Al-doped and undoped zinc oxide films obtained by soft chemistry

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Received 24 October 2008; received in revised form 14 April 2009; accepted 4 May 2009

Abstract

Zinc oxide with a hexagonal wurzite type structure is an unique material that exhibits semiconducting, piezoelectric and pyroelectric properties. These properties play a key role for applications in optoelectronic devices. In the present work Al-doped and undoped ZnO films were obtained by soft chemistry starting with zinc acetate dihydrate and Al(III) isopropoxide in absolute ethyl alcohol. Trietanolamine was used as chelating agent. The films were deposited by dip coating technique on the silicon substrate and thermally treated at 500°C for one hour. The morphological characteristics of the films were investigated by Atomic Force Microscopy (AFM). Optical constants, such as refractive index (n) and extinction coefficient (k), were established by Spectroellipsometry measurements. Electrical conductivity of the studied films was determined in the 20–500°C temperature range by "the four point method". The morphology of the films is influenced by the starting sol composition, as found from AFM. According to the ellipsometric spectral data, more porous and thinner films, with smaller refractive index were obtained in the case of Al-doped ZnO films as compared with ZnO films. Both ZnO and Al-doped ZnO films presented high electrical resistivity.

Keywords: *ZnO, Al-doped ZnO, films, electrical and optical properties*

I. Introduction

Pure zinc oxide, as an intrinsic n-type semiconductor with a band gap of about 3.3 eV, has attracted a great attention for obtaining transparent conductive films used in solar cell technology, liquid crystal displays and energy-efficient windows. Zinc oxide has a higher transmittance in the visible spectrum and is more stable in the presence of a hydrogen plasma than other conductive films but its applications are limited by its low dc conductivity and low reflectance in the infrared region [1]. By doping with the Group VII or the Group III elements, the zinc oxide films gain excellent and very stable electrical and optical properties [2].

The zinc oxide–based films have been obtained both by physical methods including sputtering, evaporation, pulsed laser deposition [3–6] and chemical methods, such as chemical vapor deposition, sol-gel, chemical bath deposition [7–10]. Interest has been increased during the last few years in the preparation of thin films and oxide powders by the soft chemistry. With this type of method, multicomponent large scale oxide powders and films can be obtained easily and with lower costs than with other methods, such as CVD, sputtering or vacuum evaporation.

In the present work Al-doped and undoped ZnO films were obtained by soft chemistry starting with zinc acetate dihydrate and Al(III)-isopropoxide in absolute ethyl alcohol and triethanolamina (TEA) as chelating agent and catalyst. The morphological, electrical and optical characteristics of the obtained films were determined.

II. Experimental

2.1. Film deposition

The experimental conditions used for preparing the solutions needed for films deposition were established on the previous paper published by Shuler and Aegerter [8]. In our work the diethanolamine was replaced by tri-

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ethanolamine which allowed a significant reduction in the amount of the required chelating agent used in order to obtain stable solutions of precursors (TEA/Zn = 1/5, as compared to DEA/Zn = 1/1).

The reagents used for obtaining ZnO and Al-doped ZnO thin films were Zn(II)acetate dihydrate, $Zn(CH_3COO)_2 \times 2H_2O$ (ZAD, Reactivul) and Al(III)-isopropoxide, $Al(OC_3H_7^i)_3$ (iPAl, Merck).

Zinc and aluminium solutions of 0.1 M were obtained by dissolving zinc acetate dihydrate (ZAD) and Al(III)-isopropoxide (iPAl) into absolute ethyl alcohol p.a reagent (Riedelde Haen). Zinc acetate solution was stirred at 50°C for 15 minutes then triethanolamine (TEA, Baker Analyzed) was slowly added drop wise in molar ratio of TEA/ZAD = 1/5 and continued with stirring at the same temperature for two hours for the obtaining Zn-sol. The Al-Zn-sol was obtained by adding the appropriate quantity of Al(III)-isopropoxide solution to the zinc acetate solution, so that finally aluminum atoms represented 5% in the Al-Zn mixture. In the Table 1 the experimental conditions for the solution preparation are presented. The clear and homogenous Zn and Al-Zn solutions were stored at room temperature for 24 hours before being used for the deposition. ZnO films were deposited by dip-coating on thermally oxidized silicon wafers.

The thermal treatment of the deposited films was realized at 500°C for 5 min with a heating rate of 5°C/min, in the temperature programmable laboratory furnace. For multilayered coatings after each deposition the same thermal treatment was applied. All samples were additionally annealed at 500°C for 1 hour. The experimental conditions of the films deposition and densification are presented in Table 1.

The obtained films were labelled as follows: ZO – ZnO films; AZO – Al-doped ZnO films.

2.2. Film characterization

FT-IR spectroscopy measurements were realized with a Nicolet 6700 apparatus in 400–4000 cm^{-1} domain.

XRD analysis of the films was performed with Bruker D8 Advance diffractometer in the Bragg-Brentano configuration. The scanning was made at room temperature in the range of 5–90°, with steps of 0.01 and 4 °/second.

The AFM experiments were carried out in the dynamic (non-contact) mode using an EasyScan 2 apparatus (Nanosurf AG, Switzerland) by means of a 10 µm × 10 µm scanner with vertical range of 2 µm and z-axis resolution of 0.027 nm. The scan rate was in the range of 1–2 Hz. The cantilever was with spring constants of about 34 N/m and the shape of the SiN tips was square pyramidal with radius of curvature of less than 10 nm and half angle 350. Scanning Probe Image Processor (SPIP™) software package (version 4.6.0.0) was used for image processing in terms of roughness and grain analysis.

The thickness of the layers (*d*) and volume fractions of the components were calculated from Spectroellipsometric data obtained with a null type ellipsometer. Experimental SE spectra have been simulated using the multilayer and multicomponent Bruggemann's Effective Medium Approximation (BEMA) model [11].

Electrical resistance measurements were performed by "the four point method". In order to obtain low specific resistance Ohmic contacts were deposited on the film surface [12] (Ti (20 nm) / Au (30 nm) ohmic electrodes)

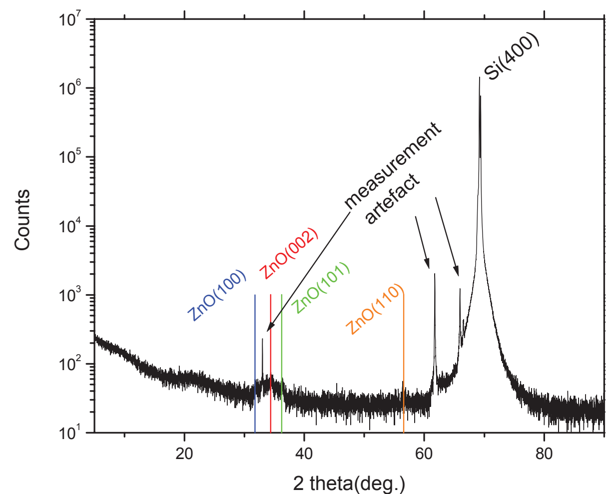
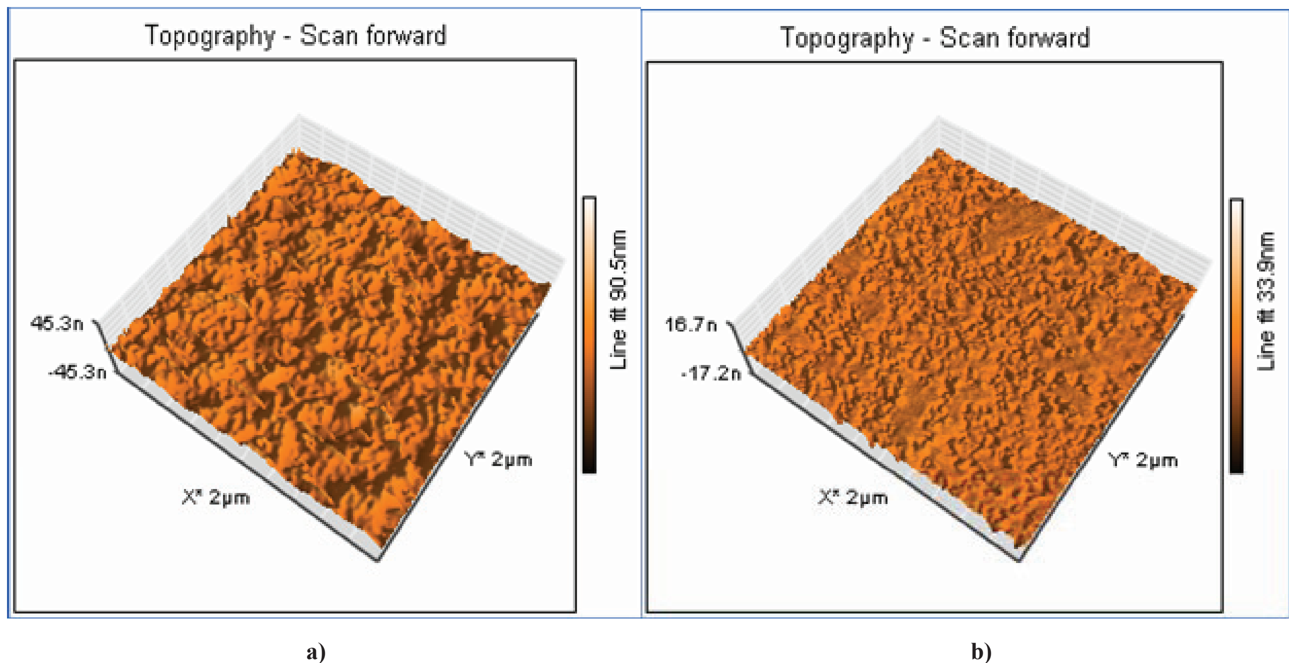


Figure 1. X-ray diffraction lines of the thermally treated ZnO film

Table 1. Experimental conditions of the solution preparation, films deposition and post- deposition thermal treatment

Sol preparation					
Sample	Concentration [mol%]		ZAD/TEA	Reaction temperature [°C]	Reaction time [min]
	ZAD	iPAl			
Zn-solution	0.1	-	5	50	120
Zn-Al-solution	0.095	0.005	5	50	120
Film deposition					
Withdrawal speed [cm/min] / withdrawal temperature [°C]					5/20
Storage time of sold before of first deposition [hours]					24
Number of deposition					1–5
Thermal treatment temperature of the films after each deposition [°C/time – min]					500/5



a) b)

Figure 2. AFM 3D images of the as-prepared one-layer films: a) ZnO film; RMS = 4.05 nm, b) Al-doped ZnO film; RMS = 1.36 nm

ex-situ, by UHV e-beam evaporation. Copper leads were attached to the electrode with silver paste and were connected to an automatic polarization system. The electric voltage (V) was then measured with applied currents (I). The films were put in an atmosphere controlled tubular furnace and the heating rate was 5°C/min.

III. Results and discussion

3.1. Structure and morphology of prepared films

Stable, clear and homogenous Zn and Al-Zn solutions were obtained in the conditions presented in the Table 1. Annealing temperature of the films was established according to the data obtained from thermal analysis of the ZnO and Al-doped ZnO dried gels, formed after removal of the solvent at room temperature from the sol-gel solutions. The as-prepared films deposited on silicon supports are amorphous and no characteristic peaks appear in the X-ray diffraction patterns. By thermal treatment at 500°C (Fig. 1), the crystallization of ZnO was observed by the presence of the diffraction lines at (100) (002) (101) and (110).

The very low intensity of the diffraction lines could be assigned to the low amount of oxide material investigated, taking into account greatly reduced thickness of the obtained films (see Table 3).

FT-IR spectra of the ZO and AZO thermally treated films present only characteristic bands assigned to Zn-O bonding at 430 cm^{-1}.

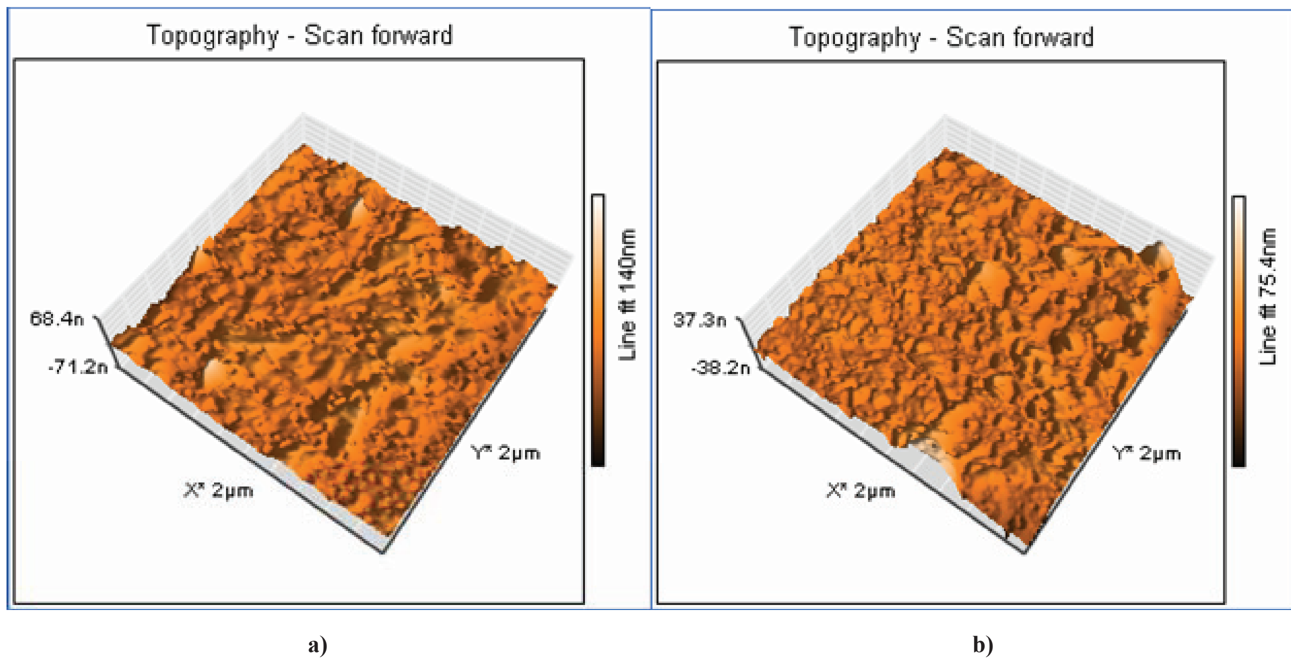
The AFM images of the as-prepared ZO and AZO films with one deposition on silicon wafers are shown in Fig. 2. The surface root mean square roughness (RMS) of the as-prepared ZnO film was determined to be about 4 nm (Fig. 2a). The smaller RMS roughness value was calculated for the as prepared Al-doped ZnO film, being of about 1.4 nm (Fig. 2b).

The AFM images of the surface of the thermally treated ZO and AZO films obtained after five layer depositions are presented in Fig. 3. It can be noticed that the films develop a distinct morphology. The surface roughness is higher than in the case of the as-prepared samples, being of about 6.8 nm for ZnO film and 20.6 nm for the alumina-doped ZnO film. The decreasing of the thickness of the films by thermal treatment could be connected to the elimination of the residual organics from the solution used for films deposition.

In the Table 2, values of median and maximum superficial grain length, width and height calculated by processing AFM images are presented. The superficial grains have been analyzed using SPIP software package based on the so-called watershed (with or without

Table 2. The average and maximum grain size

ID	ZnO film			Al-doped ZnO film		
	Length [nm]	Width [nm]	Height [nm]	Length [nm]	Width [nm]	Height [nm]
Mean	86	31	1.8	77	20	1.0
Maximum	397	125	11.7	690	132	5.8
Median	67	27	1.5	52	15	0.8



a) b)

Figure 3. AFM 3D images of the five layers thermally treated films: a) ZnO film; RMS=6.81, b) Al-doped ZnO film; RMS=20.62

gradient) and threshold methods [SPIP manual – available on www.imagemet.com] depending on the particular topography of each surface (e.g. the surface of AZO film with 5 depositions exhibits a combination of grains and pores which could be separately identified and analyzed).

From Table 2, an increase of the grain length can be seen, showing values of 2–5 times higher than the grain width. Also the height of the granules is about two orders of magnitude smaller than the length. This tendency suggests a two-dimensional development of the granules formed on the surface of the film deposited on the silicon substrate and it is more pronounced in the case of Al-doped ZnO (AZO) films.

3.2 Optical characteristics of prepared films

The results concerning the optical constants and thickness of the ZnO-based films obtained using the spectroscopic ellipsometry (SE) method (previously presented in paper [13]) are shown in the Table 3. The experimental SE spectra have been fitted by taking as fit parameters the thickness of the film (*d*) and the volume fractions of the components: ZnO, Al_2O_3 and voids (related to the film's porosity). For the as prepared films, besides the above mentioned components, there have been taken into account the dielectric constants of the solution used for deposition (denoted as "sol" in Table 3), previously measured with a Pulfrich-type refractometer.

The thickness of the as-deposited ZnO film (d = 17 nm) (one deposition) is smaller than for the similar Al-doped ZnO film (d = 43 nm). In the case of thermally treated films, the thickness of Al-doped ZnO films (d = 29 nm) is smaller than the thickness of the ZnO films (d = 34 nm) (see Tabel 3). In the literature, it is mentioned that on SiO_x/Si substrate the thickness of the ZnO film obtained by aqueous sol-gel route does not exceed 20 nm, pointing out the weak adherence of the solution to the SiO_x/Si substrate [14]. The calculated quantity of voids, about 62% for ZnO films and about 70% for Al-doped ZnO films, indicates obtaining of porous films in our experimental conditions.

Table 3. Thickness (*d*) and volume fractions of the components of the studied films

Sample	SiO_2 buffer			Film					
	d_{SiO2} [nm]	SiO_2 [%]	voids [%]	d_{film} [nm]	sol [%]	ZnO [%]	Al_2O_3 [%]	voids [%]	ε [10^{-7}]
As prepared films (one layer deposited)									
$ZO_{as\text{-}dep}$*	557	99.81	0.19	17	54.35	24.31	-	21.34	102241
$AZO_{as\text{-}dep}$	553	99.78	0.22	43	63.95	5.31	0.51	30.74	123047
Thermally treated films (5 layers deposited)									
ZO	557	99.81	0.19	34	-	38.04	-	61.96	239681
AZO	553	99.78	0.22	29	-	29.10	0.51	70.39	112326

* $ZO_{as\text{-}dep}$ - as-prepared ZO film; $AZO_{as\text{-}dep}$ - as-prepared AZO film

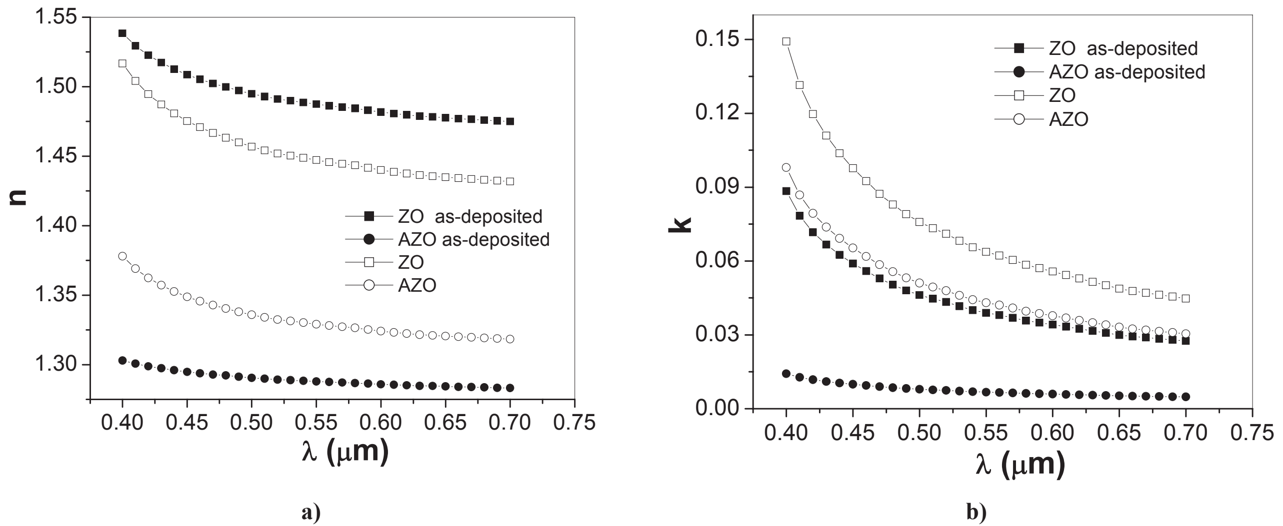


Figure 4. Optical constants of the studied films: a) refractive index, b) extinction coefficient

Optical constants (refractive index and extinction coefficient) for the studied films are presented in Fig. 4.

Refractive indexes with $1.50 < n < 1.55$ values and extinction coefficient $k < 0.06$ were determined for as-deposited ZnO film (ZO_{as-dep}). Smaller values were obtained for as-deposited Al-doped ZnO film (AZO_{as-dep}). The thermally treated ZO and AZO films have small refractive indices due to the large volume of voids (≈62% and ≈70% respectively) in the bulk of the film (see Table 3).

3.3. Electrical behaviour

The resistance of the ZnO and Al-doped ZnO films obtained after five layers deposition was measured by a standard four-probe technique. Measurements were made very carefully and repeated five times to make sure that it is the true behaviour of the studied films.

Fig. 5 shows the temperature dependence of the electrical resistance of the ZnO film on silicon wafer. The ZnO films have electrical resistance in the range of 10^2–10^5 Ohm, higher values than those mentioned in the literature data for the film obtained by sol-gel process [8]. A decrease of the electrical resistivity versus temperature indicates n-type semiconducting behaviour in the 300–600 K temperature range.

The electrical behaviour of the Al-doped ZnO film is presented in the Fig. 6.

Higher electrical resistance values in the 300–800 K temperature range were obtained for Al-doped ZnO film in comparison with ZnO film. It can be noticed that in the 300–550 K temperature interval the electrical resistivity of the AZO films remains unchanged and then decreases with the increase of the temperature up to 700 K when the resistivity increases.

This behaviour can be assigned to the high surface roughness and large volume of voids of the Al-doped ZnO film.

IV. Conclusions

Thin ZnO and Al-doped ZnO films deposited by dip-coating technique on SiO_x/Si wafers were obtained by chemical route using zinc acetate dihydrate and al-

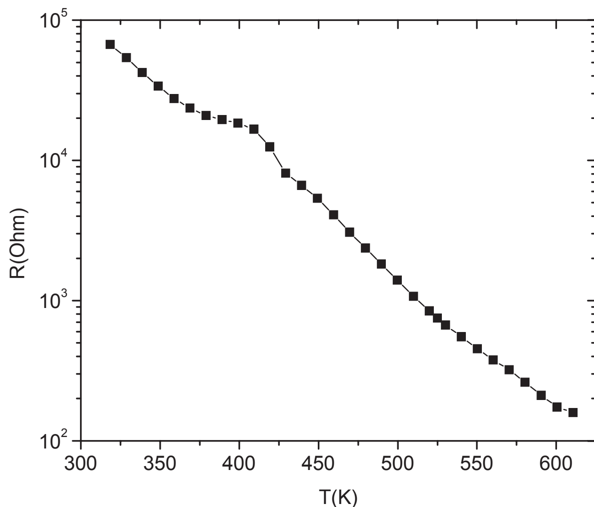


Figure 5. Electrical resistance in the 300–600 K temperature range of the ZnO film

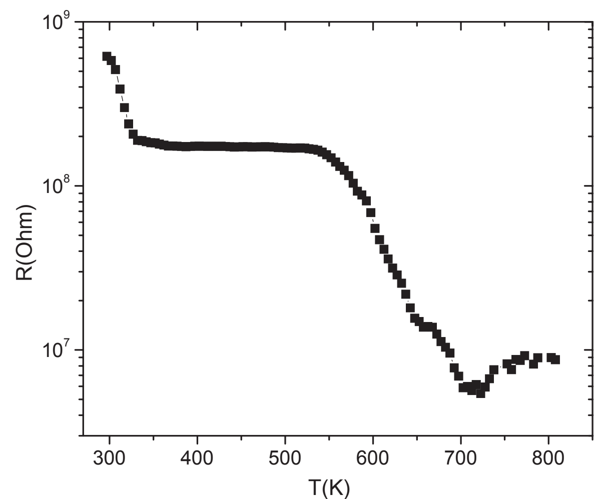


Figure 6. Electrical resistance in the 300–800 K temperature range of the Al-doped ZnO film

uminium isopropoxide as zinc and aluminium precursors respectively, absolute ethanol as solvent and triethanolamine as chelating agent.

Morphology of the films is influenced by the starting sol composition, as found from AFM.

According to the ellipsometric spectral data, more porous and thinner films, with smaller refractive index were obtained in the case of Al-doped ZnO films as compared with ZnO films.

Both ZnO and Al-doped ZnO films present high electrical resistivity.

The high electrical resistance of films deposited on silicon wafers obtained by chemical route recommend the ZnO and Al-doped ZnO films for bulk acoustic resonator (FBAR).

Aknowledgements: The financial support of the Romanian National Management Program, PN II type Project under the contract no. 11061/18.09-2007 is gratefully acknowledged. Dr. S. Mihaiu acknowledges the COST 539 Action-Elena for the support in attending the 4th Workshop “Fabrication, Properties & Applications of Electroceramic Nanostructures”, Genoa, June 26-28, 2008.

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