CHAPTER 1

INTRODUCTION

1.1 History of the laser

The acronym LASER stands for the Light Absorption by Stimulated Emission of Radiation. The history of the laser started in 1916 when A. Einstein postulated that in the matter-light radiation interaction, there must be, in addition to the processes of absorption and spontaneous emission, a third process of stimulated emission [1]. Lasers became effectively operative toward the years 1960's when T. H. Maiman constructed the first optical maser using a rod of ruby as the lasing medium [2]. Lasers are unique energy sources characterised by spectral purity, spatial and temporal coherence. As a consequence, they ensure highest incident intensity on the surface of any kind of material. The study of the interaction of high-intensity laser sources with solid materials started immediately. This interaction was termed vaporisation or laser ablation [3]. The term ablation means transport of material after dislocation, but the definition changed as far as new lasers applications were proposed. Today ablation is defined as the removal of material with laser without taking into consideration the mechanism, laser wavelength, pulse duration or any other factor [4].

The interaction of laser radiation with solid surfaces was under investigation as early as 1962, when Breech & Cross [5] analysed the emission spectrum of materials vaporised by ruby laser pulses. But the very beginning of the development of the pulsed laser deposition (PLD) technique started in 1965 when Smith and Turner used ruby laser to deposit thin films [6]. This technique did not produce significant interest, since the films deposited were of lower quality comparing to those obtained via other deposition techniques, such as sputtering, which gave better surface film quality [7].

In the years 1970's new types of lasers appeared, thus the important progresses implied laser-produced plasma diagnostic and theoretical models for description of initiation and evolution of plasma [8]. In early 1980's the creation of the first

technological installations for laser deposition and epitaxy achieved remarkable results on manufacturing of thin-film structures using laser technology [9]. Late 1980's pulsed laser deposition as a film growth technique attained reputed fame and attracted wide spread interest. Several articles on pulsed laser deposition (PLD) were published [3]. Q-switched lasers delivering ultra-short optical pulses have been developed. For this reason pulsed laser ablation deposition (PLAD) can be used to achieve congruent evaporation of multi-component targets and to deposit stoichiometric thin films.

PLAD characteristics of stoichiometric transfer of the complex-component target composition and the possibility of working in chemically active gases opened the way for depositing practically any material to any substrate. It was thus successfully used to grow high-temperature Tc superconducting films [10] and employed to fabricate crystalline thin films with epitaxy quality. The films obtained are found to be superior in quality to those previously grown using other deposition methods and triggered worldwide interest in the technique. Ceramic oxides [11], nitride films [12], metallic multi layers, and various superlattices grown by PLD have been demonstrated [13].

In 1990's lasers having a higher repetition rate than the early ruby lasers made the thin film growth easily accessible [14]. Femtosecond laser systems became largely available and new and important research and application fields appeared. The high intensity, up to 10^{20}W/cm^2, of these sources was used for fusion experiments and X-ray lasers development. PLD technique was improved by using a secondary ion gun for compensation of volatile species (ion bombardment assisted deposition). This rapid development of laser technology made PLAD more competitive. Subsequent development led to laser with a high efficient harmonic generator and excimer lasers delivering Ultra Violet (UV) radiation. From then on, non-thermal laser ablation of the target material became highly efficient. Nowadays production-related issues concerning reproducibility [15], large-area scale-up [16] and multiple-level have begun to be addressed, starting up another era of thin film fabrication in industry.

1.2 Background of thin films depositions

During the last years, interests in the study of nanostructured materials and thin films have been increasing at an accelerating rate. They are stimulated by the recent advances in nanomaterials synthesis and by the powerful nanometer characterisation techniques such as atomic force microscopy (AFM) [17], transmission electron microscopy (TEM) [18] and the Rutherford backscattering spectrometry (RBS) [19], in addition to the previously existent ones like X-rays diffraction (XRD) [20], scanning electron microscopy (SEM) [21] and Raman scattering [22].

Nanomaterials exhibit innumerable unique physical and chemical properties entirely different from that of the corresponding bulk materials [23-34]. Such unusual new physical-chemical properties of these nanomaterials are related mostly to surface/interface [28, 35], size/support effects [23, 25, 27, 29, 31] including shape/morphology [24, 27], crystallography [29, 31, 32, 34, 35] and electronic environment/charge transfer [26, 28, 30-33, 36]. Furthermore, these nanomaterials can represent only a small amount of the surface layer of the bulk material when adapted technique preserving their stoichiometry is used for their synthesis.

Several techniques for depositing thin films and nanomaterials have been used; among them chemical vapour deposition (CVD) [37], spray pyrolysis [38], electron beam evaporation [39], sputtering [40], pulsed laser ablation deposition (PLAD) and reactive PLAD [41-47]. Nowadays the last ones are mostly used. They are carried out in many applications offering several advantages. They are versatile techniques capable of producing a high quality thin films with consistent optical and electrical properties in a simple and reliable way at room temperature (RT) and higher temperatures [42-44]. They are straightforward materials fabrication methods that inherently preserve the desired mix of diverse elements while producing a high quality thin film. They have become extensively used research tools in the synthesis and studies of thin films and nanoparticles involving multilayer structures of different materials.

These techniques have gained a lot of attention in the past few years for their ease of use and success in depositing materials of complex stoichiometry. They are applicable to almost any material, in particular to compounds that are difficult to produce in thin-film form by other techniques. For instance, they were the first techniques used to successfully deposit superconducting $YBa_2Cu_3O_{7-d}$ thin films [45]. Since that time, many other complex materials, especially multi-element oxides have been successfully deposited by PLAD and reactive PLAD. Typical examples are complex ceramic materials such as CdMnS [46] and ZnO [47].

Because the stoichiometry, electrical defect density, optical and structural properties of the films determine the transport of the carriers and the conduction mechanism, the performance and properties of the films strongly depend on the method of preparation [26]. PLAD and RPLAD work particularly well for complex materials in reactive gases such as oxygen, since thin films with almost the same stoichiometry of the target can be deposited in one-step. These nanomaterials, depending on their properties, find nowadays applications in top new domain like optoelectronic, electronic, photonic, organic devices of nanoscale thickness, including visible light emitting diodes (LEDs), lasers, solar cells, photodetectors, transistors, memory cells and chemical sensors.

This work mostly involves the investigation and the successfully deposition of Indium Tin Oxide (ITO), Titanium Dioxide (TiO_2) and gold nanoparticles for Dye Sensitised Solar Cells applications (DSSC).

1.3 Why dye sensitised solar cells

For many years the problem of the world running out of fossil fuels such as coal, petrol or natural gas, that supply about 80% of all the energy consuming in the world, and the ecological problems associated with the burning of them to produce the energy for our everyday needs, is increasing exponentially. Global warming due to the greenhouse effect is one of the principal harmful repercussions [48, 49]. Thus, the need for alternative energy is growing. Nuclear power has long been one alternative, but this form of energy production is

generally viewed at best with a degree of skepticism. Some developed countries (Italy for instance) closed their nuclear power facilities amid the public fear of exposure to radiation. Other countries (in America), whilst perhaps looking towards this form of energy to answer their needs and requirements, find that the international community will now act to prevent further development of this power source amid the newer worldwide fear of terrorism. Renewable energy technologies, including photovoltaic, solar thermal and biomass-fired electricity generation, supply to date only 14% of all energy consumed in the world [50].

Taking into account that the supply of energy from the Sun to the Earth is about 3×10^{24}J a year, i.e. about 10,000 times more than what the global population currently consumes [50], one understands that managing to harvest moderate fraction of this source would lead to great improvements towards the satisfaction of our energy needs. The search for economically competitive renewable energy sources thus continues to be fuelled. The new alternative is literally natural power using renewable energy sources. Renewable energy is the production of electricity, transport fuel or process heat from sources that, for all practical purposes, do not run out.

Within this frame alternative energy efficiency, a new technology based on the natural photosynthesis process has been recently discovered. The nanocrystalline DSSC, first developed in the early 1990's by Grätzel et al. [51], have achieved solar power efficiencies up to 10% on small areas. The cells consist of thin films of porous nanocrystalline TiO_2 coated with a ruthenium metal organic dye to absorb the light energy and show highly efficient electronic charge transport properties [52]. These materials promise great potential as a cheap and efficient device compared to silicon based technology. They are adapted for large surface coatings and mass production. Furthermore, they offer easy processing and can attain new roles over conventional solar cells. The nanocrystalline DSSC possesses very important advantages over conventional solar cells based on silicon, which comprise the ability to perform well in low light and shade and to perform constantly well over a wide range of temperatures [53-55]. Their large

current density and stability as well as their low cost make numerous practical applications feasible. They present a high photon-current conversion, a long life time (15 years), a reliable chemical stability-inertness and consequential safety degree. Such cells are optimised for low or indoor lighting conditions.

Solar cells are widely used in many technological applications such as calculators, powering communication equipment and satellites. Modules (electrical association of many cells) are being pursued for applications such as radios, rechargeable torches, garden lights, security systems and battery chargers. As they can be fabricated to be visually either transparent or opaque in appearance, these cells suggest application in power generating windows (when used as a window they have a potential to reduce the heat gain into the building). Solar tiles can be used as integrated building material capable of large scale power generation. Opaque modules would be used for maximum power and transparent for day lighting. As tiles modules and as window, the cells will provide for local area power generation in urban, resort and remote locations plus load levelling in city, urban dense and high rise areas. Likewise this new solar nanotechnology is outstandingly adapted to poor and rural areas and at the same time respond to the poverty eradication issue.

1.4 Research problems and hypothesis

For a solar cell to be of any use at all, it must absorb photons in the energy range of solar emission spectrum. In the case of a semiconductor-based solar cell, the photons from the sun would excite an electron from the band edge into the conduction band. This would create what is termed an electron and hole pair. Under isolated conditions, the hole and the electron would recombine. However, depending upon the nature of the semiconductor, and on what other materials it has on its boundaries, the electron and hole can be moved further apart, increasing the time it would take for the two to recombine. If the semiconductor under illumination is then incorporated into a circuit, and the recombination time is long enough, this system can be used to perform work, thus generating a current.

The dye-sensitised solar cells belong to the group of thin-film solar cells (where the semiconductor used is TiO_2). A DSSC employs a photo-electrochemical electrode consisting of monolayers of photo-sensitiser adsorbed onto an approximately 10μm thick film or more of nanocrystalline mesoporous TiO_2 particles. Titanium dioxide has been the favoured semiconductor for these studies, following its use by Fujishima and Honda for water photolysis [56]. Unfortunately, because of its large band gap (3.0-3.2eV), TiO_2 absorbs only the ultraviolet part of the solar emission and so has low conversion efficiencies. This makes TiO_2 very inefficient as a solar cell material, since it is only capable of absorbing a small fraction of the available solar energy. Numerous attempts to shift the spectral response of TiO_2 into the visible were made. In particular, it was suggested to chemically bond a liquid dye molecule to TiO_2, since the dye molecule would absorb in the visible region. Thick layers (400-500nm) of organic dyes have been used in the past for solar cells [57]. The mobility for charge transfer within the dye layer is very low, and so it was found that only a very thin layer is active for electron injection. However, the use of a thin liquid dye may result in problems for the long-term stability and sealing of the DSSC.

The stability of the cell arises not only from aging of the dye sensitiser but from corrosion of the semiconductor due to the electrolyte. Long term stability is obtained by illuminating the cell for several weeks or months. Many efforts have been made to replace the liquid dye with solid materials as well as the volatile solvents of the electrolytes with solid hole conductors [58] or polymer gel electrolytes [59, 60]. Materials envisioned for these systems must not only possess excellent mechanical properties but also exhibit good chemical inertness in oxidising environments. Because metals usually exhibit a better resistance to corrosion, it was suggested that they could be applied either as protective coatings, producing cost effective composites, which combine both strength and corrosion resistance, or as double layer TiO_2/Au films. The use of TiO_2/Au double layer reduces the corrosion problem, since the TiO_2 film provides with a large band gap and the Au corrosion reaction is energetically not favourable.

Macfarland et al. [60] have investigated the use of a triple layer of Au/TiO_2/Ti on the absorption of merbromin and they have found a broader plasmon resonance (450-600nm) of the merbromin to the surface Au/TiO_2/TI than the merbromin in water (450-530nm). In this case photo-excited electrons are transferred to the metal and travel ballistically to and over the Schottky barrier, so providing the current output. Low energy (about 1eV) electrons have surprisingly long ballistic path length in noble metals [61, 62], allowing a large fraction of the electrons to be collected. The semiconductor shows a significant improvement for majority charge transport and separation. The device presents low overall energy efficiency, limited by low dye coverage.

Significant increase is expected with the improved of optical design (reduced surface reflection), decreased metal thickness and engineered surface morphology with significantly higher surface area, structured such that multiples passes through the dye covered surface are possible for each photon. In addition, it has been demonstrated that the plasmon resonance effect of some metals (gold, platinum, silver) could, under proper conditions, improve the energy conversion efficiency. C. Wen et al. [63] had evaluated the possibility of using the plasmon resonance effect of the silver to enhance the efficiency of the photochemical cells. They have found that the photo response in the visible region increases as the mass equivalent of the silver film thickness increases to about 3.5nm.

In order to improve the efficiency in a broad spectrum, it is suggested to use gold nanoparticles because they exhibit a broad plasmon absorption in the visible at about 520-530nm [64]. This may suggest the enhancement of light absorption either of the dye in the Visible- Infrared (Vis-IR) or of the single TiO_2 film in the UV region. It is expected that this plasmonic absorption will improve the conversion rate in the Visible- Near infrared (Vis-NIR) range.

1.5 Methodology

This work on thin films based DSSC activity is subscribed within a long terms vision. The dye-sensitised layer of TiO_2 is made on top of conducting glass. In

most cases this glass is coated with a thin layer of ITO, and this forms the working electrode of the cell. For the electrode to present a good efficiency, the ITO films should combine highly conductivity and optical transparency in the visible and near infrared region, since these properties make it very efficient for hole injection and recombination suppression.

One of the objectives of this research study is to get well trained in the field of thin film deposition by laser ablation process, and acquire the experimental and theoretical skills useful for thin film analysis, since they are emerging sciences yet difficult and very demanding in most developed countries. The research is mostly about depositing successfully thin films of ITO, TiO_2, multi-layers ITO/TiO_2 under different conditions (oxygen pressure and temperatures) and later gold nanoparticles by pulsed laser deposition technique. It is intended to investigate their different properties under selected conditions for possible application to DSSC. Besides, the multilayer film laser ablation deposition is not common in material sciences.

This work explores the physics and simulation of pulsed laser deposition processes. Experimental details of multilayer films deposition are explored with accuracy as well as the characterisations of the obtained thin films. The work is divided into seven chapters. After the introduction, the second chapter will focus on the process and techniques of PLAD and RPLAD in different aspects. The discussions include the theoretical, simulation and experimental description of the process, the general deposition process, the equipment used in the process with their description. In addition, some aspects of the techniques that can affect the quality of the thin films and the major problems of the method including some of the solutions of those problems are considered.

The third chapter covers the technical realisation of the equipment used in the Lecce Laser Laboratory (LLL) where this research works were conducted, with their specificities. More attention is paid on the type of laser, the reaction chamber with its ability to allow deposition on large scale substrates (about 10cm

diameter), the optical components, the target material and the substrate holder. Details for carefully depositing thin films are given. Details of the most important characterisation techniques used for the films of interest in this work are also introduced. The different approaches are compared with each other and their advantages and disadvantages are briefly summarised.

In the fourth chapter, preparations for depositions of each film are explained. The deposition process as carried through the system is described systematically. Some parameters like the effect of the oxygen, the number of pulse and the plume length effect on the morphology of the films are studies.

After the deposition, the electrical, optical and the structural properties of the films are measured. In Chapter 5, results of various electrical and structural experiments are presented and analysed, while in Chapter 6 optical properties from single ITO films to multilayered ITO/TiO_2/Au film are extensively discussed. Highlight of the most important results obtained and perspective developments for future works are given in the Conclusion.