

CHAPTER 3

THE LECCE LASER LABORATORY (LLL) RPLAD SYSTEM

3.1 Introduction

Great attention is paid nowadays to the deposition of thin solid films, either to study new materials or to improve the characteristics (wear resistance, hardness, chemical inertness, electrical and thermal conductivity, optical absorption, etc.) of common materials covered by special films, without wasting large amounts of rare and expensive elements. In this way, it is possible to study new materials as well as to try new method to protect substrates from environmental attack and to add value to common materials. In the initial research phase, PLADs were done on small-dimension samples (usually $\sim 1\text{cm}^2$ of area and $\sim 1\mu\text{m}$ of thickness), but large enough to allow different characterisations. In a technological phase, the problem is to deposit thin films of prospective materials on large-area substrates and finally on substrates that can find industrial applications.

As regards all these applications, the deposition method is of great importance, since it must guarantee high quality, uniformity, and economical advantage of the final product. Laser light does not introduce pollution into the deposition site and the PLAD process does not make an exception to the rules. This renders it a very promising technique, with many advantages, as already mentioned in Chapter 1.

PLAD and RPLAD have already shown good results in small deposition systems, used for research purposes. In LLL, thin films having areas of the order of 1cm^2 have been deposited and studied [see, e.g., 12, 30, 41, 42, 78, 173-175]. For technological applications, it is necessary to demonstrate that good quality, single and multilayers films, can be deposited on larger surfaces ($\sim 10\text{cm}^2$ or more) in one-step laser deposition and on three-dimensional substrates. To this aim and within the framework of this research project, the LLL PLAD system was designed and built to allow deposition of thin films on larger area and complex three-dimensional substrates.

This chapter presents the technical realisation of the PLAD system of the LLL with its specificities. The chapter will focus on the key components of the system, giving a brief summary of their technical properties and on the precautions to be taken into account during the deposition. In addition, since one of the challenges in PLAD is to deposit thin films on relatively large and three-dimensional substrates, this chapter discusses on the modifications of the experimental setup used for the PLAD experiments of the films of interest for the present work. Particular attention is paid on the vacuum system and the optical setup, which are required to scale up the PLAD process. The overall system is shown in Fig.3.1. It comprises three main parts: the excimer laser, the beam delivery system, and the optical components used to align and focus the beam, and the ultra-high vacuum deposition chamber.

3.2 Important parameters of the system

The most important parameters of the system are:

- the laser wavelength; short wavelengths produce efficient film as they reduce or even inhibit formation of craters and particulates on the film surface
- the form, the dimension, and the intensity profile of the laser beam; a homogenate profile allows a uniform ablation of the target surface,
- the focal length of the lens used to guide the laser beam; the shorter the focal length, the closer is the focal point where the laser beam is focalised. It might be easier to focalise the laser beam but, in the case where the incidence angle of the laser on the target surface is not perpendicular to the target plane, it might produce non-homogeneity of the laser beam intensity on the target surface,
- the angle of incidence of the laser beam on the target surface; small angle ($\leq 45^\circ$) gives better homogeneity of the laser beam intensity on the target surface,
- the nature of the entrance window of the laser beam; the entrance window should not absorb too much the intensity of the laser beam otherwise it could be under the ablation threshold,

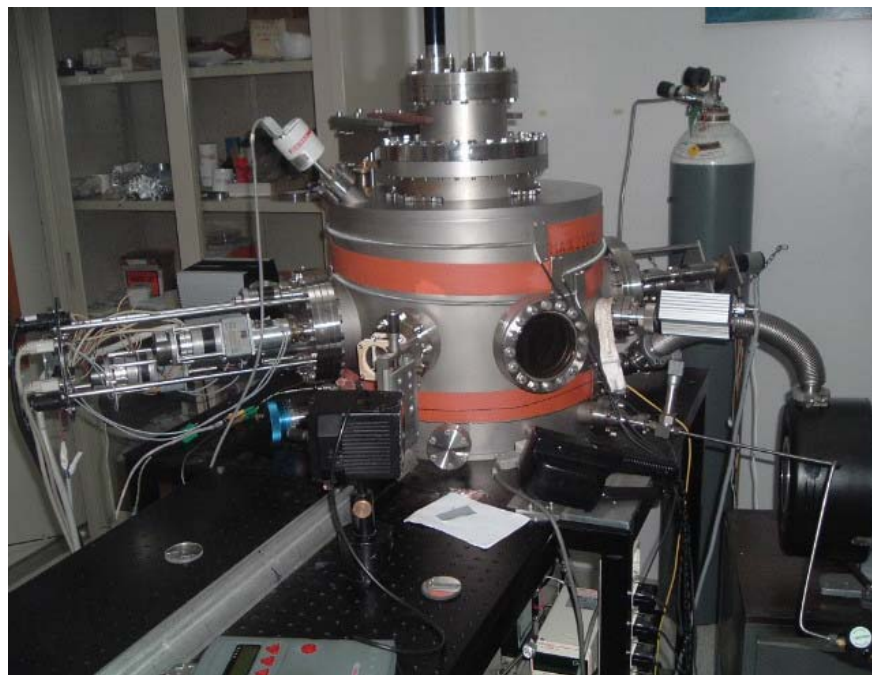
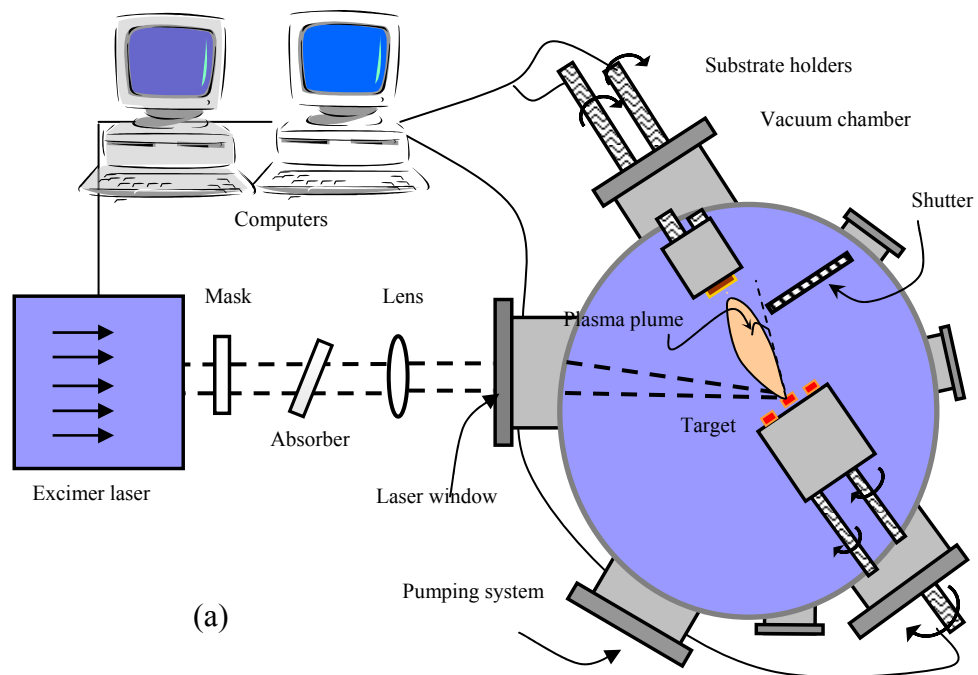


Figure 3.1 a) Schematic overview of the Lecce Laser Laboratory PLAD system;
b) Picture of the deposition chamber and vacuum system.

- the position of the target. It is better that the target be close to the centre of the vacuum chamber to allow the use of diverse geometrical configurations.
- the distance between the target and the substrate. It should not be larger than the plume length to allow efficient deposition of the film,
- the background pressure of the vacuum chamber or the reactive gas pressure, that play an important role on the film quality and in particular determines the stoichiometry of the film,
- the substrate temperature, which determines the film crystallinity.

3.3 Excimer laser

Mostly, PLAD systems use excimer lasers, since their short wavelength efficiently couples with almost all materials. The artificial word “excimer” is an acronym for ‘excited dimer’ and characterises a class of molecules that fulfil the conditions for generation of a population inversion: a thermally unstable ground state (well depth of the order of $\kappa_B T$) and excited states with a short (some tens of ns) radiative decay time [176]. The term excimer actually correctly applies only to homonuclear dimers. The correct term for heteronuclear molecules is exciplex (excited molecular complex), although excimer is commonly used also for the class of exciplex molecules.

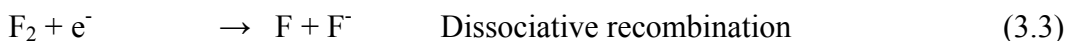
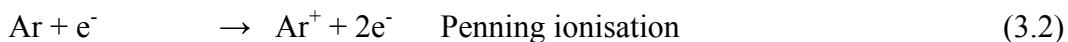
A transition from the upper electronic state to the electronic ground state results in a fast dissociation (10^{-13} s) of these molecules into their constituent atoms. For this reason the ground state remains effectively unpopulated. Any excited state population will thus constitute a population inversion, which can be used for lasing action. The wavelength of the lasing is determined by the vertical separation of the electronic states. Different excimers yield different laser wavelengths. Most excimer lasers are based on inert gas halides such as ArF, although homonuclear excimers, such as F₂, also exist. An overview of the commonly used excimer systems is given in Table 3.1, along with their associated lasing wavelength. The processes resulting in lasing are given in Eqs (3.1 - 3.5),

where the * depicts an excited state of the molecule and M is the mediating body (or third body in three body reactions).

Table 3.1 Different excimer lasing systems with their corresponding wavelengths

Excimer Laser	Wavelength (nm)
F ₂	157
ArF	193
KrCl	222
KrF	248
XeCl	308
XeF	351

The reactions are given for the ArF excimer laser, the reactions for the KrF excimer laser are similar, and the inert gas atom Ar can be substituted by Kr.



After lasing, the reaction products can reform the original reactants via reactions 3.6 and 3.7:



In theory, this regeneration scheme suggests that the laser gas mixture should last forever but, in practice, the laser has to be refilled periodically because the highly reactive F₂ (or Cl₂) degrades through reaction with the laser cavity walls and

because of laser cavity leaks. Given the importance of third body reactions, the laser is operated at high pressures (3-4 bars) and, for instance, the gas mixture for the ArF laser is 0.16% F₂ and 6.3% Ar, with the balance Ne. The pulse duration of excimer lasers depends on the pumping mechanism. Pulse durations of tens of nanoseconds are obtained when using electrical discharge excitation. Shorter pulse durations (60fs - 5ps) require pumping of an excimer amplifier with the output of a short pulse dye laser.

The LLL laser is a multigas excimer laser (Lambda Physik LPX 305i) producing high-power laser pulses. When the amplifying medium in the laser tube is a gas mixture of krypton (Kr), fluorine (F₂) and neon (Ne) as a buffer gas, it delivers an output wavelength of 248nm (KrF excimer laser). The gas mixture is ionised in order to form an excimer molecule (KrF*). This molecule can exist only in excited electronic levels: the ground level dissociates quickly into two unbound atoms. The laser transition (duration $\approx$ 20ns) between these two levels produces short Ultra Violet (UV) pulses. The discharge voltage of the ionising electrodes is typically 23-26kV producing a maximum pulse energy of 800mJ.

If the argon (Ar) is used in the mixture instead of krypton, the laser delivers an output wavelength of 193nm (ArF excimer laser) and maximum pulse energy of 500mJ. When there is a mixture of xenon (Xe) and chlorine (Cl), using neon as a buffer gas, the laser delivers an output wavelength of 308nm (XeCl excimer laser) and a maximum pulse energy of 600mJ. Usually, lasers with short wavelength (UV region) are preferred for PLAD because at shorter wavelengths the reflectivity of most materials is much lower than at visible and infrared wavelengths [176]. When the reflectivity decreases, a larger part of a laser pulse is absorbed, thus increasing the number of sputtered particles.

As a consequence, also the absorption coefficient is larger in the UV region such that the beam energy is absorbed in a thin surface layer and the ablation occurs more efficiently. The fluence of a laser pulse has to be larger than a certain threshold value, so that all the species can be stoichiometrically removed from the

target. In the case of ITO and TiO_2 , typically, values of about 2- 4J/cm² are used. Such values are large enough to allow ablation, but not too high in order to reduce the number of particulates on the deposited film. On the other words, too large a fluence may result in the ejection of large target fragments and may increase the number of droplets on the film surface, since it melts a relatively large quantity of materials. The pulse length of the laser pulse is in the range of 20-30ns. In fact, shorter pulses are not convenient for RPLAD: the thermal effect of picoseconds pulsed laser ablation is smaller than that of nanosecond pulses, and the ablation rate is very low. The pulse repetition rate is 1-50Hz. Higher repetition rates may cause interference between the plasma plume produced by successive laser pulses.

3.4 Beam delivery and optical components

The beam delivery system is formed by a set of lenses and mirrors, which allow the laser beam to focus on the target surface to achieve the preset fluence for ablation. The laser fluence at the target is usually limited to a few J/cm², while the laser beam angle of incidence at the target is of $\sim 45^\circ$. The dimensions of the nearly rectangular transverse profile of the beam are usually 10×26mm². However, the transverse energy distribution is not Gaussian. Moreover, the profile in the longer y direction is not completely symmetric. The profile also changes slightly when the pulse propagates. By carefully adjusting the laser mirrors and optimising the pulse energy, the asymmetry problem can partly be eliminated, but the resulting profile is far from the Gaussian shape. Some precautions have to be taken into account when operating with the laser.

First of all, the UV beam is dangerous. There is a risk of severe eye damage if one does not wear protective goggles when the laser is operated. Another potential hazard is the gases the device employs, in particular, the extremely poisonous fluorine. Even if the fluorine used is in 5% concentration in helium, an exposure to only a small amount of the gas damages human tissue, mostly the lungs. To minimise risks, the F_2 cylinder is stored in a separate, ventilated box to prevent the gas from leaking into the laboratory. Various optical components are required to guide, shape, and focus the laser pulses on the target surface. The output beam

first passes a $6 \times 12 \text{ mm}^2$ aperture, which cuts away the most inhomogeneous parts of the beam.

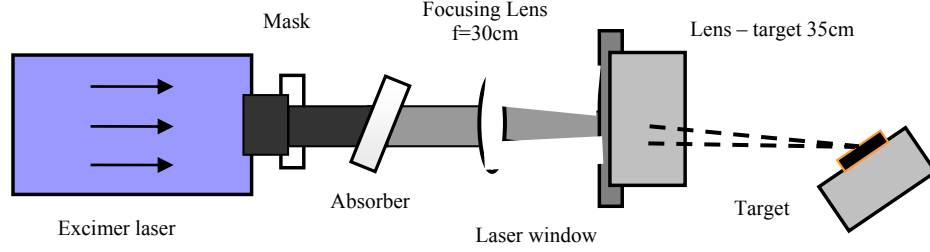


Figure 3.2 Present optical setup of the LLL PLAD system.

The collected beam is then imaged with attenuator mirrors, lenses, and windows on the target surface to produce a uniform intensity distribution with steep edges (so-called flattop distribution). The present optical setup is presented in Fig.3.2.

The optical path of the beam is chosen according to the equations:

$$\frac{1}{f} = \frac{1}{a} + \frac{1}{b} \quad (3.8)$$

and

$$\frac{a}{b} \approx \frac{A}{B} \quad (3.9)$$

Here a is the aperture-lens distance, b is the lens-target distance, f is the focal length of the lens, and A and B are the sizes of the beam and the image, respectively.

For the focal length $f=30\text{cm}$, $a \approx 150\text{cm}$ and $b=35\text{cm}$ were so chosen in order to obtain 1.1mm^2 spot on the target. Typical fluence is approximately in the range of $2.0 - 4.5\text{J/cm}^2$. However, there are some problems associated with the present system: high losses and the long optical path needed for beam shaping. To

minimise losses and to make the whole setup simpler, one of the possibilities is to replace most of the optical system with a Diffractive Optical Element (DOE). DOE is a periodic element that converts the partially coherent output of the excimer laser into a flattop distribution at a certain distance from the element [177].

Unless proper precautions are taken, UV light can be harmful both for the optical components and for the people near the optical table. Black, non-reflecting shields surround the whole system so that undesired reflections from lenses and windows would not cause eye damage for people close to the table. Optical components are best protected by keeping them clean since dust may absorb so much energy that the optical surfaces are damaged. Another cause of concern is the high intensity of the beam, which may also result in component damages.

3.5 Vacuum system

3.5.1 UHV reaction chamber

The main part of the ablation system is an about 15-inch-diameter stainless steel vacuum chamber, which can be evacuated down to 10^{-5} - 10^{-6} Pa or better, before starting PLAD or introducing the reaction gas for RPLAD. Since unwanted reactions of the ablated material with the background gas, especially with oxygen, which is highly reactive with almost all elements, must be avoided, the chamber is equipped with UHV components (flange, vacuum gauge, feedthrough, window ...) so as to minimise the contamination of the substrates and the targets.

All flanges and feedthroughs are standard CF flanges sealed with copper gaskets. In addition to ablation components, there are three windows mounted on CF flanges: an observation window on top of the chamber, a laser-beam entrance window, and a window for, e.g., external temperature monitoring with a pyrometer. Furthermore, there are additional flanges in the ablation chamber, which enable the user to add new components into the system. The entrance window through which the laser beam passes consists of a 50mm diameter quartz disc. During laser ablation, material is unavoidably deposited on these windows.

This results in some attenuation of the incoming laser light as the thickness of the film deposited on the entrance window increases with time, which hampers estimation of the laser fluence reaching the target surface. Because of this, the laser window is replaced or cleaned after every deposition.

3.5.2 Target and substrate

Despite the fact that PLAD has provided an excellent tool for producing high-quality multi-component films, it has not yet emerged as a reproducible process for commercial and industrial thin-film applications. This is mainly because the films have only a small area of structural and thickness uniformity. Especially, solar cells device applications would greatly benefit from the usage of large-area films. Several suggestions have been made to scale up the PLAD process to coat substrates with diameters of 50mm or larger. To date, three basic approaches have been reported in the literature [16, 178-180]. Two of these techniques, off-axis PLAD and rotational-translational PLAD, are so-called static-beam approaches, i.e. the optical path of the laser beam is fixed. A compatible alternative to these techniques takes advantage of laser-beam rastering across a rotating target. These three approaches are illustrated in Fig.3.3.

In off-axis PLAD (Fig.3.3.a), the target is positioned such that the centre of the ablation plume has a certain offset from the centre of the rotating substrate [180]. A modification to this alternative approach is to place the substrate almost parallel to the direction of the plume [181]. The original idea of the off-axis approach was to deposit thin films on several small substrates simultaneously, but promising results have also been obtained by using large-area substrates. For instance, high temperature semiconductors films have been deposited on 50-mm-diameter LaAlO_3 [182] and sapphire [183, 184] substrates.

In the second static-beam approach, rotational-translational PLAD, the substrate both rotates and moves back and forth in one direction (Fig.3.3.b). This method has been applied for depositing high temperature semiconductors films on 75-mm-diameter LaAlO_3 substrates [180]. In the beam-rastering approach, a focused

laser beam moves linearly across the surface of a rotating target such that the whole target material is efficiently used [181]. The rastering is realised by using a mirror held in a motorised cinematic mount. By properly adjusting the raster velocity as a function of position, the centre of the ablation plume stays for longer times near the edges of the rotating substrate, which improves the homogeneity of the film. This method has been utilised for the deposition of thin films on up to 125-mm-diameter substrates [185, 186].

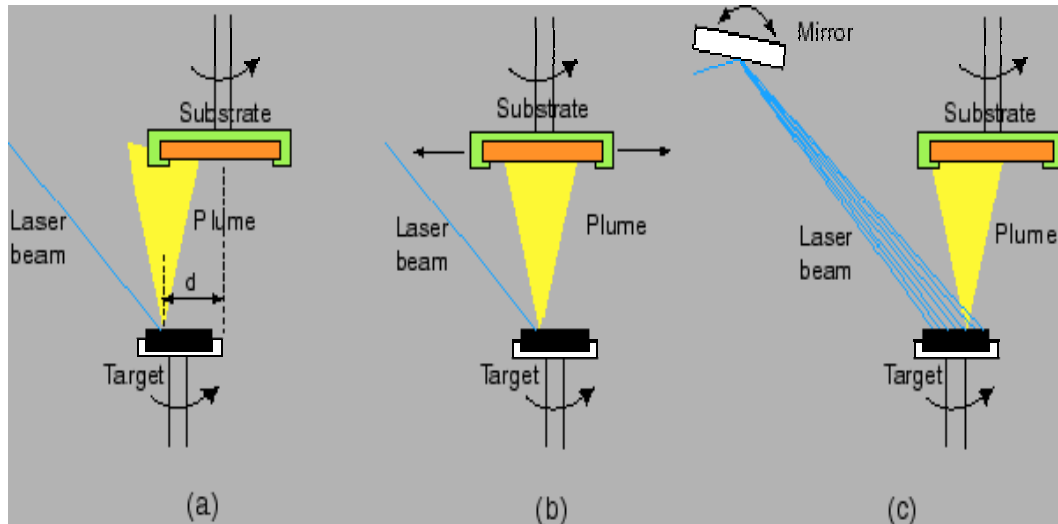


Figure 3.3 Three different large-area PLAD techniques: (a) off-axis PLAD, (b) rotational-translational PLAD, (c) laser-beam rastering [181].

A few aspects make coating of large-area substrates difficult, although deposition on smaller substrates is a straightforward process. One reason is that at a typical deposition pressure, the ablation plume has a forward-scattered, inhomogeneous and narrow flux distribution. Therefore, all large-area approaches make use of the central part of the plume, which sweeps across the whole substrate. This situation is improved when the target-substrate distance is increased. The reason is that the plume becomes wider when expanding away from the target. Uniform heating of the substrate was another challenge because it is difficult to obtain a proper thermal contact over a large area. One alternative approach is to heat the substrates radiatively with powerful lamps.

3.6 The LLL system target and substrate mechanism

In the LLL, the UHV system was designed so that targets and substrates are placed in the chamber in vertical and horizontal configurations [178]. In the vertical configuration, the laser beam propagates horizontally and passes through a fused silica window placed in front of the laser exit port. The targets are put such that the plume is directed toward the centre of rotation of the substrate plate. In the second case, the beam passes through a view port placed at the top of the chamber. The present structure, the target holder (Fig.3.4) accommodates three targets with a maximum diameter of 25.4mm and a thickness of 3mm or more.

The design of the target mechanism has to satisfy the following requirements:

- allow the rotation of each target around its own axis. This increases the uniformity of the wearing down or erosion of the target that consequently enhances the uniformity of the film growth [187];
- allow handling the mechanism from outside the vacuum chamber;
- protect the other targets during the incidence of the laser;
- permit to place the target in the corresponding holder without difficulty.

Therefore, each target revolves on its own axis and make spinning and spanning rotation as can be seen in Fig 3.5. Magnetic feedthroughs are used to transmit the rotary motion inside the vacuum chamber. The rotation speed is to be fast enough to provide a fresh target surface for every shot: however, during each deposition, every spot on the ablation track is used several times, causing a groove formation in the target. To reduce particulate formation, the target surface is polished at the beginning of each deposition. This multi-target system allows the deposition of multilayers of different materials or compounds.

Targets can be alternatively positioned in their working place and they can rotate up to a maximum frequency of 0.5Hz to avoid fast drilling. An independent scanning motion of the laser beam ensures homogeneous erosion of the targets. A combined computer controlled, motion of the target and the laser beam, allows a uniform ablation of the target, to avoid inhomogeneous drilling of the target and

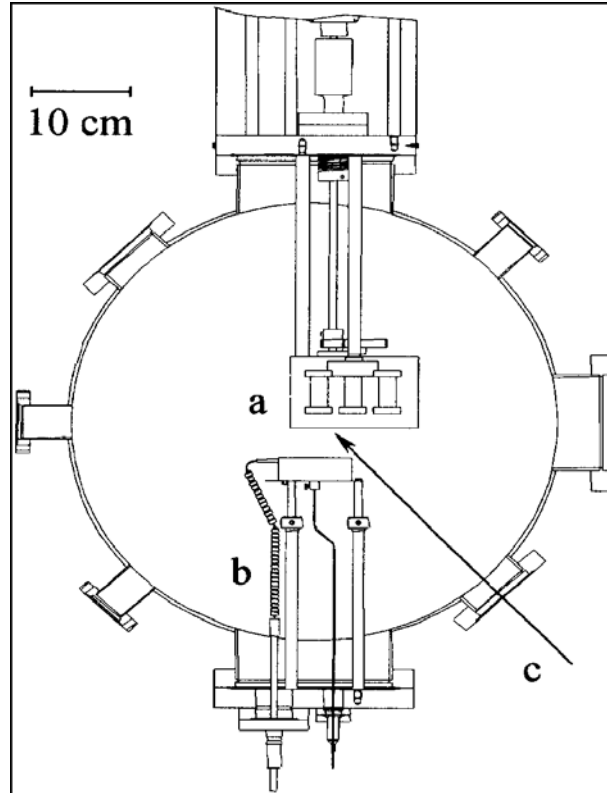


Figure 3.4 UHV chamber with target and substrate holders in horizontal configuration: (a) the target holder, (b) the substrate holder. The input of the laser beam is through the window (c) placed in front of the laser.

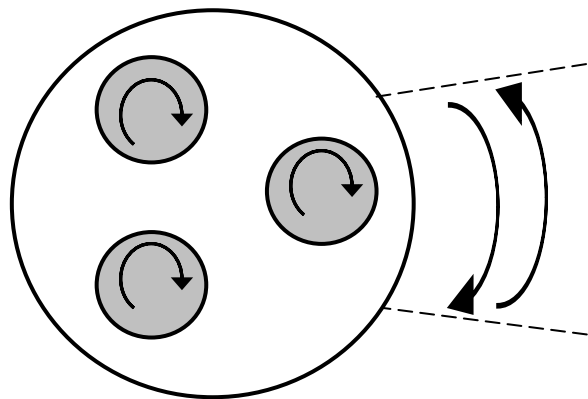


Figure 3.5 Spinning and spanning movements of the multi-target holder system: This double rotation avoids the drilling of the target, which could be very detrimental for the morphological and structural properties of the deposited layers.

efficient use of the target material. A combined computer controlled, motion of the target and the laser beam, allows a uniform ablation of the target, to avoid inhomogeneous drilling of the target and efficient use of the target material. Movement of the different optical elements for beam focusing is software driven by a program codified by Lab View 5.0.

Three different substrate holders can be used. The first one is a fixed holder accommodating one 60mm diameter flat substrate (see Fig.3.4). It can be mounted either in horizontal or vertical configuration. It can be heated up to 800°C by its resistive heating system. This temperature is sufficient for cleaning silicon wafers from native dioxide, for promoting epitaxial growth and for in-situ annealing of films.

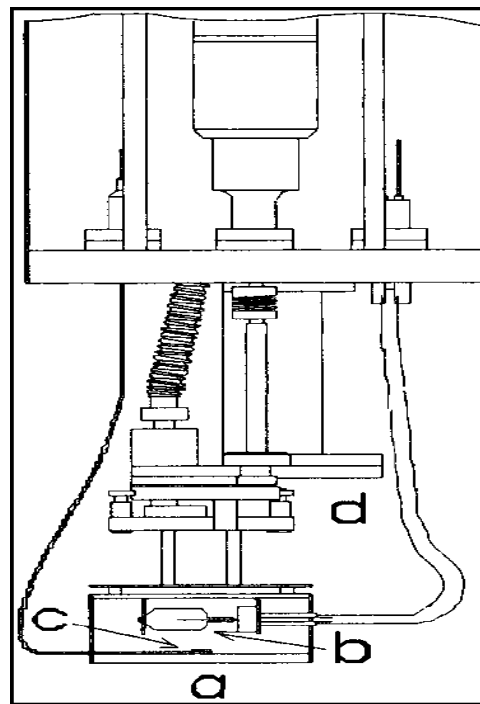


Figure 3.6 Scheme of the holder for 100mm diameter substrates, with independent x and y motions: (a) substrate holder; (b) heater; (c) thermocouple; (d) x-y movements.

The second substrate holder can accommodate 100mm diameter flat substrate (see Fig.3.6). It is allowed to have independent and contemporaneous movements along the x and y axes, in order to deposit films of uniform thickness. It can be mounted in the horizontal or vertical configuration and can be heated up to 400°C. This temperature is sufficient for eventual thermal processing of silicon wafers and for improving adhesion between the growing film and the substrate when adherence is poor in samples deposited at room temperature.

The third substrate holder can accommodate three-dimensional substrates with a maximum length of 100mm and a maximum diameter of 50mm (see Fig.3.7). The input of the laser beam is through the top window. The substrate can simultaneously translate and rotate to allow deposition of films of a uniform thickness. It can be used to deposit coatings on tools and double-face components and on substrates of various shapes. This substrate holder is only mounted in the vertical configuration and can be heated up to 300°C by a lamp system.

In PLAD technique of thin film deposition, clipping the substrate to the holder, as well as the relative position target to substrate, are important parameters. When the deposition is performed at high temperatures, generally the substrate is warmed up to obtain a good adhesion and/or epitaxial growing of the target material. For many of the target materials, the substrate heating offers good uniformity. The substrate is placed in front of the target and the distance between them depends on a reasonable compromise.

When the distance is small, the deposition rate is high, but the number of particulates is also high. When this distance is great, the film is uniform, with a low density of particulate, but the deposition rate is low. The ability to choose a proper distance is an important parameter in the PLAD design. When the films are deposited without substrate heating, it is only required a mechanism that allows to locate the substrate in front of the target. If the substrate is warmed up to relative high temperature in an oxidising atmosphere, the substrate holder necessary is more complex, as described in section 3.7.2. The necessity to have a uniform

substrate temperature entails the use of a holder of a suitable thickness, made of a material with high thermal capacity.

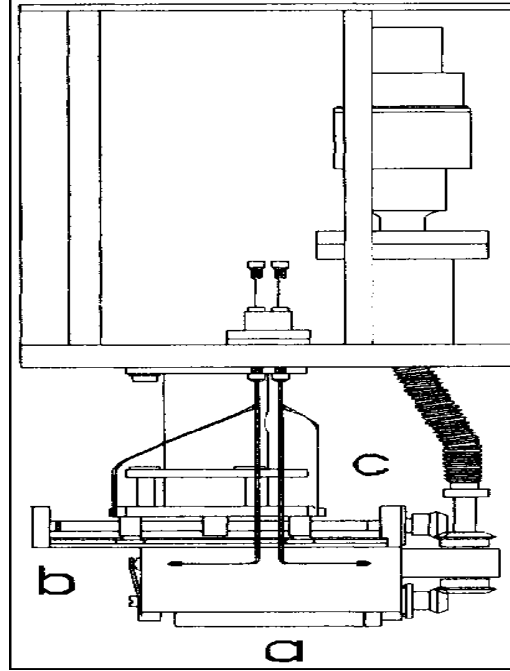


Figure 3.7 UHV chamber in the vertical configuration: (a) the cylindrical substrate; (b) the 3-dimensional substrate holder; (c) rotation and translation engines.

To the best of our knowledge, the system built in the LLL after much experimental investigations, as mentioned above, is the only one that allows controlled movements of both targets and substrates. PLAD deposition of thin films on 10cm diameter flat substrates has already been reported [179]. However, it used fixed substrates, and targets as large as the substrates. The laser spot is focused on different points on the target, to deposit the ablated material on the target portion just in front of the spot. In the LLL vacuum system, the target to substrate distance can be fixed between 40 and 120mm, when using the two holders for flat substrates. With the three-dimensional substrate holder, the target to substrate distance may range from 50 to about 75mm. It is important to note that, the shorter the distance, the higher is the deposition rate, but at shorter distances undesired plasma plume-growing film interference can develop and

micron-size droplets may be deposited on the films. Consequently, the film thickness uniformity and homogeneity increases with increasing distance [177].

3.6.1 Pumping system

The vacuum chamber is evacuated with an oil-free vacuum system formed by a rotary pump and a turbomolecular pump (TMP). The rotary pump (Leybold) has a maximum pumping speed of $48 \text{ m}^3 \text{ h}^{-1}$, allowing obtaining a pressure of $\sim 2 \text{ Pa}$. The TMP (TURBOVAC 341 MCT, Leybold) can evacuate the chamber down to an ultimate pressure of 10^{-6} Pa or better. The pressure in the chamber is measured by Pirani and Penning gauges (Edwards) and a baratron (MKS). This assembly allows a controllable and precise gas flow and enables stable and reproducible pressures over each deposition.

The gas flow through the TMP should be sufficiently low (the corresponding pressure $p < 10^3 \text{ Pa}$) in all circumstances such that the rotor of the pump would not be subjected to too high a strain. The TMP is switched on as the chamber pressure has dropped below 5 Pa . After being accelerated to the rated speed (15000 min^{-1}), the pressure in the chamber should be 10^{-5} - 10^{-6} mbar . If the pressure level is higher, there may be leaks in the chamber or in the flanges or the chamber may be contaminated. Although the TMP is a simple apparatus to use, some safety aspects should be taken into account.

In order to protect the rotor against mechanical contact, the pump should not be abruptly moved or switched off when running. Other precautions include meshes to avoid particulate entering the pump body and water-cooling circuit to eliminate the risk of overheating. Vacuum gauges and mass spectrometer allow controlling the pressure and the composition of the background atmosphere.

The mass spectrometer consists of an H100F sensor, equipped with a Faraday cup as ion detector (sensitivity of $4.9 \times 10^{-6} \text{ A/Pa}$). Its electronic operation is controlled with Transpector Ware software. Two gas cylinders (usually containing O_2 and N_2) are connected to the vacuum chamber. Inlet of reaction gases is controlled by

flux meters, in order to maintain a fixed constant pressure into the chamber during each deposition series. The background atmosphere for the reactive ablation process is supplied through a variable-leak valve. An N₂ inlet can be used for venting and preventing ambient air from entering the chamber during maintenance operations. Reaction gases can be changed without opening the system to air.

3.7 Thin films deposition

3.7.1 Target materials

PLAD is known for its ability for producing films whose stoichiometry is very close to that of the targets because of the extremely high temperatures at the focus point on the targets. However, attention must be paid to the target composition due to different species having different stick coefficients on the substrate and evaporation rates that could vary significantly, especially at high growth temperature, which is the case for ITO and TiO₂ growth. The target materials used in this work are a sintered high purity ITO disk (5cm diameter, 90 wt.% In₂O₃ and 10 wt.% SnO₂) and a TiO₂ (99.6% purity) bulk target (2mm thickness, 25mm² of surface). The ablation of gold metal was performed using a commercially available (Goodfellows) 25mm diameter gold disk.

3.7.2 Preparations for depositions

The preparations for the deposition begin usually a day before the ablation takes place. The substrate holding plate is polished with sandpaper in order to remove dirt and old deposition remnants. After that, the plate is rinsed with running water and cleaned with various chemicals (e.g., acetone). Simultaneously, the substrates are cleaned in an ultrasonic cleaner with four successive baths of: pure acetone, ethyl alcohol, deionised water and diluted (10%) hydrofluoric acid. The following day the substrate is again cleaned with pure acetone and isopropanol. Possible dust particles are removed using a flux of pressurised nitrogen.

Then the substrate is fitted to the holder and centred exactly in front of the target. At this point, one should check the condition of the targets. If they are eroded, the target holder has to be removed so that the targets can be changed or treated with

sandpaper. After having measured the laser fluence at the target site, the vacuum chamber can be evacuated by switching on the rotary pump. The gas flow through the TMP should be kept below a level corresponding to a pressure difference of the order of 20 mbar to protect the pump. The TMP is switched on when the chamber pressure has decreased below 10^{-2} mbar. The deposition can be started when the pump has evacuated the chamber to 10^{-5} Pa range or better.

The temperatures, the reaction gas pressures, and the deposition times are the important parameters that produce the best films in terms of the expected quality of the films. Before starting the deposition by turning on the laser at the selected pulse-repetition rate (usually 10Hz), the laser beam is homogenised by closing the laser window and running a minimum of 2000 pulses, then the target surface is cleaned with 1500 laser pulses or more depending on how long the target has not been used.

In this phase, the substrate is protected with a shutter. Then the reactive gas is introduced into the chamber. The laser-spot position on the target may be slightly adjusted such that the plume is directed towards the centre of the substrate or towards some other position on the deposition plate. The length, the colour, and the shape of the plume depend above all on the ambient gas pressure. At low pressures, the plume is barely visible, which makes it difficult to adjust properly the position where laser pulses hit the target.

During the deposition, the substrates are continuously moving along computer-determined paths, to obtain homogeneous deposition on the substrates. When the deposition is done at high temperatures, the substrate heating is started just after the chamber is evacuated at the desired pressure. The pressure in the chamber tends to rise with temperature because of out-gassing from the vacuum parts.

In order to avoid too large a gas flow through the pump, the pressure after the TMP should be kept below 1Pa, and, therefore, one should wait until the pressure

in the chamber begins to decrease again. This happens when the desired temperature is reached and stabilised.

3.8 Theoretical considerations

3.8.1 The plume length

If an adiabatic expansion is assumed i.e. that laser light absorption, vaporisation and plasma formation take place much faster than the expansion of the ablated material, the length L_p of the plasma is given by [188-189]:

$$L_p = A[(\gamma - 1) \times E]^{\frac{1}{3}} \times P^{\frac{-1}{3\gamma}} \times V_i^{\frac{(\gamma-1)}{3\gamma}} \quad (3.10)$$

$$V_i = v_0 \times \tau_{\text{las}} \times S_c \quad (3.11)$$

where A is a geometric factor related to the shape of the laser spot at the target surface, γ is the specific heat ratio, E is the laser energy, P is the gas pressure and V_i is the initial volume of the plasma (v_0 being the initial species velocity, τ_{las} the laser pulse duration and S_c the spot size).

It is clearly seen that if the geometry remains constant, E and P are the parameters controlling the plume length L_p . They have two opposite effects: the increasing of the gas pressure P produce the decreasing of the plasma length L_p , while the increasing of the laser energy E induces the inverse process. For a given fluence, the plume length decreases when the oxygen pressure P increase. The plume length decreases very fast when P increases from 1 to 5Pa, then slowly decreases when the oxygen pressure P increases from 5 to above 15Pa and, around 20Pa, the plume length decreases very slightly.

It is also important to notice that the plume length increases with the fluence for a given pressure. For instance, at 1Pa, the plume length is about 4.9mm at 1J/cm² and almost doubles to the value 9.9mm when the fluence is 8J/cm². However, the increase is much more sensible at low fluence (from 1 to 4J/cm², the plume length

varies from 2.8cm to 4.5cm at 10Pa). At high fluences, the plume length increases very slowly (from 4 to 8J/cm², the plume length varies only from 4.5 to 5.6cm). Fig.3.8 represents the numerical plot of the plume length dependence with the gas pressure P for five different laser fluences, as indicated on the pictures. The following parameters were considered: $A = 1.4$, $\gamma = 1.4$, $v_0 = 1.2 \times 10^6 \text{ cm.s}^{-1}$, $S_c = 1.1 \text{ mm}^2$ and $\tau_{\text{las}} = 30 \text{ ns}$.

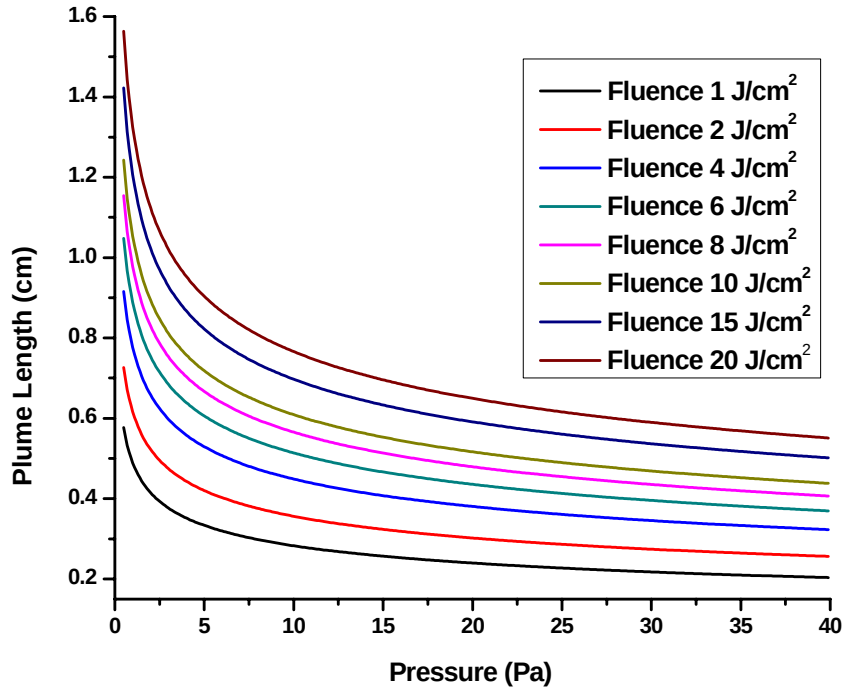


Figure 3.8 Plume lengths versus the gas pressure for five different laser fluences.

For the PLAD setup, three different regions can therefore be identified:

- i) the substrate-target distance ($d_{\text{s-T}}$) larger than the plume length L_p :
the ejected species loose their kinetic energy via collision with gas molecules. Therefore, they are transported by diffusion to the substrate and only thermalized species reach the substrate. In this case, the deposition rate depends on the diffusion coefficient in the background gas of each species and rough films with significant composition deviations are observed [189];

- ii) L_p very close to d_{s-T} : the plume remains in expansion regime and does not reach the diffusive regime before the species reach the substrate. Processes occurring at the substrate, such as nucleation, coalescence and lateral growth are prevailing, leading to smooth and stoichiometric films;
- iii) L_p larger than the plume length d_{s-T} : expansion regime and processes occurring at the substrate are prevailing. High-energy particles associated with low ambient gas pressures may both damage and roughen the surface. When the incoming particle energy is not so high to produce sputtering, they can induce the opposed effect, since the deposited energy would increase the substrate temperature, increasing the surface mobility and producing smoother films.

3.8.2 The ablation threshold

The ablation threshold (minimum laser intensity necessary for bulk material evaporation) can be calculated by an analytical way (Eq 3.12). The equation is valid for short laser pulse, i.e. considering the optical penetration depth $\delta_a \ll$ than the heat diffusion length δ_{th} and the laser spot dimension on the target surface. For a laser pulse with a rectangular temporal shape of duration τ_{las} the ablation threshold is given by [190]:

$$F_{vap} = \frac{\rho \times C_p \times \sqrt{\pi \times \tau_{las} \times \chi_{th}}}{2 \times (1 - R)} \left[(T_{vap} - T_0) + \frac{\Delta H_{fus}}{C_p} \right] \quad (3.12)$$

and

$$\chi_{th} = \frac{K_{th}}{\rho \times C_p} \quad (3.13)$$

where ρ is the mass density, C_p is the heat capacity, ΔH_{fus} is the heat of melting of the target material, χ_{th} is the heat diffusivity K_{th} is the thermal conductivity,

T_{vap} and T_0 are the temperature of vaporisation and the initial/ambient temperature, respectively, and R the reflectivity of the target surface.

For laser intensity slightly lower than the ablation threshold, very low material sputtering rates in vacuum result in collisionless low density vapour in front of the target surface. Evaporation appears to be a purely thermal process. When the laser intensity increases, the vapour density rises and collisions occur in a zone on the surface (so-called Knudsen layer). Increasing the laser intensity leads to an increase of atom density and temperature in the Knudsen layer and thus the ionisation degree rises. When the laser intensity is increased above the threshold, a fully ionised vapour plasma can be identified [191].

3.9 Characterisations techniques

Since after the deposition, the electrical, optical and the structural properties of the films are measured, the most important characterisation methods are introduced and described. Some of the different approaches are compared and their advantages and disadvantages are briefly summarised.

The different thin films deposited for the present work were submitted to X-ray Diffractometry (XRD), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM) and Raman spectroscopy. These are the techniques used in this dissertation to characterise thin films. Information such as crystalline structure, composition, surface topography, and even stacking of crystalline atomic layers were acquired. The film thickness was monitored by using a Sentech FTP 500 optical profilometer and Rutherford Backscattering Spectrometry (RBS). The electrical conductivity of the samples was measured with a Jandel 4-point resistive probe. The optical properties were investigated using a spectrophotometer.

3.9.1 Atomic force microscopy

With Atomic Force Microscopy (AFM), the surface of a material is probed with an atomically sharp tip, which is attached to a flexible cantilever. The cantilever

deforms under repulsive interactions between the surface and tip atoms. The deformation of the cantilever (which obeys Hooke's law) can be directly measured by the displacement of a laser beam reflected from it onto a 2-D photodiode array. There are two contact methods of measuring the surface topography, namely the direct contact mode and the tapping mode. In the direct contact mode, the probe measures the height profiles at a constant force (using a feedback system) or the force profiles at a constant height. The main problem with the method is that the tip can drag over the surface and the lateral forces can distort the nascent surface structure.

The problem of the direct contact method is overcome in the tapping mode by oscillating the cantilever at its resonant frequency, just above the surface. In one part of the cycle, the tip briefly interacts with the interatomic force field. This brief contact drastically reduces the effect of the lateral force. Monitoring the phase difference between the driving oscillator and the oscillation measured by the 2D detectors offers a route to information on the viscoelastic and stiffness properties of the surface [192]. When the material surface is rastered relative to the probe, the phase difference plot can provide information about the surface roughness, since the strength of the force between the cantilever and the surface drops rapidly with increasing distance. AFM analysis was performed by a digital instrument NTMDT AFM at a resolution of 5nm.

3.9.2 X rays Diffraction (XRD)

XRD gives an insight into the crystalline structure of a given material, since the interplanar spacing in regular crystal is of the order of the wavelength of X-ray radiation. Irradiating a crystal with a collimated and mono-energetic X-ray source gives rise to constructive and destructive interference via scattering of the X-rays under different crystal planes. When the incident x-ray beam is diffracted by a sample, enhanced diffraction intensity occurs only when the following Bragg's condition is achieved:

$$2d\sin(\theta) = n\lambda \quad 3.14$$

where d is the interlattice spacing in the sample, λ is the x-ray wavelength, θ is the angle between the incident/diffracted beam and the sample crystalline planes, and n is a natural integer number, as shown in Fig.3.9. Therefore, by scanning the angle θ , the intensity profile of the diffracted x-ray beam is related with crystalline information such as the d space between the crystal planes

The detecting area of XRD is normally in the range of mm^2 . Different crystal planes will have different diffraction angles. In this way, X-ray diffraction gives essential insight in the alignment of the film. Deviations from the ideal refraction angle indicate perturbations of the interlattice spacing. Such deviations can be caused by internal stresses (smaller value of d) or deviations from the ideal stoichiometry. A further determination of the crystal structure is provided by recording rocking curves of the samples. Obtaining a rocking curve involves rotating the target while the X-ray source is kept stationary.

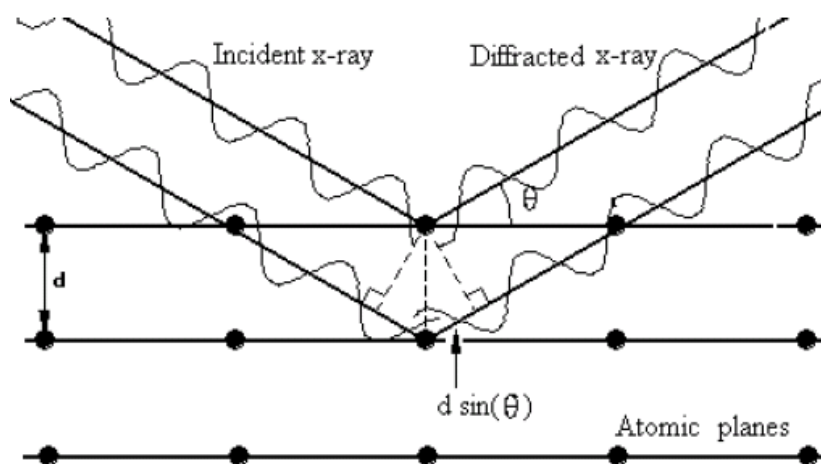


Figure 3.9 Sketch explaining the mechanism of Bragg's law.

Rocking curves can give a measure of the misalignment of the individual crystallites in the film. X-ray diffraction spectra were measured on films grown on quartz SiO_2 (100) and quartz substrates using a Scintag XDS-2000 diffractometer (radiation: Cu-K (alpha), 40kV and 35mA). Spectra were calibrated with respect

to the (100) silicon substrate peak. The Bragg equation (Eq 3.14) shows that the lattice spacing may be found from the diffraction angle.

3.9.3 Raman spectroscopy

Raman spectroscopy provides information on the phonon structure of the films. This phonon structure is critically sensitive to the quality of the films. The analysis techniques can be used as tests of the quality of films. Raman was performed at a number of excitation wavelengths 488nm laser excitation was achieved using an Ar⁺ laser (Spectra Physics 12000) coupled to a Renishaw Ramanoscope (G52836). This system provides ~4mW on the sample in a spot diameter of ~3-4μm. The same set-up was used to record spectra following excitation at the other Ar⁺ laser line (514nm), in this case with up to 20mW power focused into a ~1μm spot. Each spectrum is typically an accumulation of 10 scans and is calibrated by the Si (100) peak at 520cm⁻¹.

3.9.4 Transmission Electron Microscopy (TEM)

In TEM, a beam of electrons is spread through several apertures and lenses. This is then passed through a very thin sample (to allow transmission) and the image is focused on a phosphor screen. TEM gives the most detailed information about the nanostructure and composition of a sample, such as atomic resolution view of the sample, interface structure, defects, and crystal phase identification. Equipped with an Energy Dispersive x-ray (EDX) detector, sample composition can also be obtained by detecting the x-rays emitted from the sample because of the inelastic interaction between the incident electrons and different elements in the sample.

The advantages of TEM are high resolution, easy particle size measurement, the ability to easily determine crystallinity and selected area or nanobeam electron diffraction. This means that very small crystals can be identified and their crystal structures determined relatively easily.

Therefore, XRD shows average crystalline information of the sample, but not the information about interface and defects, which can be obtained by TEM.

However, because of the small region detected, TEM has the sampling problem, which can only be solved by checking multiple samples with sample preparation being arduous. Atomic force microscopy is limited to the sample surface only. Therefore, it is important to obtain data from multiple film characterisation techniques to characterise each film due to each technique's advantages and shortcomings. The right tools should be chosen when different properties are to be examined.

In summary, film characterisation is a task comprised of multiple techniques utilised in conjunction. Though these characterisation techniques are very important and using any one of them correctly is not trivial, detailed information about the physics behind each technique, common operation of each instrument and how to interpret data collected from these techniques are well beyond the scope of this dissertation.

3.9.5 Ultraviolet and Visible spectroscopy

The Ultra-Violet/Visible (UV-VIS) transmission spectrum of the films provides information about their optical properties, which are directly related to their electronic properties. It provides information on the optical band gap, sub-band gap absorption etc. and can be used as an indicator of the optical quality of the films. In thin conducting samples, the optical band gap (E_g) can be estimated by extrapolating from the linear part of the absorption spectrum. The point at which the line intersects with the energy axis corresponds to the approximate optical band gap of the material.

UV-VIS absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. The radiation sources in this spectrometer are deuterium and halogen lamps (lamp crossover at 326nm) giving a full range of 200-3500nm, an accuracy of $\pm 0.5\text{nm}$ and a spectral bandwidth of 2nm. All films that were analysed by UV/Vis/NIR were deposited onto quartz substrates, so that the light from the spectrometer would pass through the sample. Absorbance of films grown

on quartz substrates are taken against a background reading of a blank quartz film using UV Winlab™ software on a PC.

3.10 Thickness measurements

The thickness of the different films deposited was measured using two different techniques: the Rutherford backscattering spectrometry and a Sentech Film Thickness Probe 500 optical profilometer.

3.10.1 Rutherford backscattering (RBS)

RBS method [193] is an analytical tool that uses elastic scattering of 0.1-3 MeV charged particles to analyse the surface and the sub-regions (few tenths of microns depending on the projectile energy and ion type) of the sample. A typical RBS system consists of an accelerator and scattering chamber with sample manipulators and particle detectors. This analysing method can give both qualitative and quantitative information. When the samples are bombarded with high energetic particles, the scattered particles are detected by surface barrier detector. The signal from the detector is processed and the particle energy spectra are stored in a computer based multi-channel analyser. The data are evaluated using computer codes.

The advantage of the RBS technique lies in the quantitative analysis of the major and minor constituents lying in the first 0.5 to 2.0µm of a material. The depth distribution of the constituents can be reconstructed with a depth resolution of about 10-20nm. The RBS technique is non-destructive since the erosion and the radiation degradation of the sample material by the particle impact is negligible. Since the samples are situated in vacuum the possibility of RBS analyses of materials comprising volatile components is strongly limited.

3.10.2 Film Thickness Probe

Sentech's Film Thickness Probe FTP measures the thickness of transparent and weakly absorbing films on reflective transparent and absorbing substrates by white light reflection spectroscopy. Measurement performance and speed, solid

and reliable set-up as well as the outstanding operation software make the tool useful for very wide applications including semiconductors, glass, plastic foil, sheet metal and glazed paper coatings. In addition to the structure and composition evolution as a function of substrate temperature, optical properties of the deposited thin films in the view of future DSSC applications will be investigated. Results are presented in Chapter 5.

3.11 Conclusion

In this chapter, a coherent enhanced system for film growth by PLAD and RPLAD were described and improvements were made. It comprises an UHV chamber and optical components designed for large substrates and three-dimensional objects. It was found that large-area approach makes use of the central part of the plume, which sweeps across the whole substrate. This situation was improved when the target-substrate distance is increased as the plume becomes wider when expanding away from the target. Uniform heating of the substrate was another challenge because it is difficult to obtain a proper thermal contact over a large area. An approach of designing a multi substrate holder was investigated. The system comprises three different substrate holders. The first one is a fixed holder accommodating one 60mm diameter flat substrate, which can be heated up to 800°C by its resistive heating system. The second substrate holder can accommodate 100mm diameter flat substrate can be heated up to 400°C and the third substrate holder can accommodate three-dimensional substrates with a maximum length of 100mm and a maximum diameter of 50mm and can be heated up to 300°C by a lamp system.

The system was used to investigate the deposition of nanostructured ITO and TiO₂ thin films with controlled electrical, morphological and optical properties in view of future solar cells applications. Details for carefully depositing thin films were given. Two important parameters (plume length and ablation threshold) were discussed. Some of the most important characterisation techniques used for the films of interest in this work is described. The different approaches are compared with each other and their advantages and disadvantages are briefly summarised.