystalline Diamond (UNCD) as a function of Nitrogen (N_2) doping is presented: a, b, c, and d) AFM height sensor non-contact mode images of 5%, 10%, 15%, and 20% N_2 -doped UNCD samples, respectively. e, f, g, and h) 3D mapping of the surface terrain for the corresponding samples. It is observed that root mean square (RMS) values increase with higher levels of N_2 doping.

at 1332 cm^{-1} , a disorder (D) peak at 1347 cm^{-1} (resulting from the sp^3 – sp^2 transition), and a graphitic (G) peak at 1550 cm^{-1} (Fig.6.4a). Figure 6.4b presents a plot of Raman spectra for UNCD_{5–20} samples. Studies suggest that variations in the sp^3 – sp^2

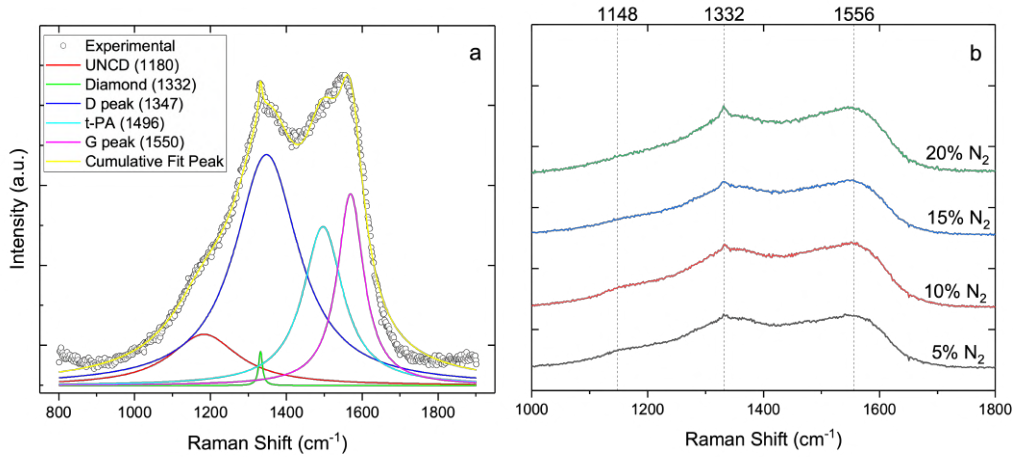


Figure 6.4 *a) Raman spectrum (514 nm) of Ultrananocrystalline Diamond (UNCD) film grown without any doping. b) Raman spectra of diamond films deposited with varying Nitrogen concentrations in the CH_4/H_2 plasma gas mixture.*

interface due to nitrogen doping and associated material transformations can be traced by changes in Raman spectral intensities and positions of diamond, D, and G peaks [224], [241], [244]–[246]. For example, the area ratio of D and G bands tracks the transformation of graphitic carbon to diamond, correlated with hexagonal and pentagonal aromatic rings within the diamond matrix [247]. Gaussian peak fitting on Raman spectra from all UNCD samples reveals shifts in phonon bands associated with t-PA (UNCD) and the G band with increasing N_2 concentration. The shift in wavenumber frequency for t-PA and the G band is related to disorder along the $\langle 111 \rangle$ crystallographic direction [248], [249], linked to the formation of hexagonal symmetry and stacking faults within the UNCD matrix due to compressive stress between nanodiamond grains [250], [251].

Moreover, the intensity ratio of the diamond peak to the graphitic peak (I_{1332}/I_{1550}) decreases with increasing N_2 concentration, indicating heightened graphitization of UNCD samples. These Raman observations align with SEM and AFM findings, where UNCD_5 and UNCD_{10} exhibit high sp^3 content, while UNCD_{15} and UNCD_{20} show relatively higher sp^2 content compared to low N_2 doping samples.

XRD diffraction analysis was performed on all N_2 -doped UNCD samples, revealing distinct diamond peaks on the (111), (220), and (311) crystal planes with

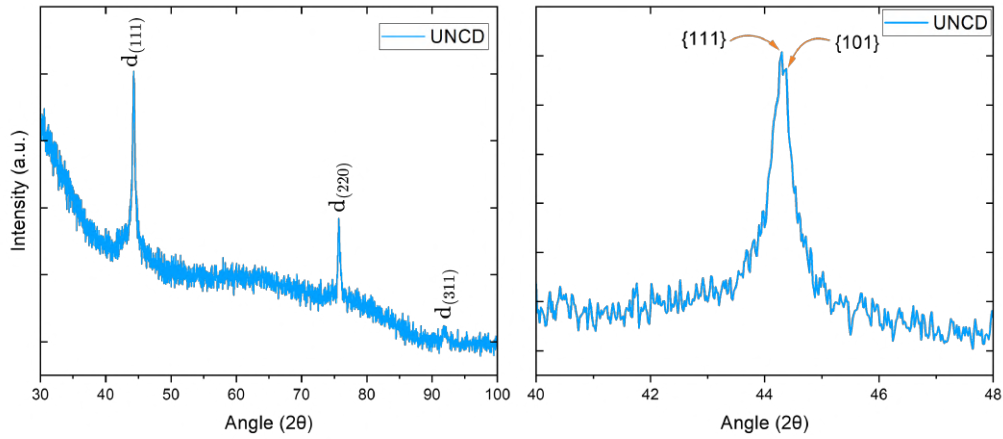


Figure 6.5 *a) X-ray diffraction (Cu K_{α} radiation) of the 5% Nitrogen (N_2) doped Ultrananocrystalline Diamond (UNCD) on a quartz substrate in $CH_4/H_2/N_2$ plasma at 40 mbar. The labels indicate the diffraction peaks associated with different planes of the nanodiamond. b) The d_{111} peak demonstrates an overlap of 111 and 100 phases, representing diamond and graphitic phases within the diamond matrix.*

corresponding 2θ values of 43.9° , 73.5° , and 91.6° , corresponding to d-spacing values of $2.06 \text{ \AA}$, $1.26 \text{ \AA}$, and $1.075 \text{ \AA}$, respectively (see Fig. 6.5a). A noteworthy discovery in the detailed analysis of the (111) peak was the emergence of a secondary peak at $2\theta = 44.4^\circ$ (depicted in Fig. 6.5b) coinciding with the primary (111) peak. This secondary peak is attributed to the presence of sp^2 carbon, a direct outcome of the development of graphene layers within the diamond structure. These specific reflections are associated with a graphene layer exhibiting a d-spacing of $2.12 \text{ \AA}$, characteristic of diaphite, as documented in previous reports [232]. It's crucial to emphasize that both the reflections associated with diamond and graphene have similar d-spacing values ($2.06 \text{ \AA}$ and $2.12 \text{ \AA}$, respectively), resulting in XRD peaks overlapping at $2\theta = 43.9^\circ$ and 44.4° . With an increase in N_2 concentration in the gas mixture, a substantial decrease in the intensity of the diamond peak (111) is observed, indicating reduced intensity with higher doping concentration. Furthermore, the Bragg's angle shifts to a higher 2θ value for the UNCD₂₀ sample, signifying a significant degree of graphitization (see Fig. 6.13). The diamond's grain size was calculated using Scherrer's formula, considering the full-width half maximum (FWHM) values of the diamond (111) crystal plane in the XRD pattern.

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (6.1)$$

Where: τ is the mean diamond grain size, K is a dimensionless factor, λ is the wavelength, β is the FWHM of the (111) crystal plane, and θ is the Bragg angle. The crystal sizes determined using Scherrer's formula are as follows: UNCD₅ - 5.2 nm, UNCD₁₀ - 5.6 nm, UNCD₁₅ - 8.4 nm, and UNCD₂₀ - 12.1 nm. Conventional

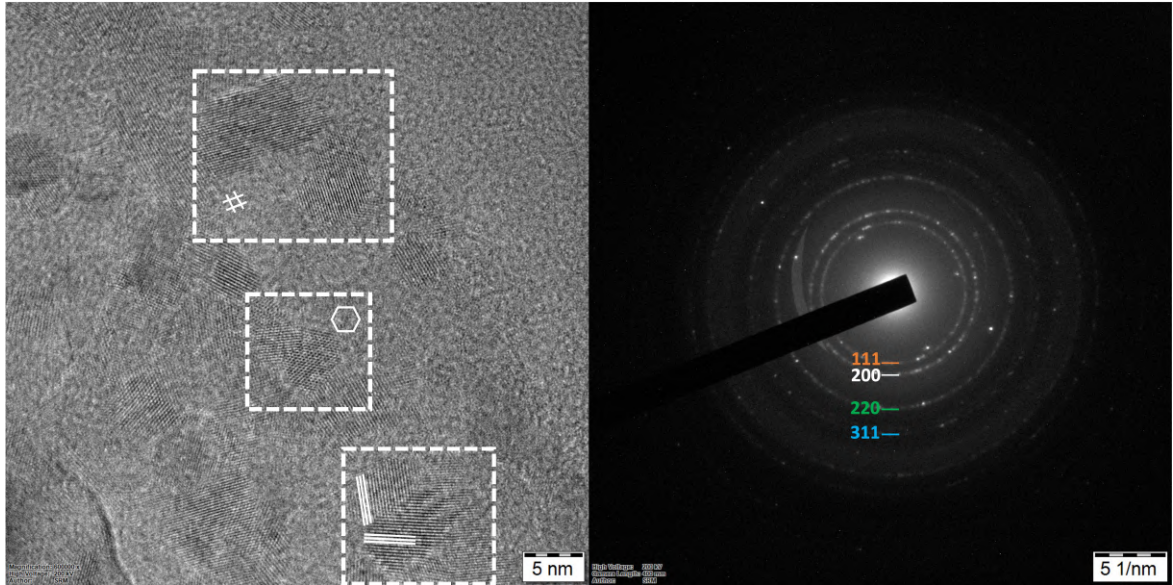


Figure 6.6 *a) HR-TEM of UNCD film unveils characteristic twin nanodiamond polymorphs in $\langle 111 \rangle$ direction. Additionally, the white box labeled with a hexagon indicates a mixed morphology comprising graphene with a hexagonal lattice and sp^3 nanodiamond. b) Selected Area Electron Diffraction (SAED) pattern of the nanodiamond film confirming the presence of the forbidden 200 crystallographic state, along with commonly observed diffraction patterns such as 111, 220, and 311.*

single crystal diamonds grown in a laboratory setting through the plasma-assisted chemical vapor deposition (CVD) technique display a well-defined cubic stacking sequence, resulting in the appearance of (111), (220), and (311) reflections associated with d-spacings of 0.206 nm, 0.126 nm, and 0.107 nm, as depicted in Figure 6.5. In contrast, nanocrystalline diamonds exhibit structural heterogeneity, encompassing various diamond polymorphs, including c-diamond. This structural diversity stems from compressive strain in the diamond layer and the thermal mismatch between the diamond and the substrate (typically Si or SiO₂), leading to the random formation of hexagonal stacking within a cubic sequence. This results in disorder in the form of twinning and stacking faults, detectable through electron diffraction techniques, as

well as complementary methods such as XRD 6.11 and Raman spectroscopy 6.13.

Figure 6.6a presents a high-resolution transmission electron microscopy (HR-TEM) image of a UNCD₅ sample, revealing hexagonal and square fringes within the highlighted white box. Initially identified as lonsdaleite, these fringes were later recognized as a disorder in cubic diamond in the form of stacking faults and nanotwins induced by compressive strain, rather than lonsdaleite[252], [253]. The hexagonal-cubic (h-c) stacking sequence, observed in sp^3 diamond layers, is common in natural diamonds and has recently been observed in laboratory-made shock diamonds[254], [255]. In our case, the hexagonal-cubic (h-c) stacking sequence observed in sp^3 diamond layers is attributed to the substrate temperature (T_{sub}), inducing compressive strain along a specific direction. Figure 6.6b shows the selected-area electron diffraction (SAED) pattern of the UNCD₅ sample, displaying common reflections associated with cubic diamond, along with the reflection linked to the Diaphite structure.

Figure 6.7 provides a detailed examination of various structural anomalies observed in the UNCD₅ sample. In Figure 6.7a, we can observe single crystals with the (111) orientation and its inset Figure shows the Fast Fourier Transform (FFT) image of the hexagonally arranged reflections. Figure 6.7 $\bar{a}$ shows the corresponding DFT calculated structure adopted from earlier report [231]. Figure 6.7b displays diamond nanocrystals separated by square fringes with a spacing of 0.206 nm. The square fringe pattern exhibits rows of diffraction spots that are perpendicular to the c-diamond 111 plane. It's worth noting that the twin domains are rotated 90° degrees with respect to each other. These fringes are not due to the overlapping of lattice fringes but are a result of twinning in c-diamond. Such domains are observed in different regions of the film, rather than being uniform throughout the entire film. Figure 6.7 $\bar{b}$ shows its corresponding structure model. In Figure 6.7c, we see cyclic five-fold 111 twins forming pentagonal rotational symmetry in the nanodiamond. The white dotted lines highlight the 111 twin planes along the $\langle\bar{1}\bar{2}1\rangle$ projections. These features have been documented earlier in natural diamonds [231], [233], [256]. Figure 6.7 $\bar{c}$ shows its corresponding structure model. In Figure 6.7d, a stacking fault in the UNCD layer is shown. Stacking faults are planar defects that occur in a perfectly ordered crystalline

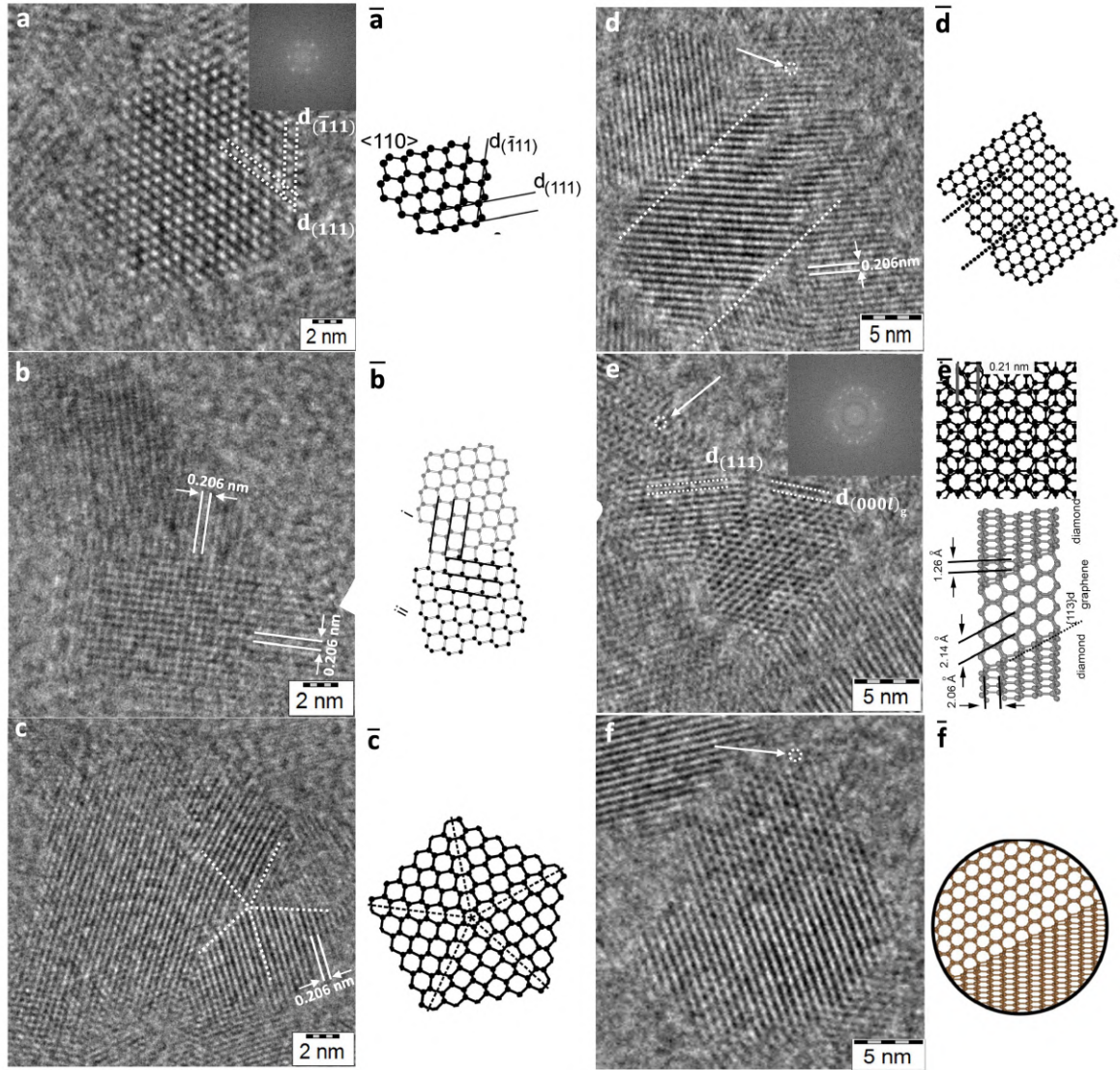


Figure 6.7 HR-TEM images of UNCD₅. a, and $\bar{a}$) cubic diamond with 111, crystal plane and its corresponding structure model. b and $\bar{b}$) hexagonal and square fringe reflections – 90° rotation twins showing two sets of 111, diffraction spots and its corresponding structure model. Here the diffraction spots indicate domains that are rotated at 90° to each other along $\langle 011 \rangle$ plane. c and $\bar{c}$) cyclic fivefold 111, twins forming pentagonal symmetry within the nanodiamond structures, and its corresponding model is shown. White dotted lines mark the twin interfaces. d and $\bar{d}$) stacking disordered nanodiamonds with cubic and hexagonal stacking are observed. e) and $\bar{e}$) Diaphite structure – interwoven graphene layers within the diamond 111, grains. Furthermore, outlines of the differently projected grains and the $d_{(000l)}$ associated with graphene d spacings are clearly visible. The white arrow indicates the hexagonal ring of carbon atoms. $\bar{e}$ and $\bar{f}$) their respective corresponding structure models. Structure models are adopted from ref.[231]

material. These defects arise from local deviations in the closely packed stacking sequence, primarily due to similarities in the sixfold symmetry packing arrangement

found in the Face-centered cubic (Fcc) and hexagonal closed-packed (hcp) structures. Both Fcc and hcp structures have atomic planes with sixfold symmetry (see Fig 6.7 $\bar{d}$). Figures 6.7e and 6.7f depict Diaphite structures, which can be interpreted as graphitic, or graphene layers embedded within the hexagonal-cubic (h-c) diamond structures. In these structures, sp^3 diamond domains are interconnected via sp^2 bonded regions that lack repetition. Previously, hexagonal fringe patterns made of d-spacing of 0.201 nm were observed in natural diamonds. These patterns are attributed to the $\langle 0001 \rangle$ projection of h-diamond domains.[256]. The hexagonal symmetry feature arises from graphene $\langle 0001 \rangle$ units intermingling with and being covalently bonded to the $\langle 121 \rangle$ surfaces of the diamond [257], [258]. Furthermore, the white arrow highlighted in Figure 6.7e indicates the presence of a hexagonal ring of carbon atoms. The corresponding fast Fourier transforms (FFTs) reveal twelve distinct spots with 0.21 nm spacings (see inset Fig 6.7e). HR-TEM images, showcasing a regular twelve-fold rotational symmetry as evidenced by FFTs, demonstrate that all twelve ~ 0.21 nm reflections are rotated by 30 degrees relative to each other. Despite the fact that a twelve-fold rotation represents a crystallographically forbidden symmetry element, it is proposed that this is generated by the orientationally directed bonding of the sp^3 diamond matrix around the type 2 diaphite core structures (see Fig 6.7 $\bar{e}$). Similar configurations have been noted in the realm of "twisted" bilayer graphene. The relative rotation between graphene sheets in such configurations yields Fast Fourier Transforms (FFTs) displaying 2×6 , or ideally 12, evenly spaced graphene diffraction spots. While the optimal rotation is 30° , various rotations within the range of $30 - 60^\circ$ between graphene sheets have also been documented. The appearance of twisted graphene layers in diffraction patterns closely resembles the arrangements and d-spacings of the reflections observed in FFTs for specific nanodiamond (ND) grains. Consequently, it is proposed that the observed regular and distorted twelve-fold rotational symmetry arises from the rotation of stacked graphene units in type 2 diaphite nanostructures.(see Fig 6.7 $\bar{e}$ and $\bar{f}$).

In Figure 6.8, we can observe cyclic twinning fringes present in the UNCD₁₀ sample. Figures 6.8b and 6.8c illustrate the dodecagonal rotational symmetry of nanodiamond grains, where the domains are rotated 30° relative to each other. This

rotational symmetry can be considered as a non-crystallographic symmetry within the nanodiamond matrix. Twinning, which is a characteristic disorder effect observed in nanocrystals, typically results in reflections and rotation twins. However, cyclic twins represent a different form of rotational symmetry seen in synthetic diamonds. These arise from cyclic twinning according to the spinnel law on the (111) plane [259]. Such a variety of cyclic twins is highly diverse and is characteristic of synthetic diamonds. Furthermore, it has been reported that the arrangement of cyclic twins in crystals can produce pseudo-pentagonal, icosahedral rotational symmetries, and other external morphologies in laboratory-grown diamonds [259]. An interesting feature of the dodecagonal symmetry is that the interface twin domains consist of five- and six-member rings as shown in Figure 6.8d. This phenomenon is a result of graphitization caused by the increased N_2 dopant, ultimately influenced by the role of hydrogen in UNCD growth.

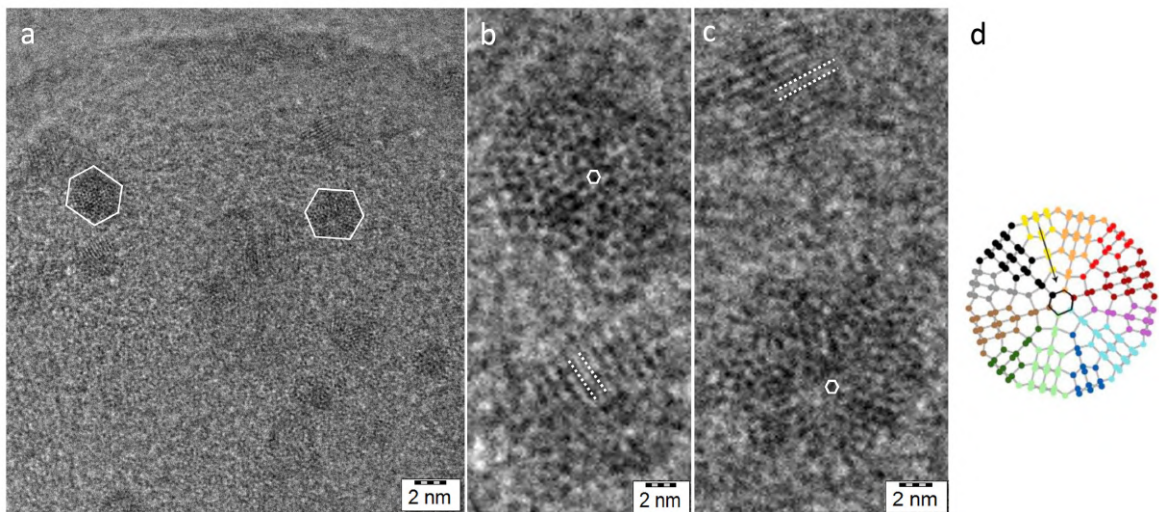


Figure 6.8 *a) HR-TEM image of UNCD₁₀ sample. b) and c) Nanodiamond structure displaying dodecagonal symmetry, which emerges from cyclic twins formed in the 10% Nitrogen (N_2)/2% CH_4/H_2 plasma-assisted CVD diamond growth. d) corresponding structure model of dodecagonal symmetry. adopted from ref.[231].*

N_2 induced growth mechanism

Carbon is often celebrated as a remarkable element due to its extensive potential, driven by the diverse self-bonding configurations allowed by its electron structure. This adaptability facilitates the creation of various carbon allotropes, each possessing

distinct properties. Traditional diamond synthesis involves the transformation of graphite (sp^2) to diamond (sp^3) by diffusing carbon onto a seed diamond's surface under elevated pressure and temperature conditions[260]. In a microwave plasma system, this conversion occurs at lower pressures, aided by the crucial role of hydrogen in reducing the activation energy barrier. The hydrogenated surface of graphene or graphite can transition to diamond at lower pressure and temperature levels compared to conventional methods, especially when nitrogen is introduced.

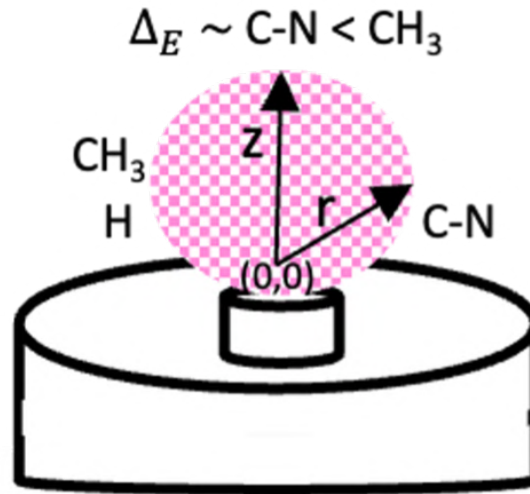


Figure 6.9 *N_2 induced growth mechanism:* The enhanced growth of CVD diamond can be achieved using C-N radicals because the activation energy barrier for attaching carbon to a diamond surface is lower with C-N radicals compared to methyl radicals.

First-principle calculations suggest that further lowering the activation energy barrier for this transition is possible with the introduction of transition metals or O- and N-terminations on the diamond surface[261]. Diamond formation in a microwave-assisted plasma system involves the periodic transition of vertical graphene sheets into a cauliflower-like morphology of diamond domains[261]. The interconversion of radicals and their diffusion onto the growing diamond surface plays a pivotal role, impacting the activation barrier and the resulting diamond quality. In a plasma chemistry involving nitrogen, carbon, and hydrogen, there are 535 possible reactions[262]. Introducing low levels of nitrogen promotes the growth of small islands that act as active sites for the diffusion of CH_2 groups, enhancing the growth rate[239], [263]–[265]. Therefore, the activation energy barrier for incorporating a carbon atom onto the growing diamond

surface is lower for C-N active sites compared to CH_3 nucleation sites ($\Delta E \sim \text{C-N} < \text{CH}_3$)[266]. A similar phenomenon is observed in the growth rates of diamond thin films in our work, where the thickness of the diamond film increased significantly as the nitrogen doping concentration increased (see Table 6.1).

However, the addition of excessive N_2 dopant can lead to heavy graphitization, degrading the film quality. With carefully balanced N_2 doping, it's possible to regulate both growth rates and film quality. The spatial distribution of the plasma and localized reacting species, including methyl (CH_3), hydrogen (H_2), and C-N radicals, influences the continuity of diamond film formation. The plasma's radial (r) and spatial (z) gradient distribution, as depicted in Figure 6.9, affects film quality and introduces defects, leading to twinning through secondary nucleation. Substrate temperature (T_{sub}) also influences the formation of sp^2 defects in diamond domains, inducing a compressive strain along a specific direction.

As N_2 concentration increases, it reduces the volume of the hot plasma core, resulting in a non-uniform heat distribution across the substrate, impacting the quality of the diamond thin film. The substrate temperature increases with N_2 concentration, contributing to crystal twinning due to stacking faults in the normal stacking of carbon atom layers along a specific direction. The introduction of N_2 in the microwave plasma-assisted growth environment enhances crystal twinning and the formation of other diamond polymorph structures, influenced by various growth parameters[57].

Conclusion

Carbon, in its natural state, typically exists as layered hexagonal graphite, where carbon atoms form sp^2 configurations. However, under high pressure and high temperature (HPHT) conditions, graphitic carbon undergoes a transformation into an ordered diamond structure, where carbon atoms are tetrahedrally bonded and arranged in six-membered ring configurations. This results in layers of carbon atoms with a cubic close-packing arrangement, known as a 3C stacking polytype[267]. On the other hand, the Diaphite structure is characterized by hexagonally arranged sp^2 carbon

within a cubic diamond stacking, creating a material with intergrown layers of sp^3 and sp^2 bonded carbon. The presence of Diaphite within nanodiamonds is significant for developing abrasives with high mechanical resistance, thanks to the strength of the $sp^3 - sp^2$ interface. Additionally, the incorporation of graphene, known for its excellent electrical conductivity, within the sp^3 domains of Diaphite holds promise for applications like 3D waveguide splitters[268].

The introduction of nitrogen during diamond growth has notable implications, incorporating sp^2 -bonded carbon within the sp^3 -bonded carbon structure embedded in the diamond matrix. The work presented demonstrates that by introducing nitrogen at specific concentrations in the gas mixture during diamond growth, Diaphite material can be grown. The $sp^3 - sp^2$ interface gives rise to hexagonally stacked cubic (h-c) diamonds with various diffraction fringes, including cyclic twinning and hexagonal carbon rings interwoven with diamond grains. The formation of Diaphite material is attributed to the regulation of hydrogen's role by the N_2 dopant concentration. The observed Diaphitic features were found in samples with controlled N_2 doping, specifically UNCD₅ and UNCD₁₀. Beyond these concentrations, heavily graphitized films were observed, confirmed by shifts in the Raman spectra associated with sp^2 carbon. The work also revealed a new feature: non-crystallographic symmetry with rotational twins leading to pentagonal and dodecagonal symmetries in the UNCD₅ and UNCD₁₀ samples, respectively. This highlights the structural diversity achievable through controlled N_2 doping in the diamond growth process.

Adjusting the balance between sp^3 and sp^2 bonded carbon opens avenues for developing novel nanostructured diamonds with unique electromechanical properties. The scalable nature of the chemical vapor deposition (CVD) synthesis process allows precise control over growth conditions (see Figure 6.10), paving the way for the creation of next-generation diamond-related materials with exciting possibilities for various applications and advancements in material science.

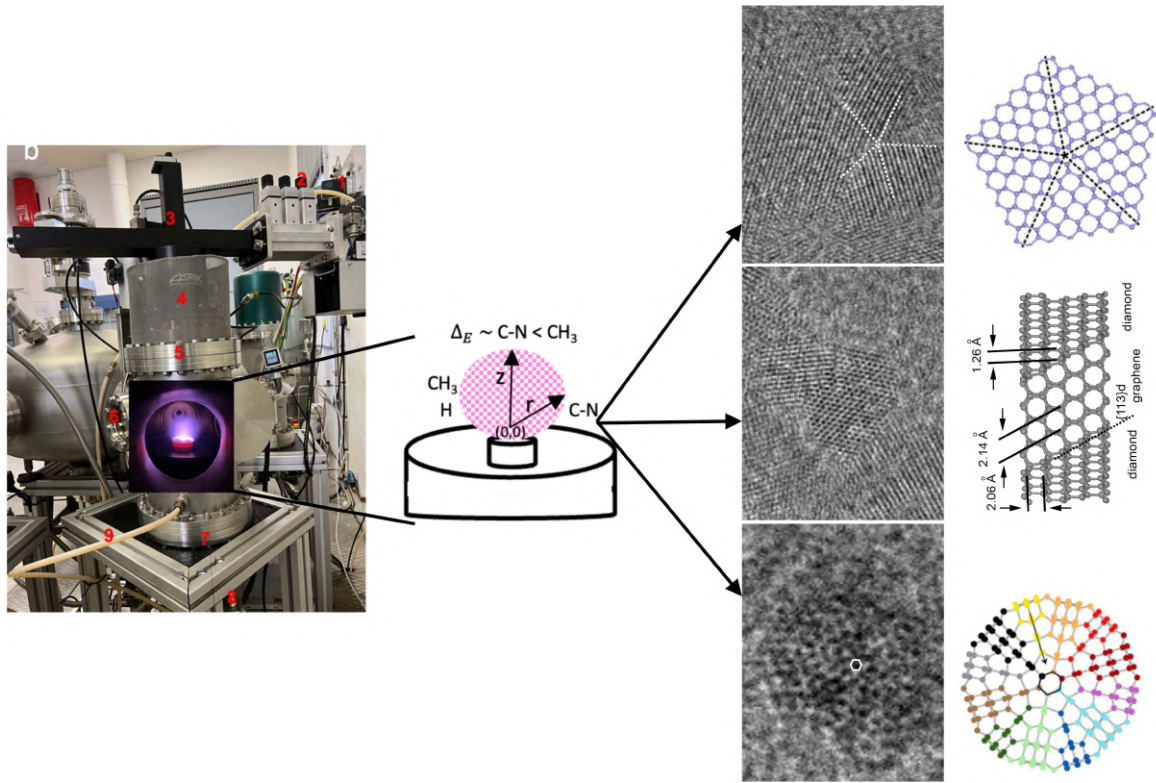


Figure 6.10 *Graphical abstract:* Tuning the plasma gas phase chemistry, the pathway for carbon-carbon bond formation can be modified, thereby allowing the creation of selective defects in diamond thin films.

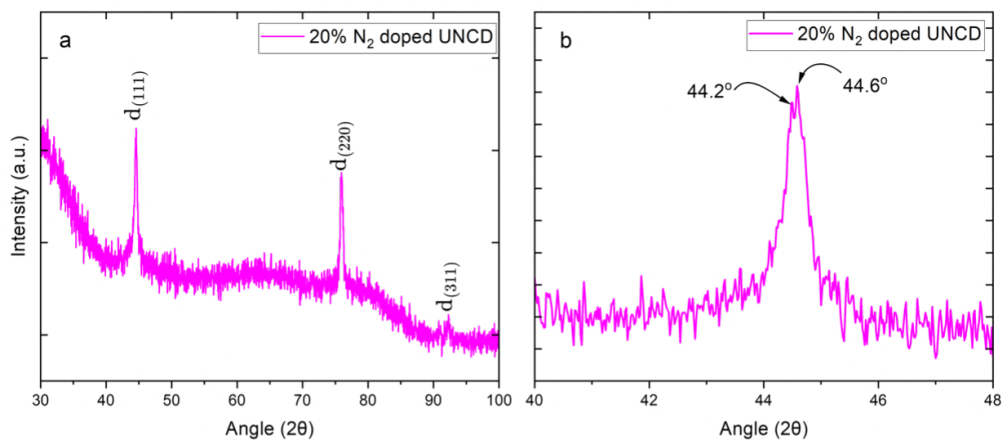


Figure 6.11 *XRD profile of UNCD₂₀ sample:* a) Commonly observed $d(111)$, $d(220)$ and $d(311)$ diffraction associated with d spacing 0.206 nm, 0.126 nm and 0.107 nm respectively. b) The $d(111)$ peak for UNCD₂₀ shift to higher Braggs angle compared to UNCD₅ and UNCD₁₀ samples.

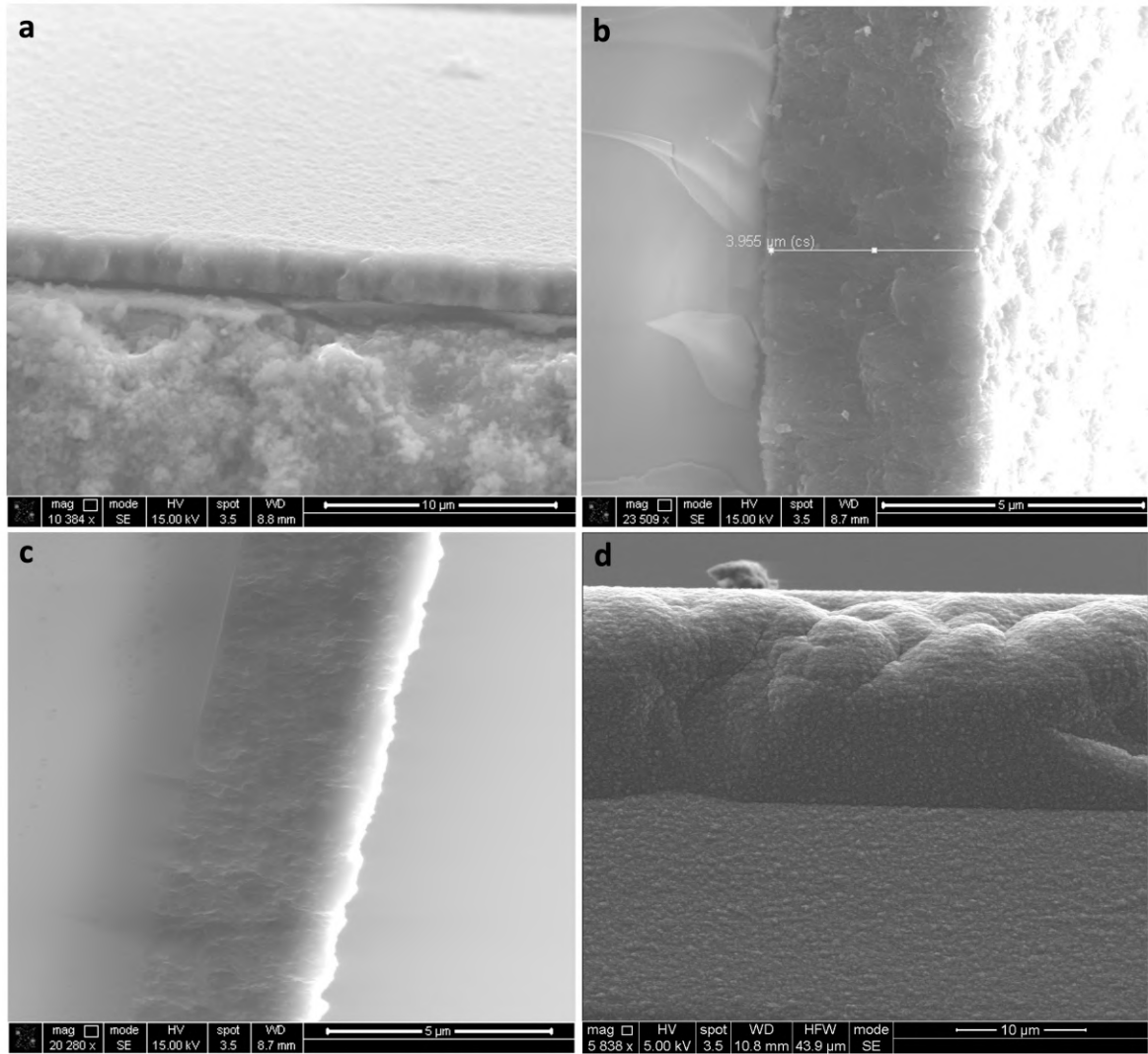


Figure 6.12 *Cross sectional imaging of UNCD_{5-20} samples: Cross sectional images of N_2 doped UNCD samples. a) UNCD_5 of film thickness $3.5 \pm 0.1 \mu\text{m}$. b) UNCD_{10} of film thickness $3.9 \pm 0.1 \mu\text{m}$. c) UNCD_{15} of film thickness $5.2 \pm 0.2 \mu\text{m}$. d) UNCD_{20} of film thickness $7.1 \pm 0.2 \mu\text{m}$.*

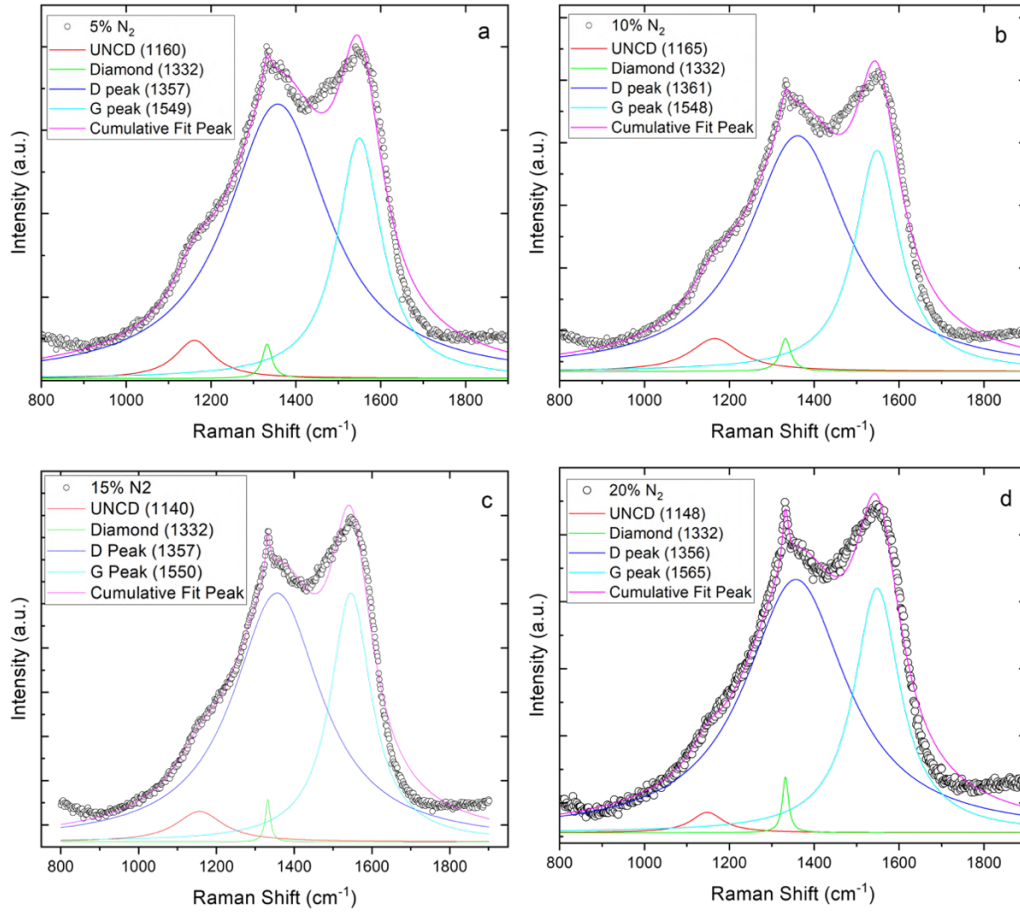


Figure 6.13 *Raman Spectra of UNCD₅₋₂₀ samples: Deconvoluted Raman Spectra of UNCD samples with varied N_2 concentration. a) UNCD₅, b) UNCD₁₀, c) UNCD₁₅, and d) UNCD₂₀ sample.*

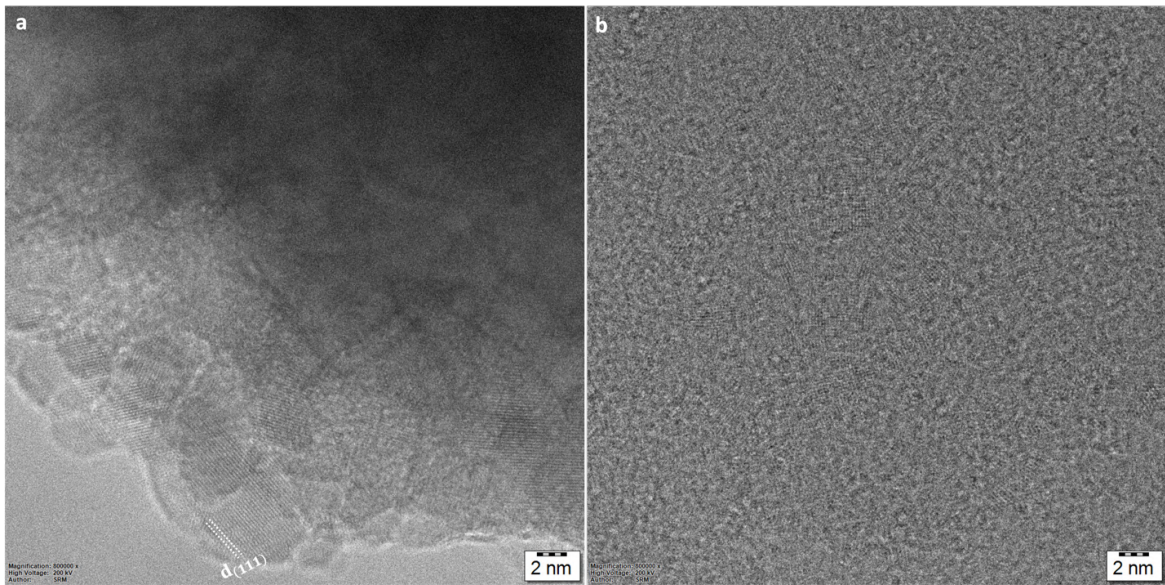


Figure 6.14 *HR-TEM image of UNCD without nitrogen doping: a and b) nanodiamond display only 111 fringes associated with cubic diamond.*

Chapter 7

Electronic Transport in N₂ doped diamond thin films

Ultrananocrystalline diamond (UNCD) films are a unique type of nanostructured carbon where the conductivity and microstructure can be controlled by adding nitrogen to the grain boundary regions [269]–[272]. The transition in conductivity from localized to delocalized states in these materials is thought to result from changes in structure, such as widening of the grain boundaries and the introduction of nitrogen doping to increase the density of free carriers [273]. However, the exact cause of the significant increase in conductivity in heavily doped films, without altering the nitrogen concentration, remains uncertain [59]. Some studies suggest that the heightened conductivity may be due to the formation of π -bonded sp^2 clusters and additional mid-gap states, which give UNCD films transport characteristics similar to those of disordered metals like graphitic carbon rather than degenerate semiconductors [274]. Alternatively, an analysis based on a non-degenerate semiconductor model considers the conductivity of UNCD films prepared with various concentrations of nitrogen, employing a combination of hopping (strong localization) and activated (band) conduction processes in three dimensions (3D) across different temperature ranges [275].

Numerous investigations have delved into the transport mechanisms of n-type conductive ultrananocrystalline diamond (UNCD). At temperatures above approximately 4.2 K [59] or 10 K [242], mechanisms such as hopping or other thermally

activated processes typically take precedence. Additionally, within this temperature range, two-dimensional localization has been identified as contributing to carrier transport [273]. However, there's a scarcity of data below 4 K, leaving the conduction mechanism in this lower temperature range still a puzzle. Some prior studies conducted around 1 K have hinted at a correlation between conductivity and sample morphology, suggesting that anisotropic weakly localized transport is facilitated by superlattice-like models of the nitrogen-doped UNCD structure [276]–[278].

The subsequent sections will present conduction mechanism concepts observed in disordered materials particularly nitrogen doped nanodiamond films and finally our work on conduction mechanism in nitrogen -doped nanodiamond films, paying significant attention to heavily doped diamond and the transport mechanism below 4 K which has not be done by many researchers.

7.0.1 Activated and Hopping conduction mechanism

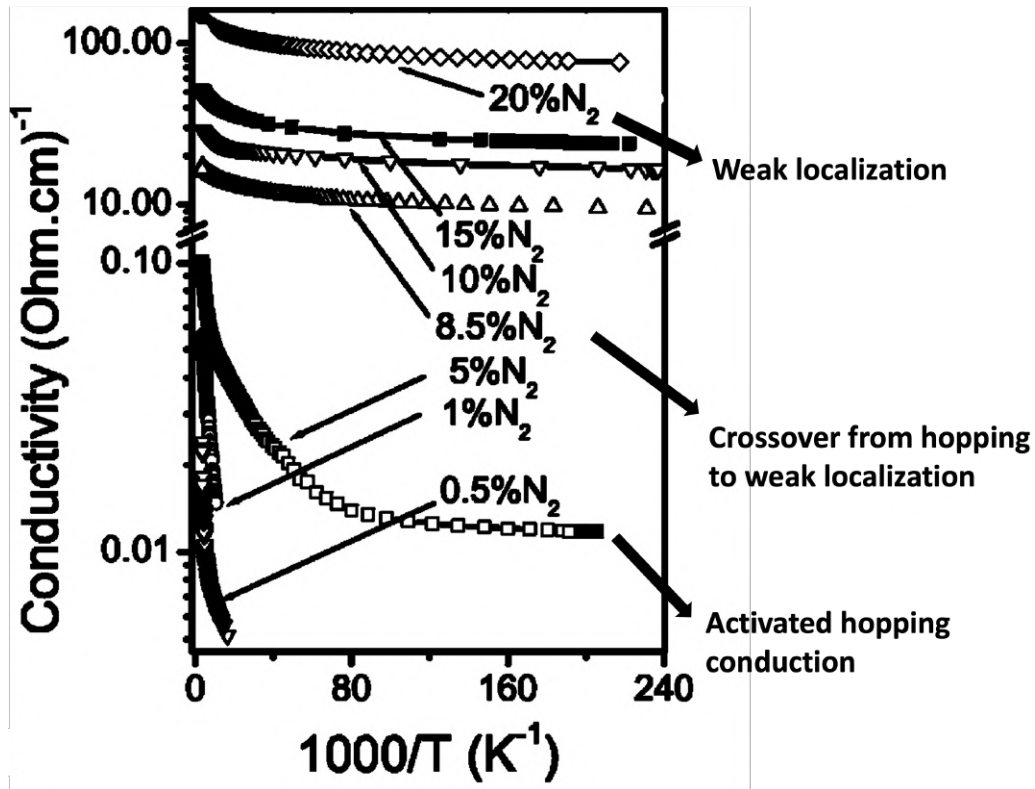


Figure 7.1 Mechanism of n-type conductivity in NCD films: The conductivity of NCD samples varies with N₂ doping introduced during NCD film growth. adapted from [59]

Electronic conduction in ultrananocrystalline diamond (UNCD) films doped with nitrogen can be elucidated through three distinct mechanisms: thermally activated conduction, variable range hopping (VRH), and weak localization (WL). These mechanisms predominate in UNCD films depending on the nitrogen concentration introduced, resulting in different densities of states. Research by Bhattacharyya et al. (2004) [279] demonstrated that UNCD films doped with 10% to 20% nitrogen exhibited metallic behavior, while diamond thin films with moderate N_2 doping levels, typically ranging from 5% to 8% nitrogen, displayed semi-metallic characteristics. In contrast, films with nitrogen content below 5% exhibited semiconducting behavior (see Figure 7.1 and 7.2).

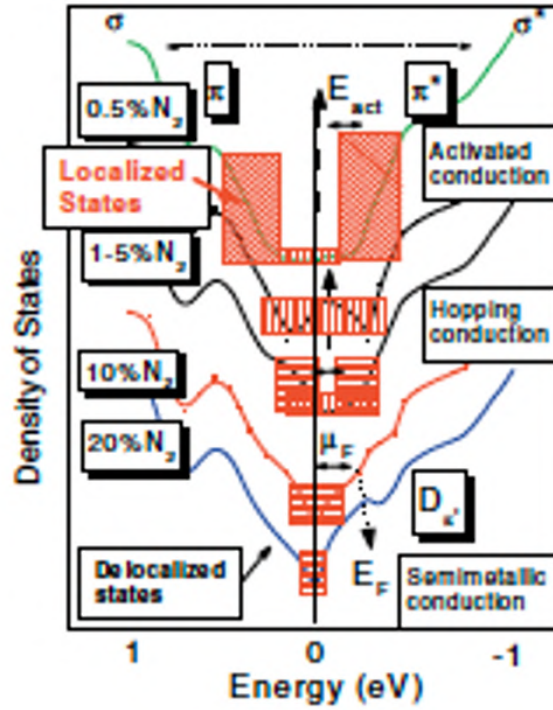


Figure 7.2 *Density of States (DoS) for NCD samples with respect to N_2 doping concentration. adapted from [280].*

In a thermally activated conduction mechanism the conductivity (σ) follows an Arrhenius-like temperature dependence.

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_\alpha}{k_B T}\right) \quad (7.1)$$

where E_α is the activation energy, k_B is the Boltzmann constant.

The VRH model predicts that the conductivity (σ) follows a temperature-dependent behavior, which can be described by the Mott VRH formula for three-dimensional systems:

$$\sigma(T) = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^p \right] \quad (7.2)$$

where p depends on the dimensionality of the system (e.g., $1/4$ for 3D systems, $1/3$ for 2D systems, and $1/2$ for 1D systems). Further σ_0 is a prefactor, and T_0 is a characteristic temperature related to the density of states near the Fermi level and the localization length.

For a Mott-Davis (MD) VRH model, where the density of states near the Fermi level is assumed to be constant and the Coulomb interactions between electrons are weak, the characteristic temperature T_0 is given by

$$T_0 = \frac{18}{k_B \xi^3 g(E_F)} \quad (7.3)$$

ξ is the localisation length and $g(E_F)$ is the density of states at the Fermi level.

For a Efros-Shklovskii (ES) VRH model, where the electron electron ($e-e$) interactions are significant, leading to a Coulomb gap—a reduction in the density of states near the Fermi level, the characteristic temperature $T_0 \rightarrow T_{ES}$ is given by

$$T_{ES} = \frac{2.8e^2}{4\pi\epsilon_0\epsilon_r k_B \epsilon \xi} \quad (7.4)$$

ϵ_r is the dielectric constant of the material. For diamond the relative permittivity is considered to be 5.5.

Both the Mott-Davis and Efros-Shklovskii VRH models describe electron hopping in disordered systems, but they differ in how they account for the density of states and Coulomb interactions. The temperature dependence of conductivity can help identify which model applies. In practice, plotting $\ln(\sigma)$ versus T^{-p} (where p is $1/4$ for MD and $1/2$ for ES) can reveal which model better describes the system.

7.0.2 Weak Localisation conduction mechanism

Heavily N_2 doped nanodiamond films, previously noted for their metallic properties, display a predominant quantum mechanical process known as weak localization (WL), characterized by diffusive behavior. We will delve into this phenomenon, as well as its complementary negative magnetoresistance, and further explore various WL models applicable to our N_2 doped nanodiamond systems.

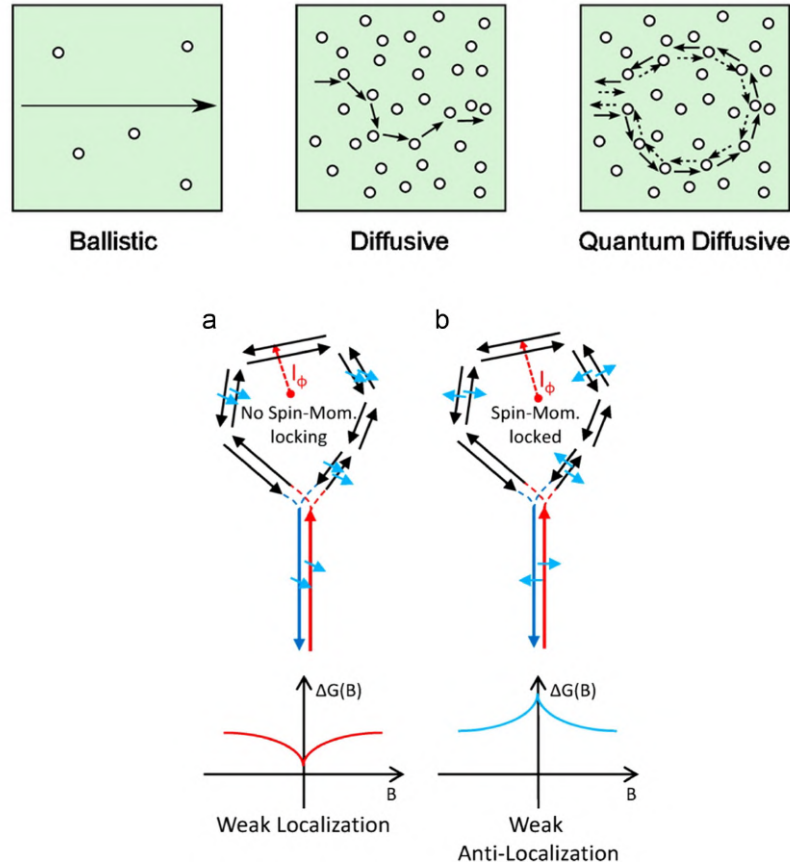


Figure 7.3 Graphical representation of weak localisation (WL) and weak anti-localisation (WAL) under Quantum diffusive transport. adapted from [281]

To understand Weak localisation (**WL**) it is essential to review the Drude's model. Resistance in a material is intricately linked with the number of electron scatterings and the length of the material. Therefore, we can expect resistance to increase proportionally with these factors. At high temperatures, the phase relaxation length of a material's electronic conduction is shorter than the mean free path. Conversely, at low temperatures, materials with low electronic mobility exhibit phase relaxation

lengths that exceed the electron mean free path. In such cases, conduction in the material occurs in a series of phase coherence units with elastic scatterers. Weak electron localization is a phenomenon that arises from interference between these various scattering events. Depending on the lattice structure, localization may occur in one, two, or three dimensions.

When electrons travel along a closed loop in opposite directions (time-reversed paths), their wavefunctions can interfere constructively if the phase coherence is maintained. This constructive interference enhances the probability of the electron returning to its original position, effectively increasing the resistance of the material 7.3a. However, this phenomenon can be disrupted by a external magnetic field, typically around 100 G, causing negative magneto-resistance, where conductance increases as the magnetic field strength increases.

Weak anti-localization (**WAL**) is a phenomenon where quantum interference effects lead to an increase in electrical conductivity. This effect is typically observed in systems with strong spin-orbit coupling. The interference of electron wavefunctions traveling along time-reversed paths can result in destructive interference due to spin-orbit interaction 7.3b. This destructive interference reduces the probability of the electron returning to its original position, effectively decreasing the resistance of the material. Unlike weak localization, applying a magnetic field in the case of WAL results in positive magnetoresistance (a decrease in conductance), as it disrupts the destructive interference.

2D WL

The dimensionality of the material, determines the type of WL. In 2D disordered materials with significantly higher doping concentration, the total conductivity can be described by equation 7.5 below [273], [282], [283]:

$$\sigma(0, T) = \sigma_0 + \Delta\sigma(0, T)_{WL} + \Delta\sigma(0, T)_{e-e} \quad (7.5)$$

The first term σ_0 represents the Drude conductivity, followed by a correction resulting from weak localization $\Delta\sigma(0, T)_{WL}$ and finally, the correction arising from electron-electron interactions $\Delta\sigma(0, T)_{e-e}$ [284]. The last term becomes very significant at very low temperatures below 10 K.

$\Delta\sigma(0, T)_{WL}$ is given by

$$\Delta\sigma(0, T)_{WL} = \frac{e^2}{\pi\hbar} \ln\left(\frac{1}{L_{Th}}\right) = B \ln T \quad (7.6)$$

here L_{Th} is Thouless length used to describe the 2DWL fit in the disordered metals [282] and the $\Delta\sigma(0, T)_{e-e}$ is given by

$$\Delta\sigma(0, T)_{e-e} = \left(\frac{e^2}{4\pi^2\hbar}\right) \left(2 - \frac{3}{2}F\right) \ln\left(\frac{\tau k_B T}{\hbar}\right) \quad (7.7)$$

Where F is electron screening factor and k_B is Boltzmann constant [276], [283]. We can examine the $\ln T$ dependence of the conductance to further assess the suitability of this model to a disordered system.

3D WL

In a conventional three-dimensional weak localization conduction regime, the conductivity is described by an equation [284].

$$\sigma(0, T) = [\sigma_0 + p_1 T^{0.35} + p_2 T^{0.5}] \frac{S}{l} \quad (7.8)$$

where σ represents the conductivity. The ratio $\frac{l}{S}$ considers materials geometrical configuration effecting the conduction, with S representing the cross-sectional surface area and l indicating the length of the sample. The parameters p_1 and p_2 are defined based on equations 7.9 and 7.10, provided below:

$$p_1 = \frac{e^2}{2\pi^2\hbar L_\phi} \left(\frac{C^2 S}{kg m^3}\right) \quad (7.9)$$

The term $p_1 T^{0.35}$ represents the correction to conductivity due to weak localization, where L_ϕ indicates how coherent electron waves remain within the material.

$$p_2 = \left(\frac{e^2}{4\pi^2\hbar} \right) \left(\frac{1.3}{\sqrt{2}} \right) \left(\frac{4}{3} - \frac{3}{2}F \right) \sqrt{\frac{k_B}{\hbar D}} \left(\frac{C^2}{kgm^4} \frac{S}{k^{0.5}} \right) \quad (7.10)$$

The term $p_2T^{0.5}$ represents the correction due to electron-electron interactions. The symbol $\mathbf{D}$ represents the diffusion coefficient, while $\mathbf{F}$ stands for the electron screening factor in the above equation. Although the equation is typically applied to isotropic systems, certain nanodiamond films display some level of anisotropic behavior in their conduction due to dimensionality factors. This behavior has been attributed to the propagative Fermi surface (PFS) model, which effectively accounts for the unconventional transport properties observed in nano-crystalline diamond films. Additionally, a correlation has been established between the anisotropic parameter and the disorder observed in artificially constructed superlattices [276], [285]. In such anisotropic materials, the MR ($\Delta\sigma(B)$) is described by the equation below.

$$\frac{\Delta\sigma(B)}{\sigma(0,T)} = \alpha \left[\sigma(0,T) \left(\frac{e^2}{2\hbar\pi^2} \right) \left(\frac{eB}{\hbar} \right)^{1/2} \right] f_3 \left\{ \frac{\frac{\hbar}{eB}}{4D\tau_\phi} \right\} \quad (7.11)$$

Here, the parameter f_3 is referred as the Kawabata function, and its expression is provided by

$$f_3(x) = \sum_{N=0}^{\infty} \left\{ 2 \left[(N+1+x)^{0.5} - (N+x)^{0.5} \right] - \left(N + \frac{1}{2} + x \right)^{0.5} \right\} \quad (7.12)$$

Where N represents the Landau quantum number, delineating the discrete energy levels occupied by electrons as they move in cyclotron orbits within a magnetic field [286], [287]. The coefficient α characterizes anisotropic transport in three dimensions. This function anticipates a B^2 dependence at low magnetic fields and a $B^{\frac{1}{2}}$ behavior at high magnetic fields. However in a semi-classical phenomena weak localisation follows a linear B dependence at high fields.

7.1 Transport in N₂ doped UNCD on Quartz substrates

The electronic transport mechanism in nitrogen-doped nanodiamond (UNCD) is characterized by a combination of activated conduction, hopping, and weak localization conductivity mechanisms. S. Bhattacharya et al., (2004) [279], reported that 0.5% N₂-doped UNCD exhibits an Arrhenius-type conduction mechanism with activation energies (E_a) of 72.0 meV at room temperature (300 K) and 3.8 meV in the temperature range of 60-136 K. For 1.0% N₂-doped UNCD, they observed hopping conduction with E_a values of 25 meV at room temperature and 15.1 meV in the range of 160-120 K. Further increasing the N₂ doping to 5% showed a hopping conduction mechanism with a hopping length (R_{hopp}) of 6.22 Å at 200 K. Additionally, 10% and 20% N₂-doped UNCD samples displayed variable-range hopping (VRH) conduction with extended delocalized states, indicating a shift of the Fermi energy (E_F) towards the conduction band.

Conversely, J. J. Mareš et al., (2006) [271], demonstrated that 20% N₂-doped UNCD samples exhibit weak localization, resulting in increased disorder and enhanced scattering events. This leads to quantum interference of electrons at low temperatures, causing weak localization-type conduction. T. C. Choy et al., (2008) [272], countered this argument by suggesting that quantum interference effects, which result in negative magnetoresistance in the VRH regime, can also occur in disordered metals. Thus, 20% N₂-doped UNCD samples are consistently in the strongly localized regime. They further stated that increasing the magnetic field would enhance the hopping length, causing quantum interference phase-breaking at $l_{hopp} = l_B$, with l_{hopp} showing $T^{-1/2}$ dependence, supporting the VRH interpretation.

Several studies (e.g., Dmitry Churochkin et al., EPL 2012 [277]; K. V. Shah, PRB 2010 [276]; George Chimowa et al., EPL 2012 [278]; L. H. Willems van Beveren et al., 2020 [288]) have shown a crossover from VRH to anisotropic 3D weak localization under artificial carbon superlattice frameworks, where magnetoresistance fitting yields an anisotropic parameter (α that dictates the phase coherence length following a power

law of T^p with $p=0.7$ (less than unity).

Understanding and generalizing the transport mechanisms in heavily N₂-doped UNCD samples is complex due to the interplay between disorder, Anderson localization, and phase coherence. The complexity further arises from the extent of disorder and its geometrical arrangement in films a few microns thick (1-5 μm). Therefore, further studies are needed to understand electronic transport in these samples.

S. Bhattacharya et al. [280], [289]–[291] attempted to elucidate various transport mechanisms in highly disordered UNCD materials with different confinement levels, localized states, and weakly localized orbits within the grain boundaries of UNCD samples. They noted resonant tunneling conduction between the 2D layers and extended π bonds in wider grain boundaries of 20% N₂-doped samples, contrasting with the hopping conduction observed in nanocrystalline diamond between neighboring crystals.

In this study, we examined the electronic transport mechanisms in both 10% and 20% N₂-doped samples grown on quartz and silicon substrates. In line with earlier reports, we also observed anisotropic 3D weak localization in 20% N₂-doped UNCD on quartz and 10% N₂-doped UNCD on silicon substrates, with films a few microns thick. Notably, by reducing the film thickness to 80 nm (similar to the phase coherence length L_ϕ), we observed for the first time a combination of weak localization and anti-weak localization at low temperatures (30 mK), corresponding to an increase in spin-orbit coupling at higher fields.

Additionally, we observed metallic behavior in heavily doped UNCD grown at higher temperatures (1200 K) in a hydrogen-rich plasma. These heavily doped samples exhibited a similar increase in resistance at low temperatures but with a sudden drop in resistivity at 4 K. However, the resistance did not drop to zero, and a conductivity minimum was observed, indicative of highly disordered UNCD material.

The microstructure of diamond thin films can vary greatly depending on the preparation method, ranging from diamond-like to graphite-like carbon. Films with low sp^2 concentrations have also been described as quasi-1D polymer chains, such as trans-polyacetylene [292]–[295]. In carbon, the electronic properties are significantly

influenced by bond disorder, which depends on the sp^2/sp^3 bond ratio and the size of sp^2 clusters. Overall, diamond thin films possess a complex microstructure, including 1D (trans-polyacetylene), 2D (graphene), and 3D phases. In this context, we attempt to fit the transport data collected on diamond thin films containing diaphitic domains to various transport models, including activated conduction, variable range hopping (VRH), and weak localization.

7.1.1 Transport in 7.5% N₂ doped UNCD

This sample was measured using the Oxford Triton DR system, which achieves a base temperature of approximately 10 mK. Figure 7.4 illustrates the resistance-temperature characteristics of 7.5% N₂ doped UNCD grown on a Quartz substrate. Figure 7.4 **b-f** displays the conductance-temperature plots against various transport models including activated conduction, 1D (Efros-Shklovskii) variable range hopping (VRH), 2D VRH, 3D (Mott) VRH, and 3D and 2D weak localization (WL) respectively in the temperature range between 10 K - 273 K.

Figure 7.4**a** illustrates a sharp drop in the resistance of the UNCD_{7.5} sample as the temperature rises, particularly within the 30 K to 100 K range, which is a typical characteristic of semiconducting materials. The sample's conductivity at room temperature was measured to be 8.720 S cm^{-1} . From Figure 7.4 **b** it is evident that the Arrhenius plot does not display a single straight line throughout the measured temperature range, indicating that activated conduction is not the predominant mechanism in the UNCD_{7.5} conduction. Generally, nanodiamond samples with 5-10% N₂ doping show a transition from hopping to weak localization behavior in their electrical conduction (see Figure 7.1). However, our sample grown on a quartz substrate does not follow this pattern, as confirmed by the various VRH model plots (see Figure 7.4 **c-e**).

Initially, the conductance-temperature plot appears to fit the 3D VRH model well over a broad temperature range from 5 K to 200 K 7.4 **e**. Further examination of the conductance at very low temperatures through resistivity (RT) and magnetoresistance (MR) measurements, within the 30 mK to 1 K range, revealed that weak localization

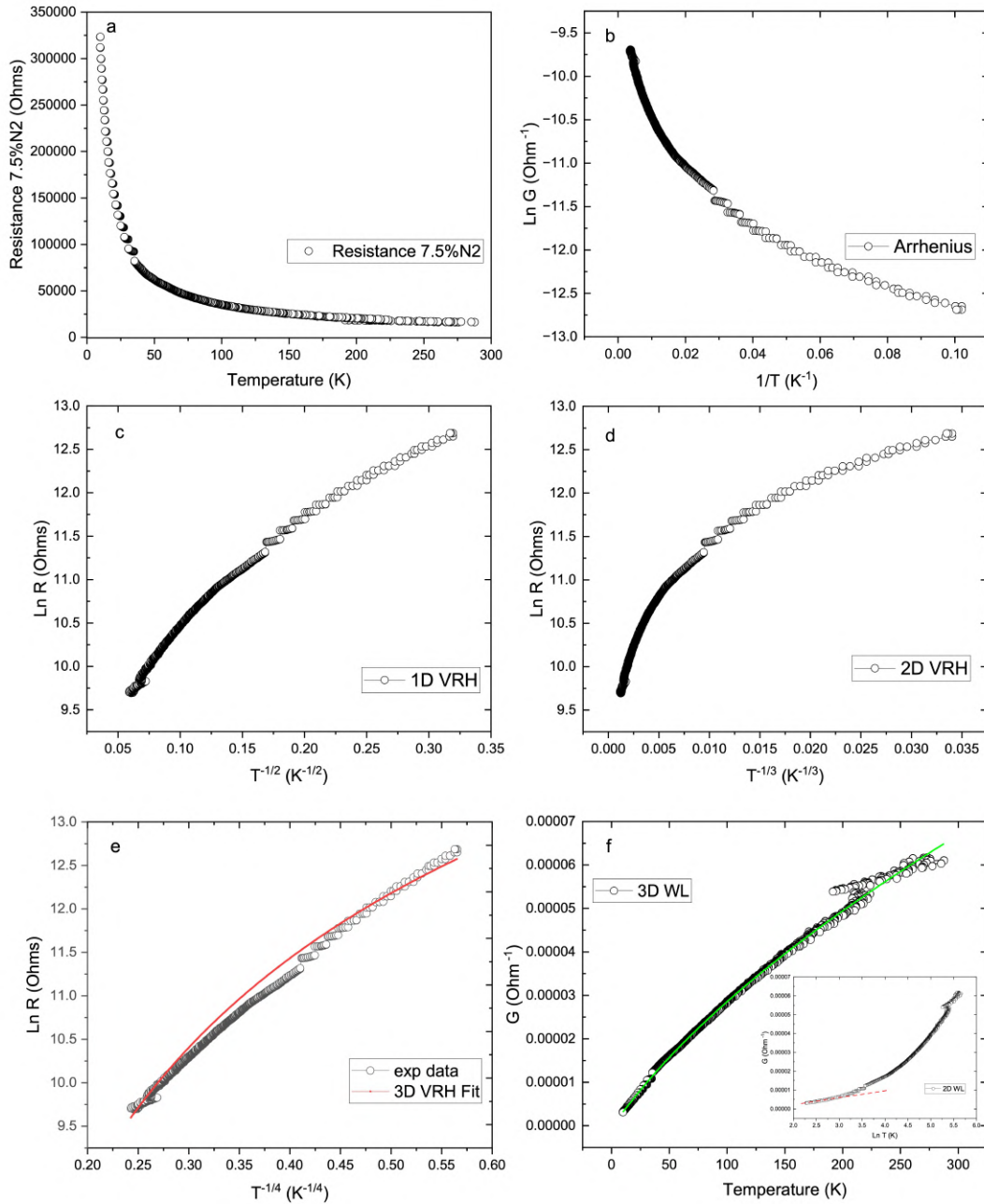


Figure 7.4 Resistance/conductance-Temperature plots of 7.5% N₂ doped UNCD sample grown on quartz substrate. a) simple R-T plot. b) Logarithmic conductance against $1/T$ for Arrhenius model. c) Logarithmic resistance plot against $T^{1/2}$. d) Ln R against $T^{1/3}$ 2D VRH model. e) Ln R against $T^{1/4}$ for 3D VRH model. f) Conductance against temperature for fit with 3D WL model and 2D WL model (inset figure).

transport is dominant in the UNCD_{7.5} sample. Figure 7.4 f presents the conductance (G) vs. T and G vs. ln T (inset figure) plots for the sample, supporting the observation of weak localization contributing to the transport mechanism in UNCD_{7.5}. The 3D weak localization fitting, performed using equation 7.8, aligns

well, confirming the 3D weak localization conduction mechanism. According to the equation 7.8, the total conductivity is the sum of the classical Drude conductivity, weak localization corrections, and electron-electron interaction corrections. From the fitting we derive the weak localization corrections ($p1T^{0.35}$), and electron-electron interaction corrections ($p2T^{0.5}$) and the values found to be $1.82 \times 10^{-5} \left(\frac{C^2}{kg} \frac{S}{m^3} \right)$, $1.1 \times 10^{-3} \left(\frac{C^2}{kgm^4} \frac{S}{k^{0.5}} \right)$ respectively, and classical Drude conductivity to be 8.91×10^{-6} ohms⁻¹. Overall the temperature dependant conductance for UNCD_{7.5%N₂} can be expressed as $G(0, T) = [8.91 \times 10^{-6} + 1.82 \times 10^{-5}T^{0.35} + 1.1 \times 10^{-3}T^{0.5}]$.

From the equations 7.9 and 7.10 and the fitting parameters (WL and $e-e$ corrections), considering electron screening factor $F = 0.3$ (as per the earlier reports on disordered nanodiamond systems [276], [279], [288]) we derive the phase coherence length $L_\Phi = 4.79 \times 10^{-8} m \ T^{-0.35}$ and diffusion coefficient $D = 1.269 \times 10^{-8} m^2/s \ T^{-0.5}$.

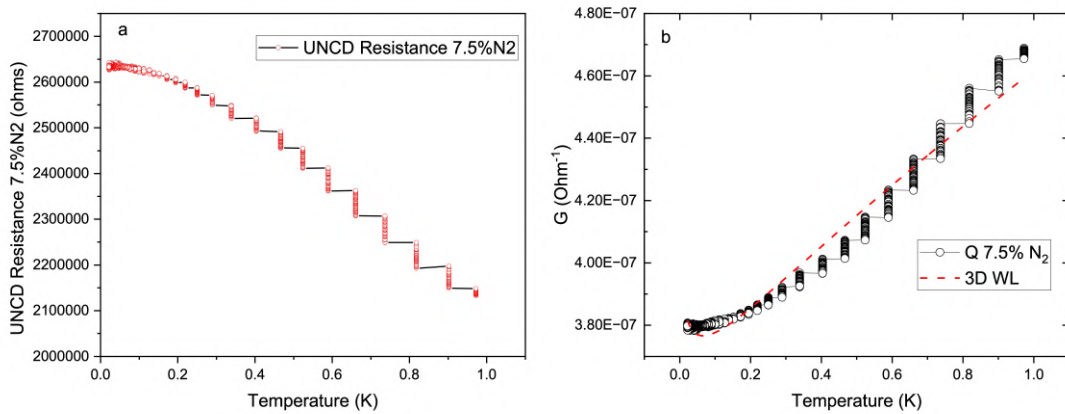


Figure 7.5 Resistance/conductance-Temperature plots of 7.5% N₂ doped UNCD sample grown on quartz substrate, measurements performed on Oxford Triton DR at 1 K to 10 mK regime. a) normal R-T. b) Conductance vs Temperature plot with 3D WL fitting.

Figure 7.5 illustrates the conductance-temperature graphs in the millikelvin (mK) regime. At low temperatures, the material exhibits 3D weak localization (WL) conduction behavior confirmed with 3D WL fit using eq 7.8.

MR in 7.5% N₂ doped UNCD

Now we verify the applicability of WL transport mechanism to UNCD_{7.5} conduction through magneto-resistance studies as followed. Figure 7.6 depicts the magneto-

resistance of a 7.5% N₂-doped UNCD sample within the temperature range of 30 mK to 1 K. A characteristic negative magneto-resistance is observed, consistent with behavior typical of 3D WL. The magneto resistance is computed as

$$MR = \frac{R_B - R_0}{R_0}$$

where R_B is the resistance at specific magnetic field B and R_0 is zero field resistance.

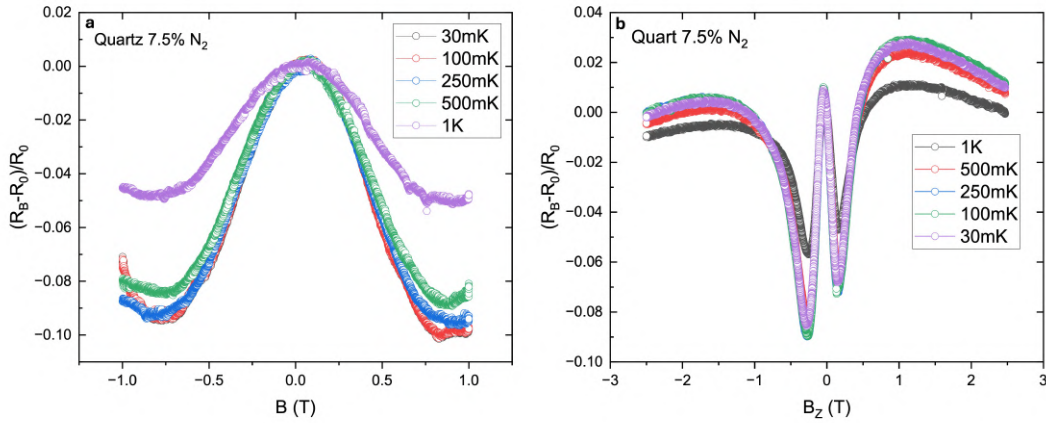


Figure 7.6 *Magneto-resistance measurements were conducted both parallel and perpendicular to the diamond thin film on quartz. a) MR (%) vs $B_{\perp}$ exhibiting a typical negative MR within the range of 0 to 0.7 T, transitioning to positive a trend at fields exceeding 0.7 T. b) MR (%) vs $B_{\parallel}$ displays asymmetric negative MR between -0.2 and +0.2 T, with a positive MR observed at fields greater than 0.2 T.*

Figure 7.6a displays the MR measurements conducted parallel to the UNCD sample in the field range of -1 to +1 T, while Figure 7.6b presents the MR measurements conducted perpendicular to the UNCD sample in the field range of -2 to +2 T. it is noteworthy that when field applied perpendicular to the thin film MR takes a typical negative values ($< \pm 0.7$ T. However, it diverges from the usual expected pattern at higher fields exceeding approximately ± 0.7 T. Conversely, when a field is applied parallel to the sample, the magnetoresistance (MR) demonstrates a decreasing trend within the range of approximately ± 0.2 T, followed by an increasing trend beyond this range. Such behavior is characteristic of highly disordered samples with a dense carrier concentration exhibiting weak localization (WL) at low fields and anti-weak localization (AWL) at higher fields. This observation aligns with the potential manifestation of the Kondo effect at millikelvin temperatures, as indicated in prior

research ([296]). Nonetheless, further analysis is necessary to validate our hypothesis.

The Hikami-Larkin-Nagaoka (HLN) model is used to describe the magnetoresistance (MR) behavior in materials exhibiting weak localization (WL) and anti-weak localization (AWL).

$$\Delta\sigma(B) = -\frac{e^2}{2\pi^2\hbar} \left[\psi \left(\frac{1}{2} + \frac{B_\phi}{B} \right) - \ln \left(\frac{B_\phi}{B} \right) \right] \quad (7.13)$$

where α parameter describes the strength of WL (α is negative) and AWL (α is positive), ψ is Digamma function, B_ϕ is phase coherence magnetic field, related to the phase coherence length L_ϕ by $B_\phi = \frac{\hbar}{4eL_\phi^2}$

Extended HLN model is used for materials with significant spin-orbit coupling that accounts spin-orbit effects.

$$\Delta\sigma(B) = \frac{e^2}{2\pi^2\hbar} \left[\alpha \left(\psi \left(\frac{1}{2} + \frac{B_\phi}{B} \right) - \ln \left(\frac{B_\phi}{B} \right) \right) - \beta \left(\psi \left(\frac{1}{2} + \frac{B_{SO}}{B} \right) - \ln \left(\frac{B_{SO}}{B} \right) \right) \right] \quad (7.14)$$

where α and β are parameters that depend on the spin-orbit coupling and $B_{SO} = \hbar / (4eL_{SO}^2)$ is a characteristic magnetic field related to the spin-orbit scattering length L_{SO} .

The digamma function and the HLN model are commonly applied for understanding WL and AWL in 2D systems. A more generalized approach to describe the magnetoresistance in 3D systems, considering both WL and AWL, can be formulated by combining the contributions from both effects. The total magnetoresistance $\Delta\rho(B)$ can be expressed as:

$$\Delta\rho(B) = \rho_0 \left(1 + \beta \sqrt{\frac{B}{B_\phi}} - \gamma \left(\frac{B}{B_{SO}} \right) \right) \quad (7.15)$$

Where β and γ are prefactors that depend on the specifics of the system, such as dimensionality and scattering mechanisms.

Carbon superlattice structures typically consist of stacked or periodic layers of different carbon-based materials, such as nanocrystalline diamond or graphene-like layers,

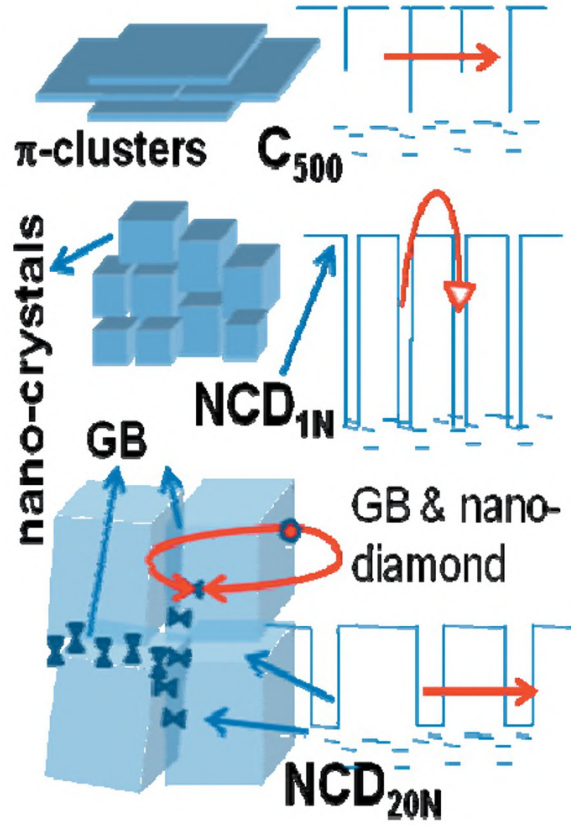


Figure 7.7 *Electron confinement with respect to size of grain boundaries in nanocrystalline diamond thin films. adopted from [280].*

separated by grain boundaries that act as barriers for electron movement. Grain boundaries in such structures create potential wells where electrons are trapped or confined. This confinement significantly alters the electronic structure of the material, leading to phenomena like the formation of localized states and modified bandgaps. In carbon-based materials, such as disordered nanocrystalline diamond, the electron wavefunctions become localized near the grain boundaries due to the disruption of the periodic lattice. The boundaries can cause scattering and localization effects, contributing to phenomena like Anderson localization or weak localization, which is often observed in these materials at low temperatures (see Figure.7.7). The strength and extent of electron confinement depend on the grain size, disorder level, and specific atomic configurations at the boundaries.

These confined states also affect the transport properties of the material. The presence of confined electrons can reduce overall conductivity due to scattering at the boundaries, but in certain configurations, the material may exhibit enhanced properties, such as positive magneto-resistance, improved thermoelectric performance

or even superconductivity under specific conditions [297]. The confined electrons in carbon superlattices thus offer a pathway to control electronic properties through careful engineering of the grain boundaries and disorder within the material. Here In this case, we observe positive magnetoresistance at higher fields 7.6a-b. This occurs because the magnetic field enhances scattering events, leading to localization or overlap of WL orbits, which results in a decrease in conductivity.

7.1.2 Transport in 20% N₂ doped UNCD-Quartz

Figure 7.8 depicts the resistance-temperature characteristics of 20% N₂ doped UNCD grown on a Quartz substrate. The resistance of the sample decreases rapidly with increasing temperature, a behavior commonly observed in semiconducting materials (see Figure 7.8 **a**). This semiconductor-like behavior is noticeable within the temperature range of 20 K to 200 K. This is in agreement with previous observations made by many researchers[277]–[279]. The sample's conductivity at room temperature was measured to be 708.4 S cm⁻¹.

Figure 7.8 **a**, **b**, and **c** display the resistance-temperature (RT) plots against the 1D (ES) Variable Range Hopping (VRH), 2D VRH, and 3D (Mott) VRH conductivity models, respectively, aimed at identifying potential conductivity mechanisms. Figure 7.8 **e** illustrates the Arrhenius plot for the conductivity of 20% N₂ doped UNCD on a quartz sample, aiming to verify the possibility of an activated conduction mechanism. However, none of the aforementioned models meet the criteria for explaining the conductivity mechanism observed in the sample.

Figure 7.8 **f** illustrates the conductance-temperature (G vs T) plot utilizing the 3D weak localization (WL) model. The red line corresponds to a fitting using the 3D WL equation 7.8. Upon analyzing the conductance-temperature graph (Figure 7.8) via equation 7.8, it is evident that the model adequately represents the conductivity behavior of the 20% N₂ doped UNCD sample across a wide temperature range (2-260 K). The relative good fit of the model at high temperature cannot be interpreted as WL but rather it is most likely due to a similar semi-classical phenomenon, in which interference of memory effects are dominate. Weak localization is dominated at very

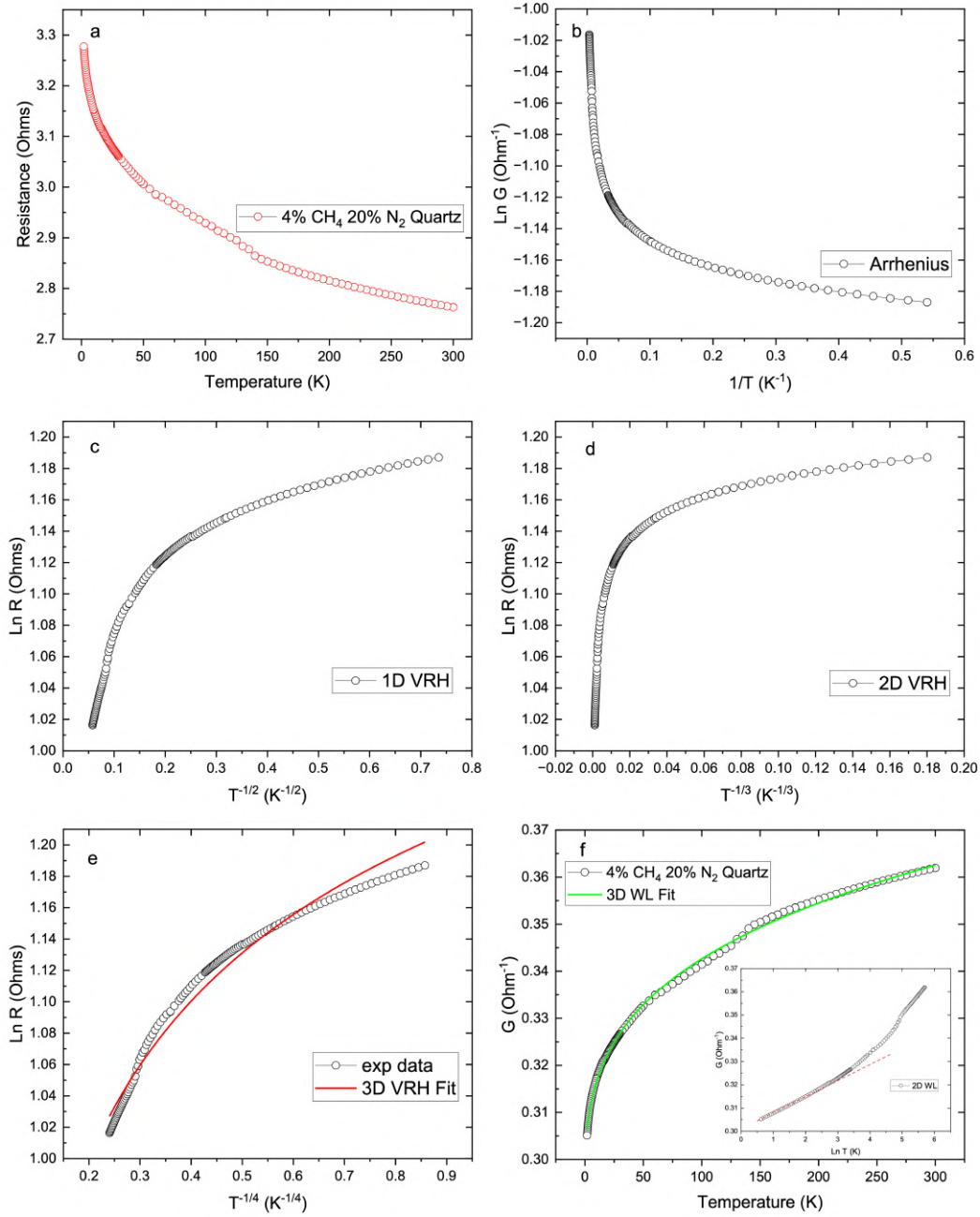


Figure 7.8 Resistance-temperature characteristics of the 20% N₂ doped UNCD sample on quartz are depicted. (a-f) illustrate different fitting models, beginning with normal R-T, activated conduction, 1D VRH, followed by 2D VRH, 3D VRH, and concluding with 3D WL, respectively

low temperatures. The fittings parameters derived from the 3D WL fit are as followed:

$$p_1 = 1.375 \times 10^{-3} \left(\frac{C^2}{kg} \frac{S}{m^3} \right)$$

$$p_2 = 6.21 \times 10^{-3} \left(\frac{C^2}{kgm^4} \frac{S}{k^{0.5}} \right)$$

$$p_0 = 0.289 \text{ Ohm}^{-1}$$

substituting the above pre-factor values we drive the phase coherence length $L_\Phi = 0.11217 \times 10^{-8} m \ T^{-0.35}$ and diffusion coefficient $D = 2.2187 \times 10^{-6} m^2/s \ T^{-0.5}$.

MR of 20% N₂ doped UNCD

To ascertain whether the observed conduction conforms to a 3D WL (weak localization) model, we conducted MR measurements on our UNCD sample grown on quartz. Figure 7.9 shows the plot of MR against the magnetic field.

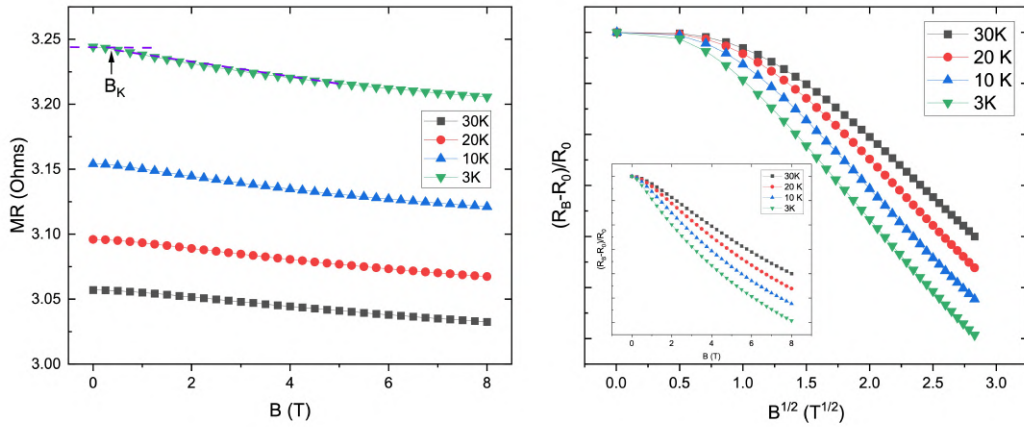


Figure 7.9 *Magnetoresistance of 20% N₂ UNCD grown on quartz. a) Resistance vs Magnetic field and b) MR(%) vs $\sqrt{B}$.*

Figure 7.9a shows a parabolic trend at lower fields and a linear trend at higher fields, indicating a three-dimensional weak localization (3D WL) conduction mechanism. At very low magnetic fields, the MR values are close to zero at all temperatures. This corresponds to the regime where weak localization is strongest, as the magnetic field is not yet strong enough to significantly disrupt the quantum interference between electron paths. This results in a minimal change in resistivity near $B = 0$. B_k is the characteristic magnetic field where the the magnetic coherence length $\ell_B = \ell_\phi$ and here the breakdown of phase coherence initiates. B_k is determined geometrically by finding the intersection point where a line parallel to the B -axis, drawn through the point representing the resistance at $B = 0$, meets the extrapolated linear fit of the curve's declining section at higher magnetic fields [271].

As the magnetic field increases, the MR becomes more negative, indicating a decrease in resistivity. This negative magnetoresistance is a characteristic signature of weak localization. The linear dependence of MR on $B^{1/2}$ at higher magnetic fields suggests that the magnetic field is progressively breaking the phase coherence of the electron wave functions, thereby reducing the localization effect. This scaling with $B^{1/2}$ is typically observed in materials where the weak localization effect is being suppressed by a magnetic field.

The magnitude of the negative MR becomes more pronounced as the temperature decreases. At 3 K, the MR shows the steepest drop with increasing $B^{1/2}$, reflecting stronger weak localization effects at lower temperatures due to enhanced phase coherence of electrons. As the temperature increases, the weak localization effect weakens, leading to a smaller change in MR with increasing magnetic field.

The observed linear relationship between MR and $B^{1/2}$ in the Figure.7.9b is indicative of the suppression of weak localization in the presence of an external magnetic field. At low temperatures, the quantum coherence of electrons is preserved, leading to significant weak localization effects that manifest as negative magnetoresistance. As the magnetic field increases, it breaks the phase coherence of electrons, reducing the localization and leading to a linear dependence of MR on $B^{1/2}$. The strength of the weak localization effect diminishes with increasing temperature, as observed from the data, where the magnitude of MR decreases at higher temperatures.

7.2 Transport in N₂ doped UNCD on Si substrates

7.2.1 Transport in 10% N₂ doped UNCD

Here, we elaborate on the R-T characteristics of the nanodiamond films fabricated using N₂ concentrations of 10%, and 20%, respectively, in the MPECVD chamber, and grown on a silicon substrate with a dielectric interface layer (refer to Figure 5.25). Variation in the N₂ doping concentration has shown a significant impact on the electrical characteristics of the films. According to Bhattacharyya et al. [59],

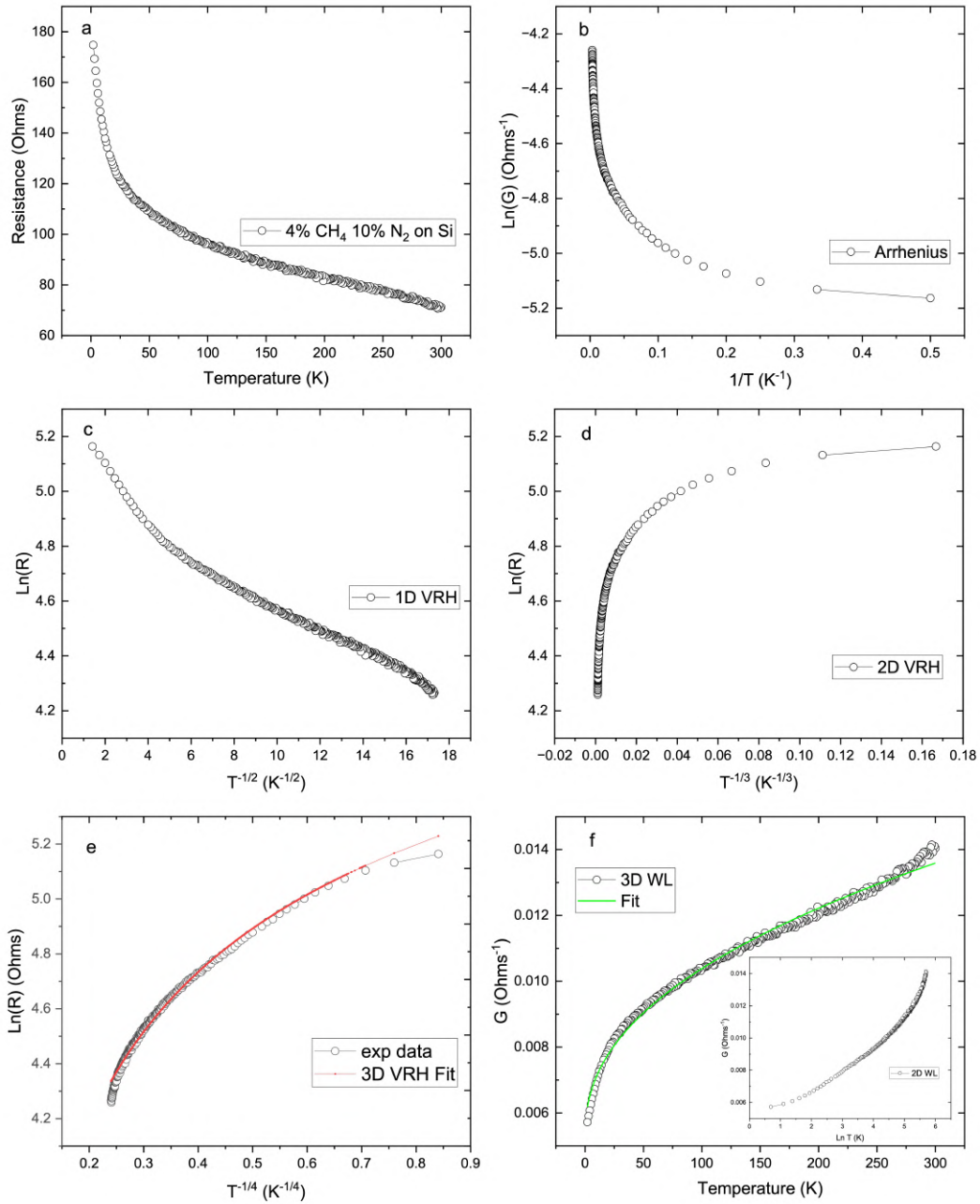


Figure 7.10 Resistance-temperature characteristics of the 10% N₂ doped UNCD sample are depicted. (a-f) illustrate different fitting models, beginning with normal R-T, activated conduction, 1D VRH, followed by 2D VRH, 3D VRH, and concluding with 3D WL, respectively.

nitrogen inclusion enhances the conductivity in nanodiamond films by a factor of 10⁴. Therefore, it's not surprising that even a subtle adjustment in the nitrogen content results in a remarkable alteration in the electrical properties of the film.

Figure 7.10 illustrates the resistance-temperature (R-T) characteristics of the 10%

N₂ doped UNCD sample. The resistance exhibits a rapid decrease with increasing temperature within the very low temperature range of 2 K to 15 K. In the intermediate temperature range of 16 K to 200 K, the sample displays typical semiconductor behavior. The sample's conductivity at room temperature was measured to be 34.72 S cm^{-1} . Figure 7.10a-f displays various fitting models, including 1D(ES) VRH, 2D VRH, 3D(Mott) VRH, activated conduction, and 3D WL, utilized to elucidate the potential conductivity mechanism. The nonlinearity observed in the graphs in Figure 7.10a-e clearly indicates that the hopping mechanism is not suitable for explaining the behavior of our films over wide temperature range. However at the higher temperature ($> 100 \text{ K}$) 3D VRH fits well. VRH fitting parameters are $R_0 = 3.117 \text{ ohm}$ and characteristic temperature $T_0 = 1.153 \times 10^{-15}$. From these we derive localisation length of 13.2 nm, hopping distance of 10.73 nm at $T = 100 \text{ K}$ and Fermi level $N(E_F) = 4.35 \times 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$.

The shift from localized hopping conductivity to delocalized conductivity in these conducting samples can be attributed to the movement of the Fermi level (E_F) to the extended states and the overlapping of bands. As the concentration of clusters increases, variable range hopping (VRH) becomes less effective because electrons no longer need to hop to distant sites; instead, nearby clusters make tunneling more feasible. This is due to the delocalized wavefunctions associated with π electrons in and around sp^2 clusters. Additionally, intercluster electron movements can occur via direct tunneling through sp^3 bonded carbon barriers separating these clusters. Consequently, the conductivity of these films does not drop to zero even at the lowest measurement temperatures but reaches a finite value (σ_0), unlike other disordered semiconductors. This is likely due to the small effective tunneling mass of electrons, which provides higher mobility proportional to the coherence length at lower temperatures [298]. For conducting and disordered sp^2 -bonded carbon, the overlapping region of $\pi - \pi^*$ states is very small, and the E_F might align with the energy level of delocalized quantum-confined regions, falling outside the localized region and manifesting delocalized tunnel conduction with finite conductivity at 0 K.

We therefore go with 3D WL and evidently, from Figure 7.10f, it appears to best explain the conduction mechanism in our films. Thus far, we have identified a

semiconducting behavior in the 10% N₂ films, where 3D weak localization processes dominate at low temperatures. The fitting parameters are:

$$p_1 = 4.399 \times 10^{-3} \left(\frac{C^2}{kg} \frac{S}{m^3} \right)$$

$$p_2 = 4.208 \times 10^{-3} \left(\frac{C^2}{kgm^4} \frac{S}{k^{0.5}} \right)$$

$$p_0 = 0.5 \times 10^{-3} \text{ Ohm}^{-1}$$

substituting the above pre-factor values we drive the phase coherence length $L_\Phi = 1.399 \times 10^{-8} m \quad T^{-0.35}$ and diffusion coefficient $D = 2.957 \times 10^{-7} m^2/s \quad T^{-0.5}$.

MR of UNCD_{10%N₂}

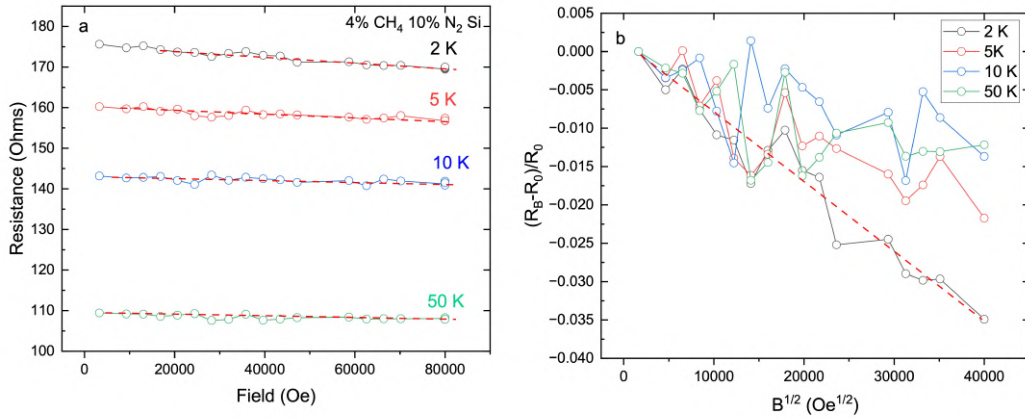


Figure 7.11 Magnetoresistance of 10% N₂ UNCD grown on Si substrate. a) Resistance vs Magnetic field and b) MR(%) vs $B^{1/2}$.

Figure 7.11a illustrates the magnetoresistance of 10% N₂ doped UNCD on a Si substrate. Notably, at higher temperatures (10 K and 50 K), the magnetoresistance exhibits mostly linear behavior with very little slope. However, at lower temperatures (2 K and 5 K), a negative slope in the magnetoresistance is observed typical of WL phenomena. Furthermore Figure 7.11b the MR shows a linear dependency of $B^{1/2}$ confirming the weak localisation behaviour at low temperature.

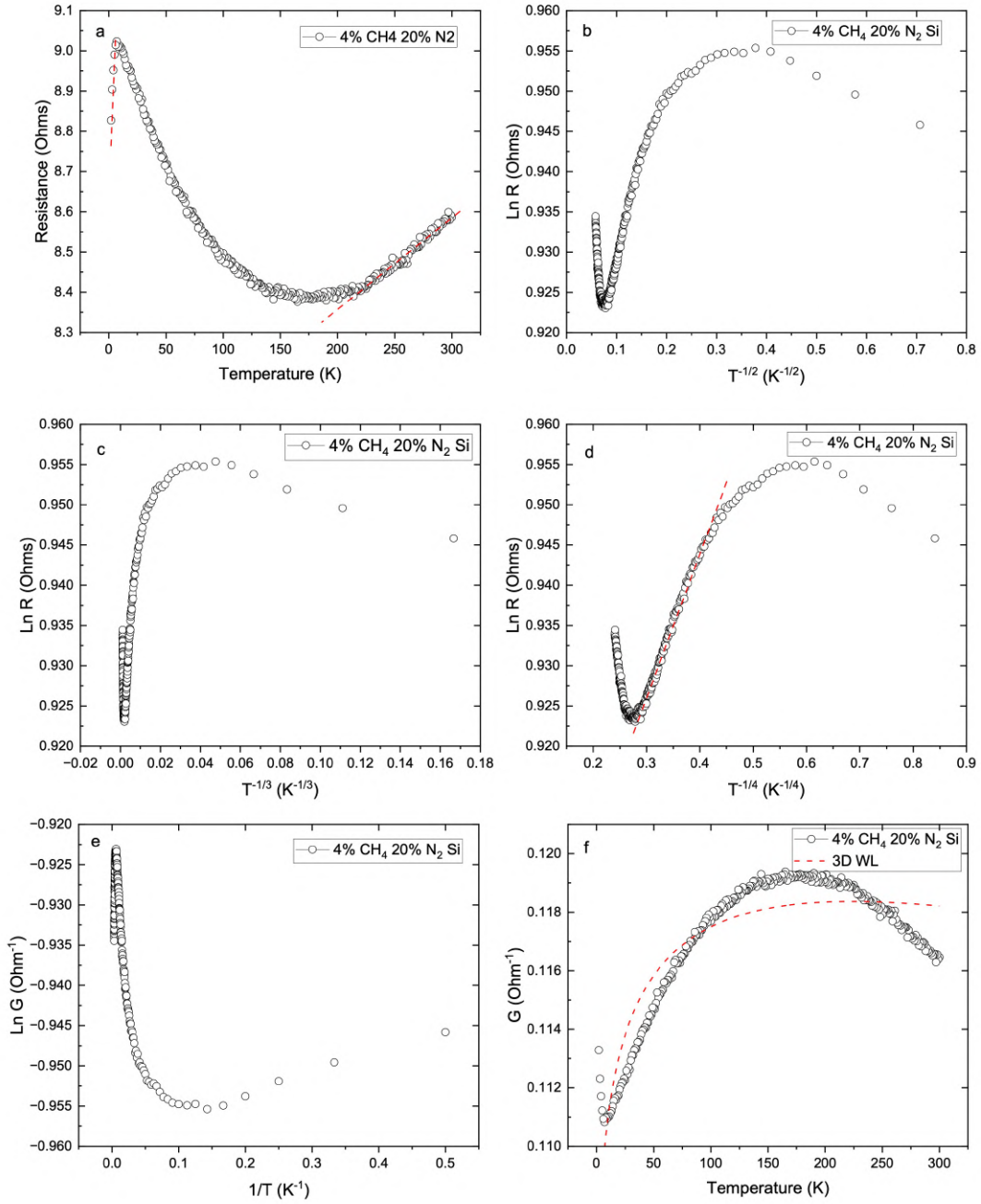


Figure 7.12 Resistance-temperature characteristics of the 20% N₂ doped UNCD sample on Si substrate are depicted. (a-f) illustrate different fitting models, beginning with normal R-T, ES VRH, followed by 2D VRH, Mott VRH, activated conduction, and concluding with 3D WL, respectively

7.2.2 Transport in 20% N₂ doped UNCD

The sample's conductivity at room temperature was measured to be 146.66 S cm^{-1} . Introducing a significant amount of nitrogen doping into the thin film during growth

increases the carrier density, which can potentially transition the conductivity from activated conduction to a semi-metallic state ([278]). The resistance-temperature (R-T) plot shown in Figure 7.12a illustrates a decrease in resistance with decreasing temperature, typical of metallic conduction due to reduced phonon scattering in the higher temperature region between 300 K and 150 K. In the intermediate temperature range (150 K - 15 K), the increase in resistance with decreasing temperature may indicate the presence of localization effects, weak localization, or the onset of a metal-insulator transition. At low temperatures (15 K - 2 K), the sudden drop in resistance suggests a low-temperature phenomenon such as the Kondo effect or a charge density wave transition.

MR of UNCD_{20%N₂}

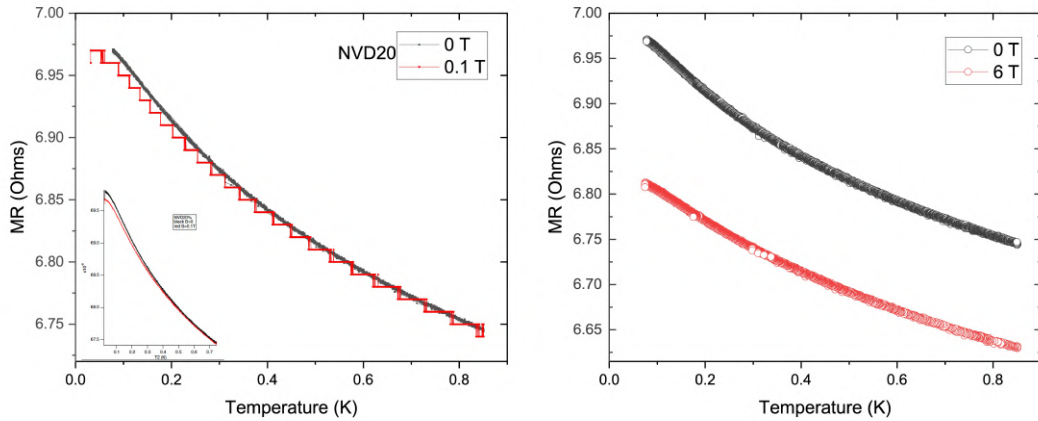


Figure 7.13 *Suppressed resistance of 20% N₂ doped UNCD sample on Si substrate from dilution fridge. a) Resistance values measured from 0.85 K down to 0.1 K at zero field, and 0.1 T magnetic field. Inset figure shows a clear deviation in resistance at low temperature between the zero field and 0.1 T field. b) Resistance values measured from 0.85 K down to 0.1 K at zero field (black color), and 6 T magnetic field (red color).*

Figure. 7.13a illustrates the magnetoresistance (MR) of a 20% N₂-doped UNCD sample, comparing measurements with the magnetic field off (zero field) and on (0.1 T). We observe a reduction in resistance as the magnetic field is increased to 0.1 T. This effect is visible at low temperatures, as shown in the inset of 7.13a and follows a similar trend at higher temperatures (above 0.25 K). The magnetic field induces dephasing in the electron's quantum coherence, disrupting constructive interference and leading

to decreased resistance. This suppression of resistance becomes more pronounced as the field is increased to 6 T, as shown in Fig.7.13b. It is important to note that while the resistance decreases with increasing field, the magnetoresistance exhibits a similar trend at temperatures above 0.25 K. However, at temperatures below 0.25 K, the trend diverges. This deviation is likely due to the enhanced weak localization effect at lower temperatures, which significantly influences the resistance behavior.

However, this observation contradicts the resistance versus temperature (R-T) data shown in Figure 7.12, where a sudden drop in resistance is observed at temperatures below 15 K. To gain a better understanding of the transport phenomena occurring in this sample, we will conduct additional repeated measurements.

7.3 Discussion on anisotropic electronic properties of nanocrystalline diamond thin films

The anisotropic characteristics of the microstructure in disordered carbon systems, such as nitrogen-doped nanocrystalline diamond, stem from the allotropic nature of carbon. Carbon's unique ability to adopt various bonding configurations is influenced by the hybridization of its four valence electrons. These configurations include four-fold coordination (sp^3 hybridization), typical in diamond, three-fold coordination (sp^2 hybridization) found in graphite, and two-fold coordination (sp hybridization) observed in the carbyne crystalline phase [299]. As a result, the microstructure of nitrogen-doped nanocrystalline diamond films consists of a combination of sp^3 and sp^2 hybridized carbon atoms. The ratio and distribution of these hybridized carbon forms change based on factors such as deposition conditions, hydrogen concentration, and heat treatments. A higher sp^3 content typically leads to a more diamond-like structure, while increased sp^2 bonding results in a more graphite-like arrangement.

Figure.7.14a illustrates a random spatial arrangement of potential wells with varying depths and widths, which correspond to sp^2 carbon clusters. These clusters are separated by potential barriers that align with the σ band edges of the sp^3 carbon matrix. As the microstructure continues to evolve, the clustering of sp^2 carbon

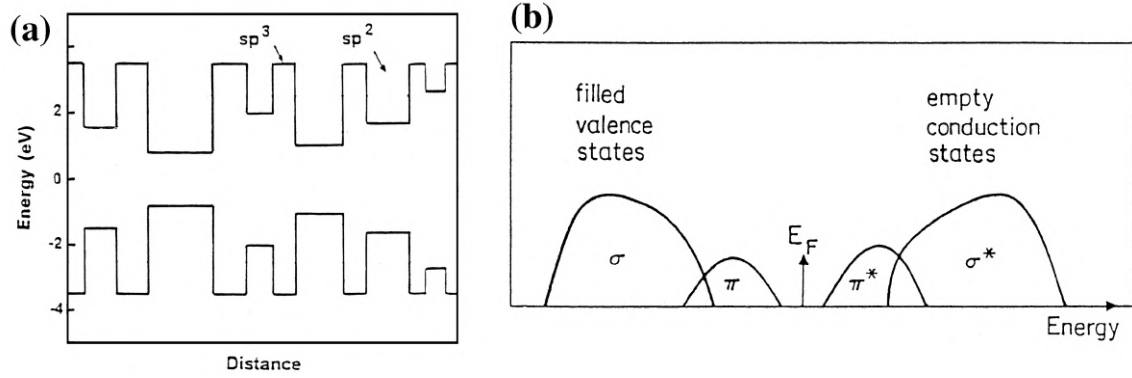


Figure 7.14 a) The cluster model illustrates the variations in the valence and conduction band edges as a function of the spatial separation between carbon grains. These fluctuations reflect the influence of the microstructural arrangement of sp^2 and sp^3 carbon atoms, where the potential wells associated with sp^2 clusters cause changes in the band edges relative to the sp^3 matrix. b) The DOS derived from the cluster model features localized states within the bandgap, primarily due to the presence of π -bonded networks in sp^2 clusters. The schematic DOS shows broadened valence and conduction bands with additional tail states and mid-gap states, resulting from the spatial variation in bonding configurations. adapted from [299].

atoms becomes increasingly important. These sp^2 clusters can form either isolated or interconnected networks, which are essential in shaping the material's electronic properties. The clustering enhances π -bonded networks, contributing to the localized states within the bandgap (see Fig.7.14b). Additionally, the level of disorder and defects in the microstructure evolves over time, impacting the spatial distribution of hybridized carbon atoms. Increased disorder introduces more localized states in the density of states (DOS), which can influence the electronic transport properties by affecting carrier mobility.

The evolving microstructure due to nitrogen doping significantly impacts electronic transport in the films. In films with greater sp^2 clustering, electronic transport is often dominated by mechanisms such as hopping or tunneling between localized π states.

Figure.7.15 illustrates that impurity clusters arranged in a triangular geometry generate localized electronic states within the energy bands, resulting in distinct resonant peaks in the DOS. These peaks are linked to the energy levels induced by the impurities and are influenced by the distance between the impurities and

the strength of their interactions. The triangular configuration often gives rise to interference effects—either constructive or destructive—which can amplify or diminish these localized states. The spatial symmetry of this arrangement also plays a crucial role in determining the distribution of these energy states. For example, closely spaced impurities within the triangle can lead to overlapping wavefunctions, producing more prominent resonant states, while more widely spaced impurities may create isolated localized states, resulting in narrower and less intense DOS peaks [300].

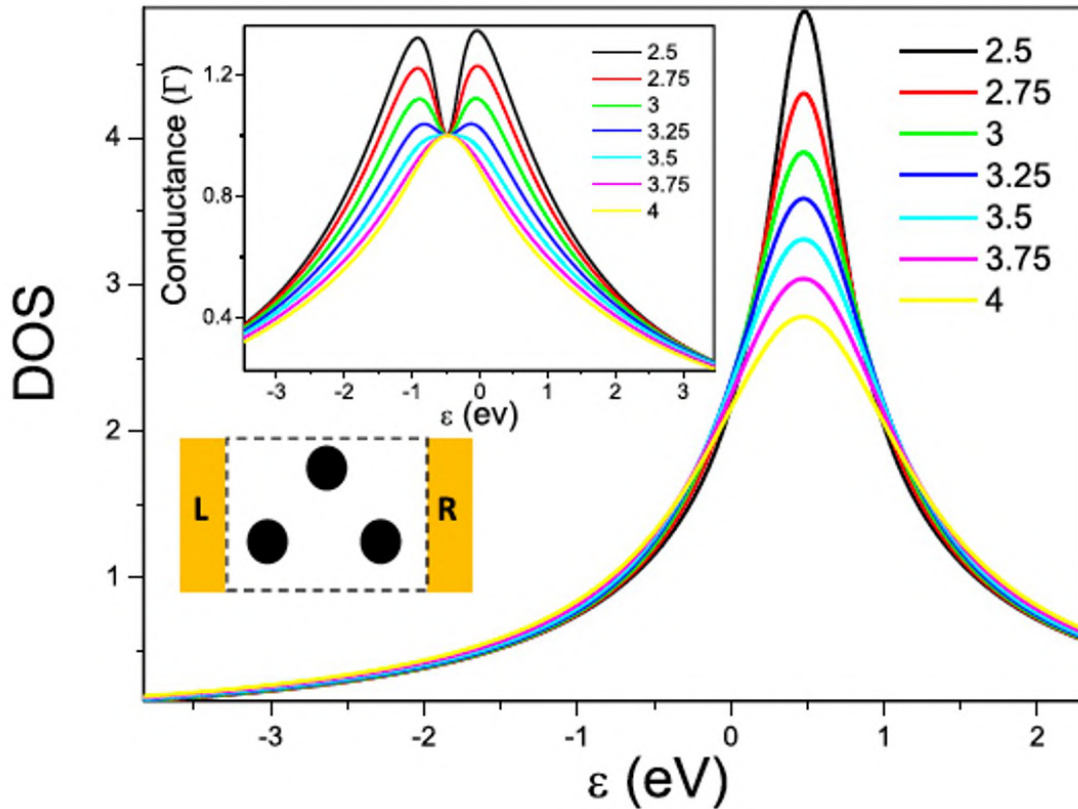


Figure 7.15 *The DOS spectra for a triangular configuration of impurity clusters, with increasing uniform inter-cluster separation from 2.5 nm to 4 nm, show a noticeable shift in the electronic behavior. Inset Figure-The corresponding conductance spectra, shown in the inset figure, reflect this where a non-linear conductance behavior is seen. adapted from [300].*

Conductance in the system is directly related to the DOS and resonant transmission. In the triangular arrangement, resonant transmission is facilitated when the energy of the incoming electrons aligns with the localized states within the DOS, increasing the likelihood of electron transmission. The presence of resonant peaks in the DOS generally corresponds with an increase in conductance, as these states offer pathways for electron flow. However, the conductance may either be enhanced or reduced,

depending on the precise geometry and symmetry of the triangular configuration, due to quantum interference effects. These interference phenomena, which are unique to the triangular arrangement, can lead to highly non-linear conductance behavior (see inset Figure.7.15), where even slight changes in the cluster geometry can significantly impact electron transport. In summary, the triangular configuration of impurity clusters introduces resonant states in the DOS that have a profound effect on conductance. These states, which are closely linked to the spatial arrangement of the impurities and their interactions, govern resonant transmission and shape the overall electronic properties of the material.

In nitrogen-doped nanocrystalline diamond, impurity clusters (formed by sp^2 carbon-rich regions) generate localized states that act as scattering centers for electrons. As the inter-cluster distance decreases, the wavefunctions of localized states from adjacent clusters overlap more, increasing the probability of quantum interference between scattering paths. This enhances weak localization effects, as electrons are more likely to interfere with themselves when scattered within smaller distances between clusters. When the impurity clusters are densely packed, the stronger overlap of electron wavefunctions leads to more pronounced weak localization, reducing conductivity as electron backscattering becomes more prominent. On the other hand, when the clusters are more separated, scattering events become less frequent, which can slightly reduce the localization effects, leading to higher conductivity. However, even with larger inter-cluster distances, the presence of disorder due to impurities still sustains a degree of weak localization.

The anisotropic nature of the weak localization in nitrogen-doped NCD arises due to the microstructural distribution of sp^2 and sp^3 bonded carbon atoms. The spatial anisotropy in the clustering of sp^2 carbon phases introduces directional variations in electronic transport. For instance, along certain crystallographic directions with a higher density of impurity clusters, weak localization effects are stronger due to increased scattering. In contrast, directions with fewer impurity clusters or wider inter-cluster separations may exhibit weaker localization and better conductivity. In the context of 3D weak localization, the overall conductivity is suppressed as quantum

interference occurs in three dimensions. Impurity clusters in the nitrogen-doped NCD introduce disorder, which extends the localization effects into all spatial directions. The degree of anisotropy in the conductivity arises from the uneven distribution of these clusters, with localized states being more prevalent in certain regions, thus affecting the strength of quantum interference differently depending on the direction of electron transport.

As nitrogen doping increases, more sp^2 -rich regions form, leading to a higher density of impurity clusters. The interplay between these clusters and the electron transport pathways evolves the system toward a regime dominated by weak localization. As the disorder increases with impurity clustering, quantum interference effects grow stronger, pushing the material further into the weak localization regime, reducing conductivity, and making it more anisotropic.

7.4 Conclusion

This study has provided comprehensive insights into the electronic transport mechanisms in nitrogen-doped nanocrystalline diamond (NCD) thin films by examining four samples with varying nitrogen doping concentrations and substrates. Through low-temperature transport measurements, we have been able to identify and characterize distinct behaviors such as weak localization (WL), anti-weak localization (AWL), and variable-range hopping (VRH), which shed light on the intricate interplay between disorder, quantum interference, and electron-phonon scattering in these systems.

The 7.5% N_2 -doped UNCD sample with a thickness of 80 nm exhibited classic 3D weak localization behavior based on resistance-temperature (RT) data fitting. At low magnetic fields (<0.7 T), weak localization was observed, while at higher fields (>0.7 T), a transition to anti-weak localization emerged. When the magnetic field was applied parallel to the sample, the magnetoresistance (MR) displayed asymmetric negative values between -0.2 T and $+0.2$ T, transitioning to positive MR beyond 0.2 T. These observations point to the significant role of quantum interference and

spin-orbit interactions in determining the electron transport in this sample.

In the case of the 20% N₂-doped UNCD sample, weak localization was more robust, fitting well across a wide temperature range. The MR exhibited a characteristic $B^{1/2}$ dependence, suggesting electron confinement and scattering mechanisms consistent with the cluster model. The larger grain size and thicker film appear to enhance localization effects, contributing to stronger quantum interference effects.

For the 10% nitrogen-doped UNCD on Si, a crossover from 3D variable-range hopping (VRH) to 3D weak localization was detected at a temperature of 100 K, and the MR followed a similar $B^{1/2}$ dependence. This indicates a temperature-dependent shift in the dominant transport mechanism, which could be linked to changes in the spatial distribution of impurity clusters, as explained by the triangular configuration of the cluster model. The gradual transition from VRH to WL reflects the competition between localized electron hopping and quantum coherence in these systems.

In contrast, the 20% nitrogen-doped UNCD sample on Si exhibited metallic conduction behavior at higher temperatures (300 K to 150 K) due to reduced phonon scattering. In the intermediate temperature range (150 K to 15 K), the presence of localization effects was suggested by an increase in resistance with decreasing temperature, possibly indicating a metal-insulator transition. At low temperatures (15 K to 2 K), a sudden drop in resistance points to a low-temperature quantum phenomenon, potentially related to the Kondo effect or charge density wave transition. This shift suggests complex interplay between electron-electron interactions and scattering mechanisms.

The findings presented in this chapter highlight the significant impact of impurity clustering and inter-cluster separation on electronic transport in nitrogen-doped NCD films. The observed weak localization and magnetic field dependencies align with predictions from the cluster model and electron confinement theory, wherein the triangular configuration of impurity clusters plays a key role in determining the quantum transport characteristics [301]. These results contribute to a deeper understanding of quantum phenomena in disordered carbon systems and suggest pathways for tuning electronic properties through controlled doping and structural manipulation.

The inter-cluster distances and impurity clustering in nitrogen-doped nanocrystalline diamond create localized states that contribute to 3D weak localization. The extent and nature of this localization—and the resulting anisotropy in conductivity—are closely tied to the spatial arrangement, density, and separation of these clusters, with smaller distances and higher impurity concentrations enhancing localization effects.

Chapter 8

Conclusion and Outlook

8.1 CNT-SMM molecular system - Efficient platform for hybrid quantum devices

The interaction between spin and phonons in carbon nanotubes (CNTs) is pivotal for the creation of hybrid quantum information devices. While individual spins can act as qubits, linking them to the mechanical vibrations of CNTs allows for the monitoring and control of spin qubits. This connection can be strengthened by modifying CNTs with magnetic ions or molecules, or by integrating them with solid-state qubits like NV centers in diamond. The successful realization of molecular electronics hinges on the precise manipulation of the magnetization of individual molecules. Therefore, to fully harness the potential of molecular magnets and incorporate them into functional devices, it is imperative to immobilize them on surfaces. This necessitates the creation of a substrate or framework onto which the molecules can be securely attached, ideally with controlled and precise positioning. However, depositing single molecules onto surfaces presents significant challenges, and numerous issues must be addressed throughout the process. Despite many efforts in this direction, maintaining the original functionality and properties of the molecules after deposition remains a formidable task. Contact between the surface and the molecules may introduce various factors that can impact their magnetic behavior, including diminished intermolecular forces, interactions between the surface and the molecules, potential distortion of molecular

crystal fields, or modification of magnetic anisotropy, all of which can influence phenomena such as quantum tunneling or magnetic hysteresis.

Here, we showcase that the acid treatment of Carbon Nanotubes (CNTs) as a variable of temperature, in conjunction with Raman spectroscopy, facilitates the functionalization of CNTs while minimizing disorder, thus preserving their electronic properties. Through the integration of CNTs with straightforward magnetic systems like Ln-EDTA, we create 1D-hybrid molecular systems exhibiting a broad spectrum of magnetic properties. This opens avenues for exploring fundamental physics in systems characterized by dilute and heavy fermions, including phenomena like spin-phonon coupling and Kondo lattice effects. Such insights lay the groundwork for the development of dependable spintronic electronic devices tailored for quantum information processing.

Outlook for Ln-CNT hybrid systems

We plan to utilize Ln-EDTA (Gd, Tb, and Dy) molecules on single-walled carbon nanotubes to investigate the fundamental physics of transport in a one-dimensional channel containing magnetically regulated impurities. Our objective is to perform transport measurements using an Oxford dilution fridge with a base temperature of 10 mK, enabling us to explore a low-temperature regime that has not been previously studied.

The successful creation of 1D CNT-SMM molecular hybrids paves the way for further exploration of their potential in quantum information and spintronic devices. Future work will focus on refining the functionalization process to improve the precision of molecular attachment while minimizing the disruption of their intrinsic properties. The challenge of maintaining magnetic anisotropy and quantum coherence in these systems must be addressed to harness the full potential of molecular magnets in real-world applications.

One promising direction is the development of hybrid quantum devices that couple the magnetic properties of CNT-SMM systems with solid-state qubits, such as NV centers in diamond. By leveraging the interaction between spin and phonons within CNTs,

it may be possible to achieve more efficient qubit control and information processing at the quantum level. This requires deeper investigation into the fundamental physics of spin-phonon coupling and its influence on quantum coherence in these 1D hybrid systems.

Additionally, heavy fermion systems and phenomena like the Kondo effect in CNT-SMM hybrids present a rich area of study that could reveal new insights into strongly correlated electron systems. Understanding these effects could inform the design of next-generation spintronic devices with enhanced functionality and performance, particularly for quantum information processing.

In conclusion, the future of 1D CNT-SMM molecular hybrids lies in their potential to bridge the gap between molecular electronics and quantum technologies. Continued advancements in functionalization techniques and a deeper understanding of their magnetic and quantum mechanical properties will be crucial for their integration into practical, reliable spintronic devices and quantum computing architectures.

8.2 CVD N₂ doped nanocrystalline diamond

Ultrananocrystalline diamond thin films were deposited on both silicon and quartz substrates using a Microwave Plasma Enhanced Chemical Vapor Deposition (CVD) system. Optimization of microwave power, gas phase chemistry, and substrate temperature, which are crucial factors determining the quality of the deposited diamond, enabled the growth of UNCD films with typical grain sizes ranging from 10 to 40 nm. This was confirmed through FE-SEM morphological studies, Raman spectra analysis, and AFM (Atomic Force Microscopy) measurements. The growth rates of UNCD film were significantly influenced by the hydrocarbon concentration in the gas phase. Growth rates of approximately 1.5 $\mu\text{m}/\text{h}$ were achieved with 1% CH₄ (2 SCCM in a total flow rate of 200 SCCM), while growth rates of up to approximately 7.0 $\mu\text{m}/\text{h}$ were attained by increasing the methane concentration to 4%. Additional enhancements to the current MPECVD assembly, such as the incorporation of a water cooling stage, absolute control of chamber pressure, optical

pyrometer, and Optical Emission Spectroscopy (OES), would significantly expand the capabilities of the reactor for producing single-crystal diamond. Increasing the substrate temperature and adjusting the concentration of N₂ in an H₂-rich plasma can result in non-equilibrium diamond growth conditions. This shift can lead to entering a new regime that enables the growth of new carbon structures, such as diamond containing mixed phases of sp³ and sp² crystalline carbon, known as diaphite.

In contrast to the HFCVD method, MPECVD allows for the growth of highly conducting UNCD thin films. This is achieved by introducing nitrogen (N₂) doping concentrations of up to 20% in an H₂-rich plasma environment.

Outlook for growth of N₂ doped UCND films

Reactor engineering by implementing the following additions.

Water Cooling Stage

The current utilization of microwave (MW) power ranges from 700 to 900W out of the

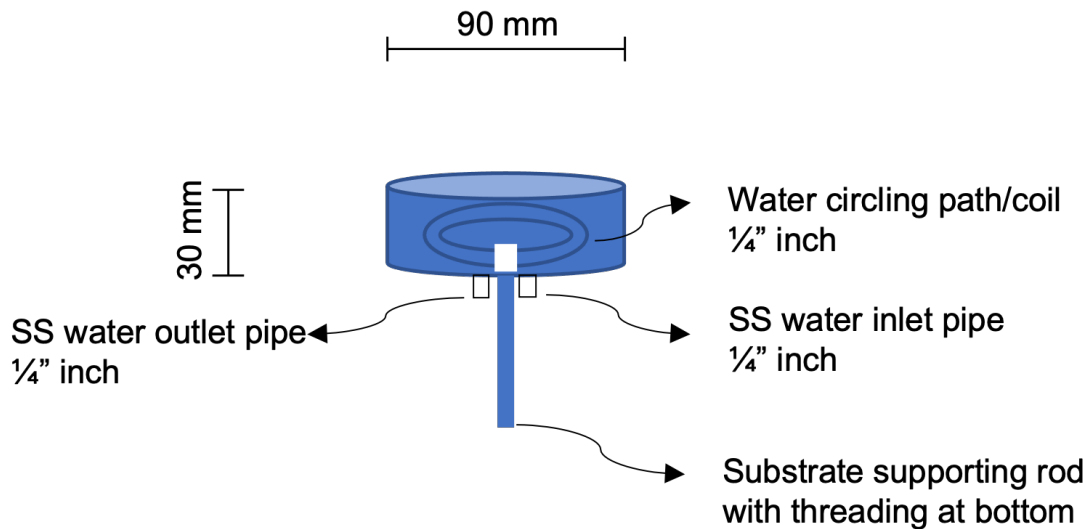


Figure 8.1 *Proposed Water Cooling stage for regulating substrate temperature simultaneously allowing to operate at higher MW power*

2 kW MW generator, resulting in substrate temperatures between 800 °C and 1200 °C. It's noteworthy that gas phase kinetics play a crucial role in governing the sequential addition of sp³ carbon at the surface. These gas phase kinetics are influenced by the amount of MW power input. Higher MW forward power generates methyl radicals,

which energetically favor the growth of sp³ carbon. Simultaneously, regulating the substrate temperature where the methyl radicals are inserted is essential. The optimal substrate temperature falls between 800 °C and 1000°C. Therefore, water cooling is necessary to control the substrate temperature while enabling operation at higher MW power levels (proposed water cooling stage - see Fig 8.1).

Optical Pyrometer The substrate temperature significantly affects the gas kinetics near the substrate surface, making monitoring this parameter crucial for achieving high-quality diamond growth. A two-color pyrometer functions by measuring the thermal radiation emitted by an object at two distinct wavelengths. The substrate temperature T_Q is directly related to the ratio of the densities ($\Phi_{\lambda_1}, \Phi_{\lambda_2}$) of the two spectral radiances ($\varepsilon_1, \varepsilon_2$) detected at these respective wavelengths (see Fig 8.2).

Electronic Gate Valve Maintaining an absolute pressure is paramount for ensuring

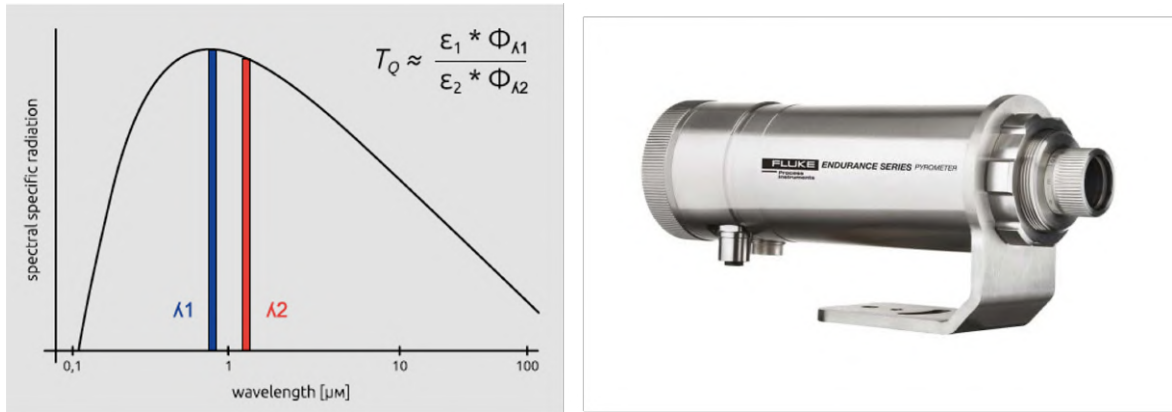


Figure 8.2 *Proposed Optical Pyrometer: for real-time substrate temperature monitoring. adapted from [302].*

the quality of diamond thin film growth. Electronic gate valves play a crucial role in this process by adjusting the vacuum flow line, thereby regulating the pressure within the chamber.

Optical Emission Spectra Optical emission spectra provide a means to monitor the formation of methyl radicals, facilitating the execution of repeatable experiments. Additionally, when introducing dopants, this instrument will enable us to study the gas phase kinetics and assess the expected quality of the diamond. Figure.8.2 shows the typical assembly OES with MPECVD setup.

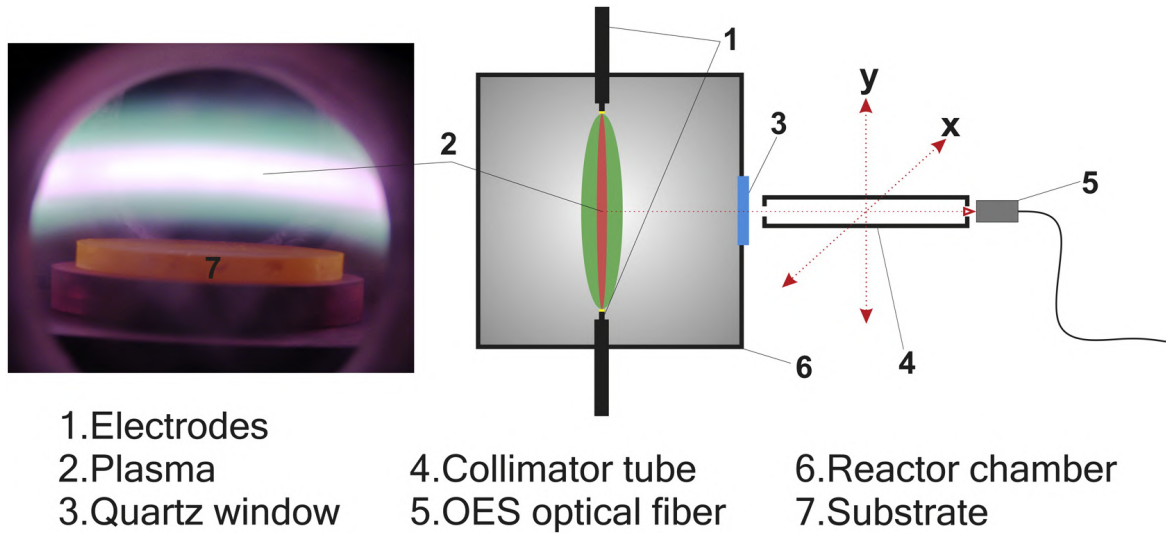


Figure 8.3 *Assembly of optical emission spectra on CVD diamond reactor.*

Transport in nanocrystalline diamond

The results presented in this chapter open multiple avenues for further research and development. Future studies can build on the insights gained from these nitrogen-doped UNCD systems by exploring additional variables such as doping levels, film thickness, and substrate effects in greater detail. A particularly promising direction involves the continued investigation of spin-related phenomena such as weak localization and anti-localization, which could inform the development of spintronic devices based on carbon materials.

Moreover, improvements in synthesis techniques, particularly through refined control of the MWCVD process, could lead to even higher quality UNCD films with reduced defect densities and more uniform grain boundary structures. Further engineering of grain boundary morphology and impurity clustering may enable the realization of novel quantum confinement effects, potentially allowing for the exploration of topologically protected states or novel phases of matter within nanocrystalline diamond systems.

In addition, low-temperature phenomena such as the Kondo effect, charge density wave transitions, and potential superconductivity in heavily doped UNCD merit closer examination. Extending transport measurements to even lower temperatures and higher magnetic fields could help uncover new quantum effects, deepening our understanding of the interplay between disorder, electron-electron interactions, and

quantum coherence.

Finally, the successful application of nitrogen-doped UNCD films in next-generation quantum technologies will require a systematic approach to integrating these materials into functional devices. This includes not only the design of prototype devices but also the development of scalable manufacturing processes that can reliably produce high-performance diamond films with tailored electronic and magnetic properties.

The ongoing exploration of electron transport in nitrogen-doped UNCD represents an exciting frontier in condensed matter physics, with the potential to drive significant advancements in both fundamental science and technological innovation.

Chapter 9

Experimental

9.1 CNT-Molecular Magnet hybrid Synthesis

9.1.1 CNT Functionalisation

The conventional acid reflux method [303] is employed to introduce organic functionalities to the surface of MWCNTs. This process involves using a mixture of nitric acid and sulfuric acid in a 1:3 volume ratio (8–16 mL) as the oxidizing agent, to which 50–121 mg of pristine MWCNTs are added. The mixture undergoes refluxing under varying conditions. Initially, the reflux experiment is performed at 55 °C for different durations (1, 3, 12, and 24 hours). In the second set of experiments, refluxing is conducted for a fixed duration of 24 hours at different temperatures (55, 60, 70, and 100 °C). After 24 hours of refluxing, the functionalized MWCNTs are separated from the viscous mixture by centrifugation, followed by vacuum filtration and repeated rinsing with distilled water. The discarded water is tested for neutral pH to ensure no residual acid contamination. The filtered product is then vacuum dried under nitrogen, resulting in the functionalized CNTs. Characterization of the functionalized material is performed before loading the samples with the Gd-DTPA or a Ln-EDTA complex.

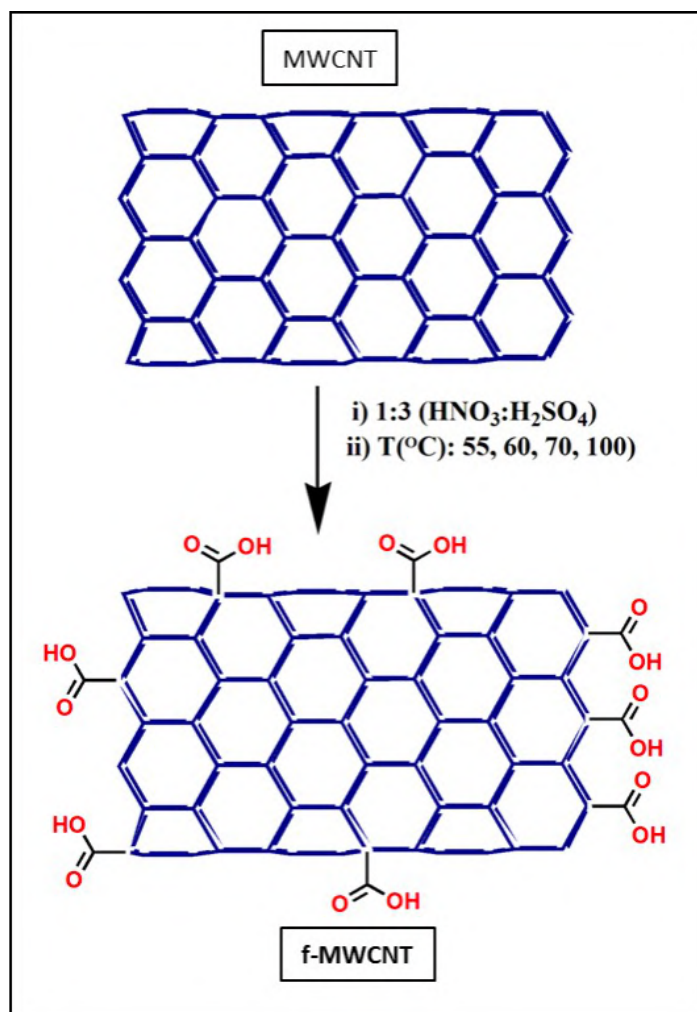


Figure 9.1 CNT functionalisation achieved through acid treatment ($\text{HNO}_3/\text{H}_2\text{SO}_4$ - 1:3).

9.1.2 Boehm Titration

The Boehm titration (BT) method is systematically examined as an analytical tool for quantifying oxygen-containing surface groups on oxidized carbon nanotubes. The method uses NaOH and HCl and its main principle is that the number of acidic sites is determined under the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups. The number of basic sites is calculated from the amount of HCl required.

Experimentally, a known amount of f-MWCNTs, was added to 15 ml of 0.001 M NaOH base. The mixture was sonicated for 24 h to disperse the carbon nanotubes and then filtered. Three aliquots with a volume of 10 mL were taken from the filtrate of each sample and was mixed with exactly 10 ml of 0.001 M HCl to achieve a neutralisation

(pH 7). The acidified solution was purged with N₂ under magnetic stirring for 2 hours for CO₂ degassification. The aliquots from acidified solution mixture were then titrated with 0.001 M NaOH to reach the neutral point at pH 7.

Since an indirect method (back titration) is adopted in this work, the carbon surface functionality (CSF) can be calculated using

$$[HCl] V_{HCl} = [NaOH] V_{NaOH} + \left(\frac{n_{HCl}}{n_B} [B] V_B - n_{CSF} \right) \frac{V_a}{V_B} \quad (9.1)$$

$$n_{CSF} = \frac{n_{HCl}}{n_B} [B] V_B - ([HCl] V_{HCl} - [NaOH] V_{NaOH}) \frac{V_B}{V_a} \quad (9.2)$$

where $[B]$ and V_B are the concentration and volume of the reaction base mixed with the carbon, providing the number of moles of reaction base that was available to the carbon surface for reaction with the surface functionalities. n_{CSF} denotes the moles of carbon surface functionalities on the surface of the carbon that reacted with the base during the mixing step. V_a is the volume of the aliquot taken from V_B , and $[HCl]$ and V_{HCl} are the concentration and volume of the acid added to the aliquot taken from the original sample. This gives the number of moles of acid added to the aliquot, and available for reaction with the remaining reaction base. The remaining moles of acid are then determined through titration using $[NaOH]$ and V_{NaOH} , the concentration and volume of the titrant in the back-titration. Thus, through the knowledge of the remaining moles of acid, which determines the amount of reaction base remaining after reaction, and by difference (knowing the total amount of reaction base available initially), the amount of base reacted with the surface functionalities can be quantified.

When NaOH is used in the Boehm titration and is directly titrated with HCl, the following equation is used:

$$n_{CSF} = [B] V_B - [HCl] V_{HCl} \frac{V_B}{V_a} \quad (9.3)$$

with a similar description of the reaction calculations as above.

The quantity of the different possible surface groups (phenols vs. lactonic groups vs.

carboxyl groups) are calculated through the difference in the calculated amount of surface functionality reacted n_{CSF} . NaOH reacts with all surface groups, (carboxylic acids/carboxyls, lactones/lactols, and phenols), and will therefore have a n_{CSF} that includes all of these groups. The selective neutralization of different functional groups by different titrating bases enables the estimation of functionalities of these groups by simply calculating the difference of the n_{CSF} calculated for different titrating bases: the differences between $n_{\text{CSF}}(\text{HCl})$ and $n_{\text{CSF}}(\text{NaOH})$ give the functionalities of carboxylic groups.

9.1.3 Ln-EDTA synthesis

Ln-EDTA complexes were synthesized using the solvothermal evaporation technique. Initially, 0.5 mM (0.146 g) of ethylenediaminetetraacetic acid (EDTA) was dissolved in 25 mL of deionized (DI) water in a 250 mL round-bottomed flask. Subsequently, 0.5 mM of Ln (where Ln corresponds to $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ (0.186 g), **1**, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (0.188 g), **2**, and $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ (0.186 g), **3**, respectively) was added to the solution. A 1 M NaOH solution was then added dropwise to enhance ligand solubility. The mixture was stirred and refluxed for 3 hours in an oil bath at 70 °C using a magnetic stirrer with a hot plate. Within the first hour of stirring post NaOH addition, the initially white suspension transitioned to transparency. The suspension was filtered through a PVDF membrane (0.22 μm) under reduced pressure. The filtered suspension was left to precipitate for the next 30 hours. Ethanol was applied as a layer to promote crystal formation. The collected crystals were further suspended in a 25 mL DCM solution to remove additional impurities.

9.1.4 Ln-EDTA Grafting onto MWCNTs

Functionalized multi-walled carbon nanotubes (MWCNTs) with predetermined carboxylic (-COOH) group concentration were prepared using Boehm titration. These functionalized MWCNTs and Ln-EDTA chelate were weighed stoichiometrically in a 1:1 ratio and mixed in 50 mL of deionized (DI) water. The mixture was magnetically stirred at room temperature for 24 hours, with intermittent ultrasonication steps to

ensure proper dispersion of MWCNTs in the liquid medium. Afterward, the resulting mixture underwent centrifugation to remove the decant, followed by filtration using a 0.22 μm PVDF membrane filter. Finally, the solid was vacuum dried under reduced pressure at 100 $^{\circ}\text{C}$ for 6 hours.

9.1.5 CNT-Ln-ETPA hybrid molecular complex synthesis

MWCNTs, characterized by known titration values (% of $-\text{COOH}$), and finely ground Gd-DTPA powder were combined in stoichiometric ratios of 1:1. This mixture was then stirred in 100 mL of deionized water (DI) using a magnetic stirrer for a duration of 24 hours at room temperature. Subsequently, the resulting solution was filtered through a 0.22 μm PVDF membrane filter employing a vacuum filtration technique. The collected solid bundle of CNTs was then dried at 200 $^{\circ}\text{C}$ under reduced pressure conditions. The concentration of Gd molecules on the CNTs was determined using the ICP-MS technique (ICAP Thermofischer Scientific).

9.2 Plasma CVD Diamond Growth

9.2.1 Sample Pre-treatment

Fused quartz substrates of size $5 \times 5 \text{ mm}^2$ and 0.5 mm thick were cleaned to remove the organic matter by treating them with piranha acid ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 - 3/1$). This is followed by cleaning the substrates under a stream of deionized (DI) water and drying them using a N_2 gun. The acid-treated quartz substrates were further treated under H_2 plasma for 5 min at 40.0 mbar pressure and 1050 K temperature to alter the surface zeta potential. Finally, the substrates were ultrasonically seeded with nanodiamond particles by treating them with a 5 nm monodispersed nanodiamond suspension in dimethyl sulfoxide (DMSO) (1 mg/mL in DMSO) for 15 min. Followed by cleaning the substrate in a stream of methanol to remove any agglomerates and then drying using an N_2 gun.

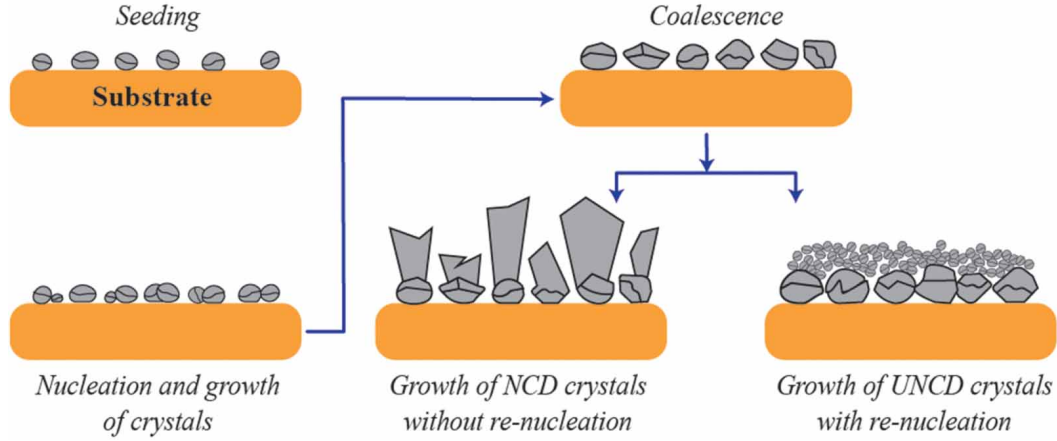


Figure 9.2 CVD diamond growth on non-diamond and pre-seeded substrate showing the nucleation of diamond film. adapted from [304].

9.2.2 CVD diamond growth

A custom-built CVD chamber with a 2 kW, 2.45 GHz solid-state microwave generator (MKS) was used for this experiment (Fig.6.10). A co-planar waveguide and an applicator from ASTeX were used. The substrate stage holder was assisted with a vernier height-adjustable gage. The temperature of the sample (T_{sub}) was measured using an optical pyrometer pointed through a transparent window of the CVD chamber. The pressure was regulated by using a needle valve placed in the vacuum line of the CVD chamber. A cooling stage was not used here. The ND-seeded quartz substrates were then placed at the center of a circular tungsten (W) resist (1" dia).

9.3 Characterisation

9.3.1 Electron Microscopy

Electron microscopy is an essential tool for acquiring high-resolution images across numerous fields, such as biomedical research, forensics, and technology. Unlike light microscopes, electron microscopes can achieve significantly higher resolution, providing detailed information that would otherwise be impossible to obtain. Each electron microscope operates by directing a concentrated stream of electrons in a vacuum toward a sample. The interactions between the electron beam and the sample generate

an image, analogous to how optical microscopes use light to capture images. The resulting image displays details of the sample's surface or internal structure, depending on the specific type of electron microscope employed. The electrons interact with atoms

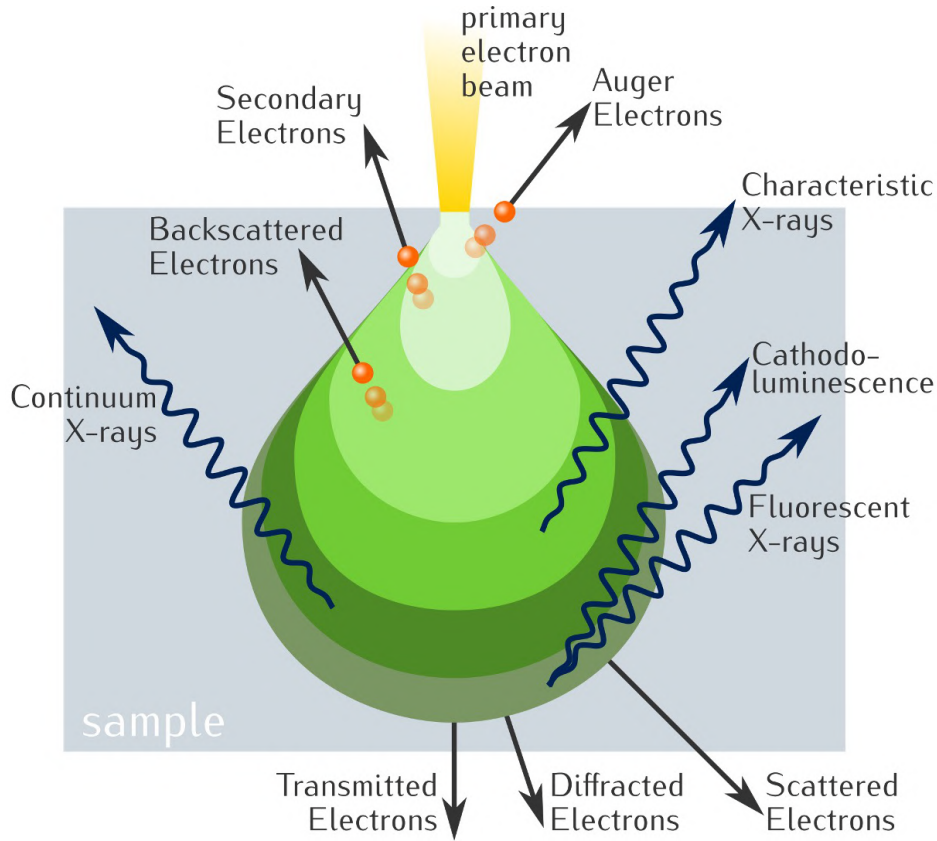


Figure 9.3 *Electron Microscopy Principle: Electron-matter interaction volume and types of signal generated. adapted from [305].*

in the sample, generating various signals that provide information about the sample's surface topography and composition 9.3. The electron beam scans the sample in a raster pattern, and the beam's position is combined with the intensity of the detected signals to produce an image.

FE-SEM

The Scanning Electron Microscope (SEM) produces images by scanning the surface with a focused beam of electrons, offering resolutions upto few nanometers. To achieve a high-resolution image, an electron source, or electron gun, emits a stream of high-energy electrons directed at the sample. Electromagnetic lenses focus the electron beam, which then scans the sample's surface in a rectangular raster pattern 9.4. The

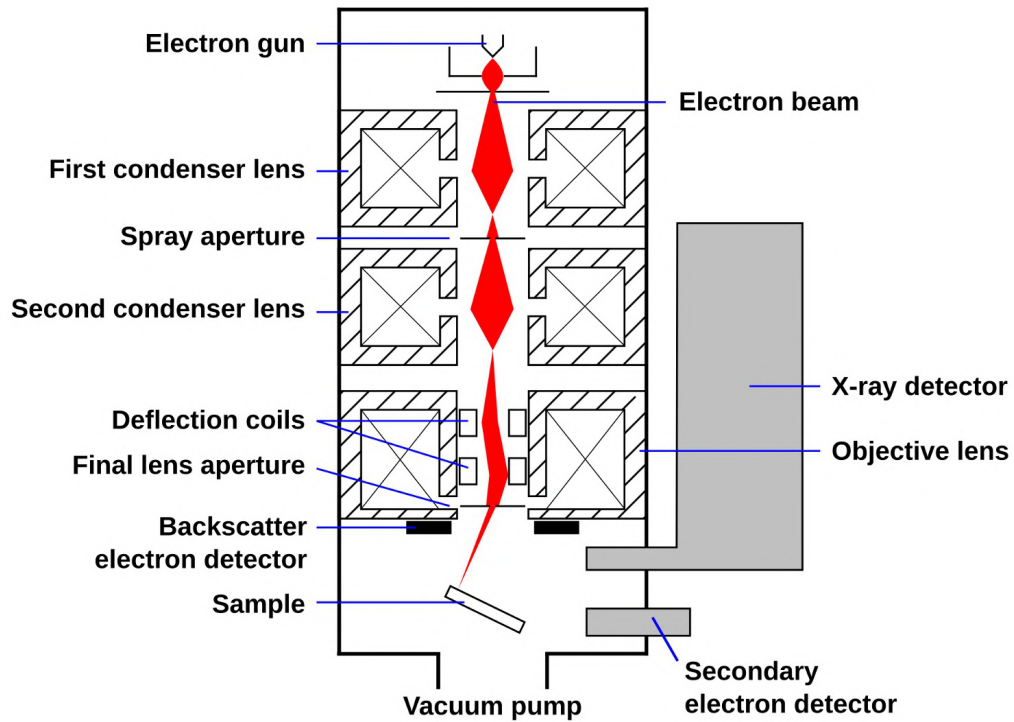


Figure 9.4 *Scanning Electron Microscopy Principle: The e-beam ejected from a metal electrode is focused via magnetic lens and projected on to the sample. adapted from [305].*

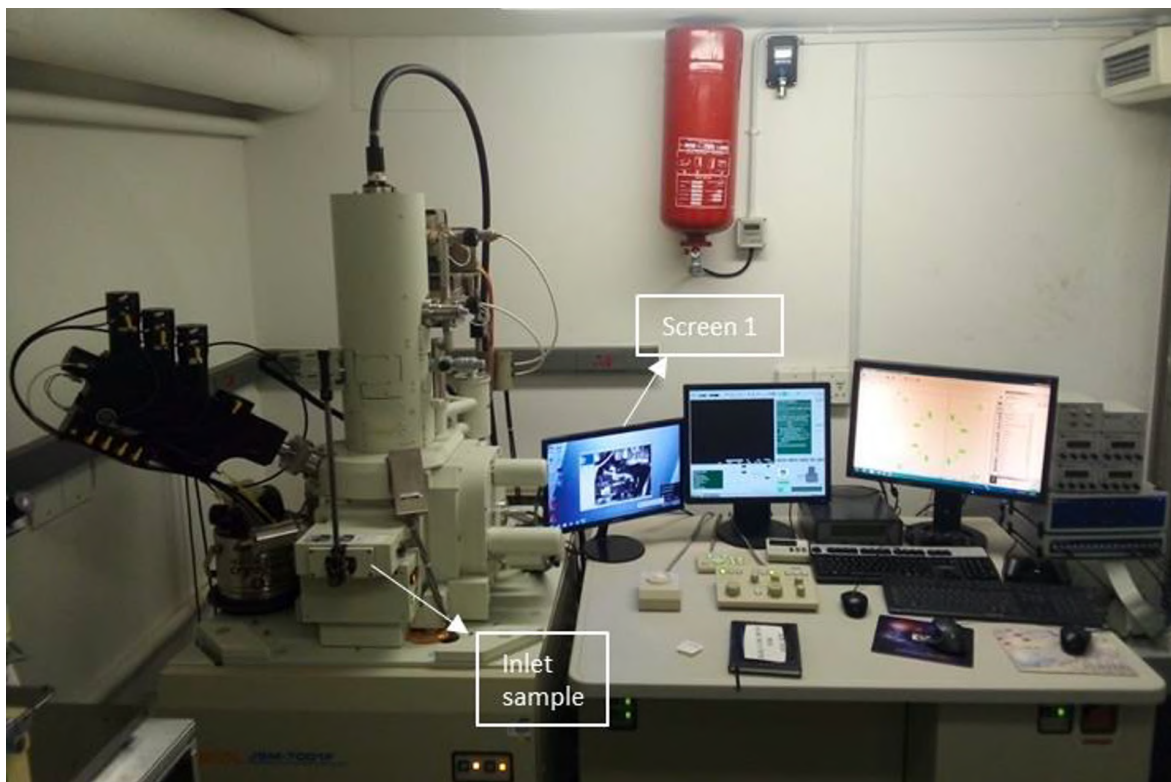


Figure 9.5 *FE-SEM (JEOL 7500F) instrument established at NSTPL, School of Physics, University of the Witwatersrand*

interaction between the electron beam and the sample produces secondary electrons, backscattered electrons, and X-rays. These emissions are detected and used to generate a magnified image. In the most common mode of SEM, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector. The number of secondary electrons detected, and thus the signal intensity, is influenced by factors such as the specimen's topography.

JEOL JSM 7001F instrument was used to carry out morphological studies on both the samples (Ln-EDTA doped CNTs) and N₂ doped UNCD 9.5.

HR-TEM

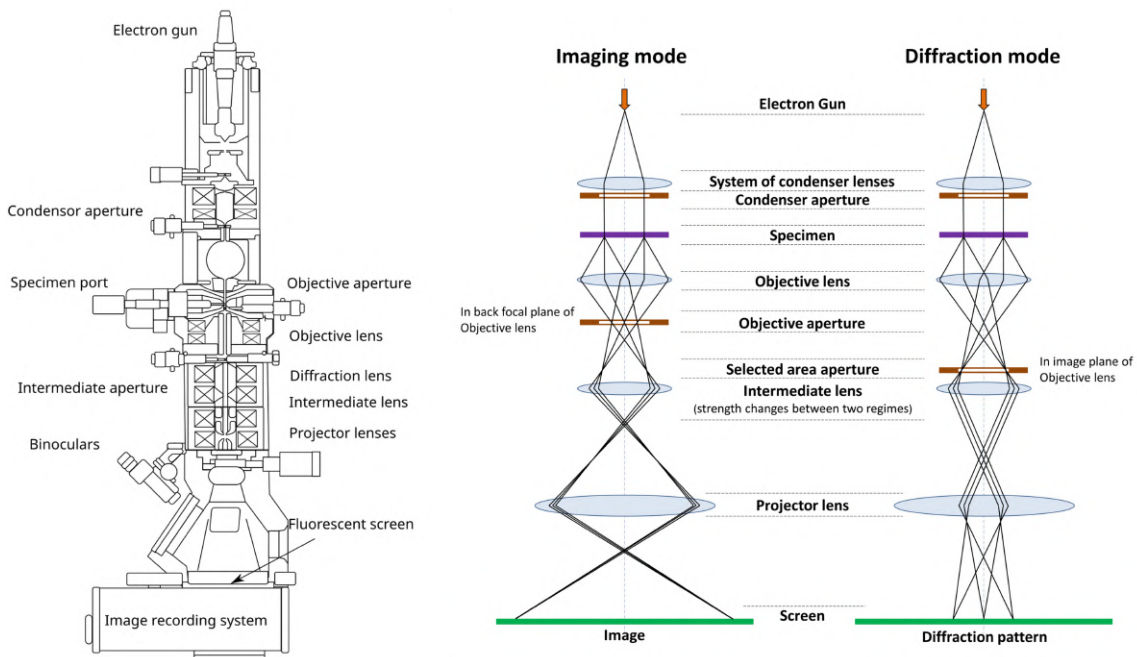


Figure 9.6 *Transmission Electron Microscopy Principle. Schematic e-beam path for a TEM instrument for various imaging modes. adapted from [306].*

A TEM is a type of electron microscope that utilizes a broad beam of electrons to generate an image of a sample's internal structure 9.6. The electron beam passes through the sample, producing an image that reveals the sample's morphology, composition, and crystal structure. An electron source directs a beam of electrons through an ultrathin sample. As the electrons penetrate the sample, they pass through lenses situated below it. The resulting data is used to create images either directly on a fluorescent screen or on a computer screen via a charge-coupled device (CCD)

camera.

High-resolution transmission electron microscopy (TEM) analysis was conducted utilizing the JEOL JEM-2100 Plus microscope operating at an accelerating voltage of 200 kV. The samples were prepared by depositing drops of Ln-EDTA-grafted carbon nanotube (CNT) hybrid molecular material suspended in ethanol solvent onto a copper grid, which were subsequently allowed to air.

9.3.2 Raman Spectroscopy

Raman spectroscopy is a powerful analytical technique used to study vibrational, rotational, and other low-frequency modes in a system. The working principle of Raman spectroscopy is based on the inelastic scattering of light, known as Raman scattering. Raman spectroscopy analyzes molecular vibrations induced by monochromatic radiation interacting with a sample. Raman spectroscopy is a method that effectively characterizes material composition, providing insights into both surface and bulk properties.

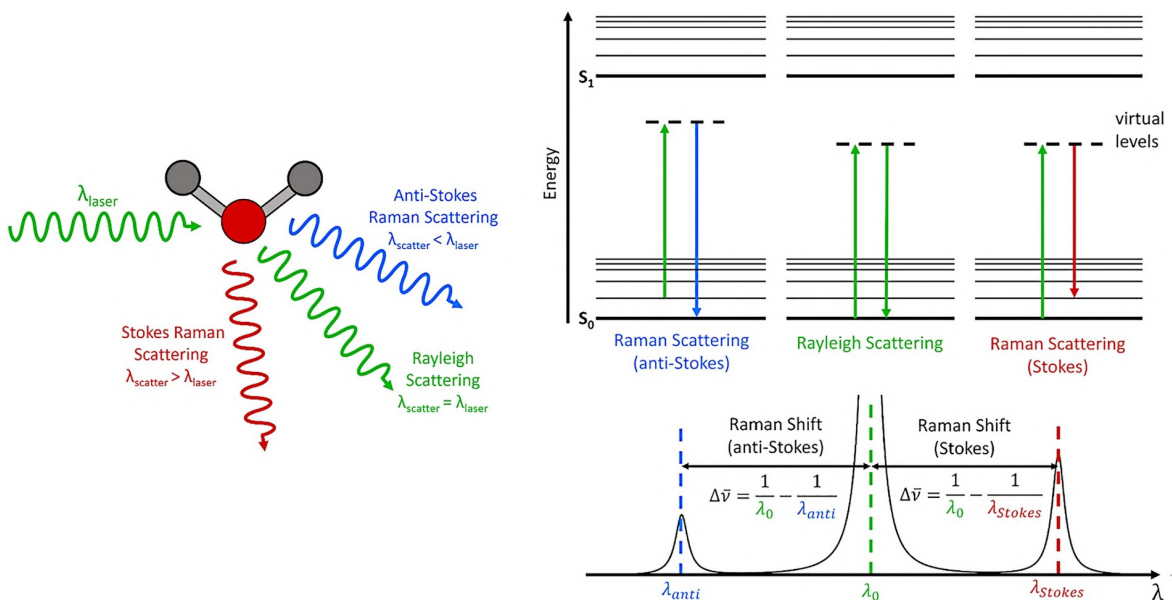


Figure 9.7 Basic principle of Raman spectroscopy and Jablonski diagram showing Raman shifts. adapted from [307].

Raman spectroscopy proves to be a suitable technique for thin film characterization due to its speed, non-contact nature, and safety for samples, requiring minimal or no sample

preparation. In the case of pure diamond, a distinct peak at 1332 cm^{-1} corresponds to the vibration of the sp^3 diamond lattice. Amorphous carbon phases exhibit two peaks. The first peak, labeled the D band (disorder), falls within the range of 1320 cm^{-1} to 1360 cm^{-1} , resulting from dislocations in the lattice. The second peak, termed the G band (graphitic), appears in the range of 1500 cm^{-1} to 1600 cm^{-1} . The intensity ratio of the D band to the G band provides information about the degree of disorder in the sample. This method proves valuable in discerning different carbon formations (sp^3 and sp^2) in CVD diamond. Given that diamond layers come in various crystalline structures such as single crystalline, microcrystalline (MCD), nanocrystalline (NCD), and ultra-nanocrystalline (UNCD), different lasers are necessary for comprehensive analysis.

Raman spectra were obtained utilizing the 514.5 nm line of a Lexel Model 95-SHG argon ion laser as the excitation source. The measurements were performed with a Horiba LabRAM HR Raman spectrograph, equipped with an Olympus BX41 microscope attachment. Incident light was focused onto the sample using a $100\times$ objective (N.A. = 0.90), and the backscattered light was dispersed via a 600 lines/mm grating onto a liquid nitrogen-cooled CCD detector. LabSpec v5 software was used for data acquisition, with a sample power of approximately 0.4 mW . Raman spectra for each sample were acquired with integration times of 60 s.

Low-Temperature Raman Spectra data acquisition

Low-temperature Raman Spectra were acquired using a $100\times$ Long-Working Distance (LWD) objective (N.A. = 0.80) and a Linkam THMS600 microscope stage and liquid nitrogen as the cryogenic fluid. The incident excitation light used is 514 nm (2.41 eV) in energy and the scattered light was collected through a $100\times$ objective using a backscattering geometry. The plane of polarization of the electric field of the incident beam was parallel to the axes of the nanotubes. The sample was initially cooled to 77 K , then kept at this temperature for 5 minutes to ensure good thermal equilibrium before spectra were acquired. After each temperature increase, the sample was allowed to achieve thermal equilibrium for 5 minutes before spectra were acquired. As the sample moved concerning the incident beam spot during heating, care was taken to

make sure the beam was focused on the same spot using Au markers on the Si substrate and by comparing the RBM peaks present in the spectrum. If the same RBM peaks were present at the higher temperature, it was taken as evidence that the beam was focused on the same spot.

9.3.3 XRD

X-ray powder diffraction (XRD) is a fast analytical technique primarily used for phase identification of crystalline materials and can provide information on unit cell dimensions. The material under analysis is finely ground, homogenized, and the average bulk composition is determined. X-ray diffraction relies on the constructive interference of monochromatic X-rays with a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to ensure they are monochromatic, and collimated to focus the beam before being directed at the sample.

When these X-rays interact with the sample, they undergo constructive interference under conditions that satisfy Bragg's Law ($n\lambda = 2d \sin \theta$), where λ is the wavelength of the X-rays, θ is the diffraction angle, d is the lattice spacing of the crystal, and n is an integer indicating the order of diffraction.

The resulting diffracted X-rays are detected, processed, and counted. By scanning the sample through a range of 2θ angles (where θ is the diffraction angle), all possible diffraction directions of the crystal lattice can be captured due to the random orientation of the powdered material. The diffraction peaks observed in the X-ray diffraction pattern correspond to specific d -spacings of the crystal lattice. Each mineral or crystalline material exhibits a unique set of d -spacings, allowing for its identification based on its distinctive X-ray diffraction pattern.

Powder X-ray diffraction (XRD) data were collected for all UNCD samples at room temperature using a Rigaku Geigerflex diffractometer.

9.3.4 Single Crystal X-ray Crystallography

Single-crystal X-ray diffraction (XRD) enables absolute structure determination by providing precise atomic positions within a crystal. This technique allows for the determination of bond lengths, angles, and the overall molecular structure within a single crystal. When a crystal is exposed to a beam of incident X-rays, the orderly arrangement of atoms within the crystal causes the X-rays to diffract in specific directions. By measuring the angles and intensities of these diffracted X-rays, crystallographers can create a three-dimensional image depicting the electron density distribution within the crystal. This technique allows precise determination of the positions of atoms, their chemical bonds, crystallographic disorder, and other structural details essential for understanding the material's properties and behavior.

Intensity data were determined on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated $M_oK_{\alpha 1}$ ($\lambda = 0.71073 \text{ \AA}$) radiation at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program SAINT+, version 6.02, and empirical absorption corrections were made using SADABS. Space group assignment was made using XPREP(Version 2014/2). The structure was solved in the WinGX(Version 2021.3) Suite of programs, using intrinsic phasing through SHELXT(Version 2018/2) and refined using full-matrix least-squares/difference Fourier techniques on F using SHELXL-2017(Version 2019/3). All C-bound hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times or 1.5 times those of their parent atoms. All O-bound hydrogen atoms were in the difference Fourier map and refined as riding on their parent atoms with isotropic parameters 1.5 times those of their parent atoms. Diagrams and publication material were generated using ORTEP-3(Version 2020.1) and PLATON(Version 130720).

9.3.5 AFM

The Atomic Force Microscope (AFM) was extensively used in studying the morphology of the nanocrystalline diamond thin films. The AFM can be employed in various

imaging modes, some of which yield topographical measurements, while others offer insights into different surface properties. Despite the diversity in imaging modes, the fundamental operation of the AFM remains similar (see Fig 9.8).

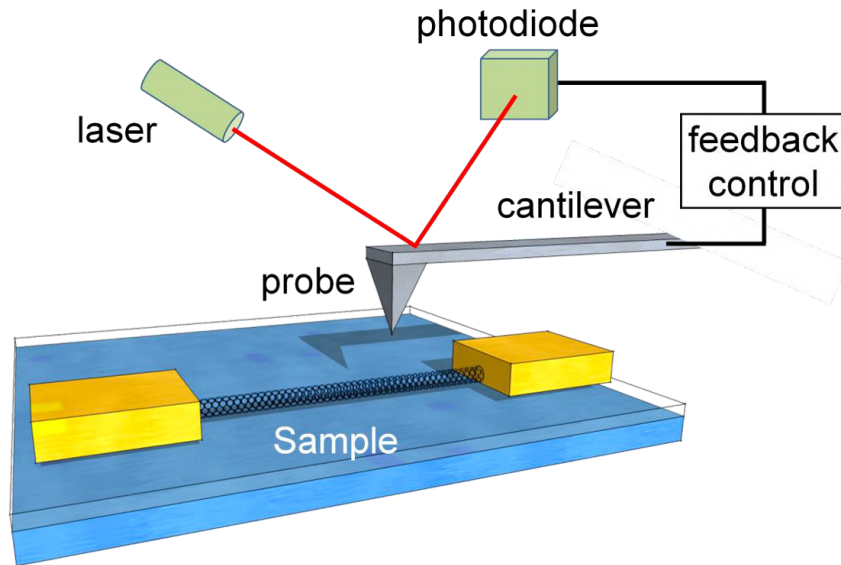


Figure 9.8 *A feedback laser shines off the back of an AFM cantilever to detect the topography signal from the tip-sample interaction. adapted from [308].*

In essence, a laser is directed onto a cantilever that houses a sharp probe with a typical radius of curvature around 10 nm. The reflected light from this setup is then detected by a photodetector. In cases where topographical measurements are sought, the probe is brought into contact with the sample and moved across the surface. The deflection of the cantilever arm is measured as a change in the angle of the reflected laser light. A feedback loop utilizes this signal to adjust the vertical height of the probe. Consequently, the surface topography can be mapped as a function of the lateral tip position. Other imaging modes operate on a similar principle, where interactions between the probe and the surface are detected through the deflection of the cantilever.

9.4 Lithography

9.4.1 Photolithography

Photolithography, also known as optical lithography or UV lithography, is a microfabrication technique used to pattern parts on a thin film or within the bulk of a substrate (commonly a wafer). This process involves transferring a geometric pattern from a photomask (or optical mask) onto a photosensitive chemical photoresist on the substrate using light. Through a series of chemical treatments, the exposed pattern is either etched into the material or allows the deposition of a new material in the desired pattern on the underlying material. In the fabrication of complex integrated circuits, a CMOS wafer might undergo the photolithographic cycle up to 50 times.

Sharing some basic principles with photography, photolithography creates the pattern in the photoresist by exposing it to light, either directly or via a projected image using a photomask. This is akin to a highly precise method used in making printed circuit boards. While the initial stages of photolithography are similar to photography, later stages are more akin to etching. This technique can produce extremely small patterns, down to a few tens of nanometers. It allows for precise control over the shape and size of the created objects and can pattern an entire surface cost-effectively. However, photolithography has limitations: it requires a flat substrate, is less effective at creating non-flat shapes, and necessitates extremely clean operating conditions. It is the standard method for fabricating printed circuit boards (PCBs) and microprocessors, although directed self-assembly is being explored as an alternative.

Heidelberg DWL 66+ Laser Writer

The Heidelberg DWL66+ Laser Writer is a versatile and high-precision direct-write lithography system designed for maskless lithography and direct writing on substrates. It is widely used in research and development as well as small-scale production due to its flexibility and high resolution.

Prior using the Heidelberg DWL 66+ Laser Writer, the pattern created with Layout

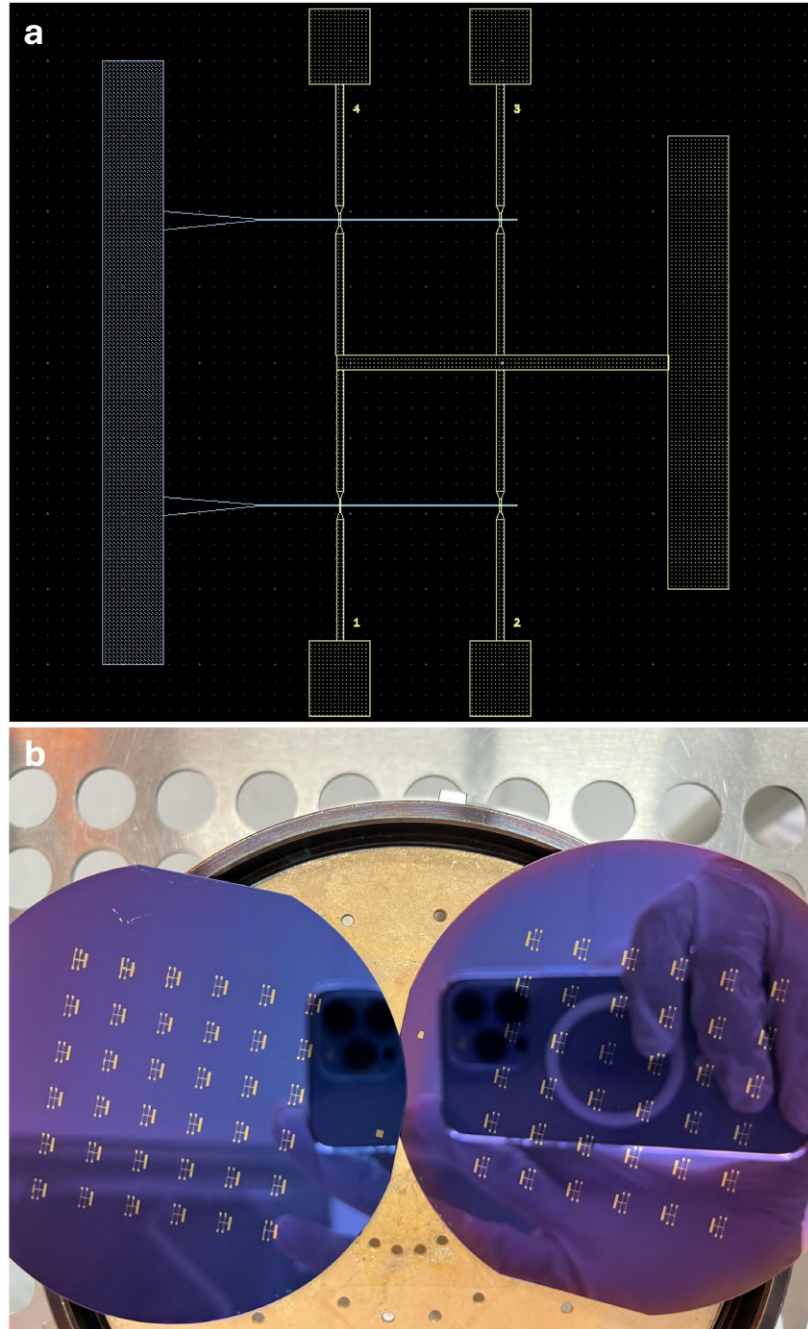


Figure 9.9 *a) CNT device pattern developed using Layout Editor. b) The same pattern developed on a silicon wafer using Heidelberg DWL 66+ Laser Writer.*

Editor (9.9a) is converted into a format readable by the Laser Writer using BEAMER and TRACER software. The cleaned wafer, coated with photoresist, is then loaded onto the stage and exposed to the laser. After exposure, the wafer is developed to remove the resist in the exposed areas using a developer. A gold layer is then deposited using e-beam deposition equipment (Kurt J. Lesker PVD 75 Pro Line series). Finally, the remaining photoresist (unexposed) is etched away using acetone (see figure9.9b for

the final CNT device pattern developed on the silicon wafer).

9.4.2 e-beam lithography

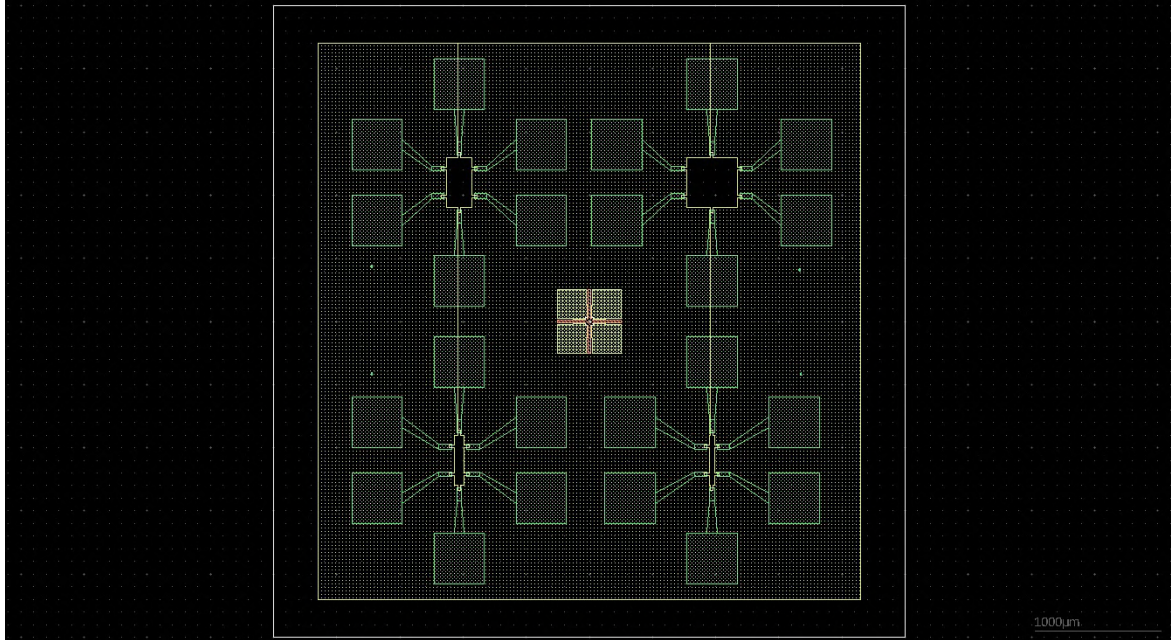


Figure 9.10 *Diamond Hallbar device of various configurations designed using Layout Editor.*

E-beam lithography (electron beam lithography) is a high-resolution technique used in microfabrication to create extremely fine patterns on a substrate. It uses a focused beam of electrons to directly write patterns onto a surface coated with an electron-sensitive resist (PMMA).

Diamond hall bar pattern designed using Layour Editor can be seen in Figure 9.10.

Elionix ELS-7500EX EBL

The Elionix ELS-7500EX is a state-of-the-art electron beam lithography (EBL) system renowned for its high resolution and precision in nanofabrication. The ELS-7500EX can achieve feature sizes down to 2 nm, making it suitable for creating extremely fine and detailed patterns.

9.4.3 Dielectrophoresis (DEP)

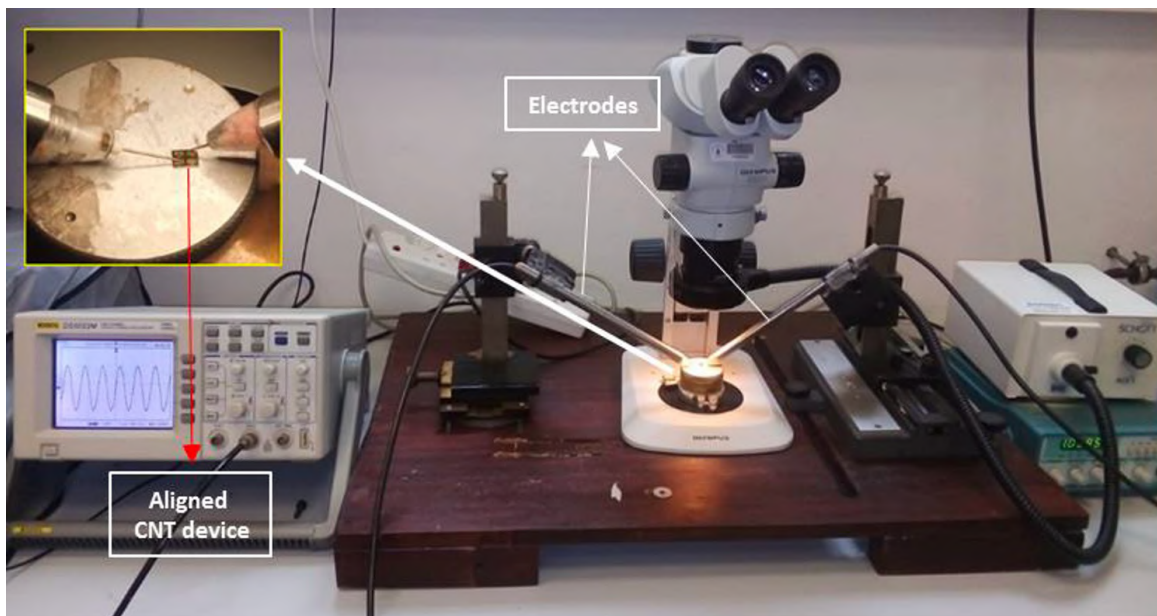


Figure 9.11 *DEP Instrument is used for aligning carbon nanotubes between two gated contacts by applying an alternating current, which is achieved by positioning two electrodes in contact with the gated terminals*

The Dielectrophoresis (DEP) technique involves applying force to Carbon Nanotubes (CNTs) through an external electric field. The application of alternating current induces a dipole moment primarily along the longitudinal axis of the nanotube, resulting in a force that moves the nanotube in a preferential direction. The alignment and packing density of CNTs on a device are influenced by the dielectric medium (the solvent dispersing CNTs and its polarizability) and the frequency of the applied electric field. A suspension of Gd-loaded Multi-Walled Carbon Nanotubes (MWCNTs) was prepared by dispersing 0.001g of functionalized CNT powder in 10 mL of ethanol solvent. The suspension underwent sonication for 20 minutes, and a 1 μL drop was collected using a pipette from the homogeneously dispersed CNT solvent. Two-terminal CNT transistor devices were created by drop-casting the CNT solvent (1 μL) onto a pre-fabricated 6-gated electrode device. The alignment of CNTs was achieved by applying an alternating current at a frequency of 1 MHz and ± 5 Vpp voltage between the respective gate electrode contacts. The integration of Gd-MWCNTs onto the transistor devices was accomplished with a packing density of 2-3 tubes/ μm refer 9.12 and 9.13.

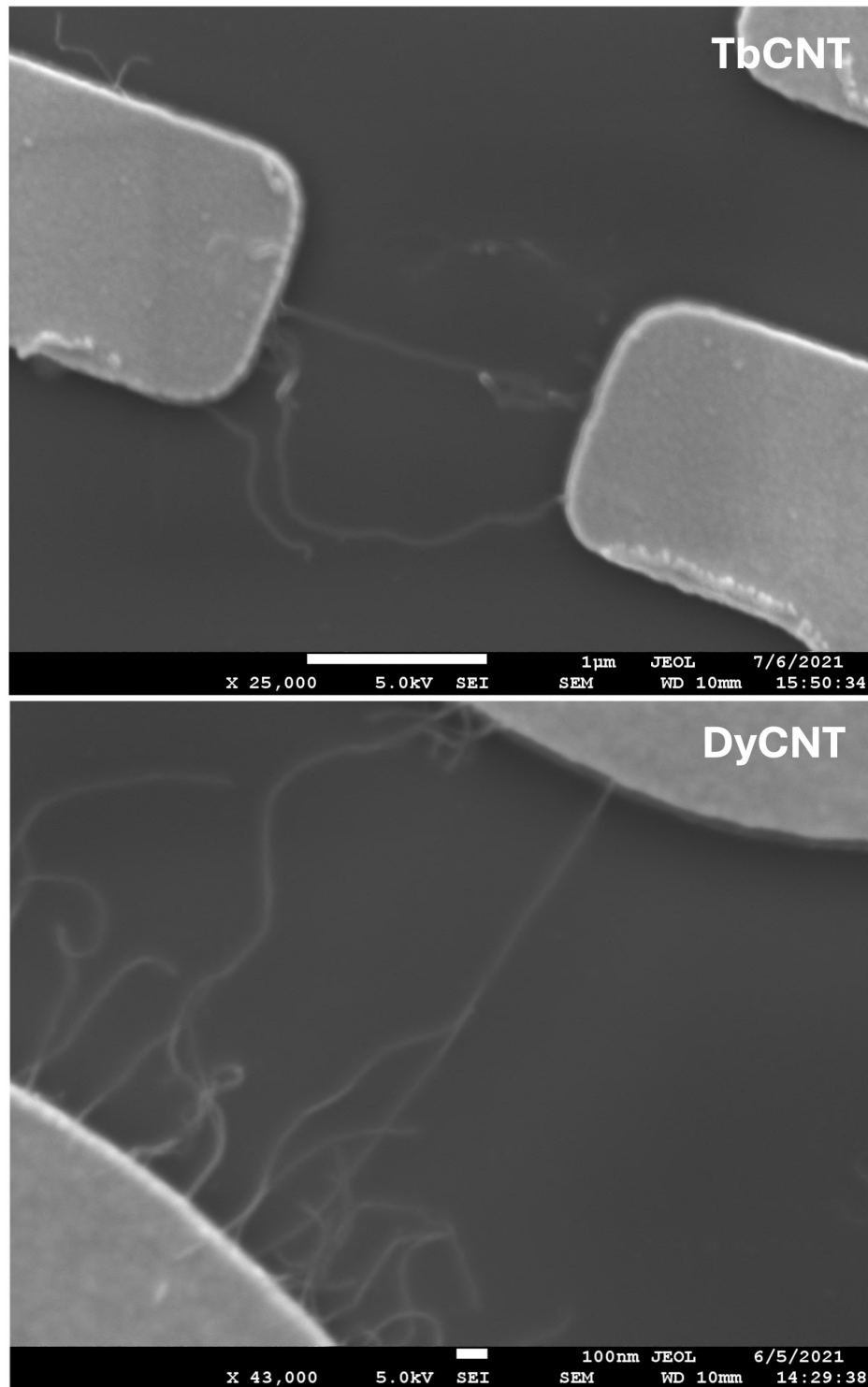


Figure 9.12 CNT device made with low density of CNTs aligned between the electrodes. CNTs aligned using DEP technique. a) TbCNT aligned between gated terminals with gap of $1.5\ \mu\text{m}$. b) DyCNT aligned between gated terminals with gap of $1.0\ \mu\text{m}$.

9.5 Low Temperature Instrumentation

Devices can be tested at low temperatures by immersing them in cryogenic liquids such as liquid nitrogen (77 K) or liquid helium (4.2 K) using a custom probe. At liquid

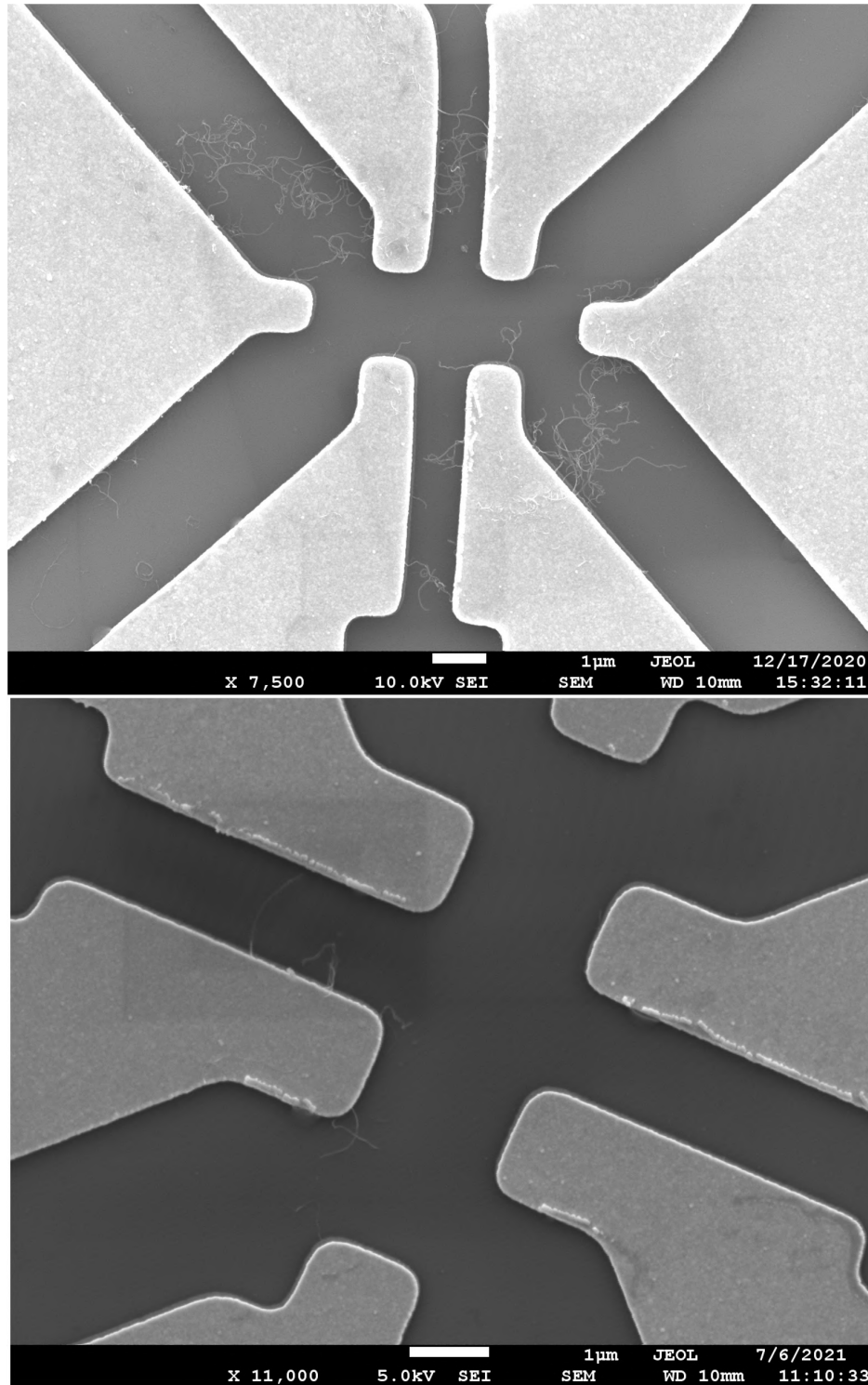
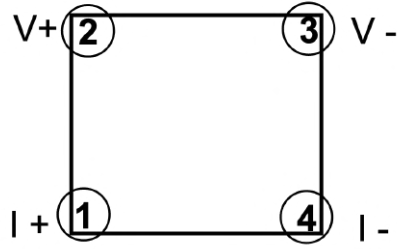


Figure 9.13 *CNT device 2 where bulk CNTs are aligned between gated terminals.*

nitrogen temperatures (77 K), the resistance of the Ohmic contacts can be checked to ensure the reliability of the contacts where the two-dimensional electron gas (2DEG) has been formed. Lower temperatures can be achieved by immersing the device in liquid helium (4.2 K) or using a cryogen-free cryostat (2.4 K) to test the samples.

9.5.1 PPMS



1-3	- 24.4 ohms
2-4	- 34.34 ohms
1-2	- 27.1 ohms
3-4	- 31.6 ohms
2-3	- 24.7 ohms
1-4	- 34.1 Ohms

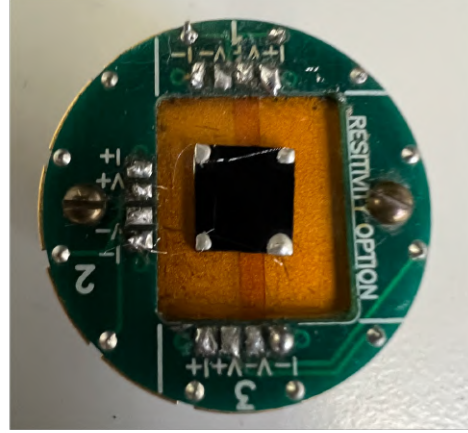


Figure 9.14 *PPMS Sample preparation: N_2 doped UNCD sample is placed on the PPMS stub with N grease for good thermal contact. The contacts are configured in Van der Pauw method.*

Low-temperature magnetic measurements were carried out using a DC-VSM (DynaCool 12T PPMS) magnetometer between the temperatures 2 K and 300 K at an applied field of 200 Oe. ZFC measurements were carried out by first cooling the sample from room temperature to 2 K under a zero magnetic field and later magnetization data were acquired in a warming cycle after applying a magnetic field of 200 Oe. FC measurements were carried out by cooling the sample from 300 K to 2 K at a magnetic field of 200 Oe and magnetization data were acquired during the warming cycle while keeping the field on.

The resolution of the DynaCool 12 PPMS in the measurement of the magnetic moment is 0.5×10^{-7} emu. Both ZFC/FC and M vs H measurements were conducted twice and the data collected were averaged to avoid discrepancies in the data, therefore increasing the confidence interval level of the data collected from the measurements. The samples is prepared in Van der Pauw configuration as detailed in the Figure.9.14.

9.5.2 Cryogenic VTI

Cryogenic VTI instrument is used to perform low temperature transport measurements with temperatures of up to 2 K. The Cryogenic Free Measurement (CFM) system

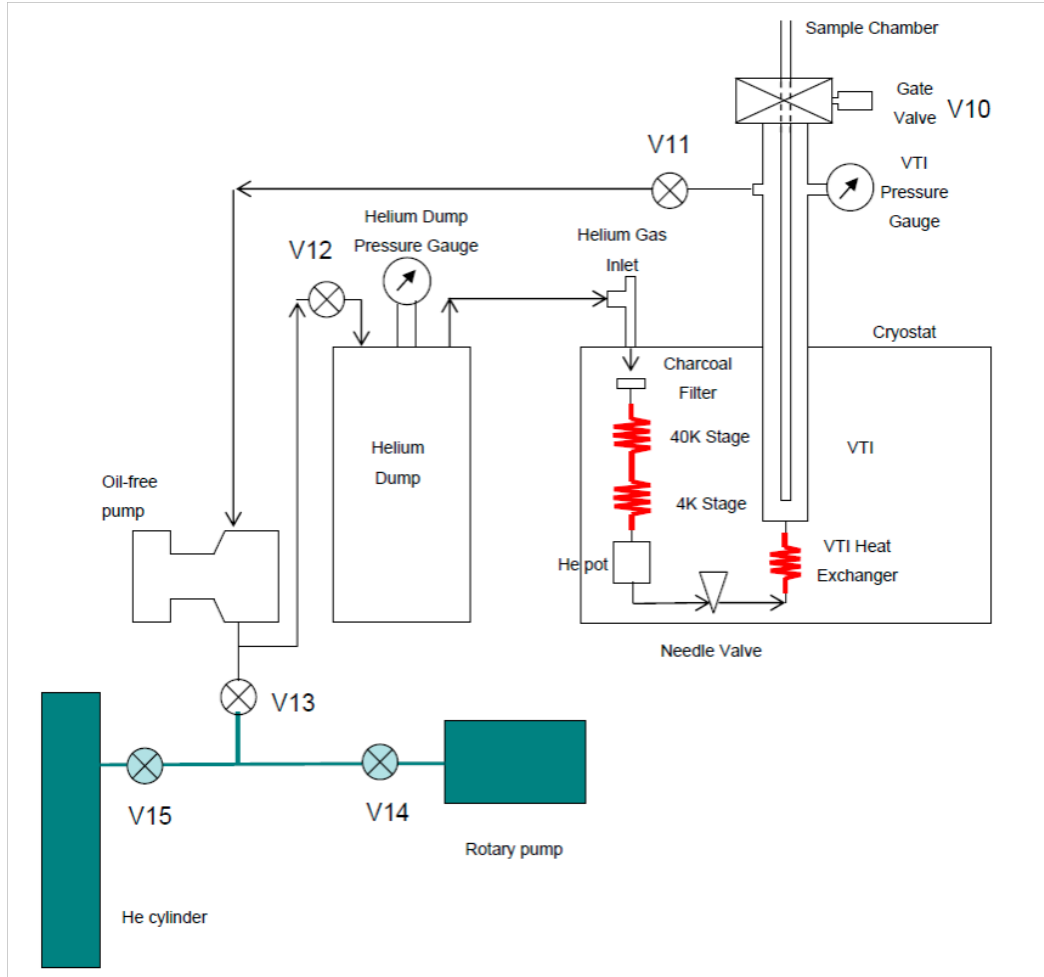


Figure 9.15 A schematic diagram of the VTI cooling stage i.e. the second Helium loop where the sample is mounted. The Helium flow is in the direction shown by the arrows.

from Cryogenic (UK), as depicted in Figure 9.15, was employed for the conducted experiments. This fully computer-automated instrument operates on LabVIEW. The system achieves low temperatures through the forced rapid expansion of helium gas circulating in two closed loops. The primary loop is propelled by a compressor, directing helium through the 40 K and 4 K stages of the cold head. The secondary loop, driven by an oil-free pump, passes helium through a needle valve, allowing temperatures as low as 1.8 K to be attained. Figure 9.15 illustrates a schematic diagram of the second loop.

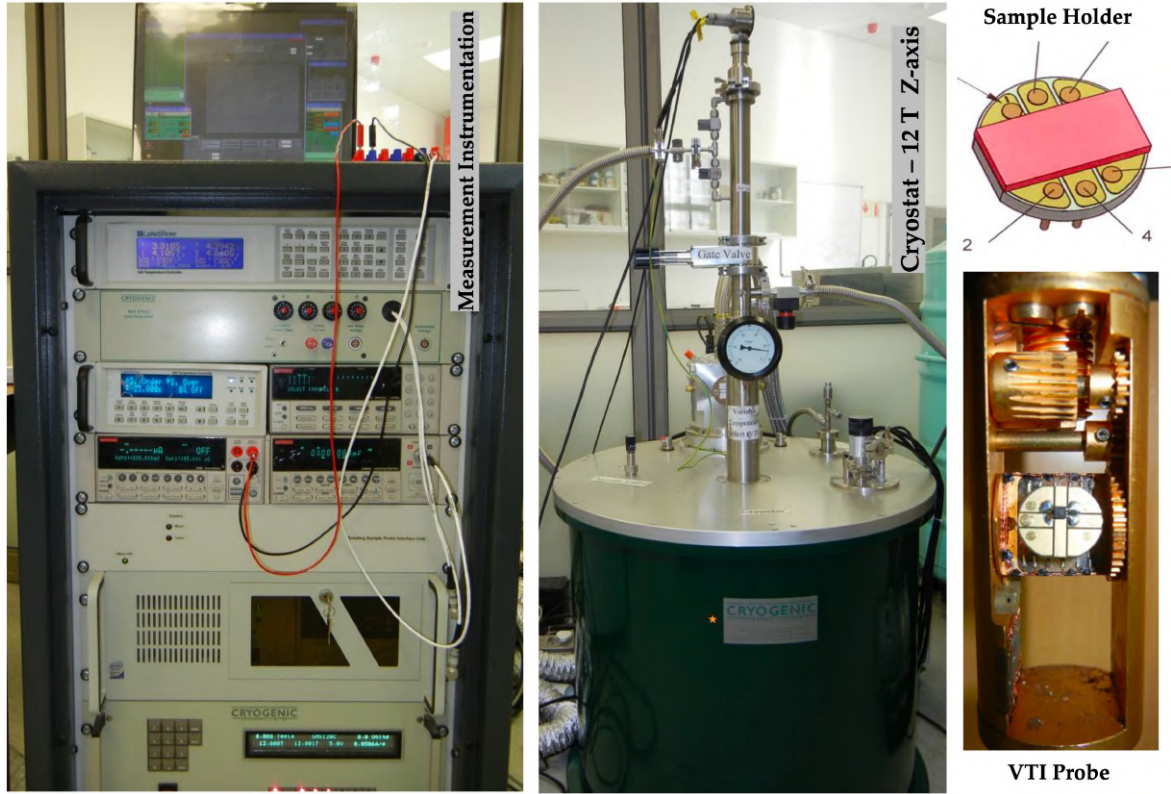


Figure 9.16 *A photograph of the cryogenic free measurement system (i) the control rack, (ii) the cryostat, (iii) the typical sample holder, (iv) the lower end of the rotator probe with a sample mounted on it.*

For resistance-temperature dependence measurements spanning 2.5 K to 300 K, both with and without a magnetic field, a Keithley 2400 served as a constant current source, and a Keithley 2182A nano-voltmeter measured the voltage across the sample. A current of 10 A was applied to the sample, balancing the need for minimal heating and a high signal-to-noise ratio. The built-in filter of the nano-voltmeter proved advantageous, ensuring high-quality measurements. Magneto-resistance measurements were conducted in the range of 0 to 12 T at variable temperatures. The nanodiamond film, approximately 300 nm thick, was deposited on quartz substrates. The van der Pauw configuration was employed for these measurements, utilizing a rectangular area with contacts positioned at the four corners.

9.5.3 Oxford Triton DR

A dilution refrigerator is a highly advanced piece of engineering capable of reaching base temperatures as low as 10 millikelvin (mK). It operates using a mixture of ^3He

and ^4He , which, below a critical temperature of 870 mK, separates into two distinct phases: a concentrated phase rich in ^3He and a mixed $^3\text{He}/^4\text{He}$ phase. The cooling effect is achieved as ^3He diffuses from the concentrated phase into the mixed phase within a mixing chamber, an endothermic process (see Figure 9.17a). The ^3He is then extracted as a gas, re-condensed, and cycled back into the concentrated phase, providing continuous cooling.

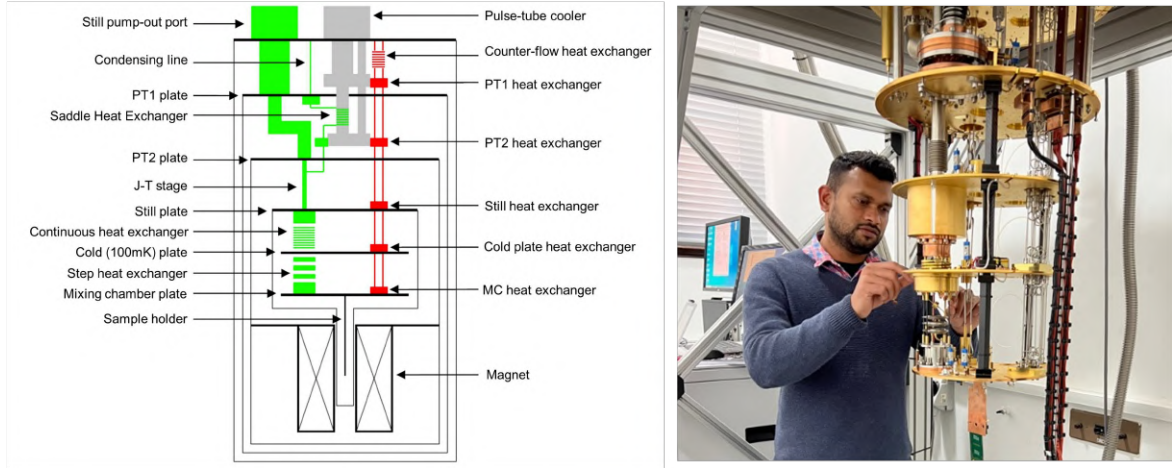


Figure 9.17 *Oxford Triton DR. a) Shows the configuration of DR assembly. Measurements up to 10 mK by placing the sample on the MC plate.*

The experiments detailed in this thesis were conducted using a cryogen-free dilution refrigerator that maintains a base temperature below 10 mK, equipped with a superconducting vector magnet capable of generating fields up to 6 tesla (T) in Z and 1 T in X and Y directions respectively. The sample is housed in a vacuum and is not immersed in the $^3\text{He}/^4\text{He}$ mixture; thermal contact with the mixing chamber is facilitated through the system's wiring. The base temperature was recorded at 10 mK, with an estimated electron temperature of 70 mK.

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