

Characterization of Undoped Spray-Deposited ZnO Thin Films of Photovoltaic Applications

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Abstract: Undoped polycrystalline ZnO thin films were produced on glass substrates at a substrate temperature $T_s = 450^\circ\text{C}$ by the spray pyrolysis (SP) technique. The films were characterized by analyzing their I-V curves, transmittance, X-ray diffractograms (XRD) and their scanning electron microscope (SEM) images. The I-V plots are all linear and the resistivity was found to be about $200 \Omega\cdot\text{cm}$. The transmittance in the visible and near infrared regions is as high as 85% which is suitable for solar cell applications. The absorption coefficient which is deduced from the transmittance measurements is continuously increasing with the photon's energy and it rapidly increases around and after the absorption edge. In the low energy side the absorption coefficient shows the exponential behavior which is known as Urbach tailing, that is related with localized states. The width of the tail was predicted and found to be 0.969 eV. By assuming a direct optical transition, the bandgap energy was estimated and found to be about 3.27 eV. X-ray diffraction patterns revealed that the films have a hexagonal wurtzite structure and that they are highly ordered with a preferential orientation (002). The grain size was estimated by using Scherrer formula and found to be 30 nm, which means that the films have a nanocrystalline nature. The presence of very weak lines in the XRD diffractograms is evidence on the presence of nanocrystallites of much smaller size than the estimated one. The SEM image shows that the surface is uniform and completely covered with material. The grains appearing in the SEM micrograph have a much greater size than that estimated from XRD diffractograms which means that they are aggregates of much smaller crystallites.

Keywords: Spray pyrolysis, thin films, transparent conducting oxide, Urbach tail, solar cells.

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1 Introduction

Zinc oxide (ZnO) is a wide band gap compound which had received a growing attention as a window material, transparent electrode and active layer in different types of solar cells, UV emitters, and UV sensors [Song (2008); Studenikin; Golego and Cocivera (1998 a); Studenikin; Golego and Cocivera (2000)]. In addition, it has interesting properties such as; low cost, availability, non-toxicity and high chemical stability in reduction environments [Song (2008)]. ZnO is emerging as an alternative candidate to more expensive indium tin oxide because zinc is about a factor of 1000 more abundant than indium in the Earth's crust. ZnO films made without any intentional doping exhibit n-type conductivity, caused by a deviation from stoichiometry due to native defects. Traditionally, two intrinsic defects most commonly are reported in the literature as dominant background donors in ZnO, namely the oxygen vacancy (V_O) and interstitial Zn (Zn_I) [Song (2008)].

There are different methods to prepare ZnO thin films; for example: reactive sputtering [Rusu, I. D and Rusu I. I. (1999-2000); Song (2008)], laser ablation [Singh; Mehra; Yoshida and Wakahara (2004)], chemical-vapor deposition [Natsume; Sakata and Hirayama (1995)], laser molecular-beam epitaxy [Segawa; Ohtomo; Kawasaki; Koinuma; Tang; Yu and Wong (1997)], thermal evaporation [Fouad; Ismail; Zaki and Mohamed (2006)], sol-gel [Musat; Rego; Monteiro and Fortunato (2008)], atomic layer deposition [Saito; Watanabe; Takahashi; Matsuzawa; Sang and Konagai (1997)] and spray pyrolysis (SP) [Ebothé; El Hichou; Vautrot and Addou (2003); El Hichou; Addou; Bougine; Dounia; Ebothé; Troyon and Amrani (2004); Studenikin; Golego and Cocivera (1998 a); Natsume; Sakata and Hirayama (1995); Ikhmayies; Abu El-Haija and Ahmad-Bitar (2010); Studenikin; Golego and Cocivera (1998 b)]. As a method of film preparation, SP is simple, cheap and flexible, and is adaptable to large area depositions [Studenikin; Golego and Cocivera (1998 a); Ikhmayies (2002)]. The optoelectronic properties of ZnO films are affected by the preparation conditions such as working pressure, substrate temperature, types of substrates, thickness of the films, and annealing temperature [Kavak; Tuzemen; Ozbayraktar and Esen (2009)].

Many authors had investigated the properties of spray-deposited undoped ZnO films. For example, Studenikin; Golego and Cocivera (1998 a) studied the optical and electrical properties of undoped ZnO films. Lokhande and Uplane (2000) studied the structural, optical and electrical properties of highly oriented ZnO films. Studenikin; Golego and Cocivera (1998 b) studied the fabrication of green and orange photoluminescent of undoped ZnO. Slow photoconductivity transients were comprehensively studied in ZnO films by Studenikin; Golego and Cocivera (2000). A study has been undertaken by Mazón; Muci; Sa-Neto; Ortiz-Conde; García (1991) to establish the influence of the principal process variables on the electri-

cal and optical properties of the films. Ebothé,; El Hichou; Vautrot and Addou (2003) studied the flow rate and interface roughness of ZnO thin films, and El Hichou; Addou; Bougine; Dounia; Ebothé; Troyon and Amrani (2004) studied the cathodoluminescence properties of undoped and Al-doped ZnO thin films. In this work we produced ZnO thin films for the use as forecontacts in solar cells. We studied the structural, electrical and optical properties of the produced films. Some of our results are consistent with the results of those authors and others are different. In the optical properties sub-section we estimated the width of Urbach tail, which-according to our knowledge- had not been obtained for undoped spray-deposited ZnO thin films by anyone before.

2 Experimental

Many researchers had prepared ZnO thin films by spray pyrolysis technique using different sources as ingredients. Zinc acetate was used by many authors, for example [Sanchez-Juarez; Tiburcio-Silver and Ortiz (1998); Musat; Rego; Monteiro and Fortunato (2008); Lokhande and Uplane (2000)]. Others used zinc nitrate, for example [Studenikin; Golego and Cocivera (1998 a); Studenikin; Golego and Cocivera (1998 b); Studenikin; Golego and Cocivera (2000)]. Others prepared ZnO films by using zinc chloride in the precursor solution of the films, such as [Ebothé; El Hichou; Vautrot and Addou (2003); El Hichou; Addou; Bougine; Dounia; Ebothé; Troyon and Amrani (2004); Ikhmayies; Abu El-Haija and Ahmad-Bitar (2010); Mazón; Muci; Sa-Neto; Ortiz-Conde; García (1991)]. In this work zinc chloride (0.8% - 2.5% varying concentration) was used as the source of Zn to prepare the precursor solution for ZnO thin films, where 7.37×10^{-3} mole of ZnCl_2 was dissolved in 600ml of distilled water. To prevent the formation of Zn(OH)_2 about 10 ml of HCl was added and so the PH of the solution reached 2.9. Films of undoped ZnO were deposited on ordinary glass substrates of dimensions ($6 \times 2.6 \times 0.1 \text{ cm}^3$). The substrates were cleaned prior to the deposition, first by dipping in distilled water, and then they were ultrasonically cleaned in methanol for (20 – 30) min. After this they were soaked in distilled water and finally polished with lens papers.

The prepared solution was sprayed through a locally designed PVC nozzle [Ikhmayies (2002)] on the hot substrates using nitrogen as the carrier gas. The spraying process was done intermittently to avoid excess cooling of the substrates and to reach thermal equilibrium. That is the spraying continues for 10s, then it stops for 5 min, and again continues for 10 s. Hence the total spraying time was 5-8 hours. This method of spraying enabled us of getting highly transparent ZnO thin films. The spray rate was in the range (3 - 5) ml/min. The optimum carrier gas pressure for this rate of solution flow was around 5 kg/cm^3 . The nozzle substrate distance was

adjusted to get the largest uniform area which was about 30 cm in diameter. The substrate temperature was about 450°C.

The transmittance of the films was measured as a function of wavelength in the range 300-1100 nm by using a double beam Shimadzu UV 1601 (PC) spectrophotometer. The reference was a piece of glass of the same kind as the substrates. The film thickness was estimated by the interference method given by Goodman (1978). The transmittance- as well as the reflectance- exhibits periodic maxima and minima as a function of the wavelength λ . The number of these maxima and minima, their separation and height depend on the film thickness. If T_{\max} is the transmittance at a certain maximum and T_{\min} is the transmittance at the next minimum, then in the case of negligible dispersion, we can define a parameter ρ_T approximately given by,

$$\rho_T = \frac{T_{\max}}{T_{\min}} \cong \left[\frac{2n_1^2(n_0^2 + n_2^2)}{(n_1^2 + n_0^2)(n_1^2 + n_2^2)} \right] \quad (1)$$

where n_0 , n_1 , and n_2 are the refractive indices of air, film, and glass respectively, and the condition $n_0 < n_1$ and $n_1 < n_2$ was satisfied. Solving Eq.1 for n_1 to have

$$n_1 = \left\{ \frac{-(n_0^2 + n_2^2)(1 - 2\rho_T) + \left[(n_0^2 + n_2^2)^2 (1 - 2\rho_T)^2 - 4n_0^2 n_2^2 \right]^{\frac{1}{2}}}{2} \right\}^{\frac{1}{2}} \quad (2)$$

and the film thickness is given by

$$t = \frac{M_{ab}(\lambda_a \cdot \lambda_b)}{2n_1(\lambda_a - \lambda_b)} \quad (3)$$

where λ_a and λ_b are the values of the wavelength of two extrema (minima or maxima) and M_{ab} the number of fringes separating these extrema. $M_{ab} = 1/2$ if one minima and adjacent maximum are chosen.

The I-V measurements were taken by a Keithley 2400 meter which is capable to measure electrical current of the order of 10^{-11} A, and interfaced to an IBM compatible PC. The sample in question was placed on a plate of PVC in an opaque metallic box, which enabled us to get results in the dark. Aluminum contacts were deposited by vacuum evaporation on the surface of the films. They were two strips of 1cm length, 2 mm width and 3mm separation. Crystal structure was measured by means of X-ray diffraction (XRD) (Philips PW1840) compact X-ray diffractometer system with Cu K_α ($\lambda = 1.5405 \text{ \AA}$). The measurements were recorded at

a diffraction angle 2θ from 2° to 81° . Scanning electron microscopy (SEM) was used to measure the surface morphology by using a LEITZ-AMR 1000A scanning electron microscope.

3 Results and Discussion

3.1 I-V characterizations

The I-V measurements for the as deposited ZnO films have been taken in the dark at room temperature and shown in Fig. 1. All of the plots are linear, so the resistivity was estimated from the slopes and found to be about $200 \Omega\cdot\text{cm}$. This large value of the resistivity is most probably due to the high substrate temperature which is 450°C and/or the presence of deep states in the films. At elevated temperatures the more perfect ZnO films are formed, which include slight defects and hence approximately no donor levels to cause lower resistivity. The presence of deep states prevents electrons from reaching the conduction band and then participating in the conduction process.

For films prepared by the SP technique our value is larger than the values obtained by the following authors; Lokhande and Uplane (2000) who got a room temperature resistivity of $10^{-1} \Omega\cdot\text{cm}$ for as-deposited spray-pyrolized ZnO thin films prepared at a substrate temperature of 698 K by using zinc acetate in the precursor solution, and Mazón; Muci; Sa-Neto; Ortiz-Conde and Jarcía (1991) who got values of the resistivity in the range $3.2 \times 10^{-3} - 1.5 \times 10^{-2} \Omega\cdot\text{cm}$ for ZnO films prepared at different substrate temperatures $360-440^\circ\text{C}$ and different deposition parameters by the SP technique by using zinc chloride in the precursor solution. Since the substrate temperature used by those authors is close to ours, we expect that the large value of the resistivity of our films is mainly due to the presence of deep states. This expectation is supported by the large value of the width of Urbach tail that we found as will be seen in the next sub-section.

For films prepared by other techniques, some authors got larger values of the resistivity, for example Lupan; Shishiyanu, Sergiu; Chow; Shishiyanu, Teodor (2007) got electrical resistivity of $1.5 \times 10^5 \Omega\cdot\text{cm}$ for as-deposited ZnO thin films prepared by successive ionic layer adsorption and reaction method. Other authors got much smaller values of the resistivity such as Rusu, I. D and Rusu I. I (1999-2000) who got a resistivity of $25 \Omega\cdot\text{cm}$ for ZnO films prepared by reactive sputtering, and Saito; Watanabe; Takahashi; Matsuzawa; Sang and Konagai (1997) got $6.9 \times 10^{-4} \Omega\cdot\text{cm}$ by the photo atomic layer deposition (photo-ALD) method without any intentional doping.

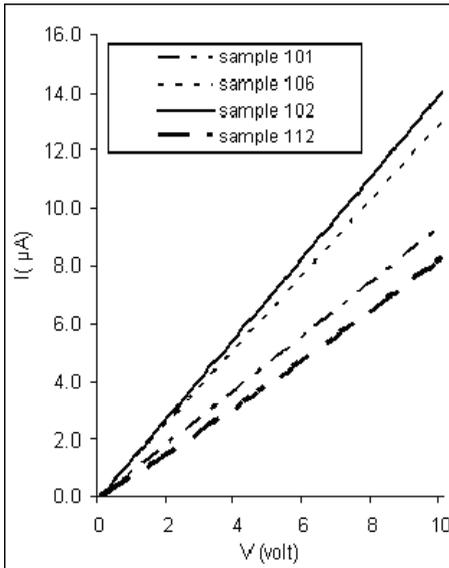


Figure 1: I-V plots for four as-deposited ZnO thin films of different thickness prepared at substrate temperature $T_s = 450^\circ\text{C}$.

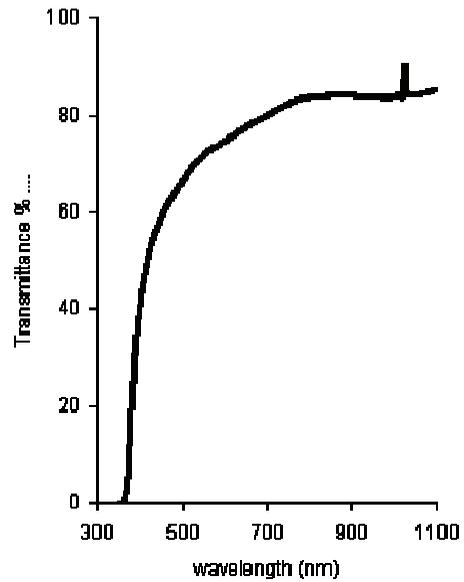


Figure 2: Transmittance curve of a thin film of as-deposited ZnO prepared at a substrate temperature $T_s = 450^\circ\text{C}$.

3.2 Optical Properties

The transmittance of the films was measured at room temperature in the wavelength range 300-1100 nm. Fig. 2 shows the transmittance curve for a film of thickness about 400 nm prepared at a substrate temperature of 450°C . As shown in the figure the average transmittance is about 85%, which is good for solar cell applications. An inspection of the absorption edge in the low energy side reveals that there is a tailing in the bandgap. The transmittance measurements were used to evaluate the absorption coefficient, and hence a plot of the absorption coefficient α and its natural logarithm ($\ln(\alpha)$) against the radiation energy $h\nu$ is shown in Fig.3, where h is Planck's constant and ν is the frequency of the radiation. The figure shows that the absorption coefficient is always increasing with the photon's energy, with a rapid increase around the absorption edge. The behavior in the low energy side near the absorption edge confirms the presence of tailing. We found that the absorption coefficient α in the low energy range empirically follows the exponential law, i.e. the Urbach tail expressed by [Natsume; Sakata and Hirayama (1995)]

$$\alpha(\omega) = \alpha_0 \exp(\hbar\omega/E_e) \quad (4)$$

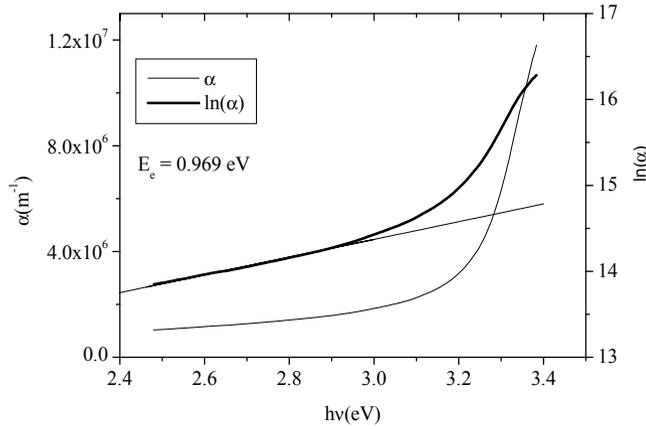


Figure 3: A plot of the absorption coefficient α and its natural logarithm $\ln(\alpha)$ against the radiation energy $h\nu$.

where α_0 is a constant, ω the angular frequency of the radiation, and E_e an energy which is a constant or according to Natsume; Sakata and Hirayama (1995) is a constant that is weakly dependent on temperature and often interpreted as the width of the tail of localized states in the bandgap. E_e is considered as a parameter that includes the effects of all possible defects [Kavak ; Tuzemen; Ozbayraktar and Esen (2009)].

As Fig. 3 shows, a linear region is observed between 2.50 and 2.93 eV which can be fitted by a straight line. The width of the Urbach tail equals the inverse of the slope of the obtained straight line. The obtained value is 0.969 eV, which is a large value. This large value is most probably attributed to the disorder caused by the existence of interstitial zinc atoms and may be interstitial oxygen atoms and oxygen vacancies too. As a result, localization of electrons due to the disorder was expected. This value is much larger than the values obtained by Natsume; Sakata and Hirayama (1995) for ZnO films prepared by chemical vapor deposition, where their values are in the range 0.08-0.10 eV. Also this value is much larger than the value obtained by Tüzemen;, Eker; Kavak and Esen (2009) for ZnO thin films of thickness 427 nm prepared by Pulsed filtered cathodic vacuum arc deposition (PFCVAD) where they got a value of 0.114 eV, and the value 0.142 eV obtained by Kavak ; Tuzemen; Ozbayraktar and Esen (2009) for ZnO films of thickness 405 nm prepared by Pulsed filtered cathodic vacuum arc deposition (PFCVAD). The large difference between our results and the results obtained by these authors most probably means that our films contain deep states and this explains the large value of the resistivity that we got. We did not find in the literature results for spray-deposited ZnO thin films to

compare with.

A plot of $(\alpha h\nu)^2$ versus $(h\nu)$ was used to estimate the bandgap energy (Fig.4). Taking into account that ZnO is a direct bandgap semiconductor [Kavak; Tuzemen; Ozbayraktar and Esen (2009)], a linear fit was established in the linear region of the curve and the bandgap energy which is the intercept of the energy axis was found to be about 3.27 eV which is consistent with that obtained by Lokhande and Uplane (2000). This value is larger than the value obtained by Tüzemen; Eker; Kavak and Esen (2009) for ZnO thin films of thickness 427 nm prepared by pulsed filtered cathodic vacuum arc deposition (PFCVAD) where they got a value of 3.19 eV. The reason that our films have a larger value of the optical bandgap energy is most probably that since our films were prepared by using ZnCl_2 and HCl was added to the precursor solution, they may contain a small concentration of chlorine, which works as a dopant that can replace the oxygen atom in the crystal lattice.

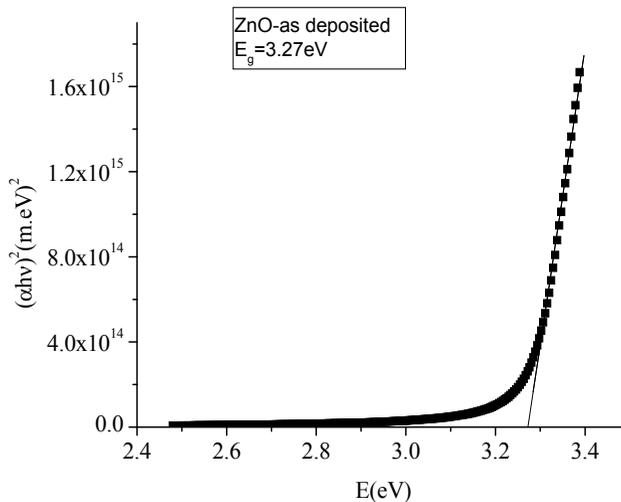


Figure 4: The plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for the as-deposited ZnO thin films deposited at $T_s = 450^\circ\text{C}$.

3.3 Structural Properties of ZnO thin films

3.3.1 X-Ray Diffractograms (XRD)

A Typical X-ray diffraction pattern (XRD) for ZnO thin films deposited by the spray pyrolysis technique is displayed in Fig.5. The diffractogram shows that the films possess a hexagonal wurtzite type crystallographic structure. The crystal growth shows a preferable orientation at (002) which means that we have *c*-axis

oriented ZnO films. Other orientations such as (100), (101), (102), (103), (004) are present but they are very weak. Studenikin; Golego and Cocivera (1998 a) produced undoped ZnO films that were highly *c*-axis oriented if sprayed from zinc nitrate aqueous solution at substrate temperatures higher than 200 °C. Below this temperature, their deposited films were without preferred orientation. But Lokhande and Uplane (2000) who prepared spray-deposited ZnO thin films by using zinc acetate aqueous solution prepared in double distilled water got one orientation of the crystallites which is (100). Many other workers got ZnO thin films with different techniques and got films with crystallites of (002) preferential orientation such as Saito; Watanabe; Takahashi; Matsuzawa; Sang and Konagai (1997).

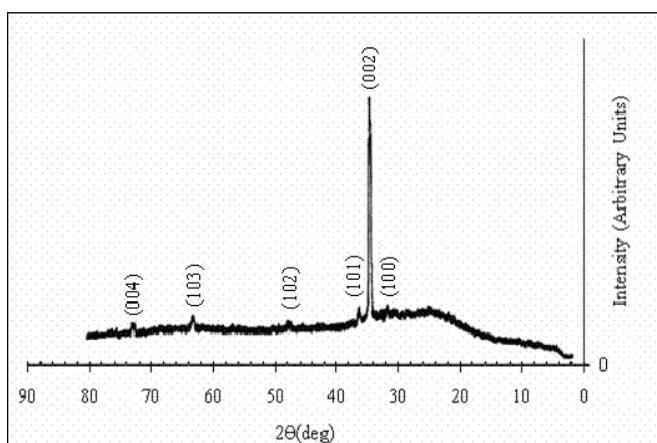


Figure 5: X-Ray Diffraction pattern for the as-deposited ZnO thin films.

From Fig. 5 it is noticed that the diffraction peak corresponding to the (002) line was located at $2\theta = 34.3^\circ$ which is consistent with the value obtained by El Hichou; Addou; Bougine; Dounia; Ebothé; Troyon and Amrani (2004), where the position of the (002) peak in their work is $2\theta = 34.2^\circ$, where these values are close to that of the standard ZnO crystal ($2\theta = 34.45^\circ$) [El Hichou; Addou; Bougine; Dounia; Ebothé; Troyon and Amrani (2004)]. Bragg equation was used to calculate interplanar distance *d* which was found to be ($d = 0.261$ nm) and the crystal lattice constant *c* was calculated and found to be ($c = 0.522$ nm) which are consistent with the results of Jejurikar; Banpurkar; Limaye; Date; Patil; Adhi; Misra; Kukreja and Bathe (2006) who got values of *c* in the range 5.258-5.188 Å for as-deposited ZnO thin films prepared by pulsed laser deposition technique at substrate temperatures in the range 100-600 °C. But our values are larger than the values obtained by Kavak; Tuzemen; Ozbayraktar and Esen (2009) where they got $d =$

0.256 nm and a crystal lattice constant ($c = 0.512$ nm) for ZnO thin films grown by pulsed filtered cathodic vacuum arc deposition (PFCVAD). This may be due to the presence of zinc interstitial and may be oxygen interstitials in our films which are responsible of the presence of the large Urbach tail.

The grain size was estimated from Scherrer formula and the line (002) in the XRD patterns.

$$d = \frac{\lambda}{D \cos \theta} \quad (5)$$

where d is the grain size, λ is the X-ray wavelength used, D is the angular line width of the half-maximum intensity and θ is the Bragg angle. The result is that the grain size is about 30 nm which means that the films have a nanocrystalline nature. This value is of the same range given by Studenikin; Golego and Cocivera (2000) but larger than that of Lokhande and Uplane (2000) which is 20 nm. The presence of very weak lines in the XRD diffractogram means that the films contain nanocrystallites of much smaller size.

3.3.2 Scanning Electron Microscope (SEM) Images

To study the topography of surface structure of the ZnO thin films, SEM observations were performed. Fig.6 shows the SEM micrograph for one of the ZnO thin films deposited at substrate temperature 450°C. The micrograph shows that there is continuous coverage of the substrate with the material. The grain size appears to be larger than that estimated from the XRD diffractogram, which means that each of these grains is an aggregate of much smaller crystallites.

4 Conclusions

Undoped ZnO thin films were deposited by the spray pyrolysis technique on glass substrates at substrate temperature $T_s = 450^\circ\text{C}$. The films were characterized by recording and analyzing their I-V plots, their transmittance, XRD diffractograms and SEM micrographs. Their resistivity was found to be about 200 $\Omega\cdot\text{cm}$ and their bandgap energy was about 3.27 eV. The transmittance of the films was high ($\sim 85\%$) which is suitable for use in solar cell applications. The absorption coefficient was continuously increasing with photon's energy, and tailing is evident in the low energy side of the absorption edge. The width of Urbach tail was estimated and related to localized states. XRD revealed that the films show the hexagonal wurtzite structure and that they are highly oriented with (002) preferential orientation. The grain size was estimated and found to be about 30 nm, which means that the films are nanocrystalline in nature. The presence of very weak lines in the XRD



Figure 6: SEM image for one of the as-deposited ZnO thin films prepared at $T_s=450^\circ\text{C}$.

diffraction pattern is evidence on the presence of nanocrystallites of much smaller size. From the SEM image it is shown that the substrates are continuously covered and the surface of the film is uniform.

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