

Structural, electrical and optical properties of undoped ZnO thin films using ion beam sputtering and spray pyrolysis techniques

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In this work, the structural, electrical and optical properties of undoped ZnO amorphous thin films prepared using Ion Beam Sputtering (IBS) and spray pyrolysis deposition techniques are presented. From the structural measurements, a transition from amorphous to polycrystalline phase has been observed at around 130 °C. From the optical measurements, the energy gap has been determined and showed an increase with the thickness of the films. The electric conductivity shows three different regimes. At low temperatures ($T < 300$ K), the electric conductivity increases linearly with temperature (semiconducting behaviour). At around 300 K, the conductivity is almost independent of temperature. For $T > 300$ K, the conductivity decreases almost linearly with temperature (metallic behaviour). This metallic behaviour might be related to the oxygen adsorption above room temperature. In addition, three regimes have been identified for the conduction mechanisms from the variation of both the electric conductivity and the seebeck coefficient as a function of temperature. Comparison between the results obtained by the two techniques is presented.

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1. Introduction

Since zinc oxide ZnO is a semiconductor material with a wide band gap of 3.27 eV and a large exciton binding energy of 60 meV at room temperature, ZnO-based thin films have been used for several applications such as transparent conducting oxide TCO, ultraviolet light emitters, solar cell windows, and bulk acoustic wave devices [1-4].

On the other hand, the reduction of thin films to nanometer dimensions for new technologies requires precise control of film thickness, conformity, and morphology. ZnO is known to be a transparent material. It is normally a non-degenerate semiconductor, but it can exhibit a relatively high conductivity [5] due to the many defects such as stoichiometric excess of zinc and vacancies introduced in the sample during film deposition. Generally, this oxide is also considered to be an n-type material due to oxygen deficiencies and interstitial Zn, which act as donors in the ZnO lattice [6].

Transport properties of these oxides depend on the deposition technique, film quality as well as film thickness. In this work, structural, optical, electrical characteristics as well as thickness dependence of undoped ZnO are investigated using two different techniques, IBS and spray pyrolysis. These characteristics provide important information about the conduction mechanisms of the material.

2. Experimental

IBS technique has been used for the deposition of the undoped ZnO films. It consists of the sputtering of an oxide target by an ion beam and in recovering ejected atoms on certain substrate [7]. The ZnO target was bombarded by an Argon ion beam accelerated to 6 keV with a current density of the order of a few mA/cm²; these parameters of the beam imposed a deposition speed of the order of a few nanometers per minute. On the other hand, the thin films were deposited at room temperature using a pure ZnO target without oxygen flow.

The second technique is the spray pyrolysis. Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface. The chemical precursors are selected such that the products other than the desired compound are volatile at the temperature of deposition. The process is particularly useful for the deposition of oxides and has long been a production method for applying transparent electrical conductors. The undoped ZnO thin films have been deposited on a glass substrate. The precursor solution has been prepared starting with a mixture of 2.4 g of Zn(CH₃COO)₂ powder in different methanol volumes (with and without deionized water).

The structural characterization of the films, for different thicknesses, was carried out by X-Ray diffraction technique using an X-Ray diffractometer (Bruker D5000) with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$).

The optical transmission of the films was determined using a double beam UV-VIS-NIR spectrophotometer (SAFAS 200 DES) with 170-1010 nm wavelength range and 1 nm resolution.

The electric conductivity and the thermopower measurements have been performed simultaneously using a home-made four probes technique, detailed elsewhere [8].

3. Results and discussions

Results using the IBS technique will be presented first and then results from spray pyrolysis technique will support and validate the IBS results. ZnO films with different thicknesses (20nm-240nm) deposited on glass have been prepared and investigated. The electric conductivity of these films has been measured and found to be in the same order of magnitude from 5 to 20 S/cm at room temperature. However, the transmission of the films is higher than 85% within the visible range and it is almost independent of the thickness.

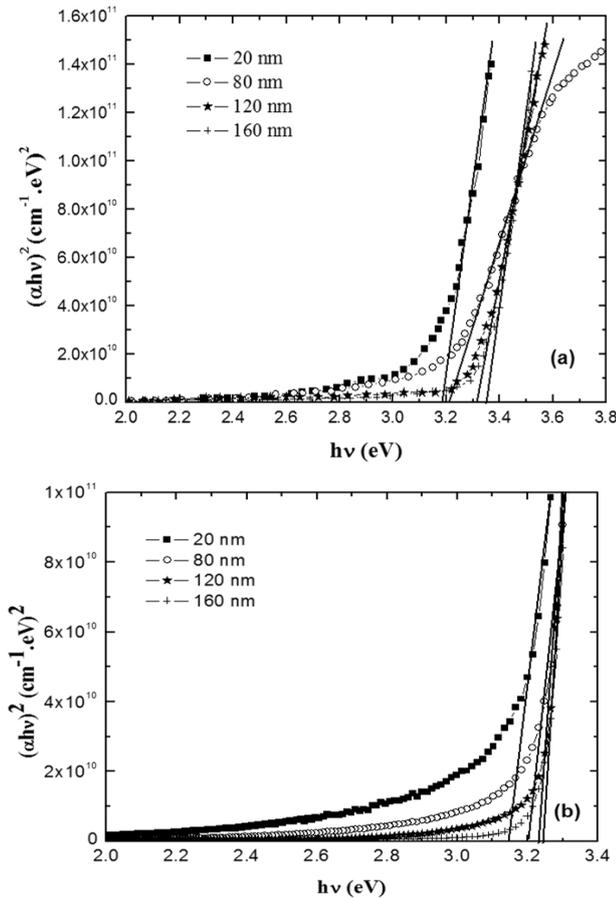


Fig. 1. $(\alpha h\nu)^2$ as a function of photons energy for different ZnO film thicknesses: a) for IBS technique, b) for spray pyrolysis technique. The intercept of the solid line with the energy axis represents the energy gap of the material for the corresponding thickness

In the contrary, the optical energy gap increases with the thickness of the film, as shown in Fig. 1; it goes from 3.16 eV (20 nm) to 3.32 eV (160 nm) for IBS technique and from 3.15 eV (20 nm) to 3.26 eV (160 nm) for spray pyrolysis. Similar results have been obtained for films deposited by sol-gel technique [9, 10]. In semiconductors with high energy gap, the gap might increase or decrease as the carrier concentration changes [11] according to Burstein-Moss formula [12, 13]:

$$\Delta E_g^{BM} = \left(\frac{\hbar^2}{2m^*e} \right) (3\pi^2 N)^{2/3}, \quad (1)$$

where N is the carrier concentration.

On the other hand, X-Ray Diffraction (XRD) analysis of the films showed no thickness dependence at room temperature. However, dependence on the deposition temperatures has been observed as shown in Fig. 2. For temperatures above 100 °C, a diffraction peak was observed. The intensity of this peak increases with increasing the temperature. This increase in the peak's intensity is accompanied by a sharp drop in the electric conductivity of a 10^4 factor, as shown in Fig. 3.

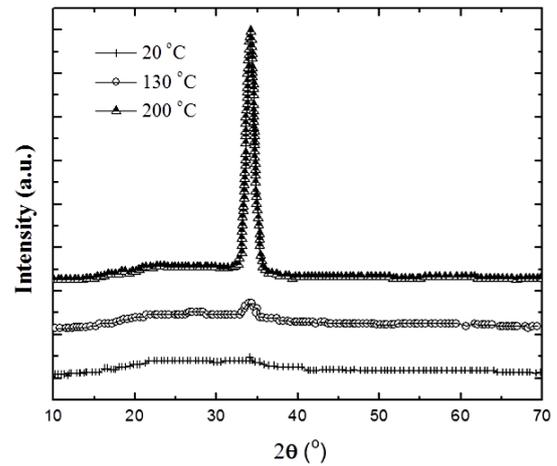


Fig. 2. XRD of ZnO films deposited for different substrate temperatures. The peak intensity of the (002) plane increase as the temperature increases above 100 °C

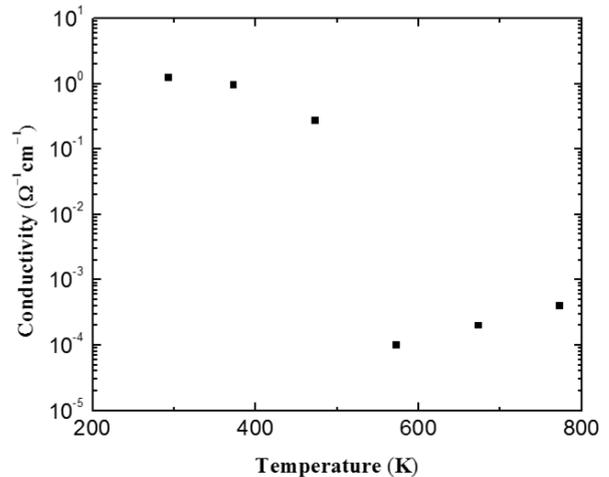


Fig. 3. Electric conductivity of ZnO films, of thickness of 80 nm, as a function of the substrate deposition temperatures

From Fig. 2, one can conclude that the film, as grown, shows an amorphous phase. However, at a temperature above 100 °C, a transition to crystalline phase occurs. In the following, the analysis will be limited to temperatures below this transition in order to make sure that the films are in the amorphous state.

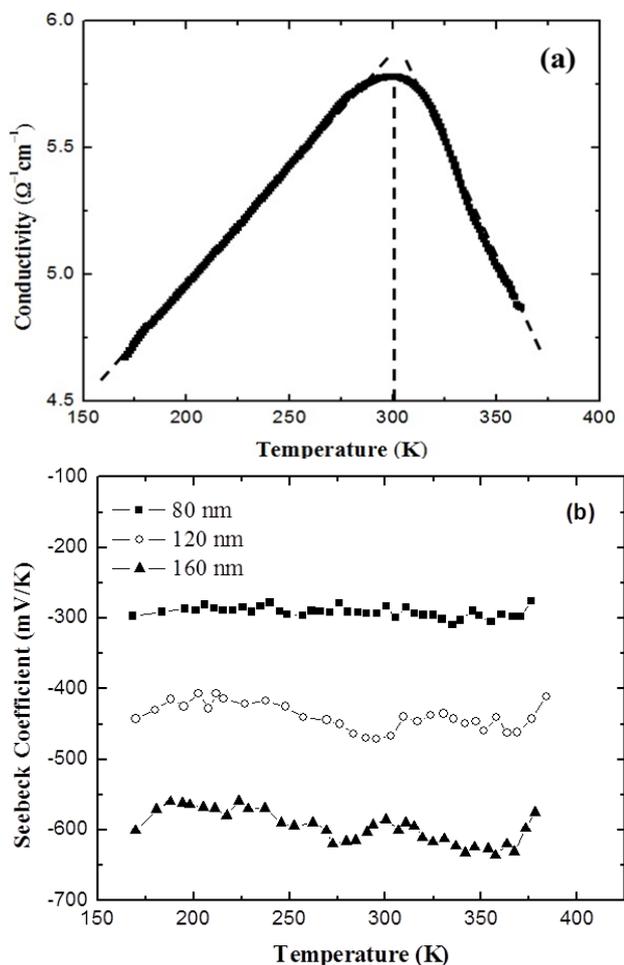


Fig. 4. (a) Variation of the electric conductivity as a function of temperature for a ZnO film of thickness 20 nm. The figure shows three different regimes: a linear increase below 300 K, an almost flat behaviour around 300 K and a linear decrease above 300 K. (b) Variation of the seebeck coefficient as a function of temperature for films with different thicknesses (80 nm, 120 nm and 160 nm)

In Fig. 4a, the variation of the electric conductivity as a function of temperature, for a film thickness of 20 nm, is shown. At low temperatures ($T < 300$ K), the electric conductivity increases linearly with temperature. In this regime, the conduction mechanism is not a thermally activated one. At around 300 K, the conductivity reaches a regime in which it is almost independent of temperature. For $T > 300$ K, the conductivity decreases almost linearly with temperature. The negative slope of the variation of the conductivity could have been explained as a metallic behaviour but it is not. Several authors have shown this behaviour in the undoped ZnO films around room

temperature and they attributed it to the oxygen adsorption; the oxygen molecules are adsorbed at the film surface and form ionic regions that are larger as much as the temperature increases. The electric conductivity of the ZnO film decreases consequently. In Fig. 4b, the seebeck coefficient doesn't show a significant variation with temperature for three different film thicknesses.

Similar behaviour of the conductivity as a function of temperature has been obtained using spray pyrolysis technique, as shown in Fig. 5a. However, the conduction regimes are better identified in the samples prepared by spray pyrolysis technique. In addition, seebeck effect measurements have been performed on samples prepared by both techniques (IBS and spray pyrolysis). The samples prepared by IBS technique didn't show a significant variation of the seebeck coefficient with temperature, as mentioned above. In the contrary, the results of the seebeck coefficient obtained by the spray pyrolysis technique show behaviour consistent with the results of the electrical conductivity, as shown in Fig. 5a and Fig. 5b. This might be attributed to the quality of the films, which are prepared by two different techniques.

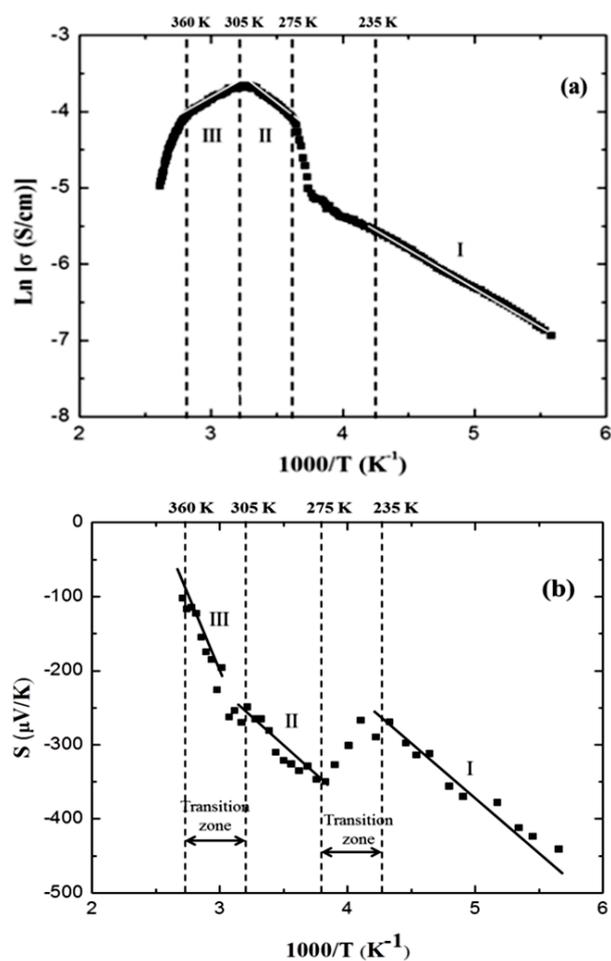


Fig. 5. Variation of the Ln of the electric conductivity (a) and the seebeck coefficient (b) as a function of inverse temperature. The Thickness of the samples is 20 nm in both measurements. The samples here have been prepared by spray pyrolysis technique

The structures observed in Fig. 5a and Fig. 5b might be interpreted as follows: a) At low temperature $T < 235$ K, the conductivity increases linearly with temperature. At the same time the seebeck coefficient decreases linearly while remaining negative. This type of behaviour might be related to certain conduction mechanism associated with the carrier displacement within the localized states (with an activation energy ΔE). From these Figures one can determine the activation energy in region I where the electric conductivity and seebeck coefficient are given respectively by [15]:

$$\sigma \propto \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (2)$$

$$S \propto \left(-\frac{\Delta E}{qT}\right) \quad (3)$$

ΔE has been found to be in the order of 0.1 eV from both curves of Fig. 5a and Fig. 5b. For temperatures around 300 K, the conductivity curve shows a brusque change with temperature and correspondingly a change in the slope in the seebeck coefficient. This behaviour might correspond to a transition zone to certain localized states close to the conduction band. b) At intermediate temperatures ($275 \text{ K} < T < 305 \text{ K}$), the region II corresponds to a thermally activated regime. A change in the slope is observed from 0.1 eV to 0.2 eV. This behaviour might be related to certain localized states close to the conduction band but with activation energy of 0.2 eV. c) For $T > 305 \text{ K}$, a sudden drop of the conductivity (region III) has been observed. This phenomenon is similar to what has been obtained and analyzed in the films prepared by IBS technique. It is related to adsorption phenomena that depend on the thickness of the film, structure (amorphous or polycrystalline), grains' dimensions, density, defects, etc.

In order to explore the thickness dependence of the films, measurements of the electric conductivity of three films with different thicknesses have been performed. Fig. 6 shows the results for films of thicknesses 20 nm, 80 nm and 120 nm. An increase in the conductivity accompanied by a clear shift of the peak towards higher temperatures with the increase in the thickness is observed. This might be attributed to the increase in the energy gap as a function of the thickness mentioned previously and shown in Fig. 1. This increase in the energy gap was attributed to the increase in the carrier concentration.

Further analysis of the results shown in Fig. 4, Fig. 5 and Fig. 6 is needed in order to understand the behaviour of the electric conductivity as functions of temperature and thickness. It is well known that the properties of the semi-conduction/conduction of undoped ZnO are related to the defects rich in Zn such as interstitials, to the oxygen vacancies, and to the hydrogen that acts as shallow donors. This would explain the behaviour of the electric conductivity up to certain temperature that changes with the thickness, as shown in Fig. 6. Above this temperature that corresponds to certain critical donors concentration a new regime of the conductivity begins. The electric conductivity starts decreasing as shown in Fig. 4 and Fig.

6. This change in the slope occurs at temperatures as low as the film thickness is lower. One might explain this behaviour as following: more is the thickness of the film a higher temperature is needed to attain the critical donors' concentration.

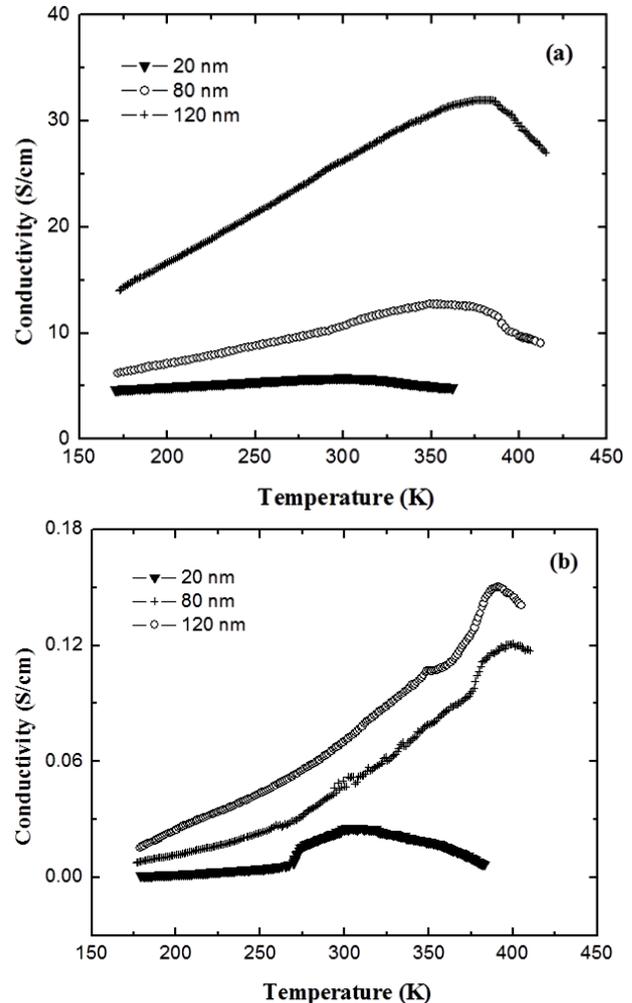


Fig. 6. Variation of the electric conductivity as a function of temperature for different thicknesses (20 nm, 80 nm and 120 nm). (a) For films prepared by IBS technique and (b) for films prepared by spray pyrolysis technique. A clear shift in the peak is observed. As the thickness increases the peak shifts towards higher temperatures

To understand the electric conductivity as a function of the thickness, many physical phenomena have to be taken into consideration. When the temperature increases, the carriers' concentration increases; this is due to the increase of the zinc interstitials. On the other hand, the adsorption process and the diffusion of the oxygen and the carriers in the ZnO for temperatures above 300 K should not be ignored, especially their resulting effects in the decrease of the carriers' concentration that leads to a decrease in the electric conductivity.

At the end, Fig. 7 shows the variation of the electric conductivity in both heating and cooling directions. This behaviour has been observed in both techniques (IBS and spray pyrolysis). The Fig. 7 shows a clear degradation of

the conductivity after one cycle. This type of behaviour has been reported in literature [15] in the case of undoped ZnO but with different technique. It was attributed to an oxidation of the remaining zinc in the film during the heating process.

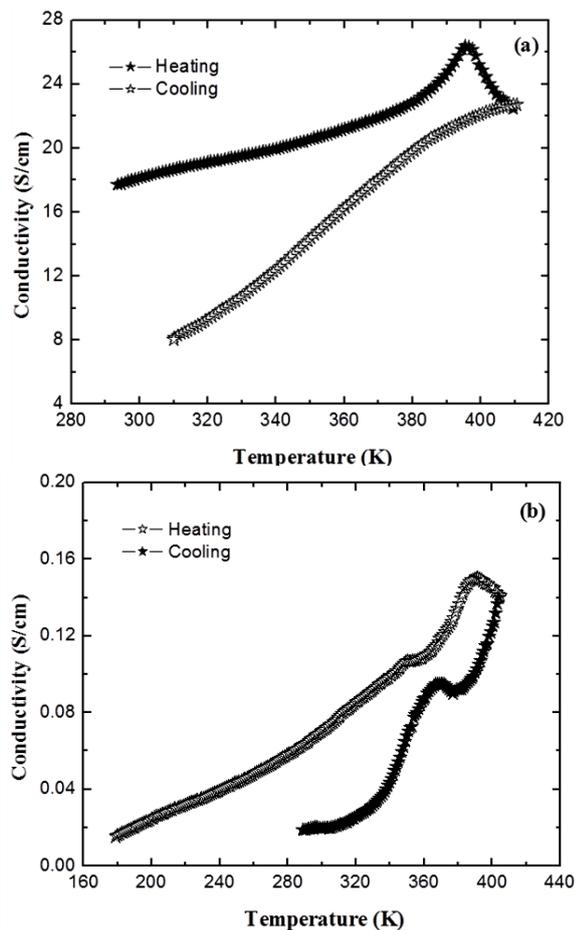


Fig. 7. Cyclic variation of the electric conductivity as a function of temperature obtained by a) IBS technique and b) spray pyrolysis technique (heating and cooling)

4. Conclusion

In this work, the structural, electrical and optical properties of undoped ZnO amorphous thin films using IBS and Spray Pyrolysis deposition techniques have been presented. From the structural measurements (XRD), a transition from amorphous to polycrystalline phase has been observed at around 130 °C. From the optical measurements, the energy gap has been determined and showed an increase with the thickness of the films. The electric conductivity and the Seebeck effect show a semiconductor-metal transition at around 300 K that might be related to the oxygen adsorption above room

temperature. In addition, three regimes have been identified for the conduction mechanisms from the variation of both the electric conductivity and the Seebeck coefficient as a function of temperature. Cyclic measurements of the electric conductivity as a function of temperature showed a deterioration of the conductivity after each cycle. This might be due to the oxidation of the Zinc as the films are heated during the measurements. Comparison between the results obtained by the two techniques is presented and showed almost the same properties except in the Seebeck effect, the structure is more pronounced in the spray pyrolysis that in the IBS technique. This might be due to some difference in the preparation conditions that might affect the quality of the films. At the end, the doping process and implementation of ZnO in certain applications especially solar cells are under investigation.

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