Influence of the Al content on the optical properties of ZnO thin films obtained by the sol-gel technique

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ZnO thin films were prepared by the Sol-Gel technique, with the addition of 0.001−1 at. % aluminum, in steps of ½order of magnitude, as well as some selected values in the 2–20 at. % range. The metal salts employed were zinc acetate dihydrate and aluminum(III) nitrate nonahydrate. The films were annealed at 400 °C in air, and show high transparency, uniformity, and good adherence to the substrate. We have found that the improvement of the optical transmission of the films, with respect to that of pure ZnO, as well as the shift of the absorption edge towards higher energies, are consequences of the formation of the corundum phase of Al_2O_3 in the films.

Keywords: ZnO; Al_2O_3; Sol-gel; Thin films; Transparent conducting oxides (TCO's); Optical properties

1. Introduction

ZnO thin films are highly attractive in the development of optoelectronic devices, due to their numerous potential applications, which in turn arise from their high transparency in the visible and near-UV spectral regions, as well as their wide conductivity range. The conductivity of ZnO thin films depends upon several factors, such as the preparation technique, the *in situ* preparation parameters, the doping agent, the annealing temperature and atmosphere, and even the measurement conditions [1-4]. When ZnO films are doped with the appropriate metal atoms, such as Al, Sn, Cd, Ga, In, etc., their resistivity can be as low as 10^{-4} Ω cm. However, in the case of Al-doped ZnO films, the presence of the dopant also usually decreases the transmittance significantly, to values under 70 % [5], a fact that is highly inconvenient for the usage of the films as transparent electrodes.
In this work, we report on the preparation of $(ZnO)_{1-y}(Al_2O_3)_y$ thin films of high optical transmission, by the sol-gel technique.

2. Experimental

The preparation of the ZnO precursor solution, based on the use of zinc acetate dihydrate, has been reported previously by the authors [6]; the dopant source was aluminum(III) nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$), and the Al atomic percentages in solution (X) were in the 0.001-1.0 % range, in steps of ½order of magnitude, as well as some selected values in the 2–20 at. % range. The precursor solutions were highly sensitive to the water content, therefore, it was necessary to dry the metal salts before the preparation of the solutions, in order to discard the ambient water absorbed; all precursor solutions were maintained at 4 °C. Both of these operations resulted in a gelation time of 11 days for the solution with the highest Al content (20 at. %), and longer for smaller dopant concentrations. Long gelation times are required for thick films made up of several coatings. All films were deposited on glass slides, at room temperature, by the dipping method. They were pre-heated at 100 °C for 60 min and then annealed at 400 °C, in air. All the films obtained were highly transparent and fracture-free. The optical measurements were performed on a Perkin-Elmer Lambda-2 UV-Vis spectrometer, on films prepared by one- and six-dipping procedures. The X-ray diffraction studies (XRD) were carried out in a Rigaku D/max-2100 diffractometer (Cu $K\alpha_1$ radiation, 1.5406 Å), with a thin film attachment. The thickness of the films was determined by means of a Sloan Dektak II profilometer, after removal of a step-like portion of them with diluted HCl.

3. Results

Representative UV-Vis spectra of one-coating films (av. thickness = 0.1 μm) have been assembled in Fig. 1., all of which show the abrupt absorption edge characteristic of ZnO, at around 380 nm. It can be observed that the spectra of the films with low Al concentrations in solution are very similar to that of undoped ZnO (Fig. 1.a), while the spectra of the films with Al contents in the intermediate range show an improvement in their transmittance in the low absorption region right after the edge (λ > 380 nm), Fig.1.b. This effect continues to increase, up to values of nearly 100 % transmission for films with high aluminum concentrations in solution (Fig. 1.c); this is accompanied by an increase in the transmission percentage in the high absorption region (λ < 380 nm), *i.e.* from ~10 % for the intrinsic ZnO film (X = 0), to ~35 % for the film with X = 20 at. % Al. When the spectra are superimposed, as shown in Fig. 2, a shift of the absorption edge toward shorter wavelengths is observed. The E_g values, obtained from a $(h\nu\alpha)^2$ *vs.* $h\nu$ plot (not shown; $h\nu$ = photon energy, α = absorption coefficient [7]), as a function of the Al concentration in solution are presented in Fig. 3.

For six-coating films (av. thickness = 0.5 μm), the spectra, superimposed in Fig. 4, show the interference

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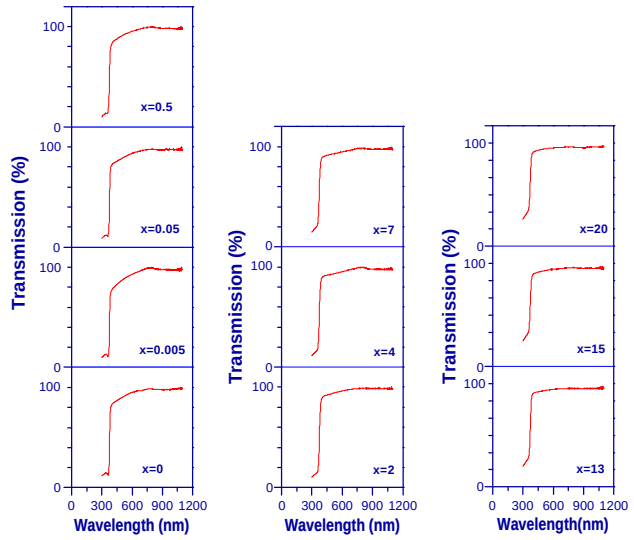

Figure 1. Representative UV-Vis spectra of $(ZnO)_{1-y}(Al_2O_3)_y$ thin films with *a)* low, *b)* intermediate, and *c)* high aluminum content in solution.

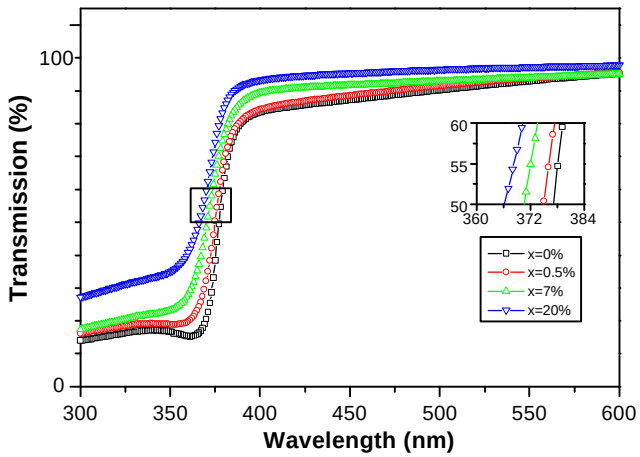

Figure 2. Superposition of representative UV-Vis spectra of "one-coating" $(ZnO)_{1-y}(Al_2O_3)_y$ thin films.

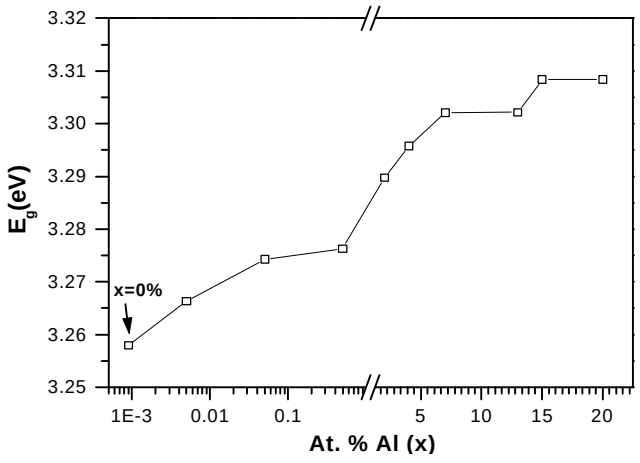

Figure 3. Calculated E_g values of $(ZnO)_{1-y}(Al_2O_3)_y$ thin films, as a function of the aluminum content in solution (X).

fringes characteristic of thick films, in the low-absorption region, however, their high transmittance is maintained; as in the case of the one-coating films, the absorption edge becomes significantly more abrupt with the aluminum content, and a shift toward shorter wavelengths is observed.

The XRD patterns of all films show the presence of polycrystalline ZnO in its hexagonal, wurtzite form, as observed in Fig. 5 for the film with 20 at. % Al in solution. The ZnO lattice parameters were calculated, by using the Bragg Law and the interplanar distance equation for a hexagonal lattice, and the results, a = 3.255 and c = 5.212, are very close to the reference values, which indicates that there is no significant structural deformation in the material. An important observation is the fact that, from a value of X = 9 at. % Al, a shoulder between the ZnO (002) and (101) peaks is evident; after a gaussian deconvolution of the above mentioned peaks (inset in Fig. 5), it was found that such shoulder corresponds to the (104) plane of the α or corundum phase of Al_2O_3. It is interesting to note that Sieber *et al*., by means of scanning electron microscopy and tunneling electron microscopy, detected the presence of Al_2O_3, as well as of other Zn-O-Al complex compounds, in their sputtering-grown ZnO films with 0.8-8.6 at. % Al, from an aluminum concentration value of 1 at. %, after thermal treatment at 500 °C [8]. Furthermore, they ascribed the decrease in grain size in their films to the presence of such phases. In our case, the ZnO grain size decreases from *ca.* 350 Å in the intrinsic films, to an average value of 100 Å in the films with high Al content in solution, as calculated from the full-width at half-maximum of the XRD peaks. The Al_2O_3 grain size is approximately 150 Å, as measured for films with 20 at. % Al.

4. Discussion

The improvement of the transmittance of the films, with the aluminum concentration, can be attributed to the presence of Al_2O_3, detected in the XRD patterns as seen before, on the basis of the following known facts: i) The absorption edge of aluminum(III) oxide is found at *ca.* 190 nm [9], therefore, it is a transparent material in the ZnO absorption edge region. ii) Compounds formed due to the presence of aluminum, have been found to show a columnar-like growth on the grain boundaries of ZnO [8]; this structural order makes a positive contribution to the transmittance.

The shift of the ZnO absorption edge can be due to two main causes: a free carrier (electron) concentration increase, or a decrease in grain size. The first is not considered to be important in our case, since a significant conductivity increase was not observed [10]; furthermore, the presence of Al_2O_3 indicates that the aluminum is not electrically active in the films. This point and the fact that we observe a decrease in the grain size of the films (from 350 to 100 Å), on increasing the Al concentration in solution, as Sieber *et al.* also found for their films [8], lead

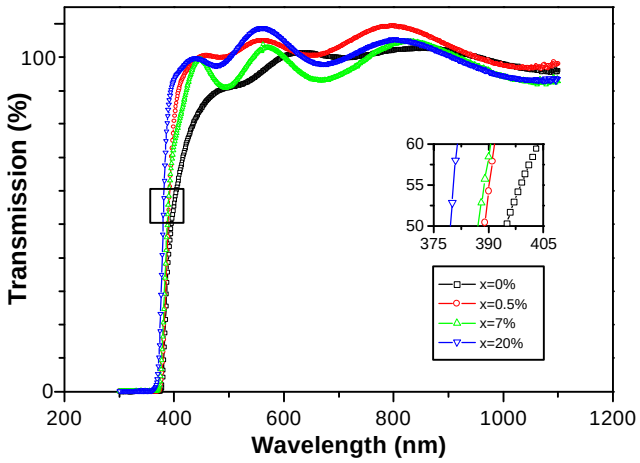

Figure 4. Superposition of representative UV-Vis spectra of "six-coating" $(ZnO)_{1-y}(Al_2O_3)_y$ films.

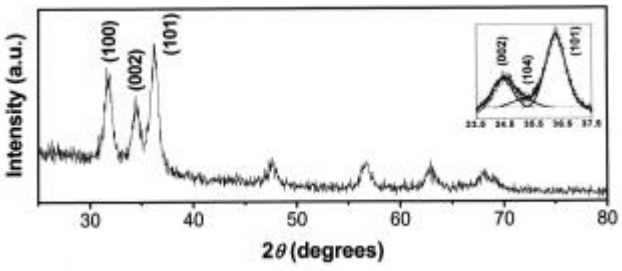

Figure 5. Representative XRD pattern (X = 20 at. % Al) of the films. The inset shows the deconvolution of the ZnO (002) and (101) peaks, and the Al_2O_3 (104) peak.

us to ascribe the absorption edge shift to the grain size decrease. If the grain is small, a quantization of the energy levels of both the conduction and the valence band is expected [11], which would, in turn, cause an E_g shift toward higher values.

The high transmittance of the films obtained in this work is an issue that must be highlighted, especially for the films with high aluminum content, since it has been reported to date that aluminum doping is detrimental to the transmittance of the ZnO films [12].

5. Conclusions

It was observed that the optical properties of the films obtained in this work were improved with the incorporation of aluminum in the ZnO precursor solution. The metal was observed to be present in the films as Al_2O_3, which presumably has a high structural order. The presence of Al_2O_3 crystals has an effect on the growth mechanism of ZnO, leading to a decrease in grain size, and therefore, to quantum size effects that produce an increase in the values of E_g.

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