



Structural and optical characteristics of spin-coated ZnO thin films

M. Smirnov, C. Baban*, G.I. Rusu

"Al. I. Cuza" University, Physics Department, 11 Carol I Blvd, Iasi 700506, Romania

ARTICLE INFO

Article history:

Received 30 April 2009

Received in revised form 22 October 2009

Accepted 22 October 2009

Available online 29 October 2009

Keywords:

Zinc oxide

Spin-coating

Optical properties

Transparent films

ABSTRACT

Zinc oxide (ZnO) thin films were deposited onto glass substrates by spin-coating method, from a precursor solution containing zinc acetate, ethanol and ammonium hydroxide. After deposition, the films were heated at a temperature of 100 °C in order to remove unwanted materials. Finally, the films were annealed at 500 °C for complete oxidation. X-ray diffraction showed that ZnO films were polycrystalline and have a hexagonal (wurtzite) structure. The crystallites are preferentially oriented with (0 0 2) planes parallel to the substrate surface. The films have a high transparency (more than 75%) in the spectral range from 450 nm to 1300 nm. The analysis of absorption spectra shows the direct nature of band-to-band transitions. The optical bandgap energy ranges between 3.15 eV and 3.25 eV.

Some correlations between the processing parameters (spinning speed, temperature of post deposition heat treatment) and structure and optical characteristics of the respective thin films were established.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, the transparent conductive oxides (TCOs) in thin films are some of the most extensively investigated materials due to their important area of applications in modern solid-state device technology [1–5]. Usually, these films are used as window layers as well as one of electrodes in modern solar cells based on the α -Si, CdTe, CdS, CuInSe₂, etc. [1–3,6,7]. The conventional transparent conductive films of SnO₂, In₂O₃, ITO (indium tin oxide), CdO, etc. were found to reduce to their metallic characteristics by exposure hydrogen plasma [8,9].

The excess of metallic Sn or In atoms in SnO₂ and In₂O₃ thin films respectively leads to a decrease of the transmission coefficient especially in the blue spectral domain. For this reason, the respective films become unsuitable for application in amorphous and polycrystalline silicon solar cells [1–3]. The photovoltaic devices based on zinc oxide (ZnO) thin films are characterized by a stable structure in the presence of hydrogen plasma. Pure and doped ZnO polycrystalline thin films are also applied for a large number of acoustical, electronic and optical devices, because they are characterized by excellent piezoelectric properties, varistor effect, etc. [6–10]. The main technological interest for polycrystalline ZnO thin films based devices lies on their very low cost.

Transparent conductive ZnO thin films have been prepared by a variety of deposition technologies such as r.f. and d.c. sputtering, spray pyrolysis, chemical vapour deposition, sol–gel method, pulsed laser deposition, etc. [1–3,9–12].

It was clearly established that structural, electronic transport and optical properties of ZnO films are very sensitive to preparation method and deposition conditions [2–4,11–15]. There are relatively few reports on the spin-coating preparation of ZnO thin films.

As compared to other preparation methods, the spin-coating method for deposition of ZnO films has some important advantages: simplicity of technological runs and low cost of the used materials and equipments [14,16–18].

In this paper, the structural and optical properties of ZnO thin films prepared by spin-coating method are investigated as a function of deposition conditions.

2. Experimental procedure

Zinc oxide thin films were deposited onto glass substrates by spin-coating method. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) was chosen as a starting material. Ethanol was used as a solvent. The solution was prepared using the following procedure: zinc acetate (1 g) was dissolved in ethanol (10 ml) and then ammonium hydroxide was added in order to obtain a clear solution with a pH 10. The solution was filtered to yield a clear and homogeneous solution and then used for preparing films by spin-coating method [13,14]. Glass slides were chosen as the substrates at room temperature. For preparation of different samples, the solution was spin-coated on the substrates with the speed ranged from 700 to 1600 rotations per minute (rpm) for 10 s. After deposition, films were dried at 100 °C for 10 min over a hot plate in order to remove the used solvent. The spin-coating deposition was performed at room temperature. The coating–drying cycles were repeated several times (1–12 cycles) until the desired thickness was obtained. Finally, the films were introduced in a special furnace

* Corresponding author.

E-mail address: baban@uaic.ro (C. Baban).

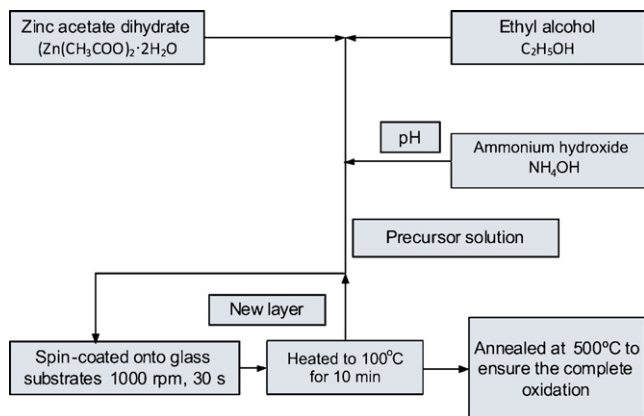


Fig. 1. Flow chart for obtaining ZnO films.

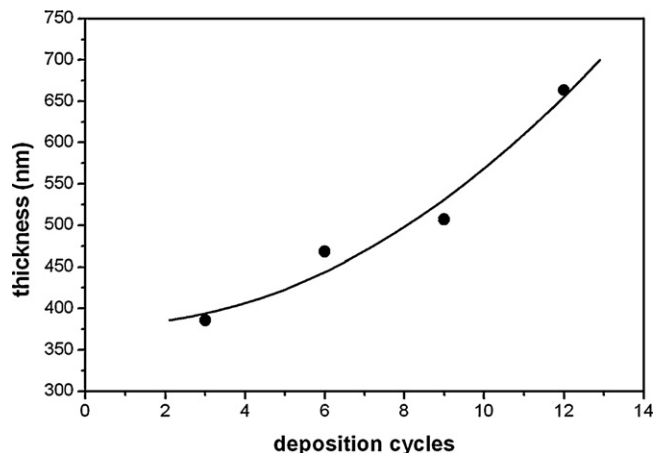


Fig. 2. Film thickness dependence on the number of deposition cycles.

and heated in air. This process consist of following successive technological runs: a heating process from room temperature to 500 °C with a temperature rate of about 8 K/min; an annealing process at 500 °C for 120 min and a cooling process (with 8 K/min) to room temperature. The experiments show that these preparation conditions permit to obtain films with stable structure and homogenous composition. The flow chart of the entire process for preparing ZnO films is schematically drawn in Fig. 1.

The obtained films were uniform, smooth and have a good adherence to the substrates. The crystalline structure of the films was investigated by the X-ray diffraction (XRD) technique with a DRON 3.0 diffractometer using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The surface microstructure was studied by means of atomic force microscopy (AFM) in the contact mode.

The temperature dependence of electrical conductivity was studied using surface-type cells. Thermoelectric power was determined using sonde electrode method [15,19].

Transmission spectra in the spectral range 300–1350 nm, were recorded (at room temperature) using an ETA-STC (Etaoptik Steag) spectrometer.

The absorption coefficient, α , was calculated from expression [20–23]

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right) \quad (1)$$

where d is the film thickness and T denotes the transmission coefficient.

The thickness of the films was determined by an interferometric method (multiple beam Fizeau's fringe method [23] using a MII-4 type microscope).

3. Results and discussion

It was experimentally established, that composition of coating solution plays an important role in preparing high quality ZnO thin films. It was found that the ratio 10 ml/1 g of ethanol to acetate in mixture solution permitted to obtain the stoichiometric and homogenous films. The increasing of this ratio lowers the ability of the coating solution to form the films onto glass substrates (the solution was not able to adhere to the substrates).

The film thickness increases with increasing of cycle number for a determined spinning speed. By this, the films with controlled thickness can be deposited. Fig. 2 shows the typical dependence of the film thickness on the cycle number at the speed of about 1000 rpm for 10 s. In the studied range, this dependence was found to be about linear. The average baked thickness was evaluated to be about 33 nm per coating cycle. Generally, the thickness of the

coating depends on the speed at which solution level falls, concentration and viscosity of the respective solution, surface tension of the solution, temperature and relative humidity.

The thickness of thicker films is in principle a multiple of thickness for only one coating. For a certain value of deposition time and cycle number the films thickness decreases slowly with increasing of rotation speed to about constant value (Fig. 3). A similar behaviour was also found for many semiconducting films deposit by spin coating.

Fig. 4 shows typical XRD pattern for a ZnO film prepared by six-cycle spin-coating of ZnO films followed by post-deposited heat treatment. It was established that all studied ZnO films are polycrystalline and have a hexagonal (wurtzite) structure (Fig. 4). As-deposited films have also an amorphous phase. The film crystallites are preferentially oriented with (0 0 2) planes parallel to the substrate surface, in addition to other (1 0 0), (1 0 1) prominent reflections. The lattice parameters calculated from XRD, are in good agreement with those indicated in JCPDS data for ZnO crystals [JCPDS, $N_c = 36145$]. For our films we found $a = 3.233 \text{ \AA}$ and $c = 5.204 \text{ \AA}$. It was found that the intensity and full width at half maximum (FWHM) of (0 0 2) peak decreases with increasing annealing temperature. This behaviour indicates that the quality of ZnO films improves when they are annealed at higher temperatures.

The crystallite size, D , can be determined using Debye–Scherrer equation [24,25]

$$D = \frac{K\lambda}{B \cos \theta_B} \quad (2)$$

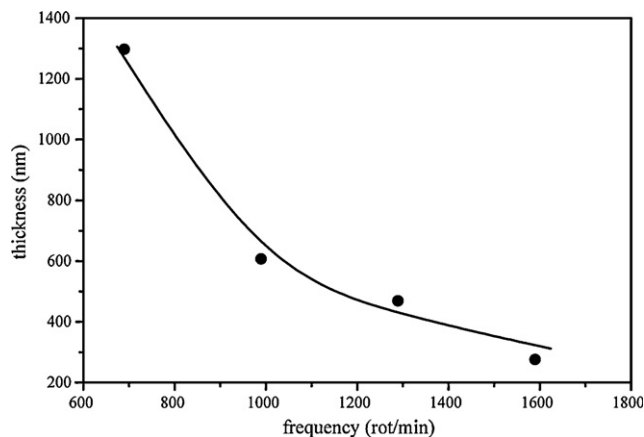


Fig. 3. ZnO film thickness as a function of spinning frequency.

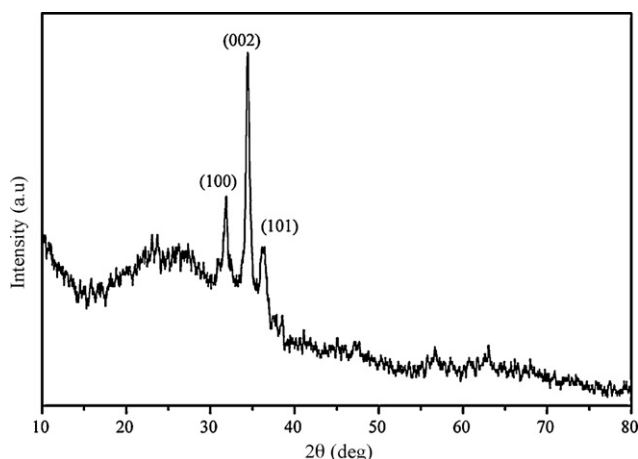


Fig. 4. Typical XRD pattern for a spin-coated ZnO film.

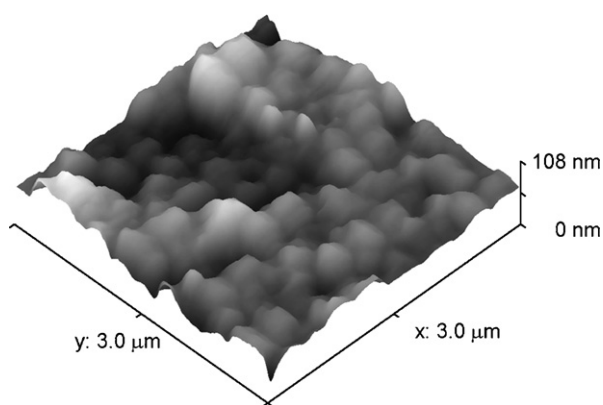


Fig. 5. AFM image for an as-deposited ZnO film (1000 rpm, $d = 510$ nm, rms = 13.7 nm).

where $\lambda = 1.5418$ Å is wavelength of CuK α radiation, B denotes the FWHM of diffraction peak, θ_B is Bragg angle and K represents the Scherrer's constant (equal to around 0.90 according to the widespread practice [24]). The calculated average crystallite size, 20–40 nm, increase with the increasing of annealing temperature.

AFM images showed that the surface topography of films was columnar (Figs. 5 and 6). We observe that ZnO films have a grain like surface morphology. The surface of as-deposited samples is characterized by some nonuniform domains (Fig. 5). After annealing at a temperature of 500 °C the films became uniform, the film crystallites having similar shape and size (Fig. 6).

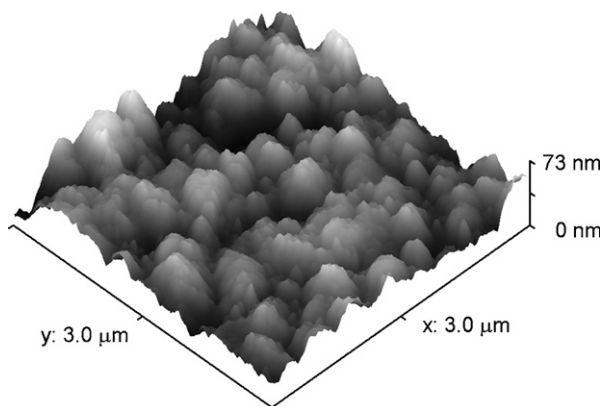


Fig. 6. AFM image for a ZnO film after annealing in air at 500 °C (1000 rpm, $d = 510$ nm, rms = 10.46 nm).

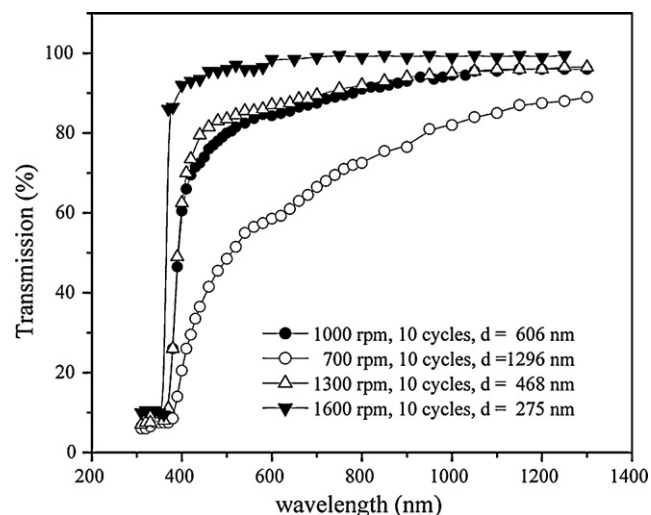


Fig. 7. Transmission spectra for ZnO films deposited in different conditions.

In the temperature range 300–500 K, the Seebeck coefficient was negative for all studied samples and decreased with increasing temperature for temperatures greater than 400 K.

The electronic transport in investigated films is strongly influenced by their polycrystalline structure [20].

Transmission spectra (Fig. 7) were recorded for ZnO thin films prepared in different conditions. The optical transmittance of the films is high in visible range (between 75% and 95%) in spectral domain 450–1300 nm, which is important for applications of respective films, such as transparent conductive electrodes and solar cell windows [3,6]. It can be observed that the transmittance decreases with increases of cycle number (in fact, in this case, there is an increase of film thickness). The increases of transmittance with the increasing of annealing temperature may be due to decreasing optical scattering caused by densification of film crystallites (crystallite size increases and crystallite boundaries domain is reduced).

It is known, that the pure compounds are characterized by a sharp transmission edge at a photon energy corresponding to the forbidden energy bandgap of the respective intrinsic semiconductor material [21,22,26–28].

Fig. 7 shows that at small values of spinning speed (<1000 rpm) the films are inhomogeneous. The films deposited at spinning speeds greater than 1000 rpm have a homogenous crystalline structure and stoichiometric composition [6,21,22,26–28].

In the lower wavelength range (300–370 nm) the values of the transmission coefficient are determined by the polycrystalline structure of the films (crystallite shape and size, roughness of the film, characteristics of grain boundaries, etc.) [2,6]. Different authors [6,14,18,28,30] have reported similar behaviour of transmission spectra.

The optical absorption coefficient, α , was determined from Eq. (1). It is known that the fundamental absorption corresponds to electron excitation from the valence band to the conduction band (band-to-band transitions) can be used to determine the nature and value of the optical bandgap [6,20,21,29,30]. Depending on the energy band structure of the studied semiconductor, theoretical considerations lead to different equations for the absorption coefficient, α , as a function of the incident photon energy.

For our studied samples the following relation, which indicates direct allowed transitions (neglecting exciton effects) is valid [6,21,29].

$$\alpha = \frac{A_d}{h\nu} (h\nu - E_{go})^{1/2} \quad (3)$$

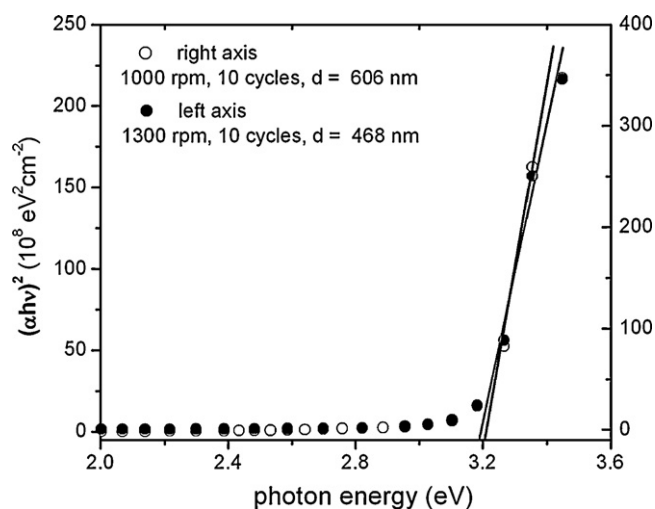


Fig. 8. $(\alpha h\nu)^2$ vs. photon energy for ZnO films.

where $h\nu$ is photon energy, E_{go} denotes the optical energy bandgap and A_d is a characteristic parameter (independent of photon energy) for respective transitions.

According to Eq. (3) the $(\alpha h\nu)^2 = f(h\nu)$ dependence must be linear.

In Fig. 8, the $(\alpha h\nu)^2 = f(h\nu)$ dependences are illustrated for two studied samples. It can easily be observed that these dependences indicate the direct nature of band-to-band transitions. The values of optical bandgap, E_{go} have been determined by extrapolating the linear portion (which correspond to higher photon energy) of respective curves to $(\alpha h\nu)^2 \rightarrow 0$. The values found for energy bandgap ranged between 3.15 eV and 3.25 eV.

The values of E_{go} are in good agreement with values indicate in literature for bulk ZnO crystals [2,4–7].

4. Conclusions

A simple and very cheap route to obtain transparent Zinc oxide films was used, starting with a precursor solution based on zinc acetate dehydrate, ethanol and ammonium hydroxide spin-coated onto glass substrates. The film properties can be controlled by spinning speed, number of deposition cycles and annealing

temperature. The obtained films were uniform, smooth and have a good adherence to the substrates. The films were polycrystalline with a hexagonal (wurtzite) structure with the crystallites preferentially oriented with (0 0 2) planes parallel to the substrate surface. The films show a high transparency (more than 75%) in the spectral range from 450 nm to 1300 nm and can be used as transparent window in solar cell technology.

Optical bandgap energy calculated from absorption spectra (considering allowed direct transitions) were in the range 3, 15–3, 25 eV.

References

- [1] H.L. Hartnagel, A.L. Dawar, A.K. Jain, C. Jagadish, Semiconducting Transparent Thin Films, IOP, Bristol and Philadelphia, 1995.
- [2] G. Harbeke (Ed.), Polycrystalline Semiconductors: Physical Properties and Applications, Springer Verlag, Berlin, 1985.
- [3] K.L. Chopra, S.R. Das, Thin Film Solar Cells, Plenum Press, New York, 1983.
- [4] F.C.M. Van Pol, F.R. Blom, Th.J. Popma, Thin Solid Films 204 (1991) 349.
- [5] S.Y. Kuo, W.C. Chen, C.P. Cheng, Superlattice Microstruct. 39 (2006) 162.
- [6] L.L. Kazmerski (Ed.), Polycrystalline and Amorphous Thin Films and Devices, Academic Press, New York, 1980.
- [7] J.F. Chang, H.H. Kuo, I.C. Leu, M.H. Hon, Sensor Actuators B: Chem. B4 (2002) 258.
- [8] J.L. Van Heerden, R. Swanepoel, Thin Solid Films 299 (1997) 72.
- [9] S. Major, S. Kamar, M. Bhatnagar, K.L. Chopra, Appl. Phys. Lett. 49 (1986) 394.
- [10] T. Miniami, H. Sato, K. Ohashi, T. Tomofuji, S. Takata, J. Cryst. Growth 117 (2002) 258.
- [11] B. Sang, A. Yamada, M. Konagai, Jpn. J. Appl. Phys. 37 (1998) L1125.
- [12] K. Ellmer, R. Wendt, Surf. Coat. Technol. 93 (1997) 21.
- [13] T. Kohoutek, T. Wagner, Mir. Vlcer, Mil. Vlcek, M. Frumar, J. Non-Cryst. Solids 352 (2006) 1563.
- [14] S. Tuzemen, S. Eker, H. Kavak, R. Esen, Appl. Surf. Sci. 99 (2009) 6195.
- [15] G.I. Rusu, M. Diciu, C. Pirghie, M.E. Popa, Appl. Surf. Sci. 253 (2007) 9500.
- [16] A.H. Jayatissa, Semicond. Sci. Technol. 18 (2003) 647.
- [17] A.H. Jayatissa, K. Guo, T. Gupta, A.C. Jayatissa, J. Mater. Electron. 20 (2009) 577.
- [18] S. Ilican, Y. Caglar, M. Caglar, J. Optoelectron. Adv. Mater. 10 (2008) 2578.
- [19] A.S. Ohotin, A.S. Pushkarsky, R.P. Borovikova, V.A. Simonov, Methods for Characterization of Thermoelectric Materials and Devices, Science, Moscow, 1974 (in Russian).
- [20] G.I. Rusu, M.E. Popa, G.G. Rusu, I. Salaoru, Appl. Surf. Sci. 218 (2003) 222.
- [21] J.I. Pankove, Optical Processes in Semiconductors, Dover, New York, 1971.
- [22] C. Baban, G.I. Rusu, Appl. Surf. Sci. 211 (2003) 6.
- [23] K.L. Chopra, Thin Film Phenomena, McGraw-Hill, New York, 1969.
- [24] B.D. Cullity, Elements of X-Ray Diffraction, Addison-Wesley, 1978, p. 356.
- [25] H. Metin, R. Esen, Semicond. Sci. Technol. 18 (2003) 648.
- [26] M. Rusu, I. Salaoru, M.E. Popa, G.I. Rusu, Int. J. Mod. Phys. B 18 (2004) 1287.
- [27] C. Baban, G.G. Rusu, I.I. Nicolaescu, G.I. Rusu, J. Phys. Condens. Matter 12 (2000) 7687.
- [28] M.T. Mohamad, A.A. Hashim, M.H.A.I. Maamory, Mater. Chem. Phys. 99 (2006) 382.
- [29] Y. Tauc, R. Grigorovici, Y. Vancu, Phys. Stat. Sol. 15 (1966) 627.
- [30] L. Bentes, R. Ayouchi, C. Santos, R. Schvarz, P. Sanguino, O. Conde, M. Peres, T. Monteiro, O. Teodoro, Superlattice Microstruct. 42 (2007) 152.