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Effect of precursor solution and annealing temperature on the physical properties of Sol–Gel-deposited ZnO thin films

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ABSTRACT

Polycrystalline transparent Zinc oxide thin films have been grown on glass substrates by the sol–gel technique using two different precursor solutions. The physical properties of the films were analyzed with X-ray diffraction, Atomic Force Microscopy, UV–Vis and Raman spectroscopy. The results show that the films grew in the hexagonal wurtzite structure. The band gap of the samples was estimated from UV–Vis measurements in values from 3.1 to 3.22 eV, these values are in agreement with those reported in the literature. Two different simple ways to obtain polycrystalline ZnO were developed and the properties of the films were studied as a function of the precursor solution.

1. Introduction

Zinc oxide (ZnO) is a wide direct band gap semiconductor ($E_g = 3.3$ eV) [1,2] with a number of interesting physical properties. ZnO has been extensively used as a window material for solar cells due to the high transmittance in the visible region and its low electrical resistivity [2]. Recently, ZnO is attractive for optoelectronic applications such as photodetectors, light emitting diodes and electro and photoluminescence devices [3] due to the direct band gap and the large exciton binding energy of 60 meV [4–6]. It has potential applications in ultra violet light emitting devices, laser devices and daylight blind UV detectors [2].

ZnO has two stable crystalline structures, hexagonal wurtzite and cubic zinc blende. The wurtzite structure is the most stable phase at ambient conditions.

ZnO thin films have been obtained by pulsed laser deposition [3,4,7,8], RF magnetron sputtering [9], spray pyrolysis [10,11] and sol–gel [12].

The sol–gel technique is a cheap versatile thin film deposition technique that allows obtaining a variety of materials. Some of the principal advantages of the sol–gel deposition process are: the good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost and good optical properties. The sol–gel processes are efficient in producing thin, transparent, multi-component oxide layers of many compositions on several substrates [13].

There are several reports on the production of ZnO thin films using zinc acetate (ZnAc) [14,15], however the use of a sol stabilizer is reported. As far as the authors are aware there is not much work on the use of zinc acetylacetonate (ZnAcAc) as a precursor for the sol–gel technique. The properties of the films grown by chemical methods are strongly dependent on the precursor used [10]. In the present work, the effect of the precursor solution as well as the annealing temperature on the physical properties of ZnO thin films prepared via sol–gel dip-coating technique using two different precursor solutions is studied. The starting solutions were prepared using zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$) dissolved in methanol and zinc acetylacetonate hydrate ($(C_5H_7O_2)_2Zn(H_2O)$) dissolved in a mixture of propanol and water. The ZnO thin films were structurally characterized by X-ray diffraction and Raman spectroscopy. The optical properties were measured with UV–Vis spectroscopy. The topography of the films surface was analyzed with atomic force microscopy. The results are discussed as a function of the precursor solution and the annealing temperature. The

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results show good quality films crystallized in the hexagonal wurtzite structure.

2. Experimental

2.1. Precursor solutions

ZnO thin films were grown on glass substrates by the sol–gel technique. Two different precursor solutions were used. In the precursor solution A, 2 g of ZnAc was dissolved in methanol and the solution was magnetically stirred at room temperature for 24 h. The resulting solution was highly transparent and stable. For the precursor solution B, 1.377 g of ZnAcAc was first dissolved in propanol and the solution was stirred with a magnetic stirrer at 50 °C for 1 h. After that a 1:1 proportion of distilled water was added and the solution was stirred for 1 h at 50 °C. The solution became whitish. Solution A is very stable, after a month of aging the appearance did not change while in solution B a segregation was observed, it is possible that in the precursor solution B the zinc acetylacetonate was not dissolved completely and after some time it was segregated.

2.2. Thin films deposition

Prior to the deposition of the films, the glass substrates were cleaned rinsing them in acetone, and then in ethanol. The deposition of the thin films was carried out in a dip immersion sol–gel coating system at room temperature. Two series of thin films were grown on glass substrates, one series for each solution.

The samples are labeled as A# for the films grown using precursor solution A and B# for the films grown using precursor solution B. Each substrate was immersed five times, after each immersion a thermal treatment was applied at a temperature of 180 °C for 10 min in air, in order to evaporate both solvent and possible organic compounds from the precursor in the films.

After the last immersion, the samples were thermally annealed at different temperatures (T_a) for 3 h. Two samples were obtained using solution A, these samples where annealed at 400 °C (A4) and 500 °C (A5). From solution B two films were grown; one sample was annealed at 400 °C (B4) and the other one at 500 °C (B5).

X-ray diffraction (XRD) patterns were obtained in a Siemens D5000 diffractometer, using the Cu-Kα line at grazing angle. Raman spectroscopy measurements were performed in a Labram Dilor micro Raman system employing the 532 nm excitation line in the backscattering geometry configuration. An UV–Vis Perkin Elmer Lambda 25 spectrophotometer was used to obtain the optical transmittance spectra. The topography studies were performed by atomic force microscopy (AFM), using a Thermo Microscope Autoprobe CP Research AP-2001 in contact mode.

3. Results and discussion

3.1. Structural characterization

The XRD patterns of the samples grown by the sol–gel technique on glass substrates using different precursor solutions are presented in Fig. 1. It can be seen that the films are polycrystalline. The samples grown using precursor solution A (A4 and A5) present seven peaks at: 31.62°, 34.24°, 36.12°, 47.62°, 56.42°, 62.78° and 67.94° that correspond to the diffraction planes of hexagonal ZnO (PDF#75–1526): (100), (002), (101), (102), (110), (103) and (200), respectively. In the patterns of the samples B4 and B5, three peaks can be clearly seen at 31.62°, 36.12° and 56.52°, these peaks correspond to the (100), (101) and (110) diffraction planes of ZnO wurtzite structure according to card PDF#75-1526. It is difficult to observe considerable shifts in the positions of the peaks as the annealing temperature increased. As can be seen the films grown using solution B are preferentially oriented in the (100) direction, while sample A4 is oriented in the (101) direction; A5 has no preferential orientation. Note that in the films obtained from solution A the (002) reflection appears, Sagar et al. [14,15] reported preferentially oriented films in the (002) direction obtained from ZnAc precursor, thus ZnAc promotes the growth of crystals in the (002) direction. From XRD using the Scherrer formula: $d = 0.9\lambda/B\cos\theta_B$, where d is the crystallite diameter, λ is the wavelength (1.5406 Å), B is the full width at half maximum (FWHM) of the peak and θ_B is the Bragg angle, the crystallite size was calculated. The crystallite sizes and the values of FWHM, are presented in Table 1.

The lattice parameters were calculated using the relation for the plane spacing equation [16]:

$$\frac{1}{d^2} = \left(\frac{4}{3}\right)\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \tag{1}$$

where d is the plane spacing, obtained by the Bragg law: $\lambda = 2d\,\sin\theta$, h, k and l are the Miller indices, a and c are the lattice parameters. The calculation results for the lattice parameters give $a = 3.26$ Å, and $c = 5.23$ Å for all the samples. These values are in good agreement with the reported values in the literature [17].

From Table 1 it can be observed that bigger crystallite sizes are obtained for films grown from solution B probably because the dissociation enthalpy [10] of ZnAc is low allowing the formation of a dense film structure with small crystals while in solution B the nucleation is slower and bigger crystals are formed. Note that the increase on the annealing temperature leaves to the reduction of crystallite sizes, this effect can be due to the strain relieved crystals reduced in size and have energy enough to move toward low energy surface sites forming a more dense and compact film [18]. Although it has to be considered that the XRD peaks can be broadening by stress and defects present in the films [19], affecting the FWHM, thus the real values of the crystallite size can be different from the calculated values. It can be assumed that the crystalline quality of the samples deposited using precursor solution B is better than the samples grown using solution A as it can be seen from stronger relative intensity of the peaks, and the reduction of the FWHM and increase of the crystallite size.

The Raman spectra of the films were taken in order to confirm the presence of the wurtzite phase in the ZnO thin films, the spectra are shown in Fig. 2. It can be observed the presence of two broad bands centered at 568 and 1100 cm^{-1}.These bands represent the 1LO (E_1) and 2LO modes of wurtzite ZnO [6], which agree with the XRD analysis. These results indicate that there is resonant Raman scattering of the E_1-LO phonon indicating good crystalline quality of the films [6]. Note that the bands corresponding to the films grown using solution B are better defined, more intense and narrower than the bands of the films grown using solution A, this effect is related to the crystallinity. The annealing temperature does not have visible effects on the Raman spectra of the films. The Raman spectroscopy results confirm the XRD results where a better crystallinity of ZnO thin films deposited from solution B was observed.

3.2. Optical characterization

Fig. 3 shows the transmittance spectra of the samples. The transmission spectra show transmission above 80% except for the film B5 that has a transmission near 75%. As it can be seen the films with the highest transmission are the samples grown using precursor solution A with a value of about 86%. These results are consistent with the observed in the precursor solutions. Solution A was