Influence of Al doping agents nature on the physical properties of Al:ZnO films deposited by spin-coating technique

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In this paper we present the morphological, structural, optical and electrical properties of aluminium doped zinc oxide films prepared by spin coating technique from a zinc acetate dihydrate and 2-methoxyethanol (0.5M) solution. $AlCl_3$ and $Al(NO_3)_3$ were used as doping agents in different concentrations (1at%, 4at% and 6at% in starting solution). After deposition, films were dried at 100 °C and then annealed at temperatures between 400 °C and 500 °C. The characterization of deposited layer was performed by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and UV-Vis spectroscopy. The results show that the optical and electrical properties of the structures strongly depend on the deposition conditions of ZnO:Al. In addition, the resistivity can be easily varied depending on ZnO:Al annealing temperatures and Al concentration.

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1. Introduction

Transparent conductive oxide (TCO) thin films have received considerable attention from many researchers because of their wide applications in optoelectronic devices such as display panel, solar cell, and photovoltaic devices, owing to their high conductivity and transparency in the visible spectrum region. Tin-doped indium oxide (ITO) is the TCO material frequently used taking into account the advantages above mentioned. However, in the last years a huge attention was accorded to ZnO, another metal oxide semiconductor suitable for use as TCO thin films because its higher thermal stability and relatively low cost product compared with ITO [1-2]. Since their conductivity is due to intrinsic defects such as zinc excess at the interstitial position and the lack of oxygen, undoped ZnO thin films are very sensitive to oxidation which will decrease the conductivity [3-6]. In this work we examined the Al doped zinc oxide films and the doping effects of Al on the electrical conductivity, surface morphology and optical properties of ZnO:Al thin films deposited by the sol–gel process using two different doping agents. The changes induced on the electrical resistivity of ZnO:Al thin films by varying the Al content and heat treatment conditions were discussed.

2. Experimental

Al-doped ZnO thin film were prepared by sol-gel process on 2×2 cm^2 glass substrates by spin-coating technique [7]. The components of the starting solutions were: zinc acetat dihydrate ($(Zn(CH_3COOH)_2\ 2H_2O$) dissolved in a mixture of 2-methoxyethanol and diethanolamine (DEA). Aluminium chloride ($AlCl_3$) or aluminium nitrate $Al(NO_3)_3$ were used as dopping agents. The concentration of zinc acetate was 0.5 mol/L and the Al/Zn concentration in the starting solution was varied in the following ratio: 0.5, 1, 2, 3 and 6 at %. The resulting solution was stirred at 60 °C for 2 hours to become clear and homogeneous. Before deposition the substrates were ultrasonically cleaned in acetone and subsequently in ethanol then rinsed with deionised water. Moreover, the substrates were subjected for 15 minutes to UV-Ozone treatment. After spin-coating, the films were drying at 100 °C for 10 minutes and annealed at 350, 450, 500 and 550 °C for 1 hour.

The electrical resistivity of the films was measured using a four-point probe system, with the appropriate correction factors. The surface morphology was studied using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Transmission spectra were recorded in 350-2500 nm spectral range. The thickness of the thin films was measured by profilometry and by ellipsometry and the films thickness values ranged between 100 and 200 nm.

3. Results and discussion

Figs. 1(a) and 1(b) show the variation of the resistivity for films annealed at a fixed temperature (350, 450, 500 or 550°C) as a function of the aluminium content of the starting solution using $AlCl_3$ and $Al(NO_3)_3$ as doping agents, respectively. In both cases the electrical resistivity

reaches a minimum value for an Al doping concentration at about 2%, after that for higher concentrations we remark a continuous increase of the electrical resistivity with the increase of Al doping concentration.

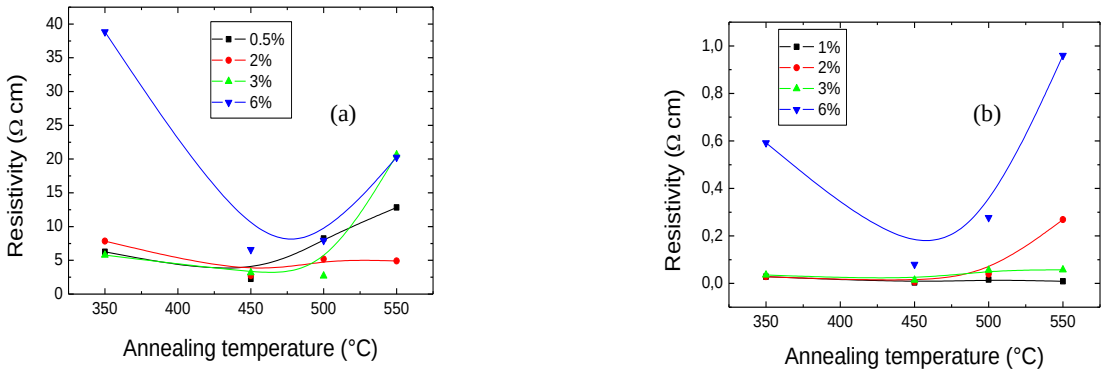

Fig. 1. Resistivity of ZnO:Al films as a function of Al doping concentration using (a) $AlCl_3$ and (b) $Al(NO_3)_3$ as doping agents.

The decrease of the electrical conductivity at high doping levels could be attributed to a degradation of the film morphology. Indeed from SEM micrographs (Fig. 2) we remark at high doping levels the occurence of microcracks at the thin films surface. These observations are in agreement with previous studies concerning the In:ZnO doped films [7]. The AFM micrograph analysis put in evidence (see Table 1) an increase of roughness with the increase of doping concentration if the $AlCl_3$ is used as doping agent and also if the doping agent was $Al(NO_3)_3$. A similar decrease of roughness with the increase of doping concentration was also putted in evidence in the case of In doped ZnO films [7, 8]. On the contrary, the differences of the roughness in function of the doping agent, could be attributed to the differences of the hydrolysation constants of the $AlCl_3$ and $Al(NO_3)_3$, which could conduct to a different growing mechanisms.

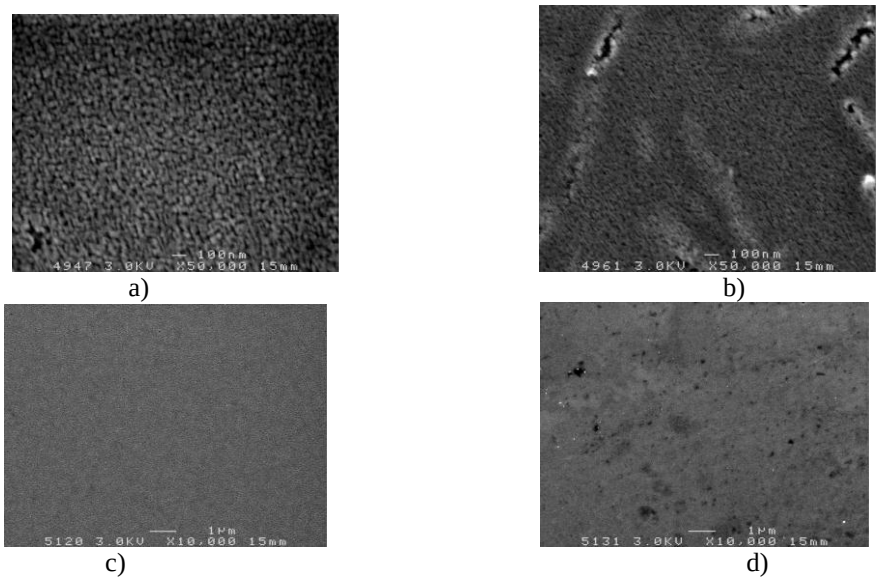

Fig. 2. SEM images for Al doped ZnO films using different doping agents in different concentrations: $AlCl_3$: 0.5% (a), 6% (b); $Al(NO_3)_3$ 1% (c), 6% (d). The annealing temperature for these samples was 450°C.

Table 1. Roughness values (RMS – root mean square roughness, RA – average roughness) of Al doped thin films annealed at 450°C using $AlCl_3$ and $(AlNO_3)_3$ as doping agents in different concentrations.

Al content	**$AlCl_3$**				**$Al(NO_3)_3$**			
%	0.5	2	3	6	1	2	3	6
RMS(nm)	5.2	4.2	3.9	3.4	22.9	17.8	13.7	8.9
RA(nm)	5.4	3.0	2.9	2.7	11.5	8.2	4.0	3.1

The analysis of the electrical resistivity in function of temperature for thin films containing the same quantity of dopant, show that no matter the nature of the dopant agent, the resistivity reaches a minimum value at about 450-470°C (Fig. 3a and 3b). At this temperature, the lowest electrical resistivity value, about 4.18×10^{-3} Ωcm, is obtained using as doping agent $Al(NO_3)_3$.

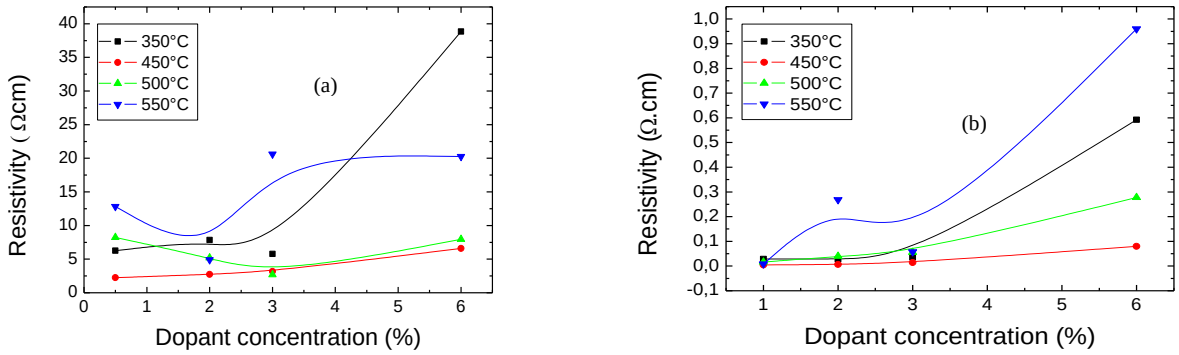

Fig. 3. Resistivity of ZnO:Al films as a function of annealing temperature using (a) $AlCl_3$ and (b) $Al(NO_3)_3$ as doping agents.

Figs. 4 show the SEM and AFM micrographs for films annealed at 350°C, 450°C and 500°C films prepared using $AlCl_3$ and $Al(NO_3)_3$, respectively, using the same ratio of doping agents. As could be remarked from SEM micrographs, no matter the doping agent nature, the films grain size increase with the annealing temperature. With the annealing temperature the crystallite grain size become larger due to the fact that the atoms of the films got more energy to migrate for forming the crystal.

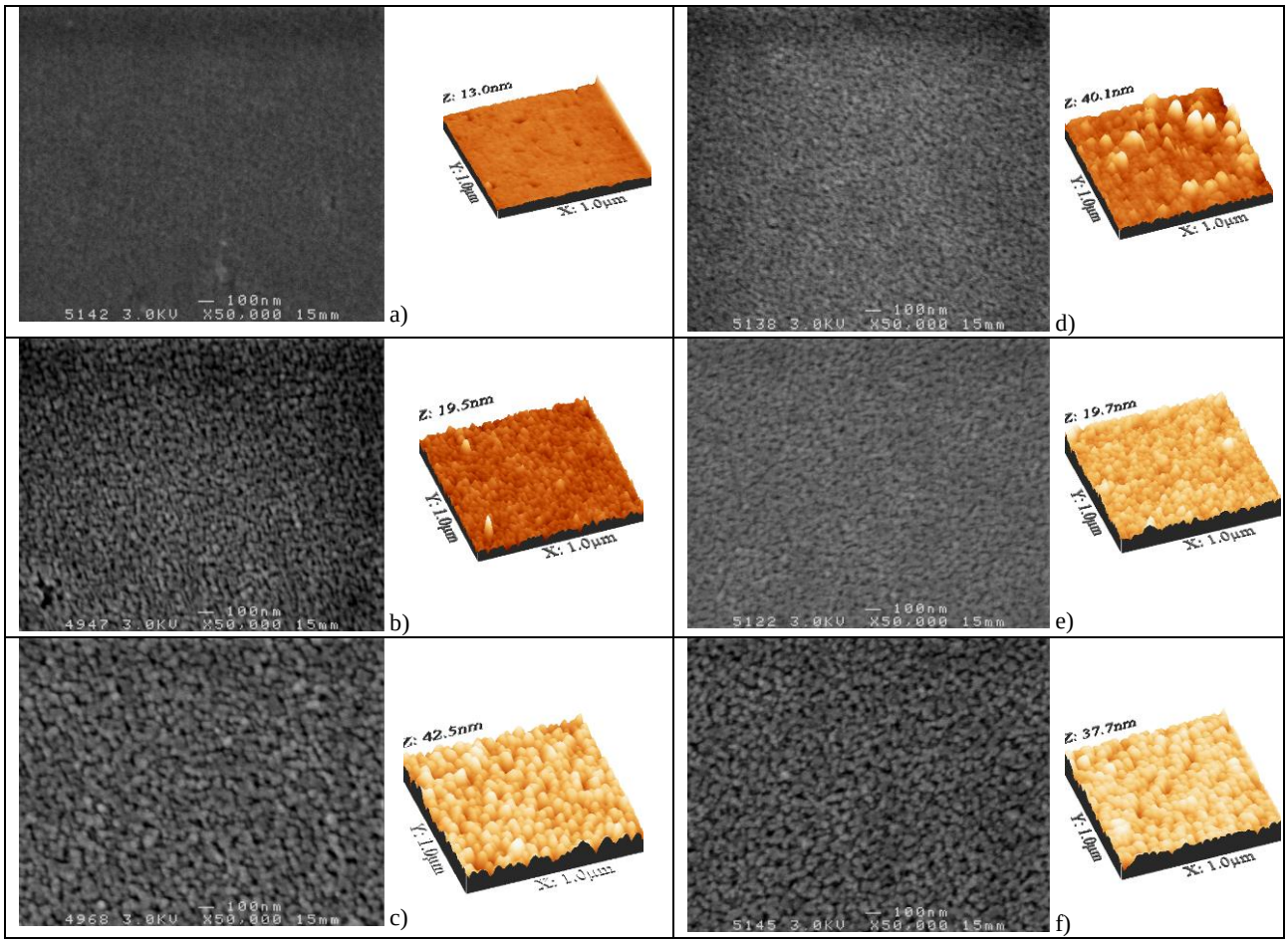

Fig. 4. SEM and AFM images for Al doped ZnO films using different doping agents and different annealing temperatures: AlCl3: 350 °C (a), 450 °C (b) and 500 °C (c); $Al(NO_3)_3$: 350 °C (d), 450 °C (e) and 500 °C (f).

Table 2. Roughness values (RMS – root mean square roughness, RA – average roughness) of Al doped thin films (1%) using $AlCl_3$ and $(AlNO_3)_3$ as doping agents annealed at different temperatures.

	Doping agent					
	$AlCl_3$			$Al(NO_3)_3$		
Annealing temperature (°C)	350	450	550	350	450	550
RMS (nm)	7.9	5.2	2.0	34.2	22.9	16.2
RA (nm)	6.2	5.4	2.6	26.0	11.5	7.9

This behaviour is generally known and was remarked also in the case of many other films [9-16]. Concerning the variation of the roughness in function of the annealing temperature, in both cases we observed a decrease of the roughness with the increase of annealing temperature (see Table 2).

From transmission spectra all films present a very high transparency (>90%) between 400 nm and 2400 nm spectral range domain. No obvious changes are induced in optical transmission for ZnO:Al with the variation of Al doping concentration or annealing temperature. From the recorded data according to [17] we calculate the optical gap for direct transitions. As an example, in Fig. 5 are represented the $(\alpha h\nu)^2$ versus energy for different Al doped concentration using $AlCl_3$ (a) and $Al(NO_3)_3$ (b) as doping agents, α, being the absorption coefficient. The modifications of the optical gap with the annealing temperature are not significant and are in agreement with the values obtained previously for the In doped ZnO films obtained by the same method [7]. On the contrary for high Aluminium doping levels (6%) we remark a decrease of the optical gap values. The optical band gap values ranged generally between 3 and 3.28 eV and are smaller than that of single crystals 3.37 eV.

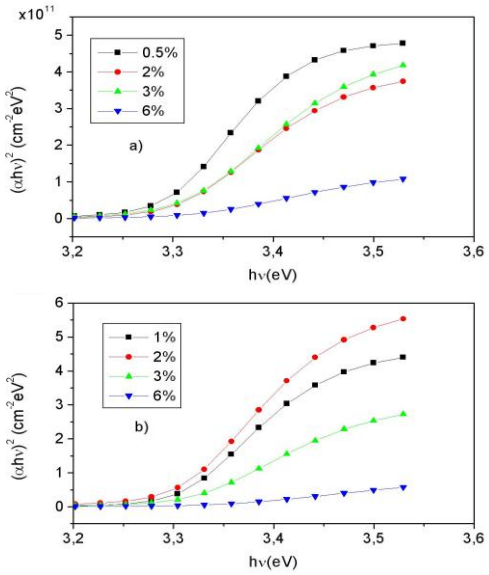

Fig. 5. $(\alpha h\nu)^2$ versus photons energy for different Al doped concentration using $AlCl_3$ (a) and $Al(NO_3)_3$ (b) as doping agents.

Table 3. Gap energy values for different Al doped concentration and for different annealing temperature using $AlCl_3$ and $Al(NO_3)_3$ as doping agents.

Doping agent	$AlCl_3$				$Al(NO_3)_3$			
(Al wt%)	0.5	2	3	6	1	2	3	6
Optical gap (eV)	3.25	3.25	3.26	3.13	3.27	3.26	3.24	3.08

Annealing temperature (°C)	350	450	550	350	450	550
Optical gap (eV)	3.27	3.25	3.28	3.26	3.27	3.26

4. Conclusions

Aluminum doped ZnO thin films were prepared by the sol–gel method using two different dopant agents $AlCl_3$ and $Al(NO_3)_3$. Films have very good transparency (>90%) and good electrical conductivities. The morphology is strongly influenced by the preparation conditions. The roughness of films decrease with the increase of doping Al content. It was putted in evidence that comparing to $AlCl_3$, the $Al(NO_3)_3$ is more suitable as doping agent. The values of the resistivity are of two order of magnitute lower using the aluminium nitrate than using the aluminium chloride. The annealing temperature also influence the electrical resitivity values. A minimum of

about 4×10^{-3} Ωcm is obtain for annealing temperatures ranged between 450 and 470 °C.

Acknowledgments

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