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Al-doped ZnO thin films by sol–gel method

V. Musat[a,*], B. Teixeira[b], E. Fortunato[b], R.C.C. Monteiro[b], P. Vilarinho[c]

[a]*Department of Metals and Materials Science, 'Dunarea de Jos' University of Galati, 111 Domneasca, 6200 Galati, Romania*
[b]*Department of Materials Science, CENIMAT, Faculty of Sciences and Technology, New University of Lisbon, Campus da Caparica, 2829-516 Caparica, Portugal*
[c]*Department of Glass and Ceramic Engineering, CICECO, University of Aveiro, Campus Universitario de Santiago, 3810-193 Aveiro, Portugal*

Abstract

Transparent and conductive high preferential *c*-axis oriented ZnO thin films doped with Al have been prepared by sol–gel method using zinc acetate and aluminium chloride as cations source, 2-methoxiethanol as solvent and monoethanolamine as sol stabilizer. Film deposition was performed by dip-coating technique at a withdrawal rate of 1.5 cm min^{-1} on Corning 1737 glass substrate. The effect of dopant concentration, heating treatment and annealing in reducing atmosphere on the microstructure as well as on the electrical and optical properties of the thin films is discussed. The optical transmittance spectra of the films showed a very good transmittance, between 85 and 95%, within the visible wavelength region. The minimum resistivity of 1.3×10^{-3} Ω cm was obtained for the film doped with 2 wt.% Al, preheated at 400 °C and post-heated at 600 °C, after annealing under a reduced atmosphere of forming gas.

Keywords: Al-doped ZnO; Thin films; Sol–gel; Electrical properties; Optical properties

1. Introduction

ZnO:M (M = Al, Ga, In) thin films with high *c*-axis orientated crystalline structure along (002) plane are extensively studied for practical applications including transparent conducting electrode materials for various electronic devices such as solar cells, electroluminescence displays, etc. [1–5]. A high degree of crystal orientation reduces the electrical resistivity due to an increase in carriers mobility by reducing the probability of the scattering of the carriers at the grain boundary.

Sol–gel method is widely used to obtain various kinds of functional oxide films, including ZnO and doped ZnO thin films with preferred *c*-axis orientation. Generally, two principal routes to obtain oxide thin films are used: the alkoxide route, using organo-metallic precursors often expensive and dangerous and the non-alkoxide route, using water or alcohol solutions of metal salts such as acetates, nitrates or chlorides [1–4,6].

The main factors affecting the sol–gel film microstructure and properties are: solution chemical equilibrium (chemical composition, concentration, pH, order-time-temperature of reagents mixing), substrate–film interaction during film deposition (sol viscosity, spin/dip coating parameters) and thermal processing of the as-deposited gel film (time and temperature of preheating between each layer deposition, time-temperature-atmosphere of postheating, time-temperature-atmosphere of final annealing).

In this paper, based on XRD data, SEM micrographs, UV–VIS spectra and Hall effect measurements, the authors present some results on the field of transparent and conductive Al-doped ZnO thin films prepared by a non-alkoxide sol–gel method.

2. Experimental

The thin films deposition was performed by dip-coating technique on Corning 1737 glass substrate, using a sol prepared with $Zn(CH_3COO)_2{\cdot}2H_2O$ (purity–99.5%), $AlCl_3{\cdot}6H_2O$ (purity–98%), 2-methoxyethanol and monoethanolamine (MEA). The concentration of metal ions in the solution was 0.75 mol/l and the molar ratio of MEA to metal salts was 1.0.

In order to study the effect of aluminium concentration and thermal treatment on the microstructure, electrical and optical properties of Al-doped ZnO thin films, two values of dopant concentration (1 and 2 wt.%) and

*Corresponding author. Fax: +40-2-361353.
E-mail address: vio52musat@yahoo.com (V. Musat).

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Table 1
Post-heat treatments (PT)

	Experimental conditions
PT1	Heating from 25 to 600 °C, maintaining at 600 °C (1 h) in air and cooling in air
PT2	Introducing and maintaining at 600 °C (1 h) in air and cooling in air
PT3	Introducing and maintaining at 600 °C (1 h) in air, cooling until 450 °C in air, maintaining at 450 °C (20 min) in inert or reducing (forming gas) atmosphere and then continuing cooling in inert or reducing atmosphere

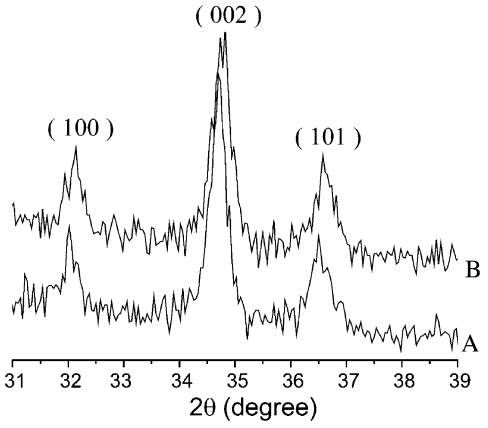

Fig. 1. XRD patterns of Al (1 wt.%)-doped ZnO thin film after PT1 (sample B) and PT2 (sample A).

three post-heat-treatments (PT1, PT2, PT3) were used. The post-heat-treatments are specified in Table 1. After each post-heat-treatment and prior measurements, all the samples have been heated for final annealing at 450 °C for 20 min in forming gas.

The XRD patterns of the samples were recorded at room temperature using a Rigaku diffractometer (model RAD IIA), with CuK_{α} radiation. The thickness of the thin films was measured using a Sloan Dektak three-dimensional surface profilometer. The surface morphology of the films was analysed using a scanning electron microscope (SEM) Hitachi S-1400. The Hall mobility was measured using a HL5500PC from Biorad.

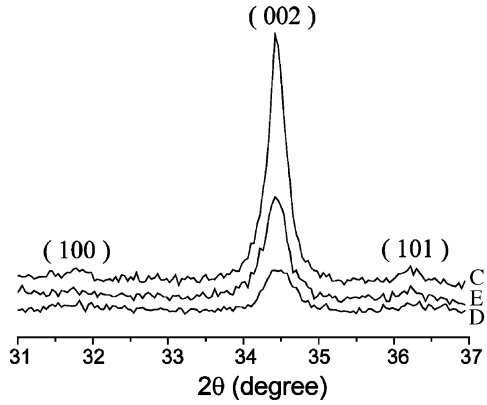

Fig. 2. XRD patterns of Al (2 wt.%)-doped ZnO thin films after PT1 (sample C), PT2 (sample D) and PT3 (sample E).

The optical transmittance was measured using a UV–VIS–NIR double beam spectrophotometer (UV-3100 PC, Shimadzu) in the wavelength range from 300 to 2500 nm.

3. Results and discussion

The XRD patterns of ZnO:Al 1 wt.% samples after PT1–PT2 and of ZnO:Al 2 wt.% samples after PT1–PT2–PT3 are presented in Figs. 1 and 2, respectively. The XRD patterns have been recorded in the 2θ range of 30–40, where the most important three peaks of hexagonal wurtzite type Al-doped ZnO structure are present.

Figs. 3 and 4 show the SEM micrographs of ZnO:Al 1 wt.% samples after PT1–PT2 and of ZnO:Al 2 wt.% samples after PT1–PT3, respectively.

The values of the electrical resistivity (ρ), Hall mobility (μ_H) and carrier concentration (N) are listed in Table 2.

3.1. Effect of dopant concentration

The XRD patterns (Figs. 1 and 2) and the SEM micrographs (Figs. 3 and 4) show a smaller grain size and a higher preferential *c*-axis orientated structure along

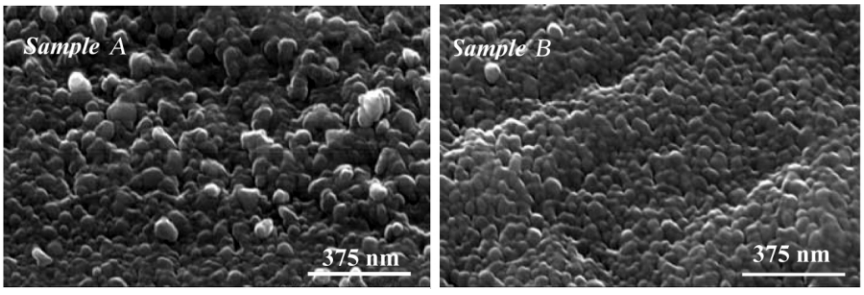

Fig. 3. SEM micrographs of the surface of the Al (1 wt.%)-doped ZnO thin films after PT1 (sample B) and PT2 (sample A).

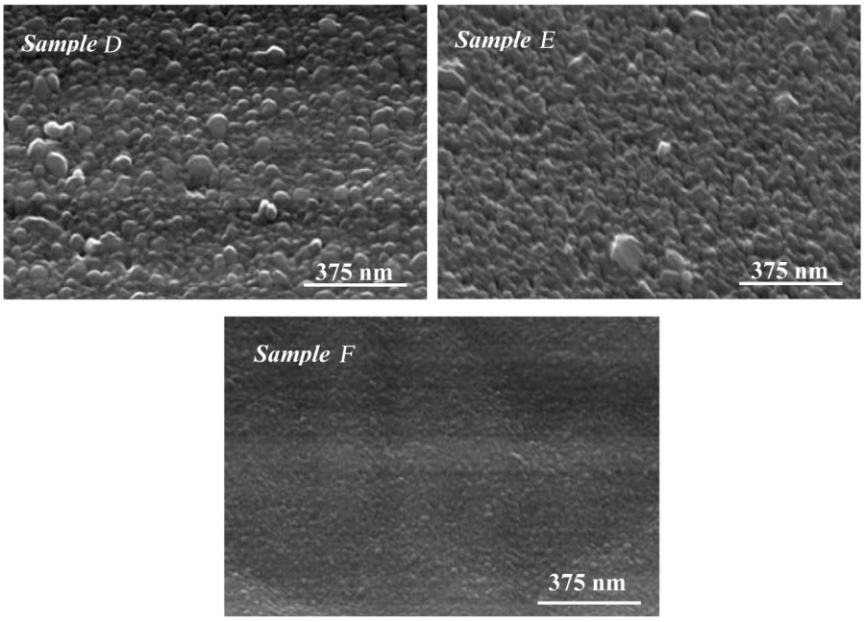

Fig. 4. SEM micrographs of the surface of the Al (2 wt.%)-doped ZnO thin films after PT1 (sample C), PT3 with cooling in N_2 (Sample E) and PT3 with cooling in forming gas (sample F).

(002) plane for ZnO:Al 2 wt.% samples than for ZnO:Al 1 wt.% thin films. The higher the crystal orientation (sample C in Fig. 2) the lower the resistivity due to the shorter carrier path length in a *c*-plane and due to the reduction in the scattering of the carriers at the grain boundaries and crystal defects, which increased the apparent mobility (sample C in Table 2) [2].

Generally, for all the samples, the low resistivity values (Table 2) show that the segregation of aluminium (as Al_2O_3) at the grain boundaries has been avoided, and an effective substitution of the dopant (Al) atoms in Zn sites of the ZnO structure took place according to the following equation [4]:

$$Al_2O_3 \rightarrow 2Al_{Zn^{\bullet}} + 2Oo + 1/2\ O_2 + 2e' \quad (1)$$

Consequently, the increase of the quantity of Al between 1 and 2 wt.% led to a subsequent increase of the carrier concentration (Table 2) indicating that, by an effective substitution, a higher amount of conduction electrons and oxygen vacancies are generated.

The effect of aluminium dopant concentration on the electrical properties also depended on the post-heat-treatment of the films.

3.2. Effect of post-heat treatment

The influence of three different post-heat treatments (see Table 1) on the electrical properties of ZnO:Al thin films has been investigated. For samples submitted to PT1, higher (002) peak intensity (Figs. 1 and 2) and larger grains (Figs. 3 and 4) were obtained, as compared to the samples submitted to PT2 and PT3. During PT1, the samples are being gradually heated from room

Table 2
Properties of thin films samples

Sample	Al content (wt.%)	Post-heat treatment	Thickness (nm)	Electrical properties		
				$\rho\times10^{-3}$ (Ω cm)	μ_H (cm^2/Vs)	N (cm^{-3})
A	1	PT2	140	7.2	24.5	3.45×10^{19}
B	1	PT1	150	5.6	29.3	3.82×10^{19}
C	2	PT1	140	3.9	34	4.67×10^{19}
D	2	PT2	160	6.6	19.1	4.35×10^{19}
E	2	PT3 (cooling in N_2)	150	1.3	26	1.85×10^{20}
F	2	PT3 (cooling in forming gas)	140	45	8	1.70×10^{19}

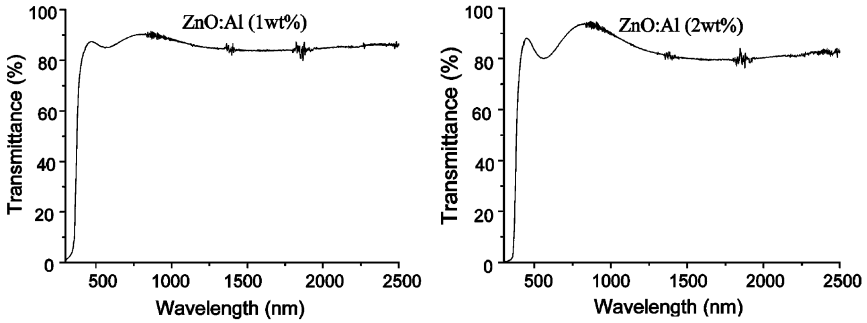

Fig. 5. The optical transmittance of Al-doped ZnO thin film after annealing.

temperature to 600 °C, the crystallization of ZnO:Al films is controlled by heterogeneous nucleation and leads to larger grains than during the PT2 and PT3. In the case of PT2 and PT3, by introducing the samples directly at high temperature (600 °C), the homogeneous nucleation competes with the heterogeneous one [1].

The atmosphere (oxidizing, inert or reducing) during cooling in the first post-heat-treatment significantly affects the electrical properties of the films measured after annealing in forming gas (see Table 2). The resistivity decreases by cooling in an inert atmosphere (sample E in Table 2) and significantly increases by cooling in a reducing atmosphere of forming gas (sample F), as compared to the results obtained by cooling in air (samples C and D). The high increase of resistivity by a factor of 35 for sample F was caused by the decrease in grain size during cooling in forming gas (Fig. 4), which lowers Hall-mobility by a factor of three and the carrier density by a factor of ten. Cooling in air atmosphere during PT1 and PT2, leads to the homogenization and stabilization of the film microstructure as a result of the larger grain size and of the decrease of the excess concentration of free Zn atoms caused by the oxidation [7]. Therefore, the microstructure of these samples is less affected in terms of grain size by the final annealing at 450 °C in forming gas. Cooling in forming gas during PT3 has a negative effect both in Hall mobility and carrier density (sample F in Table 2) as the microstructure of these samples is strongly affected in terms of grain size. The effect of cooling in N_2 during PT3 is not relevant in terms of the grain size (Fig. 4) and Hall mobility, but has an important role in terms of the type of defects and carrier density (sample E in Table 2).

The optical transmittance spectra presented in Fig. 5 show a very good transmittance, between 80 and 90%, within the visible wavelength region.

4. Conclusions

Transparent and high conductive Al-doped ZnO thin films on Corning 1737 glass were prepared by sol–gel method using an alcoholic non-alkoxide route and dip-coater technique for film deposition. The resistivity of the films ranges between 1.3 and 7.2×10^{-3} Ω cm and a very good transmittance (80–90%) within the visible wavelength region was achieved.

The increase of Al content from 1 to 2 wt.% seems to improve the electrical conductivity, but the results are not very conclusive. The atmosphere (oxidizing, inert or reducing) during cooling in the first post-heat treatment significantly affects the conductivity of the films. The conductivity increases by cooling in an inert atmosphere and decreases by cooling in a reducing (forming gas) atmosphere, comparing with the results obtained by cooling in air.

The lowest resistivity (1.33×10^{-3} Ω cm) was achieved in the film that contained 2 wt.% of aluminium, prepared with a low substrate withdrawal speed of 1.5 cm min^{-1}, preheated at 400 °C, post-heated at 600 °C (with cooling under an inert atmosphere of N_2 below 450 °C) and annealed at 450 °C in forming gas.

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