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Development of highly transparent and conducting yttrium-doped ZnO films: the role of sol-gel stabilizers

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Yttrium-doped zinc oxide (YZO) thin films were deposited with the dip coating technique. The effect of different sol-gel stabilizers (lactic acid with hydrolysis, without hydrolysis, and diethanolamine (DEA)) on structural, electrical and optical properties of the produced films were investigated. The stability of solutions prepared with DEA was much higher than that of other stabilizers. Films deposited using this solution also exhibited good adherence to the substrate, preferential orientation, and the lowest full width at half maximum of (002) X-ray diffraction peak. Average transmittance in the visible region increased by 14.6% and resistivity decreased by two orders of magnitude as the stabilizer was changed from lactic acid to DEA. The lowest resistivity, 3.5×10^{-2} Ω·cm, and an average transmittance of 85% are obtained for 200 nm thick films annealed at 450 °C in air using DEA as a stabilizer.

Key words: *ZnO:Y; transparent conducting oxide; sol-gel; stabilizers*

1. Introduction

Transparent conducting oxide (TCO) films of tin, indium and zinc oxides (doped and undoped) have been extensively studied due to their high optical transmittance and electrical conductivity. These films are useful in photovoltaic and photothermal applications [1–3]. Unlike the more commonly used indium tin oxide, zinc oxide is a non-toxic, inexpensive and abundant material. It is chemically and thermally stable in hydrogen plasma processes which are commonly used for the production of solar cells [2, 4]. Non-stoichiometric pure ZnO is an n-type semiconductor, but its optical and electrical properties are not very stable at high temperatures [5]. However, doped films can be made which have very stable electrical and optical properties [6]. Therefore, doped ZnO films are preferred for practical purposes [7]. The doping effect of In, Al, and Ga on ZnO has been reported frequently by many research groups [4–7] but the use of a rare-earth impurity as a dopant, particularly Sc, Y has been scarcely

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reported, although their ionic radii are close to that of zinc, which makes them compatible for doping. Recently, Minami et al. reported that conductivity of RF sputtered ZnO films can be increased by Y-doping [8].

Several deposition techniques are used to grow ZnO thin films, including chemical vapour deposition (CVD) [4, 9], magnetron sputtering [10, 11], spray pyrolysis [12], pulsed laser deposition (PLD) [13, 14], and sol-gel method [7]. In comparison with other techniques, the sol-gel technique has the advantage of being low cost and allowing non-vacuum, low substrate temperature deposition. Since zinc belongs to the group of elements which easily form polymeric hydroxides (a fundamental requirement for the sol-gel chemistry), this technique can be easily used to deposit thin films of zinc oxide.

The usual starting materials for sol-gel processes are metal alkoxides. They are hydrolyzed to form sols, but they are expensive and their reactants are explosive. Therefore, many thin films have been prepared using metal salts [15,16]. A problem in the sol-gel process is the stability of the sol. Sometimes precipitation or gelation occur during its storage and application, affecting the quality of the films produced. Some kinds of acids are often used to accelerate or control the sol-gel process and are known as sol-gel stabilizers. Owing to these reasons, we have made an attempt in this study to investigate the effect of adding different sol-gel stabilizers, like (a) lactic acid with water, (b) lactic acid without water, and (c) diethanolamine (DEA) in ethanol as a solvent on the structural (*c*-axis orientation and surface morphology), electrical (resistivity, carrier concentration and Hall mobility) and optical (transmittance, band gap energy) properties of YZO films prepared by the dip coating technique. The effects of annealing temperature in air on these properties have also been investigated in the temperature range of 300 −500 °C.

2. Experimental

A precursor solution of ZnO, about 0.2 M in concentration, was prepared from zinc acetate ($Zn(CH_3CO_2)_2{\cdot}2H_2O$, purity 99.5%) and dissolved in anhydrous ethanol. It was observed that the solutions prepared with concentrations greater than 0.2 M did not remain stable for a long time. Yttrium nitrate hexahydrate ($Y_2NO_3{\cdot}6H_2O$, purity 99.9%) was used as a dopant (3 wt. %) in the present study. The mixture obtained in such a manner was stirred in a magnetic stirrer for about 4 h at room temperature. It was observed that the solubility of zinc acetate was smaller in ethanol. Due to this, the associated acetate forms colloids and a milky solution is obtained. The sol-gel stabilizers were added to the respective solutions to eliminate/minimize the turbidity and precipitates. Various sol-gel stabilizers were added: lactic acid with hydrolysis (solution A), without hydrolysis (solution B), and DEA (solution C). Solution A was hydrolyzed with 2 moles of water per 1 mole of metal acetate by adding water dissolved in ethanol at 10 wt. % drop-wise, along with roughly 5 wt. % lactic acid in order to remove turbidity. Solution B was prepared using only lactic acid. It may be mentioned

that solution B had to be filtered in order to obtain a clear solution. An equimolar amount of DEA was added to solution C drop-wise to eliminate the obtained turbidity and precipitates completely. Clear, transparent, and homogenous solutions thus obtained were left to age for 48 hrs.

The corning glass (7059) substrates, after being cleaned with acetone and methanol in an ultrasonic bath for 20 minutes each, were rinsed with deionised water for 5 min and then dried in a nitrogen atmosphere. The glass substrates were dipped in the respective solutions (approximately 15 ml) at room temperature. The area of the dipped surface was 15×20 mm^2. The substrate was withdrawn with a speed of 8 cm/min. Films were dried at 250 °C for 20 min. This cycle was repeated 10–15 times until the desired thickness was obtained. The thickness of the films was in the range of 200–250 nm. The deposited films were annealed in air in the temperature range of 300–500 °C for 1 h.

The structural properties of the films were investigated with a Phillips Holland X-ray diffractometer (Model PW 1830/00). The surface morphology of the films was analyzed with Scanning Electron Microscopy (JEOL JSM 6300). The thickness of the film was measured with a DEKTECK^{3-ST} surface profilometer. The electrical resistivity and Hall coefficient of the films were measured at room temperature with the van der Pauw technique. Optical transmittance measurements were carried out in the wavelength range of 200–800 nm using a double beam spectrophotometer (SHIMADZU 330). The proportion of yttrium to zinc of YZO films was found to be nearly equal to that in the solution, as determined by an Elemental Dispersion Analysis of X-ray (EDAX) measurements.

3. Results and discussion

Some of the parameters which control the quality of the films prepared with the sol-gel technique are: (i) ageing of the solution, (ii) wettability, and (iii) the stabilizer itself. Solutions A, B and C were observed with a magnifying glass in order to watch the changes in the sol with time. 72 h after the preparation of solution, it was observed that solution A showed turbidity/suspensions; its complete gelation took place in approximately a week. Solution B remained clear for 2 weeks. However, solution C remained transparent and stable even for 2 months.

The wettability of the solution with different stabilizers was examined simply by keeping the coated solution at room temperature for a longer time. If the solution is not repelled by the substrates even after 10 minutes, it exhibits good wettability. It was observed that solution C had the best wettability, and that the coated film remained uniform and smooth as compared to the films obtained from solution A. The films produced using solution A were non-uniform and had small dots (holes) at the edges and a relatively rough surface with a yellowish-white colour. This may be due to poor wettability and residual precipitates that may have developed during aging. Films made from solution B did not contain dots, and their surfaces seemed to be moderately uniform.

3.1. Structural properties

Structural properties of the films deposited under different conditions were examined by X-ray diffraction (XRD). As grown YZO films prepared from solutions A, B and C exhibited an amorphous nature, whereas films annealed at 350 °C showed evidence of a conversion from an amorphous to polycrystalline structure with (100), (002) and (101) peaks. However, no preferred orientation was observed. As the annealing temperature was increased from 350 to 450 °C, the (002) reflection peak became intense and sharper as compared to the others, indicating a tendency of preferential growth in the films. With a further increase in temperature, i.e. beyond 450 °C, there was a decrease in the intensity of all the peaks, which suggests a degradation of the quality of the films at higher temperatures [17]. This effect was common in films derived from all three solutions.

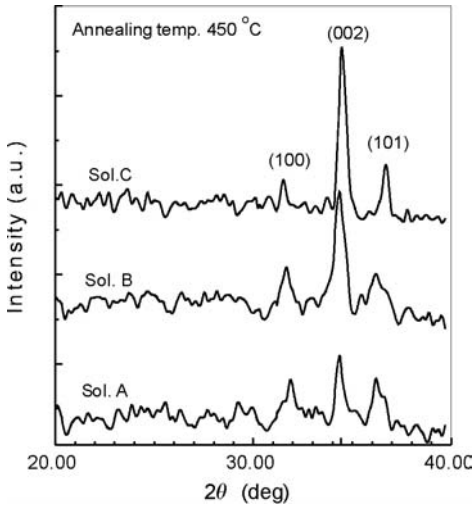

Fig. 1. XRD diffraction patterns of YZO films derived from different solutions annealed at 450 °C in air

Figure 1 shows the X-ray diffractograms for YZO films annealed at 450 °C and prepared from solution A, B and C. The highest (002) peak intensity was observed in films prepared using solution C. A shift in the (002) peak position to a higher 2θ value was also observed for these films with an increase of the annealing temperature. This shift approached the powder value of 34.44° at the temperature of 450 °C. This indicates a reduction in the tensile stress with annealing [16]. This reduction could be due to a large linear expansion coefficient of YZO films in comparison with the glass substrate, to a reduction of defects, or to the desorption of oxygen.

The effects of annealing temperature on full width at half maximum (FWHM) of the films obtained from different solutions are shown in Figure 2. It was observed that FWHM decreases with increasing annealing temperature until 450 °C for all of the

films. The value of FWHM is inversely proportional to the grain size, implying that grain size improves with increasing annealing temperature [18]. A further increase in the annealing temperature resulted, however, in an increase in FWHM. This may be due to a degradation of the structure or contamination with alkali ions from the glass substrate [19]. The lowest FWHM, 0.39°, was obtained for films made from solution C, being 11.4% lower than that obtained from films made from solution A.

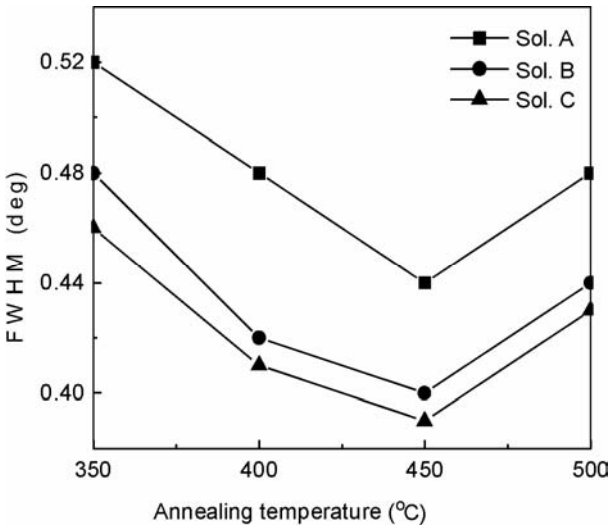

Fig. 2. The effect of annealing temperature on the FWHM of YZO films obtained from solutions A, B and C

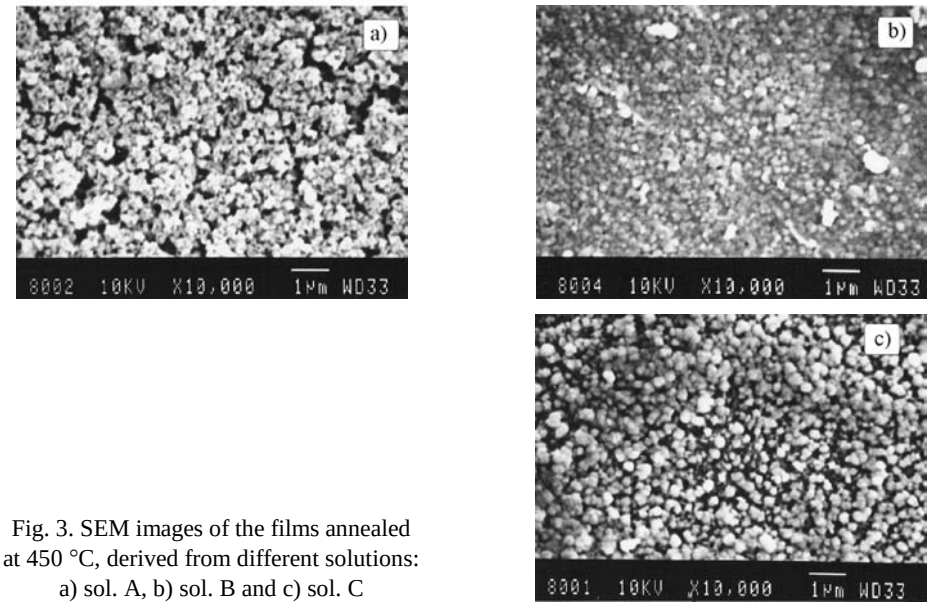

Fig. 3. SEM images of the films annealed at 450 °C, derived from different solutions: a) sol. A, b) sol. B and c) sol. C

The experiment reveals that the use of DEA enhances the *c*-axis orientation of YZO films. The solution with DEA as a stabilizer was the most stable and produced YZO films with the highest quality.

Figures 3a–c show SEM images of films annealed at 450 °C, derived from three different solutions. It can be clearly seen that the use of DEA enhances grain growth (supported by XRD analysis, Fig. 2) and improves surface morphology.

3.2. Electrical properties

The Hall coefficient data showed that the YZO films are of the n-type. Electrical properties of YZO films prepared from all three solutions were investigated as a function of annealing temperature. There was an increase in mobility with increasing annealing temperature until 450 °C, which is mainly due to the improvement of crystalline structure in films as supported by our XRD analysis (Fig. 2). This increase in mobility is also accompanied with an increase in the carrier concentration, due to interstitial zinc atoms and/or a contribution from Y^{3+} ions substituting Zn^{2+} ions. This results in a decrease in resistivity. Moreover, the desorption of oxygen from the surface, pores and grain boundaries with increasing annealing temperature may also be responsible for decreased resistivity. A slight increase in the resistivity of the films at temperatures above 450 °C may be due to a structural degradation as observed in the XRD analysis.

Table 1. FWHM, resistivity (ρ), carrier concentration (n) Hall mobility (μ_H) and average transmittance for YZO films grown at an optimized annealing temperature (450 °C) using different sol-gel stabilizers

Sol-gel stabilizers	FWHM (deg)	ρ (Ω·cm)	n (cm^{-3})	μ_H (cm^2/Vs)	Average transmittance (%)
Solution A	0.44	4.016	1.15×10^{17}	14.0	75
Solution B	0.40	0.246	1.39×10^{18}	18.2	79
Solution C	0.39	0.035	9.1×10^{18}	19.8	86

The resistivity (ρ), carrier concentration (n) and Hall mobility (μ_H) for the YZO films grown under optimized annealing temperature (450 °C) using different sol-gel stabilizers are given in Table 1. It is seen from the table that μ_H in a sample obtained from the solution C is nearly 1.4 times higher than that in a sample obtained from solution A, while there is an increase by two orders of magnitude in the value of n for films prepared from solution C as compared to those obtained from solution A. This gives rise to the lowest resistivity, $3.5 \times 10^{-2}\,\Omega$·cm, for films obtained using DEA as a stabilizer.

3.3. Optical properties

Figure 4 shows optical transmittance curves for YZO films annealed at 450 °C, prepared from different solutions. The average transmittance in the visible region

measured for films obtained from all the three solutions was higher than 75%, but it was the highest for films produced from the solution C. The optical band gap energy was calculated using Tauc's plot, as shown in Fig. 5. The maximum values for transmittance and the band gap energy were obtained for films produced from solution C, amounting to 86% and 3.331eV, respectively.

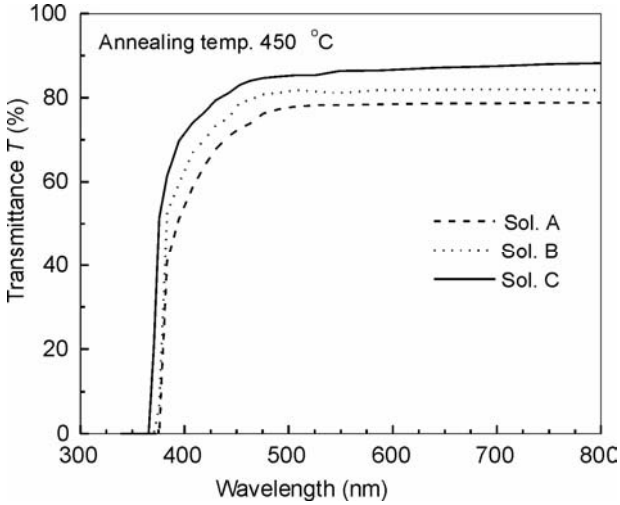

Fig. 4. The dependence of transmittance (*T*, %) in the wavelength range of 200−800 nm on sol-gel stabilizers for YZO films annealed at 450 °C

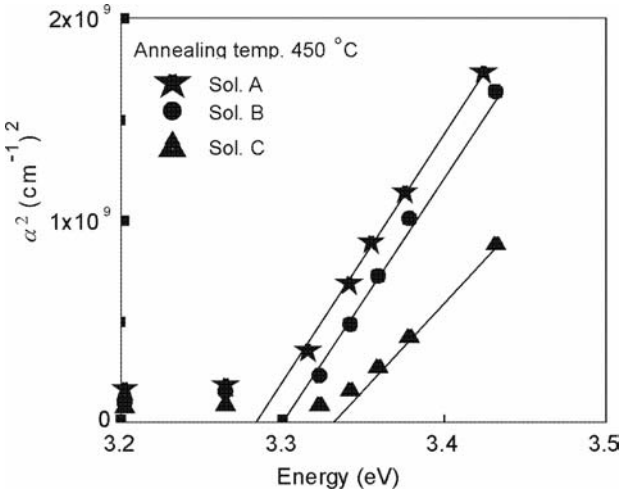

Fig. 5. Effect of sol-gel stabilizers on the band gap energy (E_g) for YZO films, shown in Tauc's plot

The effect of annealing temperature on the band gap energy of YZO films prepared from different solutions is shown in Fig. 6. It is seen from the figure that the

band gap energy is higher for films obtained from the solution C as compared to those obtained from the solutions A and B. The effect of annealing is also enhanced for films obtained from solutions using DEA as a stabilizer. The average transmittance was also found to increase with an increase in annealing temperature up to 450 °C for all three films. The variation of transmittance with annealing temperature for films deposited from the solution C is also shown in Figure 6. This increase in transmittance can be attributed to an improvement in the crystallinity and microstructure with increasing annealing temperature.

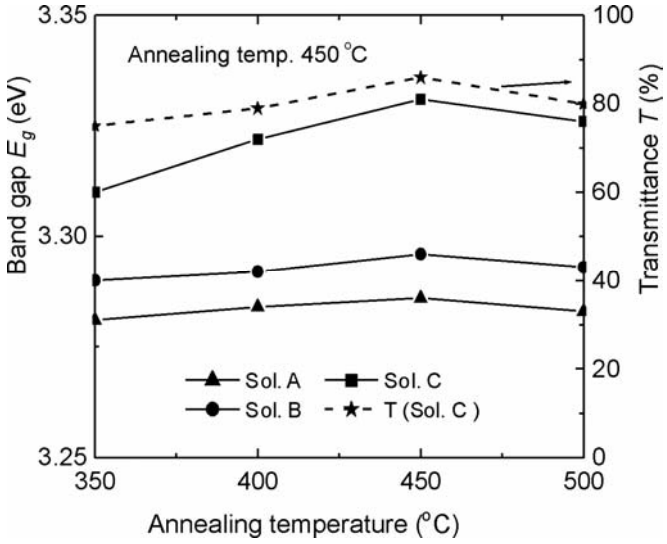

Fig. 6. Variation of band gap energy (E_g) and transmittance (T, %) as a function of annealing temperature

4. Conclusion

Sol-gel derived yttrium-doped ZnO thin films were obtained. They all exhibited polycrystallinity at an annealing temperature of 350 °C. It was observed that solutions with DEA as the stabilizer were the most stable and produced high-quality films. The crystalline quality of the films improved with increasing annealing temperature up to 450 °C. Films prepared from the solution C showed preferential *c*-axis orientation. Minimum resistivity and the maximum transmittance were obtained for films deposited from the solution C. These films also showed an enhanced optical band-gap energy.

It may be mentioned that the key to obtain high-quality films using the sol-gel technique is to prepare a clear, transparent and homogeneous solution without any chemical species. Further, in the sol-gel process of ZnO thin films starting from zinc acetate (the precursor material), one cannot use a hydrolysis reaction (as in alkoxides) in order to form Zn–O–Zn bonds in the precursor. The formation of such bonds al-

ways leads to a homogenous and/or heterogeneous nucleation of ZnO or other related compounds in the solution. When this happens, the solutions are not homogenous anymore. However, DEA acts as a bidentate ligand to the zinc ions in the solution, making it stable against any precipitates. This stability of the solution is responsible for the successful incorporation of Y into the ZnO lattice, in turn leading to reduced resistivity.

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