

CHAPTER 4

THIN FILMS DEPOSITION OF INDIUM TIN OXIDE (ITO) AND TITANIUM DIOXIDE (TiO₂).

4.1 Introduction

The pulsed laser ablation deposition of thin ITO, TiO₂ and ITO/TiO₂/gold films is performed in the Lecce Laser Laboratory (LLL) high vacuum system employing a reactive atmosphere in order to facilitate stoichiometric material growth. The use of the oxygen (O₂) as a reactive gas was investigated, as well as, the effect of the pulse number on the thickness of the films, the substrate temperature and finally the plume length and deflection. Reference sample were grown in Ultra High Vacuum UHV chamber ($\sim 10^{-5}$ Pa) and compared with the samples grown in a reactive atmosphere. The interest in this material is due to the recent demonstration of the high efficiency energy conversion of dye solar cells based on titanium dioxide films. These devices were all grown via chemical deposition techniques. In particular, the first demonstration of Dye Sensitised Solar Cell (DSSC) efficiency TiO₂ based structures was achieved from a hydrothermally processed TiO₂ colloid [52, 194] but this growth technique in addition of not having a high deposition rate, does not conserve the stoichiometry of the film.

In this chapter, the possibility of growing good quality thin ITO, TiO₂ and ITO/TiO₂/gold single and multilayers films via a physical vapour deposition technique is investigated, namely the reactive Pulsed Laser Ablation Deposition (PLAD) aiming to produce highly stoichiometric film and, possibly, to have a higher deposition rate. Details of the RPLAD are given. The preparations for the deposition are explained, and the deposition process as carried through in the LLL system is described gradually. After the deposition, thickness of the films was measure using Rutherford Backscattering Spectrometry (RBS) and Sentech FTP 500 optical profilometer. The films are highly stoichiometric and homogeneous over a large area. Thickness strongly depends on many parameters like laser wavelength and fluence, oxygen pressure, substrate temperature.

4.2 ITO films

4.2.1 Properties and applications of Indium Tin Oxide (ITO)

Materials exhibiting a high electrical conductivity and optical transparency, and that can be efficiently grown as thin films are extensively used for many applications, including architectural windows, thin film solar cells and chemical barriers [26, 41, 50, 195]. Transparent Conducting Oxides (TCOs), such as Cadmium Oxide (CdO) [196], Tin Oxide (SnO₂) [197], Zinc Oxide (ZnO) [198], Cadmium Stannate (Cd₂SnO₄) [199], ITO [41, 78], etc, as the name indicates are both transparent to visible light and electrically conductive. This opened up a whole range of technological interests. For instance, ITO film has recently been applied to automobile windows for thermal control. It has also been used to improve the environmental energy efficiency in winter and summer as it transmits light in the visible but reflects in the infrared region [200].

The scientific interest in this material is thus justified both by fundamental and applicative reasons. Fundamental reasons lie in understanding the peculiar resistivity and optical properties of these oxide materials: a very high thermal conductivity even at high temperature and very good transparency as well. It is important to note that transparency and conductivity are 2 different properties generally not easy to obtain simultaneously for the same material. In fact, for a film to be highly transparent in the visible, it should be an insulator or a semiconductor with a high band gap. On the other hand, a high band gap induces recombination of holes and electrons thus limiting significantly the conductive properties of the material. For this reason ITO, composed of about 90% of In₂O₃ and 10% of SnO₂ holds the first place in the use of TCOs. The percentage for ITO components is chosen in such a way to limit the effect of the recombination, thus enhancing the transparency in the Vis-NIR region. The applicative reasons reside in the interest to extend the semiconductor device technology into the whole range of the light spectrum.

Studies of the electrical and optical properties of ITO thin films synthesised by various techniques, including Chemical Vapour Deposition (CVD) [37], spray

pyrolysis [38], electron beam evaporation [39], sputtering [40] and pulsed laser ablation deposition [41-43, 78] have been reported. It results that ITO film possesses a multitude of properties including degenerated semiconductor (n-type) behaviour with a controllable resistivity ($\sim 2 \times 10^{-6} \Omega \text{m}$) and a high optical gap (3.6eV) [28, 78, 201]. These properties make the ITO to be highly transparent (above 80%) in the visible region with a plasma frequency in the Near Infrared (NIR) region [26, 28, 201-202]. Therefore it is highly used to form conductive electrodes, for instance in conductive solar cells heat-resistant transparent coatings, thus establishing an electric current over the device and to allow light to pass through it.

Apart from its intrinsic properties, such as low resistivity, that makes it suitable for solar cells, also the processing parameters determine which TCOs is chosen for a particular application. Traditionally, good etch ability and low deposition temperatures with high carrier mobilities have been favouring Indium Tin Oxide [203-208]. For solar cells, ITO is applied by sputtering from ceramic targets allowing stoichiometric deposition of the film.

4.2.2 Experimental procedure for the deposition of ITO films

In the framework of this research study, several samples of ITO films were prepared in one-step pulsed ablation deposition on substrates under different temperature. Several factors are to be taken into consideration when choosing a substrate for film growth and characterisation techniques. The ideal substrate should be lattice matched and chemically compatible, thermal expansion matched and transparent. For these reasons, the films were deposited at room temperature, at 200°C and 400°C on silica (SiO_2) fused-quartz glass (for absorption spectroscopy measurements) and on opaque silicon ($\text{Si} \langle 111 \rangle$) wafer cut into pieces (for RBS measurements).

The substrates were mounted either on a carousel, on which four substrates could be mounted simultaneously, or on a heated substrate holder supporting only one substrate at a time.

Before clamping on its holders in the deposition chamber, the substrates were carefully cleaned according to the detailed description given in the Chapter 2. Before depositions, the stainless-steel chamber was evacuated down to a base pressure of $\sim 5 \times 10^{-5}$ Pa. The target and substrate were placed parallel at a distance of about 55mm. First, the ITO films were deposited on substrates at room temperature using an ArF ($\lambda=193$ nm) excimer laser (Lambda Physik, LPX 305 i), operated with an energy of about 150mJ/pulse, a repetition rate of 10Hz and a pulse length of $\tau=30$ ns.

The laser beam was focused on the target to a spot area of 1.3mm^2 , using a spherical lens with focal length of 35cm, through a quartz glass window at an incident angle of 45° , thus producing a laser fluence at the target of 4Jcm^{-2} . The lens was placed 30cm apart, in front of the target. The target rotated and spanned to avoid drilling and defect creation such as droplets and craters on the surface layer of the growing film. During deposition, pure oxygen gas was introduced into the chamber by adjusting the oxygen inlet to maintain an oxygen pressure of 1Pa. These deposition conditions provided growth rates of about 11.10nm/min.

The thickness of the ITO films was fixed by setting a proper number of laser pulses. During deposition, exposure of just one substrate to the ablation flux can be assured by rotating a shield associated with the carousel to mask all but the one substrate of interest. This enables deposition of four different films without opening the vacuum chamber. At high substrate temperatures, two samples could be deposited in one step PLAD. The substrate holder was equipped with an electric heater that allowed producing films on substrates kept at temperatures that varied from room temperature to 400°C .

After film deposition on a substrate at high temperatures, the oxygen pressure was kept constant, until the temperatures holder decreases to room temperature. To investigate possible effects related to the laser wavelength, ITO films were also deposited with a XeCl ($\lambda=308$ nm) at room temperature and at 200°C .

4.3 Optimised deposition conditions

The characteristics of the films deposited can be studied as a function of different parameters, such as the partial pressure of the reactive gas, the temperature of the substrates, the fluence of the laser, and number and repetition rate of laser pulses. Among these parameters, the critical ones seem to be laser beam fluence (whether it is high enough to considerably ablate the target material), the ambient gas partial pressures (to ensure good stoichiometry of the deposited film) and the substrates temperatures (to ensure crystallinity).

For ITO and TiO₂ film depositions it is observed that a suitable fluence is in the range 4-4.5J/cm² when operating with ArF emission. The laser fluence mainly influences the growth rate. But an excessive increase also produces sputtering of micrometric sized particulates of material; this latter being clearly an undesirable effect that has to be minimised. One has then to find a reasonable balance between velocity of growth and presence of particulates in the deposited film.

The optimum partial pressures of the reactive gas differ for the two compounds: for ITO deposition the best pressure of O₂ for depositing stoichiometric ITO films is 1Pa, while for TiO₂ film deposition the best O₂ pressure is 10Pa. Under the above-mentioned experimental conditions, maximum deposition rates of 12nm/min for ITO and 21nm/min for TiO₂ thin film deposition were obtained.

4.3.1 Effect of the laser wavelength

It has been observed that, for a given wavelength and for the same deposition rate, the resistivity of the film increases with increasing thickness, while it decreases when increasing the deposition temperature. In fact, as the temperature increases, there is formation of crystalline grains which reach about 20nm at 300°C [209], thus reducing collisions of the charge carrier with the grain boundaries. Details of the resistivity measurements are given in the next chapter. It is also noticed that for the same pulse number, the thickness of the ITO film increases considerably with a decrease of a wavelength (Table 4.1 and Table 4.2).

Table 4.1 Thickness dependence on the laser wavelength (depositions are performed at room temperature)

Laser wavelength (nm)	Pulse numbers	Thickness (nm)	Deposition rates (nm/min)
308	20000	170	5.1
	40000	350	5.4
193	20000	370	11.1
	40000	790	12.0

Table 4.2 Thickness dependence on the deposition temperature for 2 different laser wavelengths

Laser wavelength (nm)	Pulse number	Temperature (° C)	Thickness (nm)	Deposition rate (nm/min)
193	80000	RT	1450	10.8
	80000	200	1150	9.0
	80000	400	950	7.2
308	25000	200	210	5.0
	40000		350	4.8
	25000	RT	400	9.6
	40000		600	9.0

For instance, for 20000 laser pulses with a XeCl (308nm) laser, the thickness of the ITO is about 170nm, while it is about 370nm when an ArF (193nm) laser is used. This effect is attributed to the different photon energy, since it is inversely proportional to the wavelength of the laser light.

4.3.2 Effect of the laser fluence

The fluence also plays an important role on the film thickness. For the same pulse number, the thickness increase with the fluence as it can be seen on the Table 4.3. It is important to notice a slow decrease of the ablation rate with increasing successive pulse number. This is a typical feature of the laser ablation process, due to the slow erosion of the target. These measurements allowed optimising the number of pulses used for the deposition, and therefore to obtain a constant film thickness in the desired range.

Table 4.3 Thickness dependence on the laser fluence

Pulse number	Fluence (J/cm ²)	Thickness (nm)	Deposition rate (nm/min)
40000	4.5	790	12.00
40000	4.0	700	10.80

4.3.3 Stoichiometry and thickness uniformity

Most solar cells applications require a high degree of compositional and thickness uniformity for the films. Fig.4.1 shows normalised thickness profiles of 50mm diameter ITO films deposited by the LLL system at room temperature in the vertical configuration (see Chapter 3). Normalised thickness profiles will not be presented for all the ITO samples, since the spectra of all the samples are very close to the data presented in Fig.4.1. This is then representative of the overall thickness behaviour of the produced RPLAD ITO films. The films were characterised after their growth via Sentech optical profilometer.

In all the films studied, the thickness uniformity and stoichiometry were easily obtained. The thickness varies quite little, the maximum variation in thickness is less than 10 %, though in this PLAD configuration, the thickness starts to decrease significantly at radii greater than 25mm. Compositional variation of some thin films is given in Table 4.4, in good agreement with the bulk material.

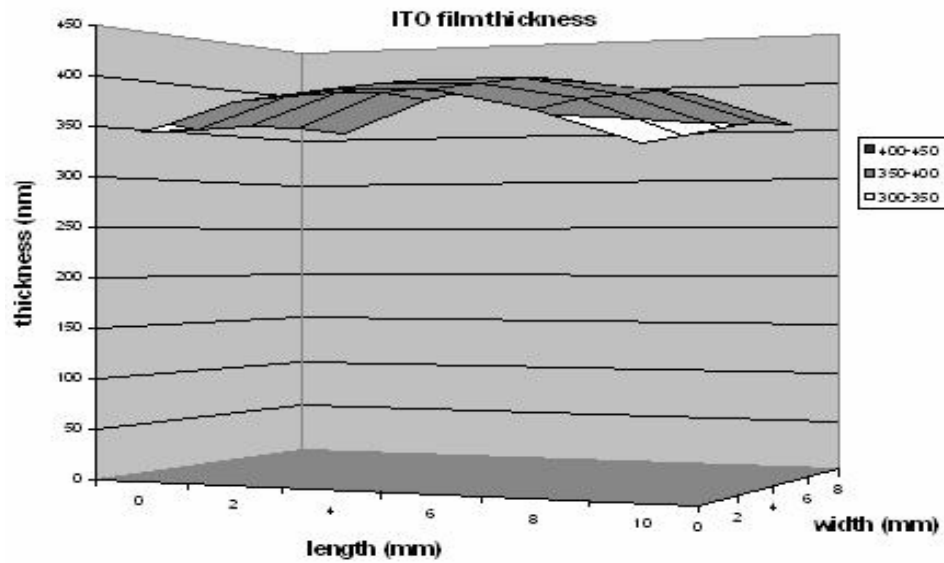


Figure 4.1 Normalised thickness profiles of 50mm diameter ITO films deposited by the LLL system at room temperature in the vertical configuration.

Table 4.4 Thickness variation of 50mm diameter ITO films deposited by LLL system in the vertical configuration. (The films were deposited under different pulse numbers)

Samples (deposition temperature)	Target composition	Number of laser pulses	Thickness from RBS (nm)	Film composition
ITO (RT)	ITO (90% SnO ₂ &10% In ₂ O ₃)	40000	620	ITO/SiO ₂
ITO (200°C)	Similar as above	80000	1150	ITO/SiO ₂
ITO (400°C)	Similar as above	80000	950	ITO/SiO ₂
TiO ₂ (RT)	TiO ₂ (98% purity)	80000	800	TiO ₂ /SiO ₂
ITO (200°C)	ITO (90% SnO ₂ &10% In ₂ O ₃)	20000	180	Poor stoichiometry
TiO ₂ (200°C)	TiO ₂ (98% purity)	20000	150	as just above
TiO ₂ /Au (RT)	Au (99% purity)	100 / 20000	2 / 300	Au- Ti/TiO ₂ /SiO ₂

Table 4.4 contains thickness and composition of films deposited on quartz SiO_2 as deduced by simulations of RBS experimental spectra. For a multilayer structure represented by A/B, A represent the first layer and B is the film layer deposited on top of the first one. Fig.4.2 shows a typical RBS spectrum, along with the corresponding simulation (first sample on the Table 4.4). The arrows indicate the position of elements if at the surface of the film.

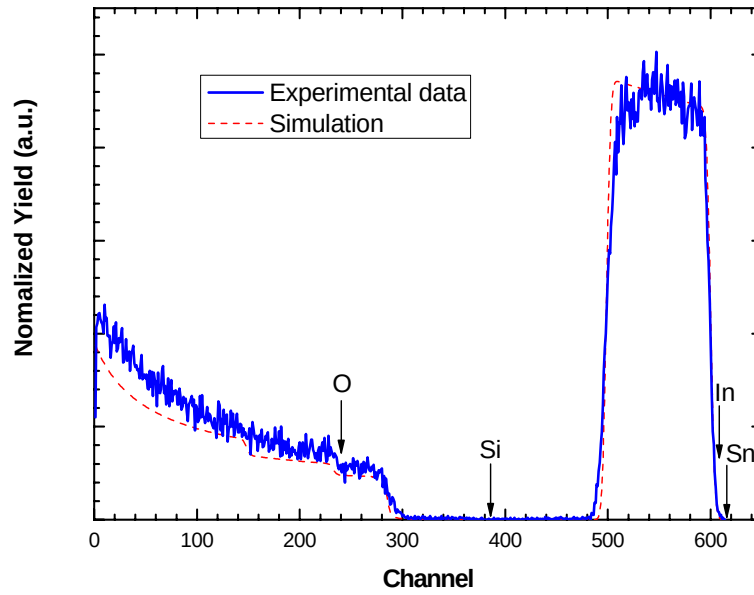


Figure 4.2 RBS spectrum of the TiO_2 film deposited on a quartz substrate. The Solid line represents the experimental result, while the dotted line is the corresponding computer simulation. The high peak (channels around 520 - 570) refers to the ITO metallic components (In, Sn), while the signal at channels inferior to 300 is related to oxygen and to the silica substrate.

RBS investigations showed that ITO films free of any kind of contamination were deposited. The film thickness and composition is fairly uniform over the whole substrate. Stoichiometric ITO and TiO_2 films were deposited both on the substrate at room temperature and on heated substrates. Compositional and thickness uniformity may start to degrade with increasing substrate area. This is because the ablated material is preferentially ejected at small angles with respect to the target normal. Despite the promising results obtained with the large-area PLAD

approaches, several improvements are required before the techniques can be effectively utilised for production-oriented purposes [188].

4.4 Effect of the oxygen pressure

4.4.1 ITO films deposition

It is well known that the oxygen background gas serves two purposes under PLAD of metal oxide and oxides [210]. It may control the oxidation state of the film surface, which, in fact, is important for production of all metal oxide and oxide films. The second important feature is the slowing down of the ablated atoms by collisions with background gas molecules. Oxygen gas is widely considered a velocity moderator for the PLAD of ITO.

An interesting experiment also performed during this study involved the PLAD growth of an ITO film directly onto an InP solar cell. Auger profilometry revealed no inter-diffusion between the two layers, underscoring the gentility afforded using the PLAD method and signalling an alternative method for fabricating ohmic contacts on photovoltaic chemical cells. Though the benefit was not investigated in this particular study, a separate study was referenced in which an ITO coating actually improved the performance of an InP cell [211].

4.4.2 Film colour/morphology

As it could be seen from the above tables, ITO films were also deposited at different oxygen pressure of 1, 5, and 10Pa at room temperature with a consecutive number of laser pulses of 40000 pulses for the samples deposited at 1 and 5Pa, and 50000 pulses for the sample deposited at 10Pa, respectively. When visually observed (Fig.4.3), the colour of the films changed with increasing the oxygen pressure. The dark aspect is typical of materials having a sub-stoichiometry of oxygen as it was reported for other materials (silicates and tellurites) [212]. This behaviour was confirmed by the optical transmission measurement performed in the NIR-visible-UV regions (300-2000nm), by means of a double beam spectrophotometer (Perkin Elmer Lambda 900).

More details on the optical properties for ITO thin films are given in the next chapter. At high O₂ pressures ~ 10 Pa, the adherence of the ITO film on the substrate is poor and the film appears very porous. This is related to the effect of the gas pressure on the plume expansion dynamic and to the mechanism of nanocluster condensation [213].

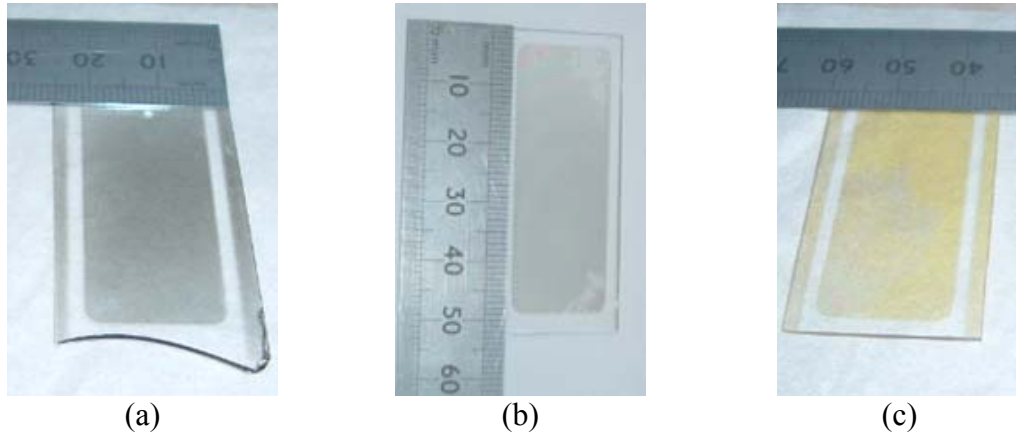


Figure 4.3 Typical pictures of different ITO films deposited at room temperature (fluence= $4\text{J}/\text{cm}^2$) under a) 1Pa O₂ pressure, b) 5Pa O₂ pressure c) 10Pa O₂ pressure.

At low O₂ pressure, interactions between the ablated species and the background gas molecules are very weak. Thus, the kinetic energy of the ablated species and the mobility of the species arriving at the substrate surface remain high, which promotes the formation of smooth and adhesive thin films. At higher O₂ pressures, the collision rate between the ablated species and the gas molecules increases leading to a decrease of the ablated species kinetic energy. At high O₂ pressure, the kinetic energy of the ablated species is therefore almost completely lost during the collisions with gas molecules inducing a reduced surface mobility of the species. The kinetic energy of the particles being too low, they cannot be correctly stuck on the substrate.

On the other hand, since the nanoparticles growth occurs during the plume expansion, a change of the gas pressure and therefore of the plume confinement

influences the collision and the growth rate. When the gas pressure is increased, higher confinement of the laser plume occurs, which allows to achieve supersaturation. The formation of nanoparticles by condensation is therefore favoured.

4.4.3 Film thickness

It could also be noticed that for a given pulses number the thickness of the film decrease when the oxygen pressure increases (Table 4.5). For instance, for 40000 laser pulses at room temperature with the same ablation rate, ITO films of about 790nm at 1Pa were obtained, while at 5Pa the thickness was about 700nm and at 10Pa the thickness decreased again to 630nm. For a given background pressure, the thickness obviously increases with an increase of a pulse number.

Table 4.5 Film thickness dependence on the oxygen pressure and pulse numbers

Pressure of oxygen (Pa)	Pulse numbers	Deposition rate (nm/pulse)	Thickness (nm)
1	20000	0.018	400
1	40000	0.020	790
5	40000	0.018	700
10	40000	0.016	630
10	50000	0.018	900

The average thickness of some ITO films deposited on Quartz under various oxygen pressures is summarised in Table 4.5. As it can be seen, ITO films with thickness varying from 400 to 900nm were produced. O₂ ambient pressure (PO₂) was found to affect the deposition rate and the film thickness during growth. For the same pulse number the deposition rate reduced significantly as PO₂ increased. For example, a growth rate of 0.2nm/s obtained under PO₂ of 1Pa was reduced to about 0.1nm/s as PO₂ was increased 10Pa. The reduction in the growth rate is attributed primarily to increased collisions of the ablated ITO particles with the ambient gas during deposition. A similar effect of PO₂ on the growth rate and

thickness was previously reported for ITO films prepared by PLAD and sputtering [201, 205].

4.4.4 Film resistivity

As already observed by Thestrup et al [44], Zheng and Kwok [204, 205] and Jia et al. [211], the resistivity of the films produced at room temperature strongly depends on the oxygen pressure. At high pressures, the resistivity of room temperature deposited ITO films increases because the particles arriving at the surface have lost so much energy that their surface mobility will be reduced considerably. However the best ITO films were found at 200°C, since it combines a low resistivity and a high transparency. Consequently, poorly crystallised films were produced.

A 1999 paper by Thestrup, et al. [44], describes the deposition of ITO films onto 10mm commercial cover glass slides and their resulting resistivity and optical transmission values over deposition temperature ranges, as well as for different O₂ partial pressures during depositions. Results indicate that at a 200°C substrate temperature, an O₂ environment resulted in the lowest overall resistivity films. In that same year, another study [214] investigated the difference in electrical and optical properties of PLD grown Aluminium-doped Zinc Oxide (AZO) and ITO, both on 10mm commercial cover glass substrates. It was found that for certain temperatures of deposition, AZO films were more conductive than ITO films grown under identical conditions. However, over a range of temperatures and partial pressures, the ITO films reached values of specific resistivity which were smaller than the lowest value for AZO.

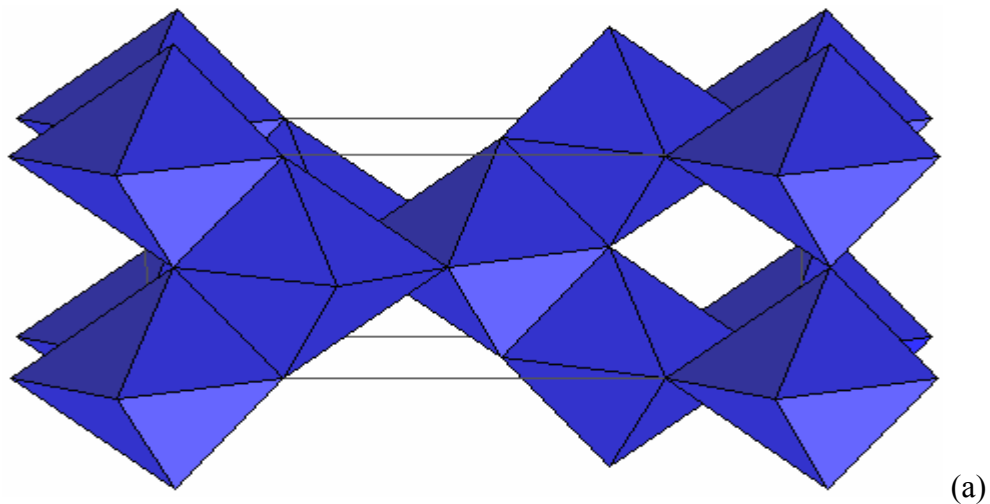
Overall, it was argued that since the resistivity of AZO and ITO varied in a similar manner over temperature and pressure ranges, with comparable values, and that the optical transmission values over the ranges were found to be comparable, AZO might in some instances serve as a suitable alternative to ITO. Craciun et al. [215], grew various amorphous ITO films on silicon and glass and characterised them both optically and electrically. UV-assisted PLD was found to produce

slightly better results in both areas, and all films were grown at 22°C. It was observed that the conductivity of the films improved with increasing working pressure, up to a maximum at 10mTorr (deemed the optimal deposition pressure by this study), and sharply decreased thereafter. Over the range of increasing conductivity, the optical transmittance was found to increase as well. It should be noted that films grown at the optimal 10mTorr were fully oxidised. A possible explanation for the UV enhancement offered in this work was that UV-induced photo dissociation of molecular oxygen gas into ozone and atomic oxygen provides a more reactive environment, one that has a cleaning effect on the substrate and promotes accelerated oxidation of metals.

In 2002, Holmelund et al. [216], deposited ITO films onto glass slides using a 355nm wavelength laser. They found that, in order to obtain films comparable to those produced by using 248nm and 193nm wavelengths, either a higher laser fluence (~ 1.5 to $2\text{J}/\text{cm}^2$) or heated substrate (200°C in this case) must be used, due to a low absorption coefficient of the 355nm irradiation. The similarity between the films was determined by resistivity measurements and optical transmission readings.

4.5 TiO₂ films

4.5.1 Crystal structure of Titanium Dioxide (TiO₂)



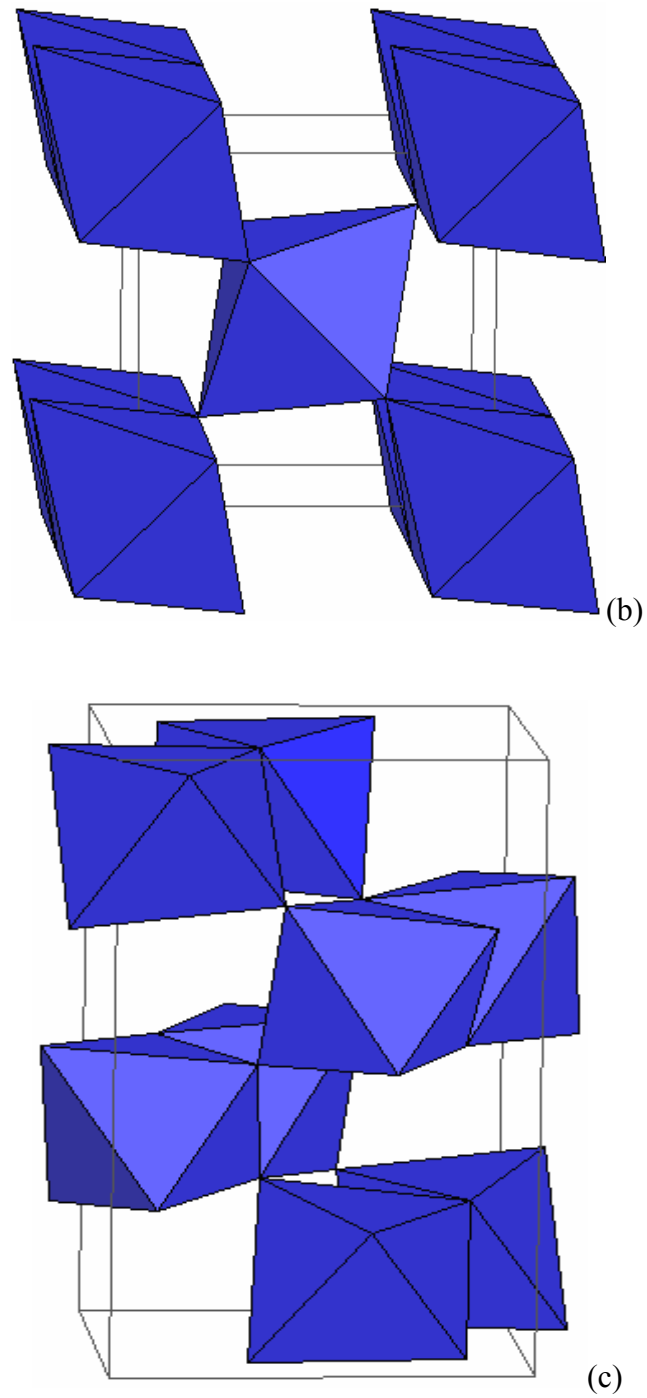


Figure 4.4 Crystal structure of different TiO_2 ; a) anatase b) rutile c) brookite.

TiO_2 occurs in three crystalline polymorphs: rutile, anatase and brookite. The basic unit cell structures of these phases are shown in Fig.4.4. The crystal parameters, the Ti-O interatomic distances, and the O-Ti-O bond angle for the three phases are summarised in the Table 4.6 Rutile and anatase are both

tetragonal with six and twelve atoms per unit cell, respectively. In both structure, each Ti atom is coordinated to six O atoms and each O atom is coordinated to three Ti atoms. In each case, the TiO_6 octahedron is slightly distorted, with two Ti-O bonds slightly greater than the other four, and with some of the O-Ti-O bond angles deviating from 90° .

The distortion is greater in anatase than in rutile. The structure of rutile and anatase and brookite crystals has been described frequently in terms of TiO_6 octahedral having common edges [217]. Two and four edges are shared in rutile and anatase phases with four and 6 active modes, respectively.

Table 4.6 TiO_2 crystal structure data

	Anatase [217]	Rutile [217]	Brookite [218]
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Lattice constant ($\text{\AA}$)	a = 3.784 c = 9.515	a = 4.5936 c = 2.9587	a = 9.184 b = 5.447 c = 5.145
Lattice Volume($\text{\AA}^3$)	136.25	62.07	257.38
Point group	4/mmm	4/mmm	mmm
Space group	I41/amd	P4 ₂ /mnm	Pbca
Molecule/cell	4	2	8
Volume/molecule ($\text{\AA}^3$)	34.061	31.2160	32.172
Density (g/cm^3)	3.9	4.28	4
Ti-O bond length ($\text{\AA}$)	1.937 1.965	1.949 1.980	1.87 ° -2.04 °
O-Ti-O bond angles	77.7 ° 92.6 °	81.2 ° 90.0 °	77.0 ° -105 °

The third form of TiO_2 , brookite, shown in Fig 4.3c, has more complicated structure with height edges in the orthorhombic cell corresponding to 36 active modes. The interatomic distance and the O-Ti-O bond angle are similar to those of

rutile and anatase phases. The main difference is that there are six different Ti-O bonds ranging from 1.87 to 2.0Å. Accordingly, here are 12 different bonds from 77° to 105°. In contrast, there are only two kinds of Ti-O bonds and O-Ti-O bond angles in rutile and anatase.

4.5.2 Properties and applications of TiO₂

For the past several decades, TiO₂ thin films have been extensively studied since this material has singular chemical [219], electrical [220, 221], magnetic [222], catalytic [223] and optical properties. Various optical applications have been proposed for titania thin films because of their high refractive index and stability [224]. Transparency in the visible and absorption in the ultraviolet make them candidates for filters [225]. It has also been used as pigmentation for paints and polymers. In particular, since about 1971 when Fujishima et al. [56] reported their work on a photo electrochemical cell possessing an anode of TiO₂, photocatalysis has developed into major area of intensive investigation. From that time on, TiO₂ has continued to hold a dominant position in photo catalysis [226].

Numerous investigations on the electronic properties of TiO₂, both on experimental [56, 227-229] and theoretical [230-233] aspects have been carried on. TiO₂ is a large band gap semiconductor with a direct forbidden gap of 3.03eV, which is degenerated, with an indirect allowed transition of 3.05eV for rutile phase, and 3.2eV for anatase. The rutile phase is the most stable at high temperatures (800°C). It has a high dielectric constant and a high index of refraction (2.7) and therefore it is used in thin film form as antireflecting and protective coatings on optical elements [234] and as dielectrics in thin film capacitors [235].

On the contrary, the anatase has not been well understood in the fundamental properties because it is difficult to realise the metastable phase by controlling the stoichiometry. However it is known to develop at temperatures below 800°C. Its index of refraction is 2.5 [236]. It is widely used as:

- photo catalysts [237-238], for decomposition of water and other

- contaminants on TiO₂ surface, as a sensors [239-240],
- gate electrodes for metal-oxide-semiconductor devices in solar energy converters [241],
- electrodes in photochemical solar cells; it is also known that anatase plays a key role in the injection process of photochemical solar cells with a high conversion efficiency [242].

Rutile phase has been studied extensively for the main reason that most crystal growth techniques yield TiO₂ in the rutile phase. Its electronic structure has been experimentally investigated by various techniques [243]. In contrast to the rutile phase, there were few investigations of anatase and brookite phase. Actually they are attracting a great deal of interest also in connection with their photo catalysis and electrochemical applications [242, 244], but the anatase is more actively investigated. Its Fermi level is higher than that of rutile by about 0.1eV [245]. Moreover, it has been reported that anatase thin film have different electrical and optical properties from the rutile films [246]. The anatase thin film appears to have a wider optical absorption gap and a smaller electron effective mass, resulting in a higher mobility for the charge carriers.

TiO₂ thin films were deposited by different techniques such as sol-gel [247], chemical vapour deposition [248], reactive magnetron sputtering [249] and PLAD [250-255]. It is known that PLAD has numerous advantages over the classical deposition methods. Indeed, it allows for the control of crystalline status and stoichiometry of the synthesised material. Moreover, the obtained thin films are highly adherent to the substrate. In addition, the incorporation of contaminants in the growing film, which usually happens during the deposition process, is avoided [14, 176]. Previous studies of PLAD of titania have reported amorphous films [251] or film containing rutile and anatase and off-stoichiometry phases [252].

On the other hand, the synthesis by PLAD of polycrystalline films composed primarily of brookite TiO₂ was reported along with anatase and a small amount of rutile [250]. They were deposited using KrF radiation on (111)-oriented silicon,

fused quartz and sapphire substrates under 200mTorr (26.6Pa) of oxygen pressure and at 750°C. Other authors found that the crystalline phase of the films is also influenced by the ambient oxygen pressure [256], as well as the substrate material and its orientation [34, 77].

4.5.3 Experimental procedure for the deposition of TiO₂ thin films

Part of this study is the synthesis of TiO₂ thin films under different temperature in the view of having anatase thin films. The work on TiO₂ anatase thin films is motivated by the distinct properties already displayed by anatase crystals, as well as the fact that thin films are often required for practical uses. Moreover, thin films have certain advantages over crystals for investigation, since in thin films can be more easily heat-treated. The procedure of the deposition of the thin films is almost the same as the one described in Chapter 3.

The TiO₂ films are deposited using the excimer ArF laser at room temperature, 200°C and 400°C on transparent quartz SiO₂ and opaque Si substrates for producing single layer thin films. They were also deposited on the 200°C pre-deposited ITO thin films for producing double layer thin films ITO/TiO₂. In this case the deposition was performed only on substrates at relatively high temperatures. It is observed that the films were all amorphous at temperatures below 200°C. It was said that the anatase phase changes to rutile phase at the range of 500-700°C [257]. But in the present case, the rutile phase appeared in films deposited on substrates heated at 400°C.

For all the TiO₂ film depositions, the oxygen pressure was kept at 10Pa, high enough to allow formation of anatase TiO₂ films at relatively high substrates temperatures [258]. At higher oxygen pressure, the collision of species and the oxygen molecule increases. Collisions with the oxygen molecule lower the temperature of ablated species. Hence, the suitable pressure for the anatase phase formation shifts in the direction of high pressure as the substrate temperature increases [258]. The laser fluence varied from 4 to 4.5J/cm².

To prevent the formation of cracks on the film surface (which are due to the different thermal expansion coefficients), the thickness of the TiO₂ films was maintained in the range 300 to 800nm, which is obtained after 40000 to 80000 pulses. The repetition rate was maintained at 10Hz although it has been demonstrated that a higher laser repetition rate enhance the formation of anatase phase [259]. The variation of the deposition rate might cause the difference of supplied energy to the growing films surface and thence modify all its properties.

As already demonstrated in the case of ITO film ablation deposition, a linear increase of the thickness with the laser pulse number is observed. Moreover, the results showed that the PLAD TiO₂ films with the thickness of about 700nm deposited at 400°C include both rutile and anatase phase crystallites, but anatase crystal increases as the film thickness increases. The same behaviour was observed by others authors [257, 258]. DeLoach et al [257] explained this behaviour showing that the film became more insulating as its thickness increased, and so the heat flow from the substrate through the film to the surface was diminished in their RF sputtered films. The same reason may be given for the present films.

In these depositions at room temperature, the base vacuum pressure was ranging from 5×10^{-4} to 8×10^{-4} Pa, while the substrate-target distance (d_{S-T}) was about 45 mm. According to the plume model introduced in Chapter 2, two different qualities of grown films are expected: smooth films for the plume length lower than the substrate-target distance and films with a high roughness for the plume length higher than the substrate-target distance typically for the given O₂ pressure.

One of the most important applications of these films is to use them for solar cells electrodes. As the only part of the solar spectrum the TiO₂ will absorb in is mostly in the ultra violet, this makes the TiO₂ layers very inefficient as a solar cell material, so in the framework of this research study, Au (gold) nanoparticles was also deposited on the TiO₂ top layer in order to improve, together with the absorption efficiency in the NIR region, the conversion rate of the resulting cell.

Au thin film was deposited with 100, 200 and 400 ArF pulses laser number under vacuum (3×10^{-4} Pa). This gave a maximum thickness of 5 nm Au thin film. After the deposition, annealing at 500°C for 3 consecutive hours in a vacuum furnace was performed. This step is necessary to allow the formation of the anatase phase for the TiO₂ films configuration.

4.6 Experimental results: Plume deflection

The luminous plume arising during excimer laser ablation of ITO in vacuum and under oxygen pressure was clearly visible to the naked eye and was recorded by a digital camera. When viewed from above, at lower fluences (fluence = 4 J/cm²), the plume appears as a small volume of intense white plasma localised at the laser focus, and a more extensive diffuse blue emission, which appears almost symmetrically distributed around the surface normal and fills the major part of the forward hemisphere. Occasional thin bright tracks originating from the focal volume with seemingly random trajectories are also evident. These may be attributed to incandescent sputtered macroparticles [260].

At higher fluence, these emissions are supplemented by a shaft of violet fluorescence, also originating from the focal volume. This emission appears to be distributed asymmetrically around the surface normal. Indeed, when the long axis of the rectangular laser output is parallel to the viewing axis the violet shaft appears to follow an axis that approximately bisects the laser propagation axis and the surface normal. These laser fluences fall in the regime characterised by significant absorption of the laser light by the ablated plume.

In Fig.4.5a, a picture of the plume (blue) generated during laser ablation at room temperature of an ITO target after 500 pulses/site (fluence=4 J/cm²) in the vacuum is shown. One can notice that the plume generated by the ablation under oxygen pressure present a different aspect: it is less expanded and looks more intense (Fig.4.5b). The higher the pressure, the shorter the plume length and the brighter the luminosity, as can be seen in Fig.4.6. At a fixed pressure, the plume luminosity under different pulses number differs as well, as can be illustrated in

Fig.4.7. The plume density seems to increase and saturate at a certain value. It is important to notice that the colour of plume depend on the material, as it can be seen in Fig.4.8, the plume of the TiO_2 is yellow, different from the one of ITO (the plume behaviour described during ITO ablation has been observed for the TiO_2 ablation as well).

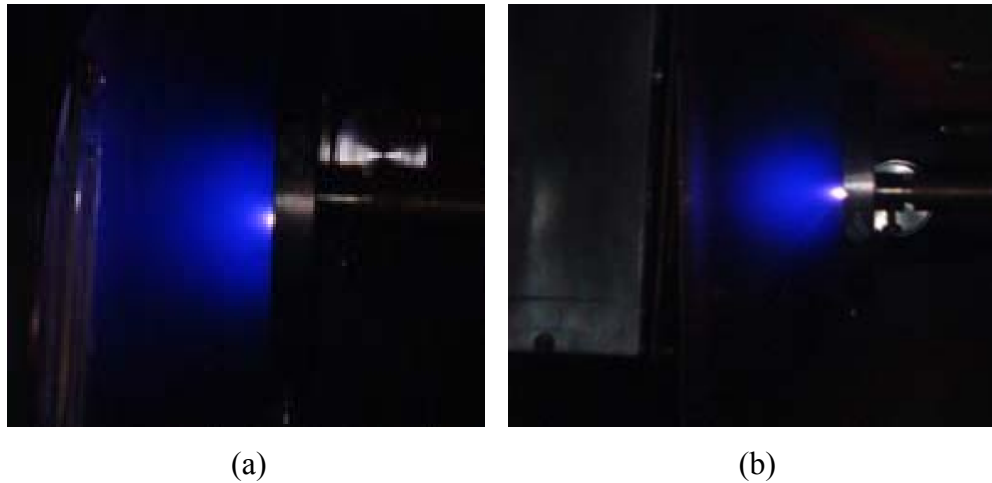


Figure 4.5 Typical picture of the plume generated during laser ablation of an ITO target after 500 pulses (fluence= $4\text{J}/\text{cm}^2$) a) in the vacuum and b) under 1Pa oxygen pressure.

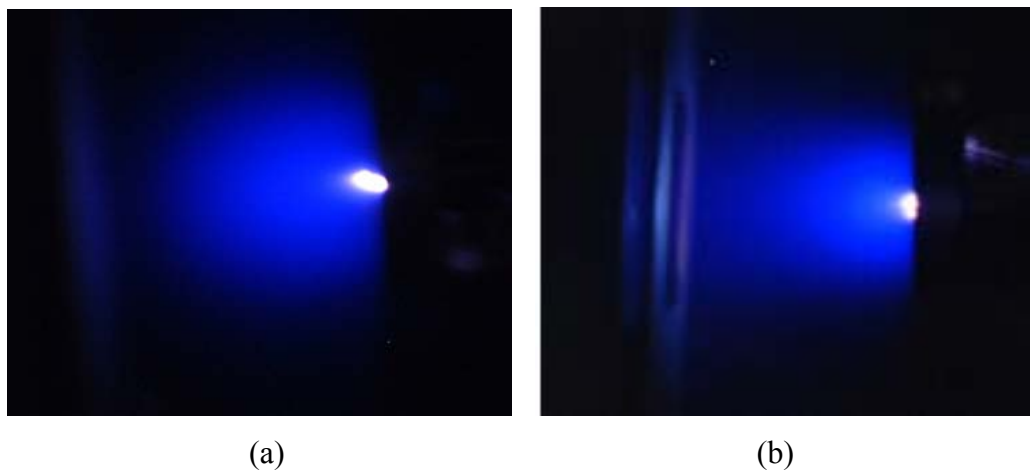


Figure 4.6 Typical picture of the plume generated during laser ablation of an ITO target after 200 pulses (fluence= $4\text{J}/\text{cm}^2$) a) in the vacuum and b) under 1Pa oxygen pressure.

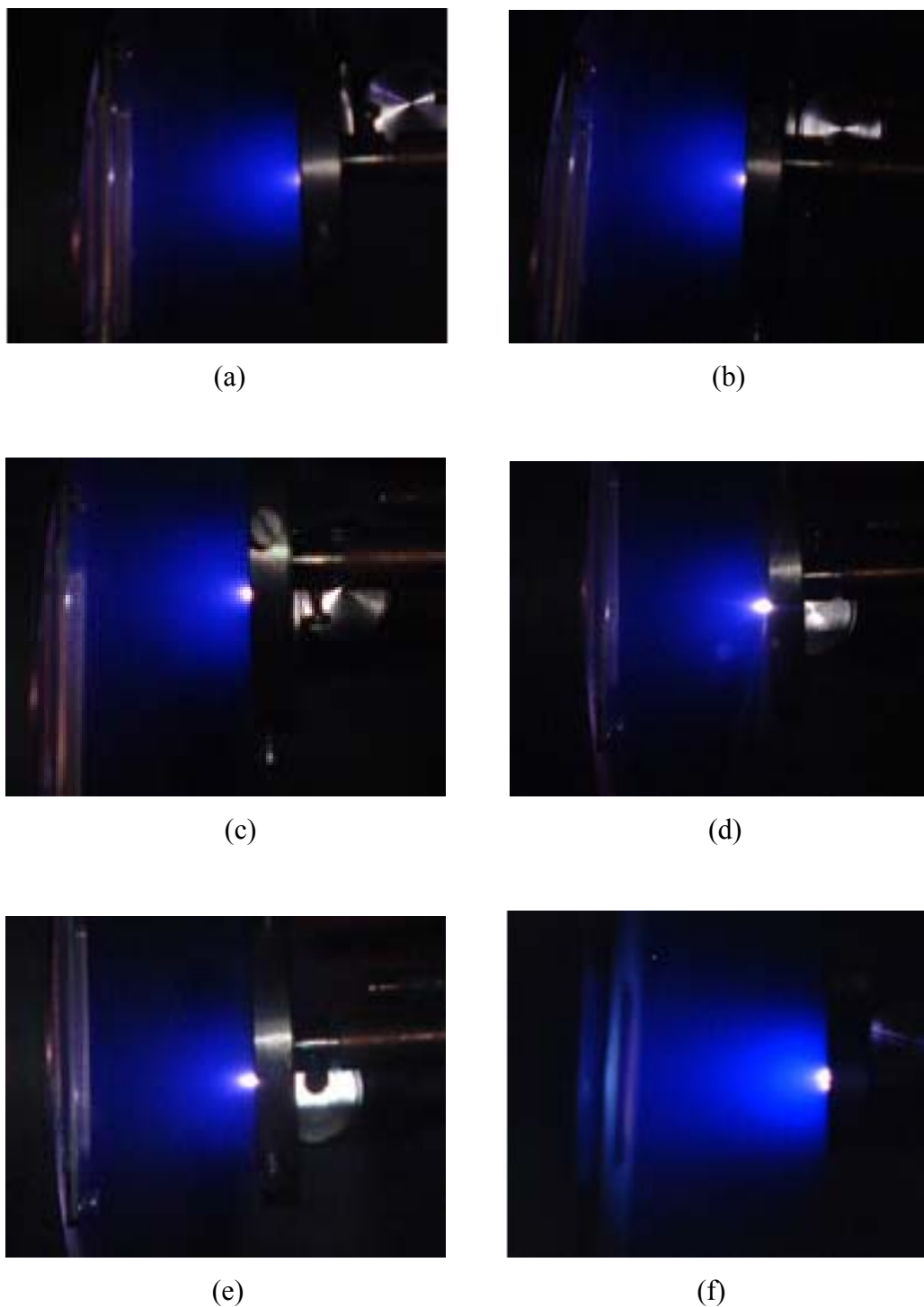


Figure 4.7 Typical picture of the plume generated during laser ablation of an ITO target (fluence= $4\text{J}/\text{cm}^2$) under 1Pa oxygen pressure, a) after 50 pulses b) after 200 pulses c) after 600 pulses d) after 1200 pulses e) after 2000 pulses and f) after 5000 pulses.

The plume deflection from the target normal was observed. It is dependent on the angle between the laser beam and the target and can have a strong effect on the morphology properties of the different films deposited. As it can be seen from the different plume images, the deflection of the plume is strongly evident at the beginning of the laser ablation of the target. After a certain number of laser pulses, the plume is stabilised and looks more symmetric. Generally, it is advised to start the deposition at this instant to ensure more homogeneity of the surface and thickness of the films.

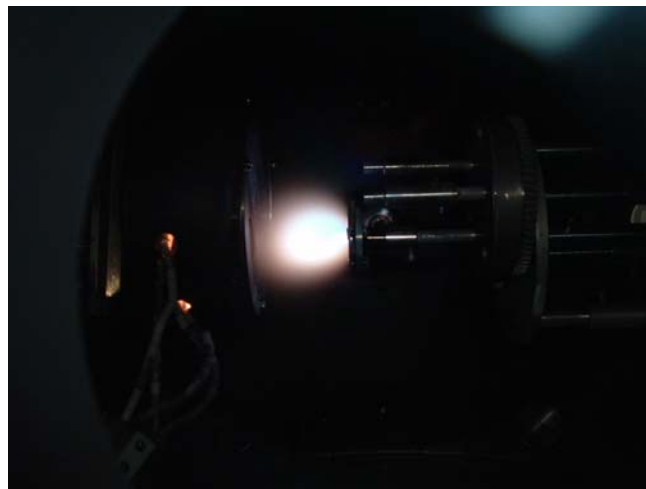


Figure 4.8 Typical picture of the plume generated during laser ablation of a TiO_2 target at $4\text{J}/\text{cm}^2$ and 1Pa .

The groove formation has been one of the first explanations for the deflection of plume towards the direction of the incoming laser beam [181]. The presence of columnar structures, oriented towards the laser beam direction, has been taken as possible explanation. The idea was that the ablated material, being constrained during the first stages of the expansion inside the confined empty spaces between adjacent columns, acquires a well-defined component of the momentum aligned to the directions of growth of the columns [261]. Other explanations were proposed, based on the interaction between laser and plasma [262] or on the magnetic fields created by the gradients of the electron density [263].

However, the plume deflection effect was showed to be always present, in some cases during long laser irradiation whenever the roughness of the irradiated area increased because of the exposure to multiple laser pulses. The models so far reported in literature are not able to explain the origin of this effect, because they are not able to justify the evolution of the plume deflection angle during the ablation experiments. Nevertheless, since today, this effect is still not well understood and there is not a general theory that can explain it. In the last years, the plume deflection effect has been observed for a large variety of laser-ablated targets.

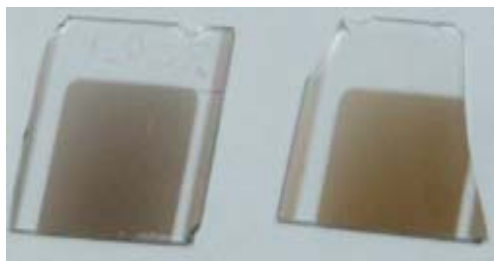
In 1993 Van de Riet et al. [261] tried to associate the deflection of the plume to the formation of oriented μm -size columnar structure on the surface of different irradiated materials. According to them, during the first stage of the gas expansion, the ablated material is constrained to move along the direction of the columns. Then, the average momentum of the ablated material acquires a component towards the direction where the columnar structure point to, namely along the direction of the incoming laser beam. Thus the important role of the target surface roughness with respect to the plume deflection and to the liquid droplets deposited on the substrate has stimulated the study the target morphologies modification induced by laser irradiation. This study of ITO and TiO_2 ablation processes has been performed for the importance, in terms of a symmetric expansion of the plume and on the yield of the ablated material, with respect to the dynamics of each species of the target nanocluster component.

4.6.1 TiO_2 films aspects

The single and double layers thin films submitted to visual inspection were completely transparent, independently of whether they were deposited at room temperature or on heated substrates. In Fig.4.9, the TiO_2 thin films deposited at room temperature, 200 and 400°C on quartz SiO_2 glass substrate can be observed; the films are visually transparent to the naked eyes. Note however that in Fig 4.10, the films were deposited in UHV without oxygen gas. The dark aspect of the film does not encourage any further investigations.



Figure 4.9 TiO_2 thin films deposited at room temperature, 200 and 400°C on quartz SiO_2 glass substrate, the films are visually transparent.



(a)



(b)

Figure 4.10 ITO (a) and TiO_2 (b) thin films deposited at 200°C on Quartz glass substrate in UHV without a reactive gas. No investigation is required as the films are visually non stoichiometric and thus not useful.

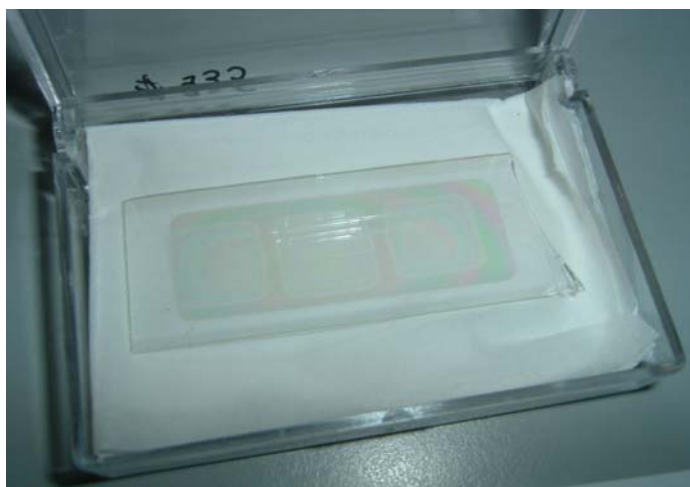


Figure 4.11 TiO_2 thin films (square surface) deposited at 400°C on ITO/ SiO_2 , the films are visually transparent.

A picture of an ITO films deposited at room temperature and 200°C is shown only to emphasise the beneficial effect on the surface quality and visually transparency (a critical parameter for the performance of the films) of the insertion of an O₂ reactive atmosphere into the chamber during the deposition. It has to be noted that the thickness of the three films is different: a lower thickness is observed for the films deposited in UHV without a reactive atmosphere. Details of thickness are given in Table 4.4. Fig 4.11 shows an example of multilayer films ITO/TiO₂ deposited in oxygen reactive atmosphere, again, the transparency is evidenced at naked eye. The ITO film was deposited onto a quartz glass substrate. In order to deposit the TiO₂ films, the ITO film was protected with a lab fabricate mask formed of 3 squares with 2mm separation distance between the squares, as seen in the film picture.

4.6.2 Thin film adhesion

All the films were shown to adhere well to the glass substrates. Although no highly quantitative adhesion tests were performed on these films, several qualitative methods can be utilised to give an indication of their relative adhesive strength. The first of these is the canonical adhesive tape test. It has been used and reported by many researchers and is thus of some utility [262]. This test consists of applying adhesive tape to the surface of the sample to be tested, and pulling the tape off at relatively fast and relatively slow rates. If the sample does not delaminate for fast or slow pull rates, it is judged ‘well adhered’. If the sample does delaminate, the degree and nature of the delamination is noted.

There are several difficulties in obtaining useful results from this method; perhaps the most obvious is that the type of tape used is seldom, if ever, reported. Despite these difficulties, the tape test indicates that prepared samples are ‘well adhered’ to the substrate in some sense. Several ITO, TiO₂ single and multilayers films were examined in this manner, and none showed any degree of delamination for a variety of adhesive tapes. This is particularly important, since some reported samples have had poor adhesion to glass, showing a high degree of delamination, and in severe cases, peeling after exposure to air for several days [262]. In

RPLAD, adhesion is certainly promoted by the relatively high (tens of eV) kinetic energies of plasma plume components.

4.7 Conclusion

Pulsed laser deposition of ITO, TiO₂ and multilayers ITO/TiO₂ thin films, in UHV and O₂ (1-10Pa) atmospheres was successfully demonstrated. Deposition were performed at room and high temperatures on quartz SiO₂ (100), silicon (111) substrates using different laser fluences (4 - 4.5J.cm⁻²). Deposition conditions for each film were described and explained. A representative set of parameters for growing in optimised and un-optimised was presented. All the samples were produced and optimised during this work. The properties of the films deposited are highly dependent on the deposition conditions. In particular the thickness has been studied as a function of the wavelength, temperature, fluence and oxygen pressure. Interesting aspects of both the oxygen pressure and the behaviour of the ablation plume were highlighted. The films obtained were uniform and highly stoichiometric over a large area.

The oxygen pressure has a strong influence on the films deposited properties as well as the laser wavelength and fluence and the substrate temperature. Films deposited in UHV without oxygen atmosphere are found to be thinner and non stoichiometric. Therefore, a proper environment should be selected, depending on the application. For solar cells applications, nanostructured thin films with a high surface roughness produced in O₂ environment are preferred [264-268], since they provide films with a larger surface to volume ratio, nanocrystalline grain size and nanoporosity. To prevent the poor adhesion of the films on the substrate at these high oxygen pressures, heating of the substrate during the deposition is performed. This leads to increase the mobility of the species arriving on the surface [82, 269, 270] thus enhance the uniformity as well as the crystallinity. The deflection of the plume is strongly evident at the beginning of the laser ablation of the target. After a certain number of laser pulses, the plume is stabilised and looks more symmetric.