Synthesis and characterization of thermally oxidized ZnO films

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Abstract. Metallic zinc thin films were deposited onto glass substrates using vacuum thermal evaporation method. By thermal oxidation of as-deposited Zn films, in ambient conditions, at different temperatures (570, 670 and 770 K, respectively, for 1 h) zinc oxide thin films were obtained. The structural characteristics of the obtained films were investigated by X-ray diffraction technique and atomic force microscopy. Characteristic XRD patterns of oxidized films show small and narrow peaks superimposed on the large broad background of the amorphous component of the substrate. Optical transmittance spectra were recorded and it was observed that the transmittances of the studied films increased with increasing oxidation temperature. The values of the optical bandgap, E_g , evaluated from Tauc plots, were found to be ranged between 3.22 and 3.27 eV. Electrical conductivity measurements were performed and it was observed that, after performing a heat treatment, the electrical conductivity of analysed samples decreased with one or two orders of magnitude. The gas sensitivity was investigated for some reducing gases such as acetone, methane and liquefied petroleum gas and it was observed that the films studied were selective to acetone.

Keywords. Zinc oxide; structural analysis; optical parameters; electrical conductivity; gas sensitivity.

1. Introduction

In recent years, transparent conducting oxide (TCO) thin films have received considerable attention because of their wide applications in different areas such as solar cells, display panels, photovoltaic devices, gas sensors, etc. Among them, zinc oxide (ZnO) presents some interesting characteristics which make it suitable for use in different applications. Zinc oxide (ZnO) has a wurtzite (hexagonal) structure with a wide bandgap of 3.37 eV, at room temperature. The bandgap has a major influence on the properties of the material. This includes properties like optical absorption, electrical conductivity and refractive index. The exciton binding energy, the important property for any optical device like light emitting diodes (LEDs), ultraviolet photodetector, UV blue semiconductor laser and so on, is 60 meV in ZnO, which is 2.4 times higher than that of GaN (Laurent *et al* 2008). This is the reason why ZnO is considered as a prospective candidate for these devices. The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the use of ZnO in mechanical actuators and piezoelectric sensors.

In order to use ZnO thin films for different applications, it is very important to obtain films with desired and reproducible properties. Taking into account that the depo-

sition parameters of each deposition technique can be varied, the properties of thin films obtained may differ significantly. Therefore, the researchers are still conducting studies to establish the most convenient deposition parameters for processing ZnO thin films with excellent optical and electrical properties.

Many techniques have been employed by different authors in order to prepare ZnO thin films. These include: electrodeposition (Laurent *et al* 2008), pulsed laser deposition (Stamataki *et al* 2009), magnetron sputtering (Prepelita *et al* 2012), sol-gel (Srinivasan and Kumar 2006), spray pyrolysis (Gumus *et al* 2006), etc. A simple, but less used method employed for preparation of ZnO thin films is thermal oxidation of Zn metallic films. This method offers many possibilities to modify the values of the deposition parameters and to prepare films with determined structures, electrical and optical properties.

The main goal of this paper is to establish some correlations between the oxidation conditions and optical, electrical and gas sensing properties of ZnO thin films.

2. Experimental

The preparation method of ZnO thin films consists of two steps: (a) deposition of zinc metallic films by thermal evaporation under vacuum and (b) by thermal oxidation of the last ones.

As substrates, glass slides were used. Before deposition, the substrates were properly cleaned.

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The evaporation of metallic zinc was performed from a resistively heated tungsten boat, in a chamber evacuated to a pressure of 4×10^{-5} Torr. The metallic films were prepared using the following deposition parameters: the evaporator (source) to substrate distance was 16 cm; substrate temperature was 300 K; source temperature was about 700 K and deposition rate was about 2 nm/s. The source material used was zinc metal (in the form of pellets) with a purity of 99.9%. The as-deposited zinc thin films had a grey metallic luster.

After deposition, Zn films were heated in ambient atmosphere, from room temperature to a final temperature. This was fixed at 570, 670 and 770 K, respectively with a temperature rate of about 6 K/min and were maintained for 60 min at a maximum temperature and finally were cooled down to room temperature. The oxide films were named A/13, A/14 and A/15, respectively.

XRD analysis was carried out by means of DRON 3 diffractometer, employing $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

Atomic force microscopy (AFM), in tapping mode, was used to study the surface topography of the films. Surface roughness was estimated over an area of $10 \times 10 \mu\text{m}^2$.

The optical transmittance measurements, recorded within the wavelength range from 340 to 1400 nm, corrected from the effect of glass substrate, were used to calculate the absorption coefficient, α , and the optical energy bandgap, E_g .

In order to investigate electrical properties, the analysed films were equipped with two parallel thin-film silver electrodes. The temperature dependences of electrical conductivity were investigated during two heating/cooling cycles.

Gas sensitivity was calculated taking into account the following relation:

$$S = \frac{\Delta R}{R_a} = \frac{|R_a - R_g|}{R_a}, \quad (1)$$

where R_a is the sensor resistance in the air and R_g is the sensor resistance in the presence of test gases, at a given temperature.

More information regarding the gas sensitivity measurements are provided elsewhere (Rambu *et al* 2011, 2012).

3. Results and discussion

3.1 Structural investigations

Figure 1 shows the typical XRD patterns of as-deposited zinc metallic film (figure 1(a)) and three ZnO films prepared by oxidation of zinc films, at temperatures of 570, 670 and 770 K, respectively (figure 1(b)).

From figure 1(a) it can be observed that zinc metallic film exhibits a polycrystalline structure, whereas XRD

patterns characteristic for oxidized films, presented in figure 1(b), indicates only the start of the crystallization process. In figure 1(a), diffraction peaks at $2\theta = 36.48^\circ$, 39.15° and 43.33° , respectively were assigned to be hexagonal Zn (planes (002), (100) and (101) respectively) based on comparison with JCPDS standard (JCPDS Data file 4-831). It was observed that after the oxidation process, at different temperatures, the diffraction characteristic of zinc metallic film disappear, indicating that the metal is completely transformed into ZnO.

Characteristic patterns of oxidized films show small and narrow peaks superimposed on the large broad background of the amorphous component of the substrate. Two peaks appear in the range of 2θ from 30° to 40° in the XRD patterns characteristic of ZnO films. They correspond to the (002) and (101) planes of the hexagonal (wurtzite) ZnO crystalline structure (JCPDS Data file 36-1451).

In order to improve the films' crystallinity, all samples were submitted to a heat treatment which consists of an annealing from room temperature to the oxidation temperature and maintained at the respective temperature for 60 min. Therefore, sample A/13 was heat treated at a temperature of 570 K, sample A/14 at a temperature of 670 K and sample A/15 at a temperature of 770 K,

Figure 1. XRD patterns of as-deposited and oxidized Zn.

Figure 2. AFM images of oxidized ZnO films at different temperatures: (a) $T = 570$ K; (b) $T = 670$ K; (c) $T = 770$ K.

respectively. In all cases, the heating rate was about 6 K/min. The structure of the heat treated films was studied again, by means of X-ray diffraction technique. Analyzing the characteristic XRD patterns (not presented here), it was observed that, no important structural modifications took place. The same small and narrow peaks were presented in the characteristic diffractograms of heat treated samples.

Surface scanning was done for the studied films, using AFM technique. As it may be observed, from figure 2, the surface morphology of respective films is characterized by high-density columnar structure. The columnar structure reveals that the microcrystallites are preferentially oriented. From the two-dimensional AFM images,

we can observe that the investigated surfaces are covered by crystallite with a well defined shape and small sizes. The colour distribution is homogeneous on the analysed surface, indicating a uniform composition of the films. One can observe that, as the oxidation temperature is increased, from 570 to 770 K, the surface average roughness increases from 9.2 to 15.1 nm. An increase of the surface roughness may be a consequence of the structural modification produced by the increase of oxidation temperature. Theoretically, at high oxidation temperature, the atoms have higher diffusion activation energy and occupy the correct sites in the crystal lattices. The film crystallites become larger and consequently the surface roughness is larger. An increase of the surface roughness with

annealing temperature increase was observed by Al-Kuhaili *et al* (2008).

3.2 Optical properties

Optical transmittance spectra of the ZnO films, recorded in spectral range from 340 to 1400 nm, are presented in figure 3. The experimental results indicate that the increase of the oxidation temperature determines an important increase of the film transmittance. As we can observe, the investigated films exhibit relatively high transmittance (between 75 and 92%) in visible region of the spectrum and a sharp fundamental absorption edge at about 380 nm.

The values obtained for optical transmittance depend on different factors such as film thickness, structural defects, etc (Li *et al* 2005; Prasada Rao and Santhoshkumar 2009). In our case, the lower values of optical transmittance obtained for sample A/13 (oxidized at 570 K) may be explained by the presence of unoxidized Zn in film structure. The complete oxidation of the metallic films depends on various parameters such as film thickness, oxidation temperature, oxidation time, etc (Wolf 1971). Many authors have investigated the transition from Zn film to ZnO and different values for a

complete oxidation temperature are reported. For example, Aida and coworkers (2006) reported that the total oxidation is achieved at a temperature of 300 °C, the oxidation time being 2 h. Alivov *et al* (2005) concluded that the entire transformation of Zn into ZnO depended only on substrate temperature. In our case, even XRD patterns does not indicate the presence of metallic zinc characteristic peaks; it is possible that remaining amount of Zn atoms is too small to be observed by XRD measurements. Probably, the un-oxidized zinc will act as scattering centres for light and, consequently, the optical transmittance is low. By increasing oxidation temperature, from 570 to 670 K and further to 770 K, the optical transmittance, in visible domain, increases. We consider that, at higher oxidation temperatures, all metallic atoms are oxidized and the decrease of optical scattering followed by crystallite growth and the reduction of crystallite boundary density will cause an increase of the optical transmittance.

The optical transmittance spectra, obtained after the samples were heat treated, are plotted and presented as inset in figure 3. As it may be observed, only for sample A/13 the optical transmittance increases after a heat treatment. For the other two samples no important modifications are identified. As we mentioned before, probably the sample oxidized at 570 K, was not oxidized entirely and therefore optical transmittance was low; by

Figure 3. Typical transmission spectra for studied samples. Inset: transmission spectra after heat treatment.

Figure 4. Typical $(\alpha h\nu)^2 = f(h\nu)$ dependences for studied films.

Table 1. Values of some characteristic parameters.

Sample	T (K)	τ (min)	R_a (nm)	E_g (eV)	σ ($\Omega \times \text{cm}$) ⁻¹
A/13	570	60	9.2	3.22	1.15×10^{-2}
A/14	670	60	10.2	3.24	4.81×10^{-3}
A/15	770	60	15.1	3.27	5.43×10^{-3}

T represents the oxidation temperature; τ is the oxidation time; R_a is the surface average roughness; E_g is optical bandgap; σ is the value of electrical conductivity before the two heating/cooling cycles.

applying a heat treatment the remaining Zn metallic was oxidized and the film became more transparent.

It is known that a stoichiometric semiconducting compound has a sharp transmission edge at that photon energy which corresponds to the forbidden energy gap of the respective compound. Assuming a direct transition between the edge of the valence and the conduction band, the variation of the absorption coefficient with the photon energy can be described by the following relation (Hodgson 1970; Pankove 1971):

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (2)$$

where α represents the absorption coefficient, $h\nu$ is incident photon energy, E_g denotes the optical bandgap, for allowed direct transition and A is a characteristic parameter, independent of photon energy.

The optical bandgap energy is calculated by extrapolation of the linear part of $(\alpha h\nu)^2$ vs $h\nu$ to $\alpha h\nu \rightarrow 0$. Using this procedure, the values of energy bandgaps corresponding to investigated ZnO films were determined (figure 4) and summarized in table 1.

The energy bandgap values were found to be in the range of (3.22–3.27) eV. These values were found to increase with increasing oxidation temperature. It is observed that the values obtained are smaller than 3.37 eV and can be attributed to the greater density of donor states near the conduction band determined by the oxygen vacancies (Wang 2004). Even when the obtained values of E_g are smaller than 3.37 eV, they are in good agreement with the values reported before (Al-Kuhaili *et al* 2008; Rambu and Rusu 2010; Rambu *et al* 2010; Prepelita *et al* 2012). It was observed that, after performing a heat treatment, the values of optical bandgap did not vary significantly.

3.3 Electrical behaviour

The electrical characterization of studied samples was carried out, by performing the temperature dependence of electrical conductivity measurements. In fact, the variation of electrical resistance was measured with film temperature up to about 570 K, the same dependences being recorded during the cooling as well. Once it reached the room temperature, the films were taken through a second heating-cooling cycle. The electrical conductivity was calculated taking into account the geometrical configuration of the electrodes.

Figure 5. $\ln \sigma = f(10^3/T)$ dependences for Zn metallic film.

The temperature dependence of conductivity for a zinc metallic film was measured in order to emphasize the oxidation process. As it may be observed from the characteristic plot (figure 5), the electrical conductivity decreases with increasing temperature, indicating the metallic behaviour of the sample. Up to about 510 K, the film conductivity varies in a relatively narrow range and then begins to decrease quickly. This behaviour indicates that some important structural changes take place due to metal oxidation. The same tendency is observed at the second heating. After two heating-cooling cycles, the electrical conductivity of the films decreases with few orders of magnitude, indicating the oxidation of metallic film.

For ZnO films the $\ln \sigma = f(10^3/T)$ dependences were studied and the characteristic plots are presented in figures 6(a)–(c). From the characteristic plots, it is observed that the film heating determines an exponential increase of electrical conductivity. This behaviour indicates the semiconducting properties of studied samples.

It was reported before (Laurent *et al* 2008; Prepelita *et al* 2012) that, by performing a heat treatment, the structural characteristics of the films are improved. Also, it is well known that physico-chemical properties of thin films depend on the structural characteristics. Consequently, a

Figure 6. $\ln \sigma = f(10^3/T)$ dependences of (a) sample A/13; (b) sample A/14 and (c) sample A/15.

heat treatment will modify electrical properties of the studied samples. Analysing the $\ln \sigma = f(10^3/T)$ dependences obtained for ZnO films, it is observed that, after the first heating, these dependences become reversible. It is supposed that a heat treatment stabilizes the structure of the studied samples and this is the reason why the $\ln \sigma = f(10^3/T)$ dependences become reversible. It is worth noting that the thermal stability of electrical resistance during successive heating-cooling cycles makes ZnO film a good candidate for applications in optoelectronics (as contact electrodes).

A decrease of the electrical conductivity with one or two orders of magnitude, after the first heating, was observed. A similar behaviour was reported before by Bouderbala and co-workers (2009). They observed an increase of ZnO film resistivity with five orders of magnitude after these ones were annealed in air.

As it is observed from table 1, the electrical conductivity of the samples, before the heat treatment, σ_i , depends on the oxidation temperature. For the sample oxidized at 570 K, the value obtained was $1.15 \times 10^{-2} (\Omega \times \text{cm})^{-1}$ and, by increasing the oxidation temperature, the values of electrical conductivity decreased with one order of magnitude. Also, it was observed that surface roughness

increased with the increase of oxidation temperature. We presume that, as the surface roughness increases, the effective surface area and the number of absorption sites increase and more oxygen is chemisorbed at the film surfaces, resulting in more resistive films.

4. Gas sensitivity

The gas sensing was performed in the temperature range of 370 to 550 K, for the following gases: acetone, methane and liquefied petroleum gas. All measurements were performed at a constant gas concentration (900 ppm).

Figures 7(a)–(c) show the sensitivity to tested gases as a function of work temperature for all investigated films. It can be seen that the sensitivity of all investigated films increases with an increase in the operating temperature, reaching a maximum value corresponding to an optimum operating temperature, and above this temperature, the sensitivity decreases. The optimum operating temperature was found to be at 470 K.

It was reported before that the response of a gas sensor is determined by the speed of the chemical reaction on the crystallite boundaries and the speed of diffusion of

Figure 7. Relationship between operating temperature and sensitivity, for different gases: (a) sample A/13; (b) sample A/14; (c) sample A/15; (d) relationship between sensitivity and ethanol concentration for all investigated samples.

the gas molecules to that surface, which are activation processes (Shinde *et al* 2007). Depending on the morpho-structural characteristics of the investigated gas sensor film, its chemical composition and the tested gas, there is a temperature at which the speed values of the two processes become equal. At that point, the sensor response reaches its maximum. As it was observed from figures 7(a)–(c), the investigated ZnO film sensors reach their maximum at a temperature of 470 K. Below this temperature, a low response is obtained probably because the gas molecules do not have enough thermal energy to react with the surface adsorbed oxygen species.

It was observed that the temperature at which the gas sensitivity reach the maximum value, named the optimum operating temperature, is a function of the kind of target gases and the chemical composition of the oxide, including additives and catalysts, nature of contact electrodes, etc. (Eranna *et al* 2004; Shinde *et al* 2007). For example, Wagh and co-workers (2006) reported that RuO₂ doped and surface ruthenated ZnO sensors yielded a large response to NH₃ at a low operating temperature (250 °C) whereas pure ZnO yields the maximum response at temperatures higher than 350 °C. Also, Bhattacharyya *et al*

(2007) have studied the resistance change with two different metallic contacts to ZnO (e.g. gold and palladium-silver) in air and in the presence of methane in N₂ carrier gas. They observed a significant improvement of the sensor performance for Pd–Ag contact.

Analysing the plots from figures 7(a)–(c), it can be observed that, by increasing the oxidation temperature from 570 to 770 K, the gas sensor properties of ZnO films are improved; the sensitivity to acetone increases from 4.12 to 6.46. This behaviour is explained by the fact that the sensor films' performances are directly related to the exposed surface/volume ratio. A rougher surface has an increased exposed surface to gas sensitivity and, consequently, increased detection sensitivity.

As it can be observed, the sensitivity of ZnO films to test gases is relatively poor. But, the optimum working temperature and the gas concentration at which we obtain the maximum sensitivity, are better than those of others (Xu *et al* 2006; Iftimie *et al* 2008). For example, it was reported before that ZnO/glass thin films have a maximum sensitivity of 5.65 to acetone at a temperature of 250 °C, while ZnO:(Sn + Al)/glass thin films exhibit a higher maximum sensitivity value of 7.65 at a tempera-

ture of 225 °C (Iftimie *et al* 2008). Xu *et al* (2006) reported as having obtained an optimum working temperature of 370 and 420 °C, respectively for a gas concentration of 3000 ppm.

A plot of the sensitivity of all investigated samples, as a function of acetone concentration, is presented in figure 7(d). As it can be observed, the magnitude of film sensitivity increases with increase in gas concentration up to 900 ppm and, after this value, no changes are found. We believe that the values of sensitivity are low and at small gas concentrations, because there is a low coverage of gas molecules on the sensor surface and, hence, lower surface reaction occurred. By increasing the gas concentration, a larger surface is covered and the surface reaction increases. At a certain gas concentration (900 ppm in this case), gas vapours form a monolayer on the whole surface of the film and vapours from that layer would reach the active sites of the surface, thus reaching the saturation point.

5. Conclusions

The conclusions from this study are summarized as follows:

(I) Zinc oxide (ZnO) films were prepared by thermal oxidation of zinc metallic films, deposited by vacuum thermal evaporation. Structural investigations, performed by means of XRD measurements, showed that Zn metallic films possessed a well defined polycrystalline structure, whereas oxidized Zn films, at different temperatures, presented small and narrow peaks which were assigned to be wurtzite ZnO.

(II) The investigated samples were characterized by high transmittance ranging between 75 and 92%, in visible domain. The values of optical bandgap were recorded and were found to range between 3.22 and 3.27 eV. These values were in good agreement with the values reported for bulk ZnO crystals.

(III) The electrical conductivity measurements were performed and it was observed that values ranged between $1.15 \times 10^{-2} (\Omega \times \text{cm})^{-1}$ and $5.43 \times 10^{-3} (\Omega \times \text{cm})^{-1}$. After a heat treatment consisting of two heating/cooling cycles, it was observed that there was a decrease of electrical conductivity values with one or two orders of magnitude. By performing a heat treatment, the film structure was stabilized. This idea is sustained by the $\ln \sigma = f(10^3/T)$ dependences, which become reversible after the first heating.

(IV) Gas sensing measurements indicate that investigated films are most sensitive to acetone and the operating temperature is 470 K. The oxidation temperatures influence the morphological characteristics of the oxidized films. Taking into account that gas sensor characteristics are related to the exposed surface/volume ratio, it can be

concluded that oxidation temperature influences the gas sensing characteristics.

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