

CHAPTER 5

RESULTS AND DISCUSSIONS OF THE ELECTRICAL AND STRUCTURAL PROPERTIES

5.1 Structural Properties of Indium Tin Oxide (ITO)

5.1.1 X-rays Diffraction (XRD) measurements

The crystalline structure of the films was studied by XRD. The XRD measurements were performed using a Scintag XDS-2000 diffractometer with a Cu-K α ($\lambda=1.54\text{\AA}$) radiation, 40kV and 35mA power. The diffractometer has a radius of 250mm and is equipped with incident slits of 2mm, incident scatter slits of 3mm, receiving scatter slits of 0.5mm and receiving slits of 0.2mm. Scan step size of 0.02° were used for all the scans. The $\theta/2\theta$ scan will not be presented for all the ITO samples since the XRD spectra of all the samples are very close to the data presented in Fig.5.1 for each category, which is representative of the overall XRD behaviour of the produced ITO films. The XRD spectra of the ITO films deposited at room temperature, 200°C and 400°C are given in Fig.5.1. The spectra show evident amorphous “humps”, with a peak intensity in the range $2\theta=21.9^\circ$. These data are characteristic of the glass substrate, since this hump appears in the XRD spectrum of each ITO film.

The ITO film deposited at room temperature is almost amorphous (Fig.5.1). The spectrum shows only two weak peaks due to the (211) and (222) Bragg reflections. They are shifted towards higher angles, indicating a lower value of the lattice parameter. This may be due to a different stoichiometry of the compound or to compressive stresses, owing to the low substrate temperature and thence low mobility of particles impinging of the cold substrate. This kind of film has been observed by several authors using different deposition methods with a low substrate temperature [271, 272]. The height of the (211) peak indicates a preferential growth of the film in this direction, with grains having a mean lateral dimension of 1nm. Amorphous ITO films could be changed to crystalline ITO films with increasing substrate temperature over 150°C , because the grain size for ITO films increased with increasing of substrate temperature [273].

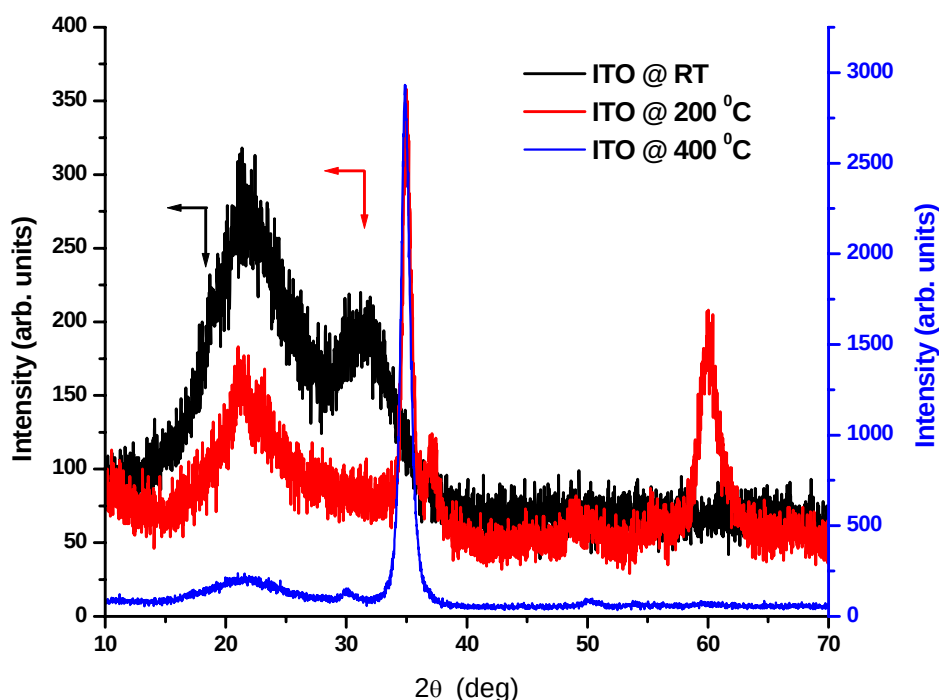


Figure 5.1 XRD patterns of ITO films deposited on SiO₂ substrates at room temperature, 200°C and 400°C.

In the sample prepared at a substrate temperature of 200°C, the amorphous hump (peak at 22.8°) is much less pronounced. Bragg reflections around 34.98°, 37.10°, and 60.00° are observed. These peaks are sharper than the ones recorded in the film deposited at room temperature, suggesting a larger nanocrystalline grain size than in the room temperature case. One could also see small peaks in the 2θ range of 45°, 49°, 50° and 55.5°, which may be useful for phase identification. Thus this film results better crystallised with respect to the room temperature one. The film grows preferentially oriented along the (100) direction and the mean grain size is evaluated to be ~10nm. The (400) peak is shifted towards lower angles, indicating a different stoichiometry of the In₂O₃ compound or a tensile stress.

When the substrate temperature is further increased to 400°C, the amorphous hump appears at 21.65° and the Bragg reflections at 30.10°, 34.89°, and 50.19°. There are hints of small peaks at higher angles in the range of 54° and 60°

(Fig.5.1). The film is highly oriented and results better crystallised than the ITO deposited at 200°C, with grains having a mean lateral dimension of 15nm and a preferential growth along the (100) direction. The (400) peak is a little shifted towards lower angles, indicating a limited tensile stress or a small difference of the compound stoichiometry with respect to the nominal one (In_2O_3).

Where more intense peaks such as (100) and (400) exhibited a very pronounced shoulder towards lower diffraction angle, the relative intensity of this shoulder was noted to decrease with the increase of the substrate temperature. This fact indicates that the layers which produced this diffraction peak are located near the interface with the substrate. The results suggest that the existence of stress in the ITO layers is predominant in films deposited at high temperatures than at room temperature. Residual stress can be separated into: (a) intrinsic and (b) thermal components. The former, which is often called growth stress, is the cumulative results of chemical and microstructural defects included during deposition, while the latter is due to thermal expansion of the film and the substrate during cooling [274]. In the ITO films, it is assumed that the intrinsic stress component, resulting from chemical and microstructural defects, is dominant.

The lattice parameter of the films deposited at high temperature, as determined by XRD data, was found to be $a=10.22 \pm 0.012$ and $c=12.67 \pm 0.016\text{\AA}$ which is larger than the Joint Committee on Powder Diffraction Standards (JCPDS) [275] value ($10.11\text{\AA}$) for the In_2O_3 powder. Same values have been obtained by Kim et al. [211]. They have explained the increase in lattice parameter of the ITO films over bulk materials by the substitutional incorporation of Sn_4^+ ions into In_3^+ sites and/or by the incorporation of Sn ions in the interstitial positions. Lattice parameter data are generally consistent with near-stoichiometry, but experimental errors and the lack of internal stress data rules out any estimate of composition via XRD data. Even if internal stress were accounted for, the accuracy of lattice parameter measurements on the thin films measured is unlikely to be sufficient.

So, one can say that there is a transition from room temperature to 200°C where

the thin film becomes well crystallised. As observed by other authors [272], the transition occurs at temperatures a little bit under 200°C. In the low temperature range studied, the initial growth of ITO films is always via island formation (on the glass substrate). The islands grow and coalesce either via a 2D or 3D process [272]. Below 150-200°C, these islands grow in 3D similar to the Volmer-Weber mechanism. Above 150-200°C, these islands become typically 1 unit cell thick and then grow laterally in a 2D manner according to the Frank-van der Merwe mechanism. The argument is as follows. In the Frank-van der Merwe mechanism, the building blocks grow laterally in a 2D manner. Sun and al. [272] found that the growth of ITO on glass always starts with formation of islands on activated nucleation sites.

At low substrate temperatures, these islands are amorphous. They grow laterally both and in height in a 3D manner. At higher temperatures, when the islands are polycrystalline, the islands first grow to a thickness of about one lattice parameter. They will then grow only laterally in a 2 dimension (2D) manner. The transition temperature between the two modes occurs at 150-200°C. Interestingly, it is found that the transition in growth mode coincides approximately with the change from amorphous film to polycrystalline film formation. X-ray analysis revealed that the ITO films are highly orientated nanocrystals with their a-axis normal to the glass substrate surface. The average particle size of the precipitated nanocrystals was calculated by applying Sherrer's formula [276]. The ITO films are nanopolycrystalline with cubic structure. Lattice constants can be calculated using the formula

$$d_{hkl} = \frac{1}{\sqrt{4 \left(\frac{h^2 + k^2 + l^2}{3a^2 + 1/c^2} \right)}} \quad (5.1)$$

where a, c are the lattice constants and d_{hkl} is the crystalline surface distance for hkl indices.

The present results indicate that highly orientated nanocrystalline ITO films can

be prepared on a moderately heated SiO₂ glass substrate without post annealing treatments. It is seen that apart from the changes in the diffraction peak intensities with increasing substrate temperature, splitting of the peaks also occurred at 400°C. This feature may be caused by the increasing high-energy of the sticking particles on the substrate, due to the increase of the substrate temperature. It must be also taken into account that the kinetic energy of ablated particles was measured to be several electron volts (eV) high, and in the case of PLAD superconducting films, the kinetic energy of the particles was found to be higher than 13eV [203].

It is known from X-ray diffraction that the structure of ITO films deposited by various techniques is strongly dependent on the deposition conditions, such as working gas pressure; substrate temperature and deposition rate [277-279]. Several studies have showed that the ITO thin films diffraction peak splitting is caused by the presence of a two layer structure [273, 280-282]. During the initial growth stage a defective structure that is stressed is formed at the interface with the substrate. As the films becomes thicker than 100nm, a new layer with a lower defect density and less stressed is observed. The fact that it is possible to observe this peak splitting for ITO film thicknesses below 100nm indicates that the transition from the first defective layer towards the higher crystallinity layer started earlier during the growth than in other deposition techniques.

During laser-ablation deposition the substrate is bombarded by energetic species. The kinetic energy of the incoming species colliding with the substrate is transformed into heat and conducted away through the substrate. Since glass has a much poorer thermal conductivity, this might result in a localised heating which will improve crystallinity, thus explain the observed results. However, why the peak position shifts is still puzzling and requires further studies.

5.1.2 Morphological measurements

5.1.3 Thickness and reflectance measurements

The thickness of most of the thin films was measured using two different

techniques: Rutherford Backscattering Spectrometry (RBS) with 2MeV He^+ ions and optical profilometry with a Sentech Film Thickness Probe 500. Using this later technique, it was possible to plot the thickness profile of ITO films deposited. Fig.5.2 represents the thickness profile of the ITO films deposited at room temperature under 1Pa oxygen pressure.

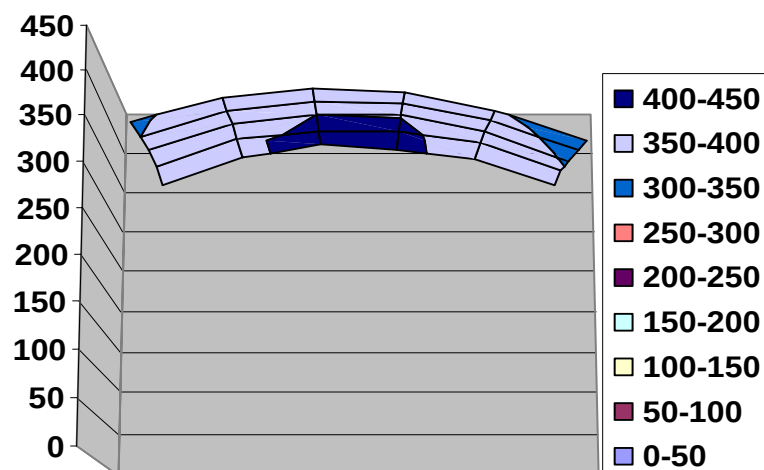


Figure 5.2 Thickness profile of an ITO film showing the thickness uniformity.

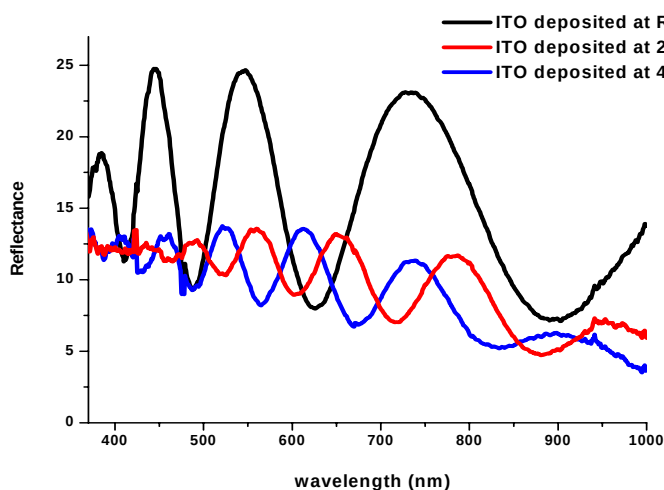


Figure 5.3 Reflectance spectra of ITO films deposited at room temperature, 200 and 400°C, as indicated in the graphs. The behaviour of the oscillations demonstrates the thickness uniformity of the films.

The profile demonstrates that the thickness (~375nm) is very uniform over a large area. This uniformity is also demonstrated by the reflectance measurements (Fig.5.3) of the different ITO films deposited under different temperature. When the film is homogeneous and uniform, one can observe periodical oscillations, due to interference that are proportional to the thickness of the thin film. The oscillations must decrease in intensity as the wavelength increases, while its length should rather increase accordingly.

The thickness value was confirmed with the RBS measurements. Thickness of films deposited at higher temperatures result much lower than the one deposited at room temperature. More details of values of films thicknesses are given in Chapter 4. As the film grows, the reflectivity exhibits a sinusoidal curve, due to the interference effects related to the thickness of the film. In the ideal situation of no absorption and perfect superficial flatness the curve would be perfectly sinusoidal; the effect of the absorption of the film is to damp the curve around a constant average value, while the effect of the superficial roughness is to decrease this average value monotonically with the time.

5.1.4 AFM measurements

The surface topography for ITO films has been studied by several authors using scanning electron microscopy [283-285], and scanning tunnelling microscopy [286]. The morphology, intergrain properties and grain configuration are very important not only for the electro-optical characteristics of the films but also for junction formation, contacting and photon engineering.

In the present work, Atomic Force Microscopy (AFM) was used to study the influence of the substrate temperature on the surface morphology of the laser films deposited. The surface roughness was then estimated. Characteristics are given in Table 5.1. AFM is a recent technique for the investigation of the topography of conducting and non-conducting materials [287-288] and can provide spatial resolution in the nanometer range as well as the atomic resolution under certain conditions.

Table 5.1 Characteristics of ITO films obtained under different deposition temperatures

Substrate temperature (°C)	Grain size (nm)	Mean roughness (nm)	Holes average size (nm)	Holes density (holes/ μm^2)
RT	1	20.6	200	154
200	10	25.9	150	144
400	15	29.9	110	125

Another advantage of AFM is that the images obtained are digital, which means that the data are stored as pixels (each pixel representing the intensity of the signal for that location). This allows measurements of surface features such as angle and roughness and the analysis of the images from different perspectives including simulated three-dimensional representations. For a better analysis and comparison between ITO films surface and substrate surface, a typical 2D image of SiO_2 glass substrate is given in Fig.5.4. The image shows a smooth film, with some holes whose density is about $160\mu\text{m}^2$. Typical images of an ITO film surface deposited at room temperature are shown in Figs.5.5 (2D image) and 5.6 (3D image), respectively. The image shows a rough surface with trenches, which are better seen in the 3 dimension (3D) plot. The Root Mean Square (RMS) roughness of the films is $R_a \approx 26\text{nm}$.

Holes of an average size of 200nm are also present. The density of holes is $\sim 154\text{holes}/\mu\text{m}^2$. The grain size, mean roughness, holes average size and holes density of ITO thin films as a function of the substrate temperatures are presented in Table 5.1. 2D images of ITO films deposited at 200 and 400°C are represented in Figs.5.7 and 5.9, respectively. In Fig.5.8 the 3D image of ITO film deposited at 200°C is represented. As can be seen from the table and pictures, the grain sizes rise with increasing temperature and reach a maximum of about 15nm at 400°C.

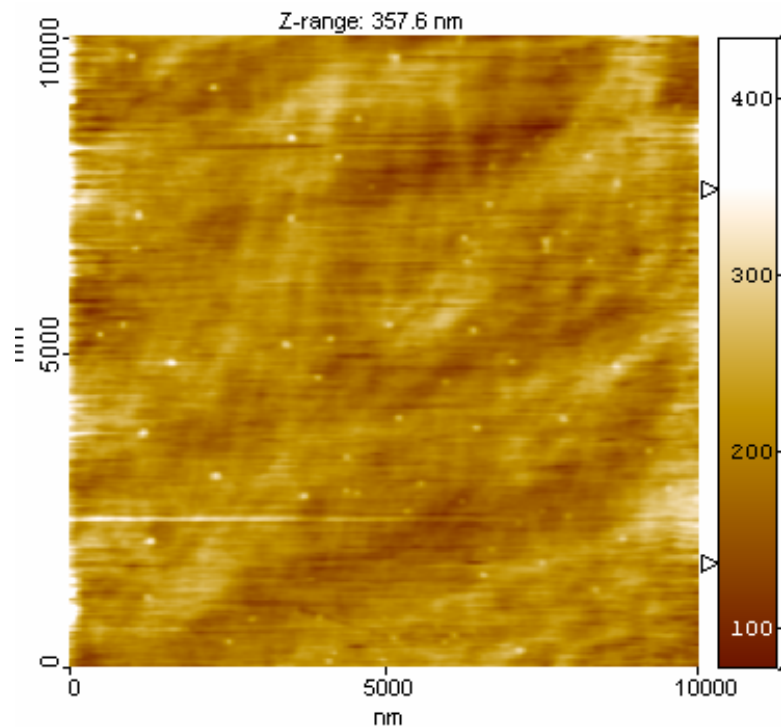


Figure 5.4 2D in top view AFM image of the SiO₂ substrate.

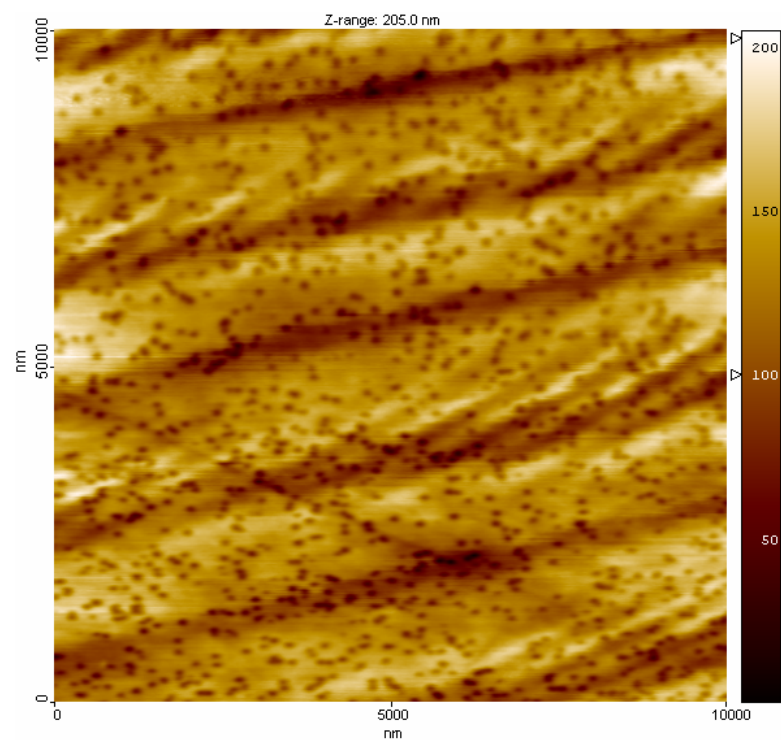


Figure 5.5 2D in top view AFM image of an ITO film deposited at room temperature.

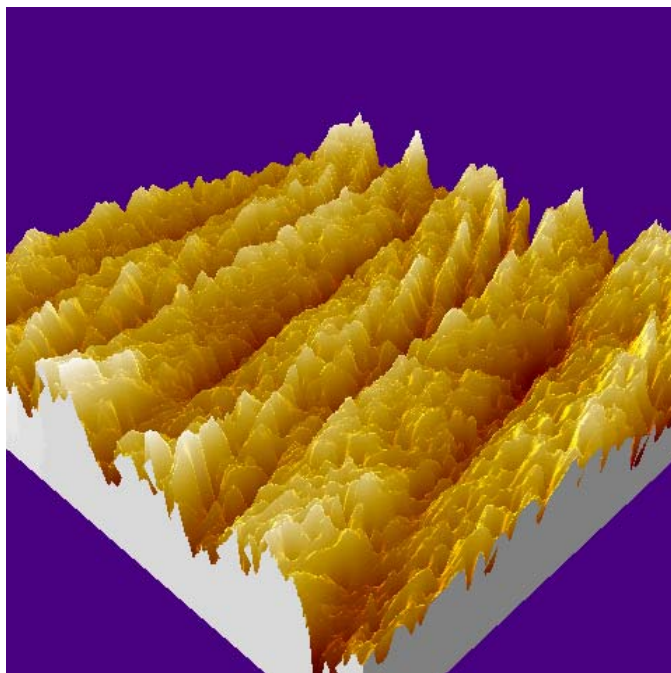


Figure 5.6 3D in top view AFM image of an ITO film deposited at room temperature.

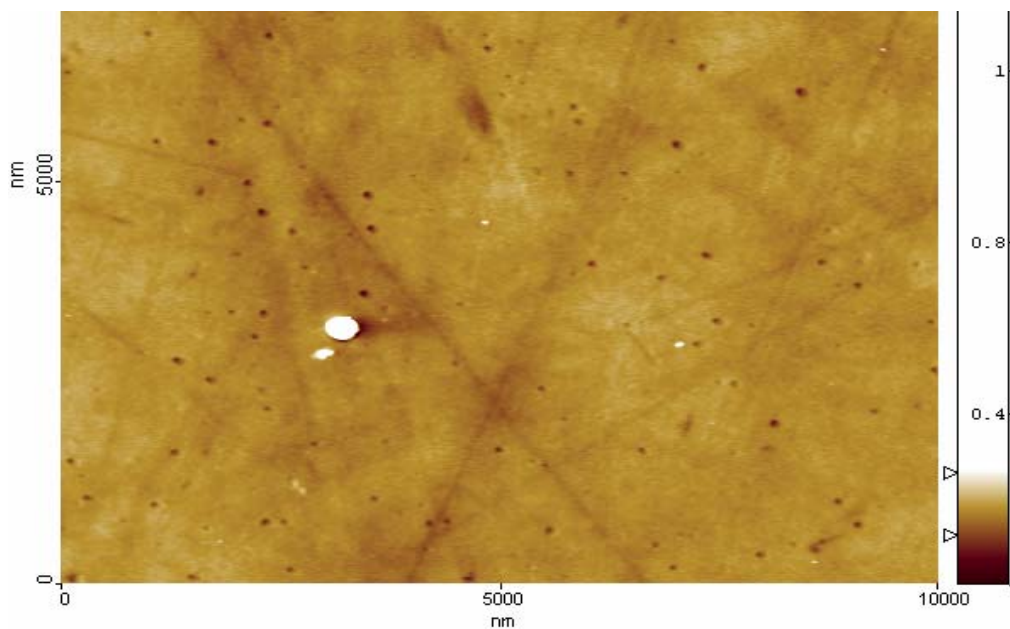


Figure 5.7 2D in top view AFM image of an ITO film deposited at 200°C.

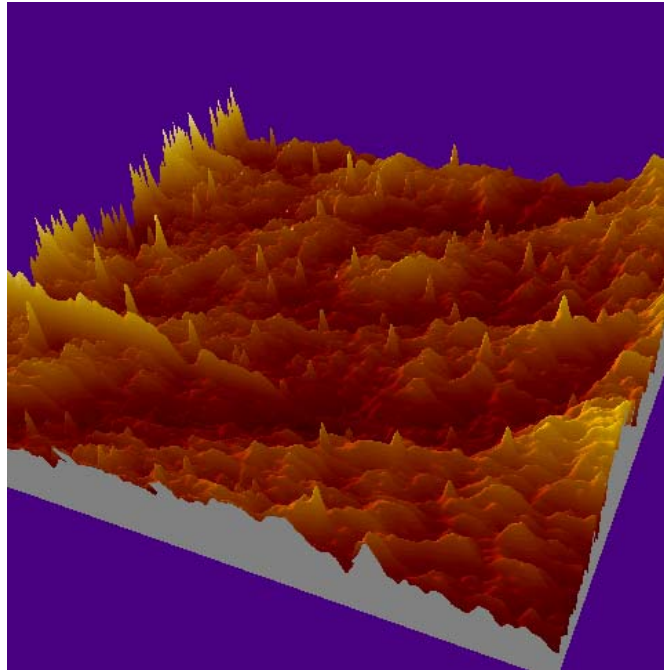


Figure 5.8 3D in top view AFM image of an ITO film deposited at 200°C.

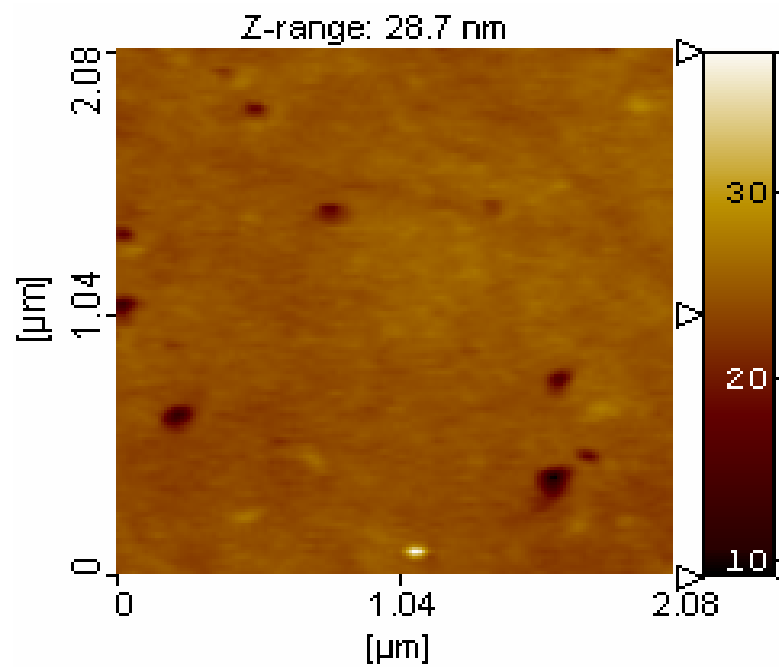


Figure 5.9 2D in top view AFM image of an ITO film deposited at 400°C.

At 400°C, the density of holes is low $\sim 125 \text{ holes}/\mu\text{m}^2$, whereas at room

temperature, it is much higher and reaches $\sim 154 \text{ holes}/\mu\text{m}^2$. The mean roughness at 400°C is about 29.9 nm . Hence, the films at this temperature are the less porous but rougher. Porous substrates attract much interest in solar cell technology, where electrodes with large surface area are especially useful, since they can provide a large surface for supporting a large amount of functional materials such as electrolyte.

A Dye Sensitised Solar cells (DSSC) [51, 196] formed by titania, dye, electrolyte, and a couple electrodes, can be an example. Correlating the results between AFM and XRD, one can observe that for the ITO thin films deposited at 400°C , large grains correspond to well crystallised films with a preferential orientation along the (400) axis. From these results, it is clear that crystallinity improves while porosity of the film decreases with increasing substrate temperature.

These results can be qualitatively explained by using the critical optimisation concept described by Vincett [289-290]. In fact, he observed, from several experimental results, that the films deposited at low temperatures contain crystallised regions and also amorphous or disordered regions. Increasing the temperature to one-third of the boiling point of the substance, the amorphous regions vaporise during the film growth. Thus, their crystallinity improves leading to well-ordered films with a high quality.

Furthermore, the diffusion in the bulk becomes relatively important at the optimal temperature and contributes to the filling of the gaps created by the evaporation of the disordered regions. The formation of pores on top of the ITO films surface is due to the existing pores on the SiO_2 substrate whose origin is unknown. The pores and roughness contribute in enhancing large surface area required for solar cells. The appearance of trenches however remains puzzling and requires further studies.

Roughness profiles for ITO films deposited at room temperature, 200°C and 400°C are represented in Figs.5.10, 5.11 and 5.12, respectively. One can see the

porosity for ITO film deposited at room temperature because holes dominate the profile. These profiles confirm that ITO films deposited at room temperature are more porous and rough than the ones deposited at high temperatures. Over all, the ITO films remain very rough and porous at high temperatures.

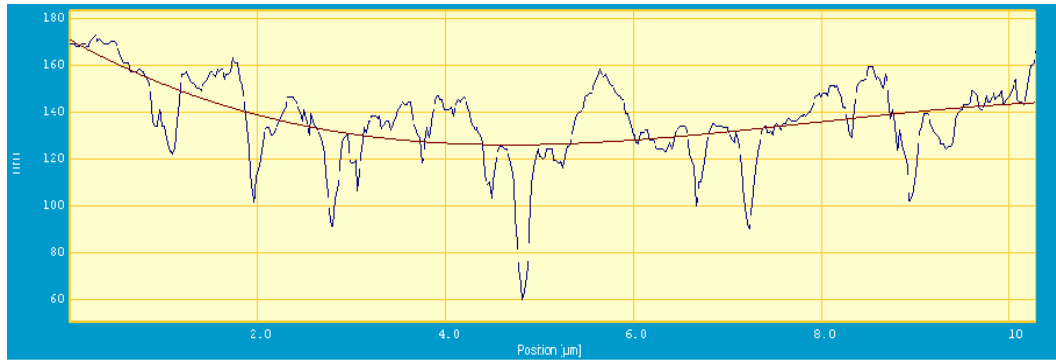


Figure 5.10 Roughness profile of an ITO film deposited at room temperature.

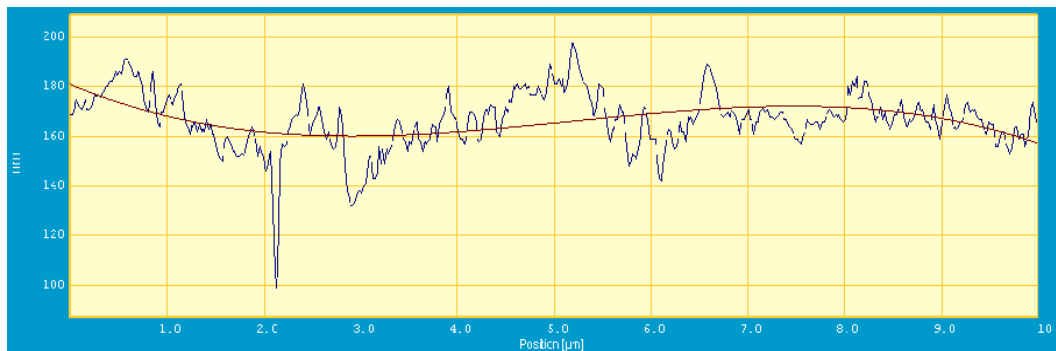


Figure 5.11 Porosity profile of an ITO film deposited at 200°C.

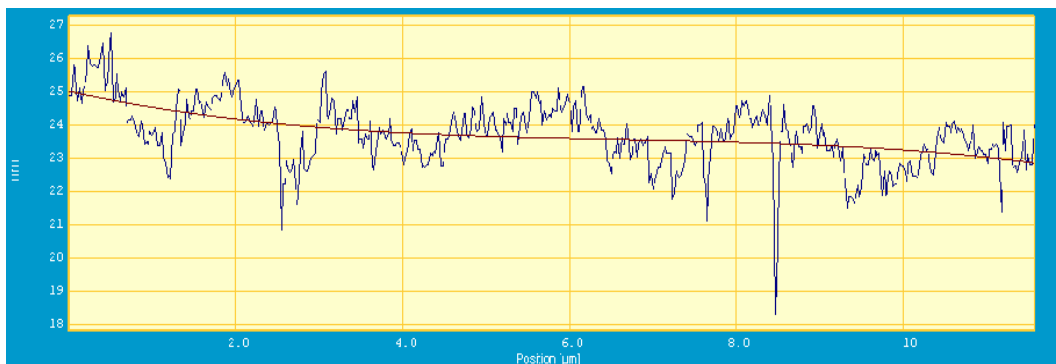


Figure 5.12 Porosity profile of an ITO film deposited at 400°C.

These morphological changes may contribute to the improved optical and electrical properties through reduced scattering. The morphological properties observed for ITO films deposited at room temperature, 200 and 400°C are shown to be well adapted for solar cells applications. Generally it is difficult to prepare porous ITO films with a low resistivity. It was reported that porous ITO film was prepared by introduction of ITO into pores of a Porous Glass (PG) matrix with nano-size pores and thus forming an ITO/PG nanocomposite [291]. The films had pore diameter of 50nm. In the present study, ITO films were prepared on SiO₂ with large pore diameter (~150nm and above) larger than the one reported in previous papers [292]. Thus, the present ITO film is well suited for many practical applications in photoelectric devices.

Moreover, the preparation method can also be used when the pores of the ITO nanocomposite need to be sealed with a flat, dense conductive film. For example, when the ITO nanocomposite is used as an electrode of DSSC, the pores of the electrode need to be sealed because liquid electrolyte will be in the pores. In the other hand, since the ITO films will be used as substrates for deposition of bilayer films ITO/TiO₂ for DSSC applications, the morphology obtained is well adapted because the higher the surface area of TiO₂, the higher the current that is generated by the DSSC [196, 293].

5.1.5 Resistivity measurements

The electrical properties of the films were measured with a Jandel four point resistive probe according to the Van der Pauw configuration, which eliminates the influence of lead resistance. This is necessary in the present case due to the relatively low resistances (less than 1Ω.m). The values for resistivity (ρ) and Hall mobility (μ_H) were then established. In the Van der Pauw configuration the sample is square like, with a contact in each of the corners. Actually any shape is permissible, although this will lead to complications in the data analysis. If we assume that the contacts are numbered from 1 to 4, consecutively around the periphery of the sample, and V_{ijkl} the voltage read between i and j , when the current flows between k and l , then knowing the film thickness, the electrical

parameters may be expressed by [294]:

$$\rho = R \times \pi d / \ln 2, \text{ where } R = 1/4 \times [V_{12}/I_{43} + V_{23}/I_{14} + V_{34}/I_{21} + V_{41}/I_{32}] \quad (5.2)$$

$$\mu_H = 10^8 \ln 2 / B \pi \times [2(V_{1324} + V_{2413}) / (V_{1243} + V_{2314} + V_{3421} + V_{4132})] \quad (5.3)$$

where d is the thickness, B is the magnetic field and R the resistance of the film. The thickness measurements were performed using RBS technique. More details of the thickness values have been given in the previous chapter. The values of the resistivity of the ITO films deposited at room temperature have been found to be significantly affected by the background pressure. Despite their amorphous-like structure, the resistivity of the room temperature ITO films was observed to be fairly low.

Table 5.2 gives the different values of the resistivity and hall mobility of the ITO films deposited under different oxygen pressure and substrate temperature. These values are in agreement with the ones reported in the literature [206, 207]. Details on relationship between oxygen pressure and resistivity for ITO films have been extensively explained in Chapter 4. It is however important to mention that charge carriers play an important role in the resistivity of film as the increase in oxygen pressure leads to a decrease of charge carrier and an increase of the resistivity.

The resistivity of the ITO films deposited at 200°C has been found to be equal to $1.8 \times 10^{-6} \Omega m$ for a film thickness of 400nm. At substrate temperature of 400°C, the resistivity further decreases to $1.5 \times 10^{-6} \Omega m$. Under different substrate temperatures, the resistivity decreased with increasing substrate temperature from room temperature to 400°C. The achievement of the lowest possible resistivity is of practical significance because it provides some freedom in selecting the film thickness to achieve a high optical transmission, while still maintaining low resistivity. In this case, the decrease in resistivity from about $3 \times 10^{-6} \Omega m$ for films deposited at room temperature to $1.5 \times 10^{-6} \Omega m$ for films deposited at 400°C is quite significant.

Table 5.2 Resistivity and hall mobility of the ITO films deposited at different oxygen pressure and substrate temperature

Temperature (°C)	Oxygen pressure (Pa)	Resistivity of the thin films ($\times 10^{-6} \Omega\text{m}$)	Hall Mobility ($\text{cm}^2/\text{V s}$)
Room temperature	1	3.0	22.3
	2	3.3	22.1
	5	3.7	21.2
	10	4.0	20.5
200	1	1.8	51.3
400	1	1.5	52.1

This is due to highly oriented films (400°C) with larger grain size (15nm according to the XRD spectra) versus poorly oriented films (room temperature) with 1-2nm grain size. These values of the resistivity are quite low (relatively to the ones reported in the literature).

The decrease of resistivity at 200 and 400°C may be due to an increase of carrier density with increasing substrate temperature and this in turn can be attributed to the improvement of the crystallinity, which results in decreasing donor sites trapped at the dislocations and boundary scattering [295]. These results strongly suggest the importance of oriented growth along (400) direction and large grain sizes in improving the conductivity of ITO thin films.

Similar results were also observed by other investigators [38, 296]. The resistivity is found to vary very little with the oxygen pressure at high temperature substrate. The best resistivity combining with a high transmittance were found in ITO films deposited at 200°C. For this reasons the multilayers ITO/TiO₂ thin films were deposited with ITO films deposited at 200°C.

5.1.6 Hall mobility

The overall Hall mobility for the films deposited was high. Lower Hall mobility was measured in the films deposited at room temperature. This indicates the existence of high scattering centers in room temperature films deposited, since the mean free paths of the free carriers may be shorter than the average grain size [297]. The room temperature films were characterised with small grain sizes (1nm). At 200 and 400°C, the increase of the Hall mobility could be a consequence of low scattering or migration enhancement of Sn by thermal effect. In this investigation, the highest Hall mobility at room temperature was estimated to be 22.3cm²/Vs under PO₂ of 1Pa and 52.1 and 51.3cm²/Vs for films deposited at 200 and 400°C, respectively. The values of Hall mobility fit very well with all the reported literature data [297, 298].

5.2 Structural properties of TiO₂ and multilayers

5.2.1 Raman measurements

Raman spectroscopy is very helpful in clarifying structure, especially where XRD data are insufficient. Raman spectroscopy was carried out using the 514.5nm line of an Ar⁺ ion laser (laser ionic) at a power level of 100mW in backscattering configuration. The scattered light was analysed with a Spex 1403 double monochromator. The signal was detected with a photomultiplier and a standard photon counting system. Raman spectra of TiO₂ films prepared at room temperature, 200°C and 400°C are represented in Fig.5.13. The spectra of TiO₂ films prepared at room temperature and 200°C present two broad bands near 515 and 639cm⁻¹. They are due to the strong absorption of Rayleigh scattered light by the notch filter at the excitation wavelength. Such a broad Raman spectrum indicates that TiO₂ films produced at room temperature and 200°C are amorphous. Raman spectra of amorphous TiO₂ are sometimes similar to that of rutile but the peaks are sharper in the rutile phase. At 400°C, the presence of the peak situated at 519cm⁻¹ is an indication that some anatase TiO₂ crystallites were obtained but the transition was not completely done.

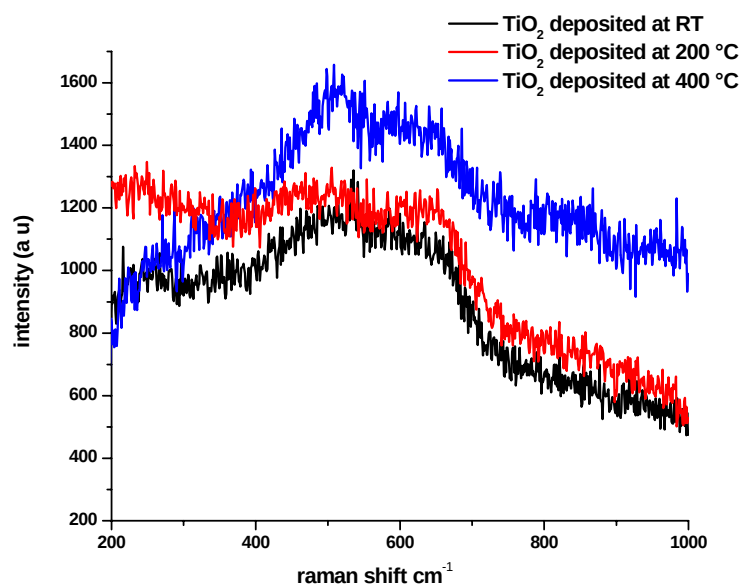


Figure 5.13 Raman spectra of an amorphous TiO_2 film deposited at room temperature, 200 and 400°C. At 400°C the TiO_2 film begin crystallisation into the anatase phase.

This peak (519cm^{-1}) corresponds to the fundamental B_{1g} vibrational mode of the monocrystal anatase TiO_2 [299]. Since these films are deposited with the aim to use them as DSSC electrodes, the low crystalline structure of TiO_2 film deposited onto SiO_2 fused quartz compared to well crystallised TiO_2 film may give rise to the significant increasing of charge recombination, resulting in the significant photocurrent drop [300]. An attempt to obtained better crystalline films has been made by annealing at 300°C and 500°C for 3h consecutively the TiO_2 deposited at 400°C. Raman measurements were performed and results are given in Fig.5.14.

The Raman spectrum of the annealed films clearly shows that the transformation in anatase was almost complete: there are no indications of amorphous phase. A strong sharp band at 148.85cm^{-1} , three mid-intensity bands at 402.93 , 518.65 , and 638.49cm^{-1} and a weak band at 197.35cm^{-1} can be observed. Including the superimposition of two fundamental peaks near 518.65cm^{-1} [219], these six peaks correspond to the six fundamental vibrational modes of anatase TiO_2 with the symmetries of E_g , E_g , B_{1g} , A_{1g} , B_{1g} , E_g , respectively [299].

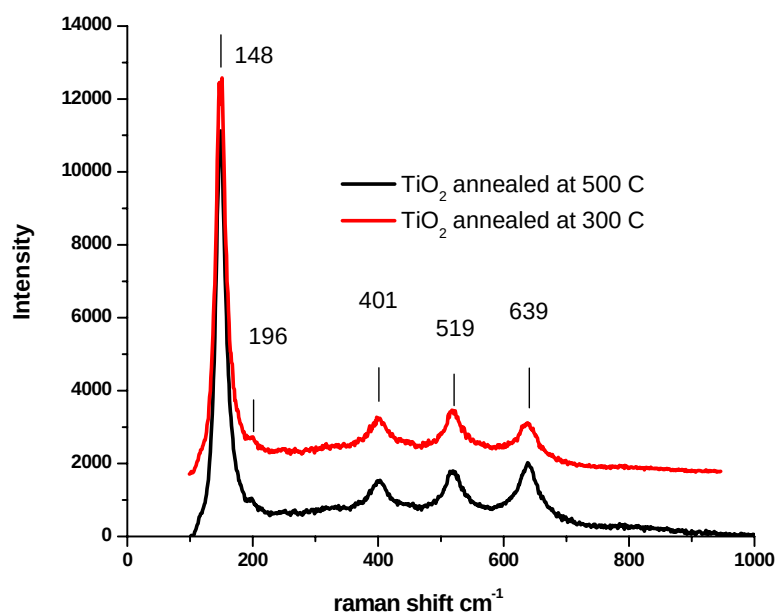


Figure 5.14 Raman spectra of TiO₂ films deposited at 400°C and then annealed at 300°C and 500°C (as indicated on the graphs) for 3 consecutive hours. The transformation of TiO₂ structure into anatase phase is almost complete.

The shift toward higher angle may be an indication of the low lattice parameter or of smaller crystal size. The spectroscopic characteristics of Raman peaks of TiO₂ films are related to crystal size. If the effect of surface defects is neglected, the anatase Raman peaks shift to higher frequencies and their Full-Width at Half-Maximum (FWHM) increase when the crystal size decreases [301, 302]. The FWHM of the most intense peak of the TiO₂ film annealed at 300°C is about $18.30 \pm 0.33\text{cm}^{-1}$, while the one of the TiO₂ film annealed at 500°C is around $19.60 \pm 0.30\text{cm}^{-1}$. From the peak position and FWHM of the most intense structure one can derive the dimensions of the nanocrystals of TiO₂ [42]. Crystal average size was about 22.1nm for the TiO₂ film annealed at 500°C, while it is about 18.7nm for the TiO₂ film annealed at 300°C (Table 5.3). In this study, the Raman peak positions for the TiO₂ films after annealing at 300 and 500°C are almost coincident with those of the monocrystal and the polymorphs to within $\pm 4\text{cm}^{-1}$ at 638.49, 518.65 and 402.93 cm^{-1} .

Table 5.3 Peak positions and FWHM's of the different modes of anatase TiO₂ films annealed at 300 and 500°C for 3 consecutive hours

Preparation conditions	Peak positions/FWHM (cm ⁻¹)				Crystal size (nm)
TiO ₂ annealed at 300°C	150.86/ 16.32	402.93/27.71	519.20/23.60	638.49/ 33.67	18.71
TiO ₂ annealed at 500°C	148.85/ 15.25	402.93/24.75	518.65/23.42	638.49/ 26.60	22.1

When the annealing was done at 300°C, the peaks at 148.85, 197.35, and 518.65cm⁻¹ corresponded to 150.86, 200.45, and 519.20cm⁻¹, respectively as seen in Table 5.3. There was no shift for the other two Raman bands at 402.93 and 638.49cm⁻¹. As shown in Table 5.3, all the FWHM values of anatase peaks decrease when the annealing temperature increases from 300 to 500°C. Kelly et al. [301] reported in detail the effect of crystal size on the Raman spectra of TiO₂ aerogels. They showed that the Raman bands of anatase at 638 and 148cm⁻¹ had apparent shifts only when the crystal size was smaller than 15nm, while the FWHM values continued to decrease with increasing crystal size up to 25nm. Busca et al. [302] reported a small E_g band shift from 638 to 640cm⁻¹ but a large FWHM increase from 20 to 30cm⁻¹ when the crystal size decreased from 50nm to 9nm. Therefore, the FWHM values are more sensitive than peak position to the size change, especially in the crystal size range of 20 to 50nm [219].

The crystal size of these thin films is in the range where the Raman band positions are weak functions of crystal size. Hence, there are only slight shifts in the band positions, probably due to quantum size effects.

5.2.2 XRD measurements

The XRD spectra of the bilayered ITO/TiO₂ films are represented in Fig.5.15. The ITO films were deposited at 200°C while the TiO₂ films were deposited at room temperature, 200 and 400°C. The data show that the current TiO₂ film deposited on ITO does not give additional peaks related to TiO₂, aside from a small onset peak at about 19.5°, which occurred for TiO₂ film deposited at 200 and 400°C. Knowing that XRD anatase peak generally occurs near $2\theta \approx 23^\circ$, one could easily say that this one is related to the TiO₂ layer with the peak shifted to lower diffraction angle because of the existence of strains [256].

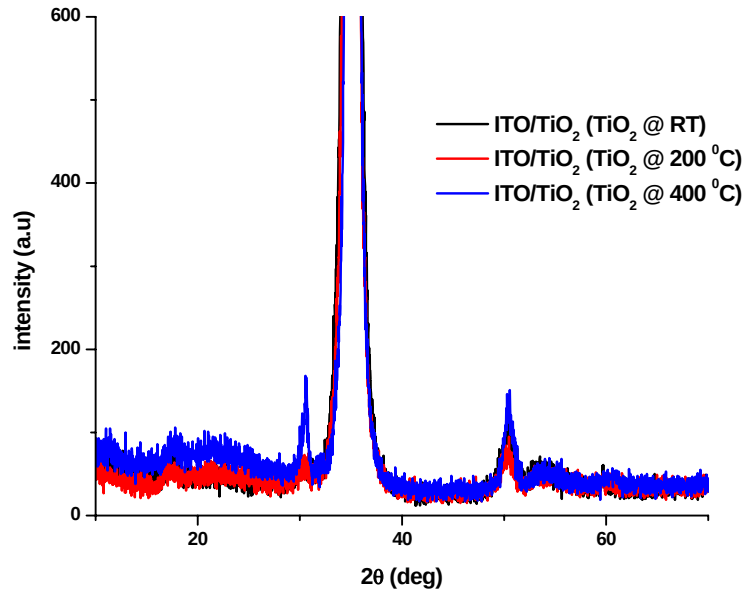


Figure 5.15 XRD patterns of ITO/TiO₂ thin films deposited on SiO₂. The ITO is the previously deposited ITO film at 200°C, while the TiO₂ films are deposited at room temperature, 200°C and 400°C.

The peak is attributed to the (101) lattice plane reflection of the tetragonal anatase TiO₂ monocystal phase [275]. In contrast with TiO₂ film deposited on SiO₂, onset formation of crystalline TiO₂ anatase occurs at 200°C when it is deposited on the predeposited ITO film. The possible formation of anatase crystal at temperature lower than 400°C could be fostered by the crystalline structure of the ITO films,

which is the substrate in this case. These measurements are in agreement with the Raman spectra, where onset formation of anatase crystal was apparent for TiO₂ film deposited without annealing.

All these films show strong Bragg reflections at 30.7°, 35.0° and 51.0°, corresponding to the ITO layer. All peaks sharpen with annealing at increasing temperature, due to phonon confinement effect. The strong amorphous hump characteristic of the substrate is essentially absent, and this is especially noticeable upon comparison with prior ITO films scans. The XRD spectra of the bilayered ITO/TiO₂ films with and without annealing are represented in Fig.5.16. The ITO films were deposited at 200°C, while the TiO₂ films were deposited at 400°C. The presence of the peak at about 23.48° in the spectrum of ITO/TiO₂ after annealing, which did not exist in the spectrum of ITO/TiO₂ without annealing, is a good indication that anatase TiO₂ film was obtained. The peak has a FWHM of 0.48° corresponding to crystal size of ~ 6-7nm.

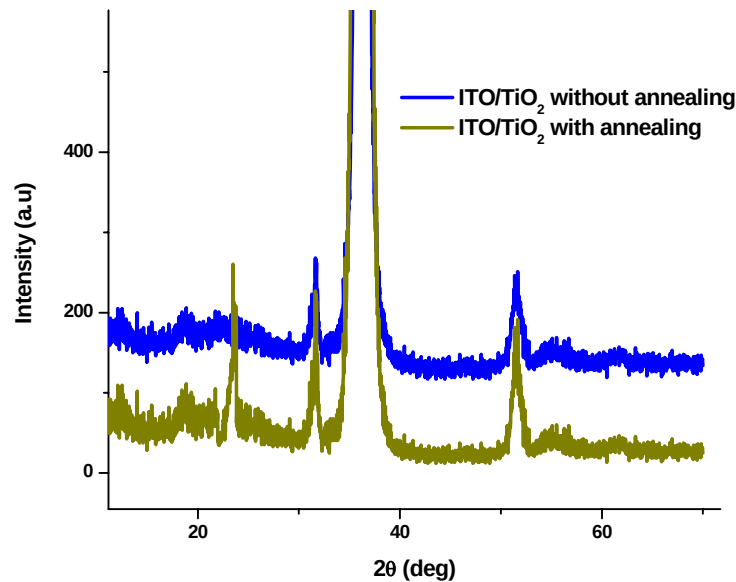


Figure 5.16 XRD patterns of ITO/TiO₂ thin films deposited on SiO₂. The ITO is the previously deposited ITO film at 200°C, while the TiO₂ is deposited at 400°C and annealed at 500°C as indicated on the graphs.

5.2.3 Surface morphology and cross section measurements

The surface morphology and cross-sections of the thin films were observed by Scanning Transmission Electron Microscopy (STEM). The thin films were cut into 5x10mm pieces, and two pieces were glued face-to-face using an epoxy resin. Thin slices of about 1mm were cut from this sandwich and further polished. These thin strips were mounted on 3mm STEM grids, and further thinning was carried out with a Gatan Argon sputter ion mill until the sample was electron transparent for observation using STEM. The STEM cross section of the ITO films deposited at 200°C on SiO₂ is represented in Fig.5.17. The picture shows a uniform and porous surface without cracks or other defects. The film thickness from light interference was estimated to be around 600nm. The actual film thickness from STEM observation, however, was found to be 0.8μm. This difference can be attributed to the porosity observed in the films.

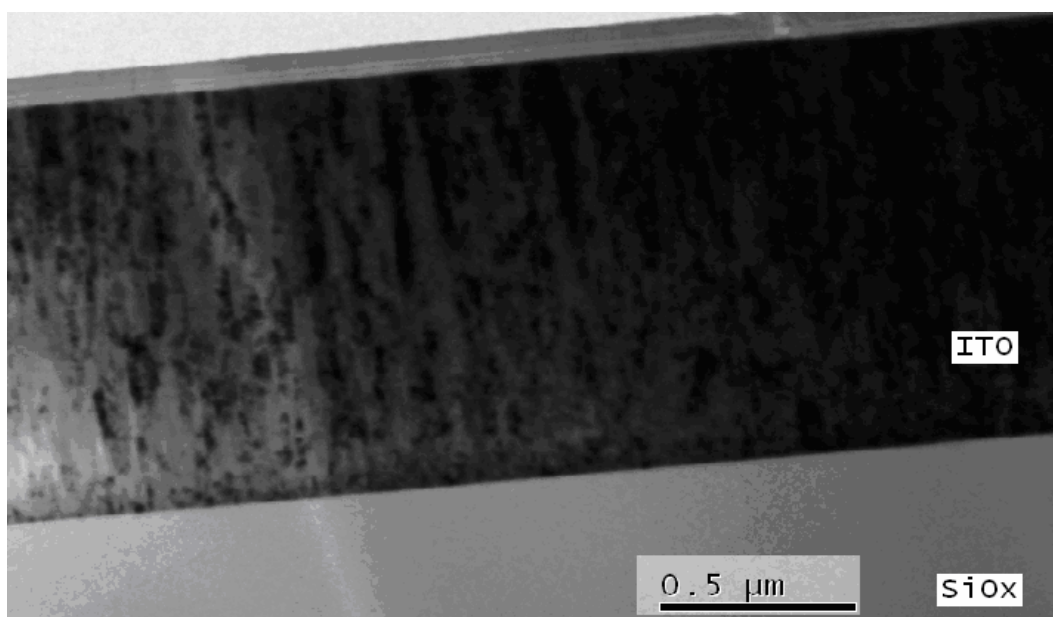


Figure 5.17 Cross section of an ITO film deposited on SiO₂.

Fig.5.18 shows the STEM micrographs of the surfaces of TiO₂ films deposited on SiO₂ at room temperature (a), 200°C (b) and 400°C (c). In (d) the surface of the ITO/TiO₂ film deposited on SiO₂ is shown in lower resolution, before the post annealing treatments. The ITO film was deposited at 200°C, while the TiO₂ film

was deposited at 400°C. Rough surface is observed for the film deposited at room temperature. The roughness decreases as the temperature increases. Moreover, TiO₂ film deposited on the predeposited ITO film present a porous surface, as can be seen in Fig.5.19. In this figure, one can observe the surface of a TiO₂ film deposited on ITO, after post annealing treatments (a). In (b), the cross section of the bilayer ITO/TiO₂ is given.

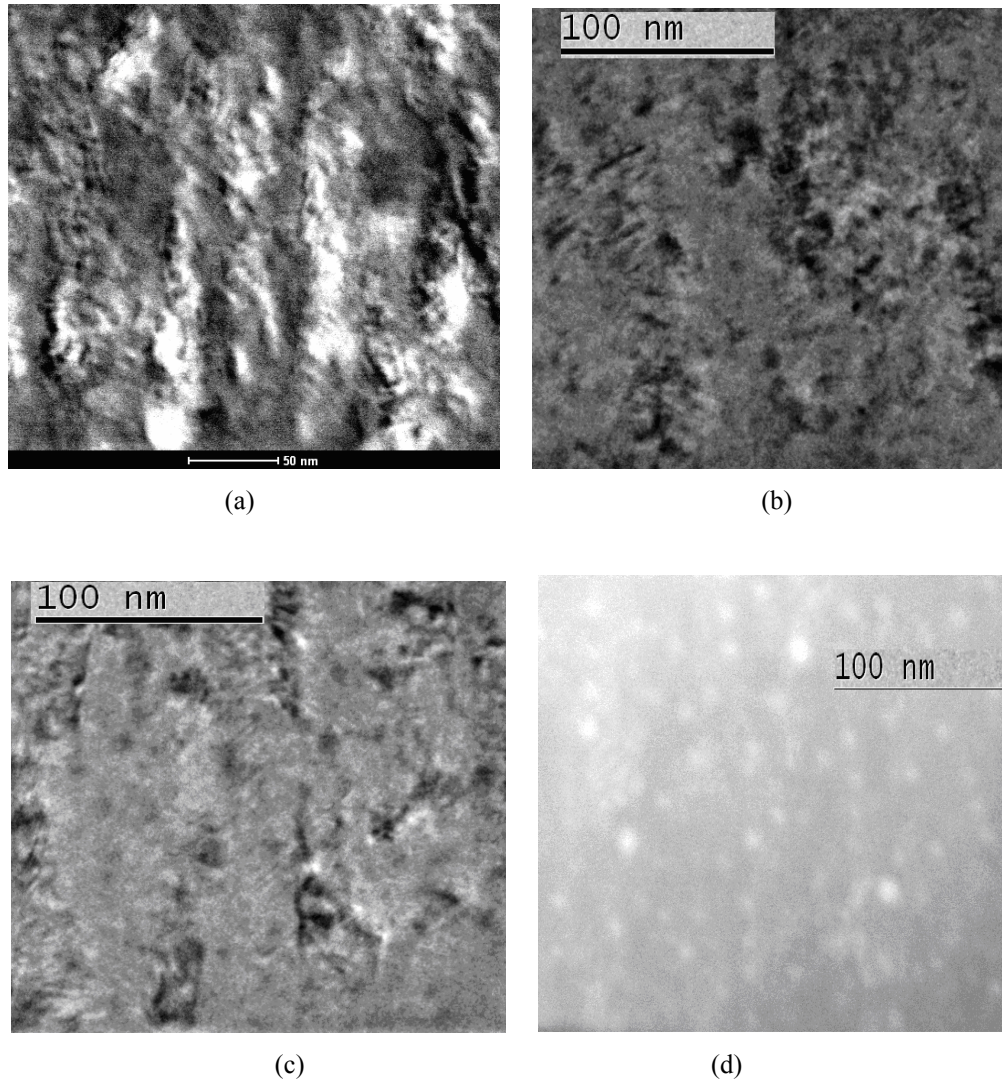


Figure 5.18 STEM surface of TiO₂ films deposited on SiO₂ at room temperature (a), 200°C (b) and 400°C (c). In (d) the surface of the ITO/TiO₂ film deposited on SiO₂ at 200°C before the post annealing treatments is shown.

The fact that the surface of the TiO_2 film deposited onto ITO is porous is due to the porous surface of the ITO films itself. The STEM images of the films confirm the relatively high pore size, with an average pore diameter of $\sim 40\text{nm}$ and excellent uniformity. It is interesting to note that the pores are randomly arranged, in contrast to the ordered structures reported for dip-coated films [303]. Such morphology was obtained for mesoporous TiO_2 films prepared by modifying sol-gel methods [304], where pore size was about 7nm . The random arrangement of the pore network may actually be beneficial for producing a uniform electrode. The cross-sectional analysis of these films showed a columnar structure, but no evidence of voids in the structure.

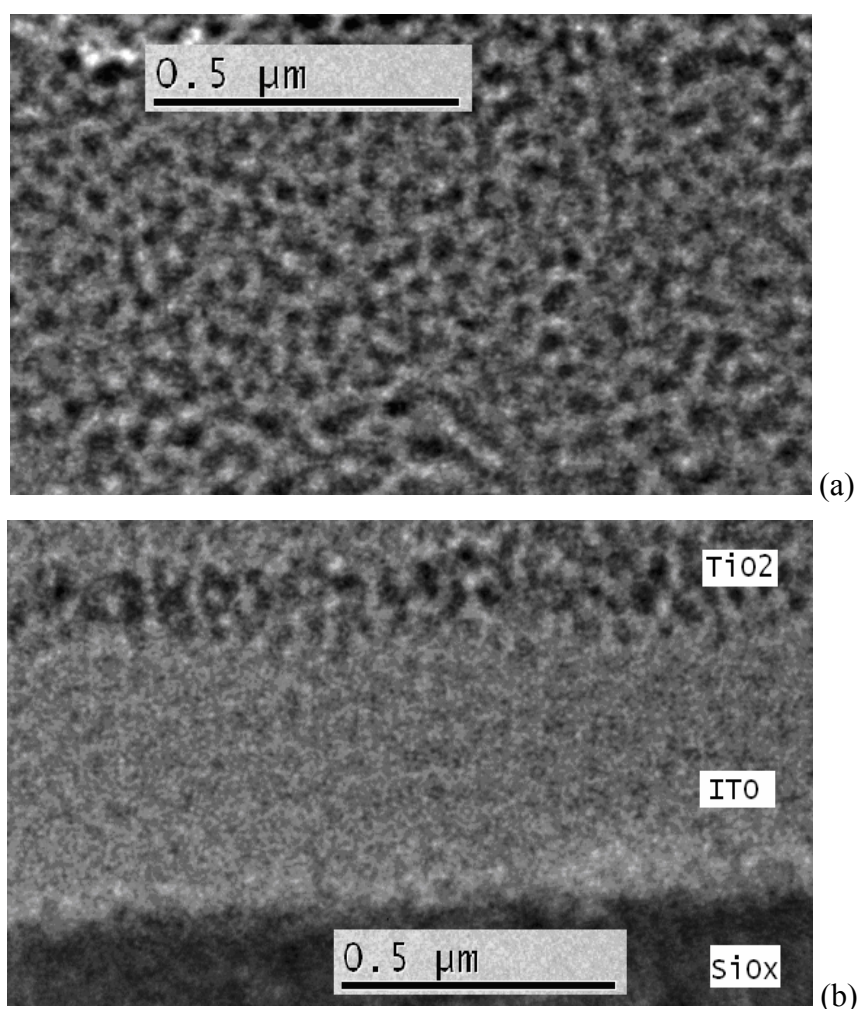


Figure 5.19 (a) Surface of a TiO_2 film deposited on ITO after post annealing treatments; (b) Cross section of an ITO/ TiO_2 bilayer.

Nanoporous titania with thickness of several μm and a large surface area is usually required to support a large amount of dye for obtaining a high light-to-energy conversion efficiency. There may be, however, limitation for further increase of the thickness of titania, because thick porous titania may increase its electric resistance, which in turn restrain electron transfer from titania to electrode [303]. If the electrode used in dye-sensitised solar cell is nano-porous, the pores are expected not only to provide a huge surface, which can support a larger amount of functional materials of titania and dye, but also to decrease the thickness of titania layer, therefore to decrease its resistance as stated above.

Consequently, the large surface area formed by the porous electrode may increase photoelectric device's functions such as the energy conversion efficiency drastically. Moreover, the specific surface area of TiO_2 is closely related with its particle size. The smaller the particle sizes of TiO_2 film, the larger the specific surface area thereof. For the TiO_2 nanocrystal between 1 and 10nm in size, the band-gap energy of TiO_2 film depends on the particle size due to the quantum size effect: the smaller the particle sizes, the higher the band-gap energy [304, 305].

5.3 Conclusion

The aim of this investigation was to deposit high quality ITO thin films by RPLAD with the intention of using them as substrate for TiO_2 thin film deposition. Experimental conditions necessary to obtain crystalline layers with a high porosity and roughness were determined. From structural measurements, it results that ITO films deposited at room temperature temperatures show very poor crystallinity, while ITO films deposited at 200 and 400°C are much better crystallised. At 200°C, the film grows preferentially oriented along the (100) direction and the mean grains size is evaluated to be $\sim 10\text{nm}$. The (400) peak is shifted towards lower angles indicating a different stoichiometry of the In_2O_3 compound or a tensile stress.

At 400°C the ITO films with grains having a mean lateral dimension of 15nm and a preferential growth along the (100) direction was obtained. The (400) peak is a

little bit shifted towards lower angles, indicating a limited tensile stress or a small difference of the compound stoichiometry with respect to the nominal one (In_2O_3). The onset of crystallisation resulted in the formation of a two layer structure containing a defective layer that decreased the carrier mobility. AFM studies revealed that the ITO thin films deposited were highly porous. The porosity decreases with increasing the substrate temperature during deposition.

The optimisation between the morphological feature, specific and surface area of TiO_2 was found to give rise to significant enhancement of a overall conversion efficiency of DSSC [300]. To achieve such properties, TiO_2 films with a high specific surface area due to porosity were annealed at 300 and 500°C for 3 consecutive hours. Raman spectra showed that results of annealing produced pure anatase TiO_2 films both on SiO_2 glass substrate and on ITO films predeposited[305]. STEM measurements suggested that TiO_2 deposited at room temperature is rougher than the films deposited at 200 and 400°C. Porous oxides represent an interesting material for DSSC. Synthesis methods based on the use of block copolymers lead to materials with very small pore diameters ($< 10\text{nm}$). In this work, uniform pores size of an average diameter of 40nm was obtained for TiO_2 film deposited on the ITO film predeposited.