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Abstract. This paper presents a sol-gel technological process for preparing thin films of ZnO and ZnO:Al. The effect of annealing treatments (500, 600, 700 and 800 ^{o}C) on their properties was studied. The structural evolution with the temperature was investigated by using X-Ray diffraction (XRD). Fourier Transform Infrared (FTIR) and UV-VIS spectrophotometry were applied to characterizing the films' vibrational and optical properties. The ZnO and ZnO:Al films possessed a polycrystalline structure. The films studied are highly transparent in the visible spectral range. The optical band gap values and the haze parameter were also determined.

1. Introduction

Nanostructured metal oxide films have been extensively studied due to their numerous applications, especially in optoelectronics. Among these materials, ZnO has prompted extensive scientific research with respect to its interesting properties, such as a wide band gap (3.37 eV) with a large exciton binding energy (60 meV), a high chemical stability, a low dielectric constant, a high thermal conductivity, antibacterial and UV protection properties [1]. On the other hand, the ZnO thin films exhibit a high transmittance in the infrared and visible spectral regions and a high refractive index, which extends their application range [2]. ZnO films are used as transparent conductors, chemical and biological gas sensors, ultraviolet light emitters, thin film transistors, solar cell windows [3-4].

Doping and mixing ZnO with different metals leads to changing and enhancing some of their electronic and optical properties. Recently, Al, P, N, Mg, Sb, Mn, B etc. [5] have been studied extensively as promising dopants for ZnO using various technological approaches. Aluminium-doped zinc oxide coatings manifest high transparency and low resistivity [6]. The doping concentration influences the optical and structural properties. The sol-gel technology offers the possibility to produce high-quality homogeneous thin films over a large area, excellent control of the stoichiometry, composition modification (mixing on a molecular level), a cost-effective process, and inexpensive equipment. [7].

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This paper presents a sol-gel method for depositing ZnO and ZnO:Al thin films. The effect of the doping concentrations of Al on the optical and structural properties is investigated. The influence of the annealing temperature is also studied. The measurement techniques used are XRD, FTIR and UV-VIS spectrophotometry.

2. Experimental

Two sol solutions were prepared for depositing ZnO and Al_2O_3 films. They were synthesized as follows:

Solution 1) Zinc acetate was dissolved in absolute ethanol (0.4 M concentration). The complexing agent and stabilizer was monoethanolamine (MEA/Zn molar ratio = 1);

Solution 2) Alumina-sec-butoxide was dissolved in isopropyl alcohol (0.2 M concentration). Acetylacetone was used as chelating agent. The full details are given in [8].

The two sol solutions were found to be stable and to retain their film forming properties for more than three months. The mixing of the two sols was made in molar ratios (Al sol/Zn sol) of 0.01, 0.03, 0.05 and 0.1; the films thus prepared are referred to with these names throughout the text. The films were deposited by spin coating at 4000 rpm on Si and quartz substrates; the samples underwent five layer depositions. The preheating temperature was 300 ^oC/10 min. After repeating the coating procedures five times, the films were annealed at 500, 600, 700 and 800 ^oC in air for one hour.

The XRD spectra of the sol-gel films were recorded by a Bruker D8 XRD diffractometer at the grazing angle of 2°, a step time of 8 s at a step of 0.1^o. The FTIR measurements were performed on an IRPrestige-21 Shimadzu FTIR Spectrophotometer. The optical measurements were conducted by using a UV-VIS-NIR Shimadzu 3600 spectrophotometer in direct, diffuse and total transmittance modes.

3. Results and discussions

The XRD spectra of ZnO and ZnO:Al (0.01) films are presented in figure 1 after thermal treatments at different temperatures. The five strongest lines are assigned to a wurtzite phase (JCPDS 01-07-8070). The corresponding lines for ZnO:Al (0.01) films appear with lower intensities suggesting that the crystallization has decayed. This means that the Al additive affects the films' crystalline structure.
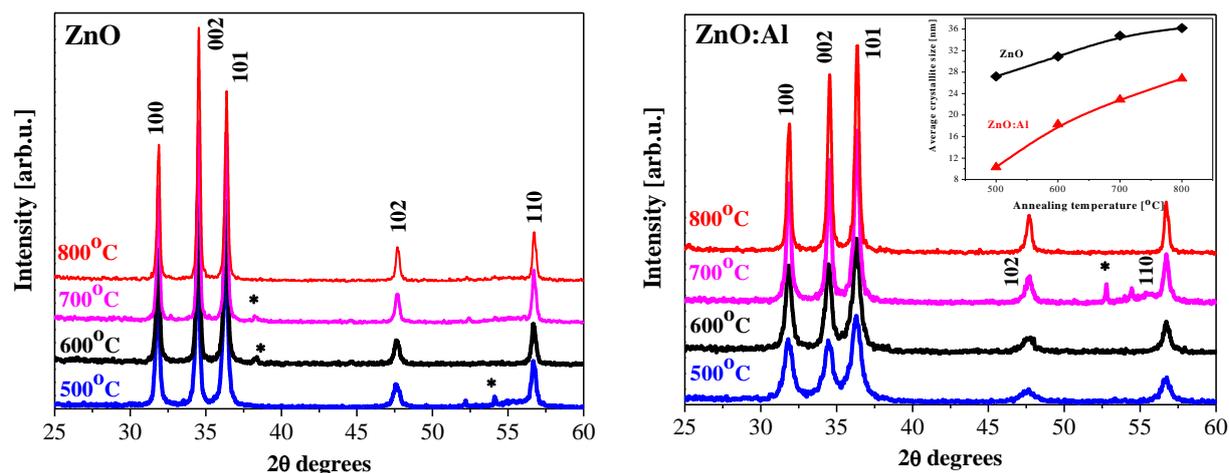

Figure 1. XRD spectra of ZnO and ZnO:Al (0.01) films. The asterisks show lines due to ZnO_2.

The ZnO film annealed at 500 ^oC shows five intense peaks of wurtzite ZnO and a small line at $2\theta = 54.1$, attributed to the ZnO_2 cubic phase (200) (JCPDS 13-0311). The ZnO:Al film (500 ^oC) manifests XRD lines corresponding to wurtzite only. The ZnO film (600 ^oC) crystallizes in a wurtzite. phase with a weak reflection at 38.4, associated with cubic ZnO_2. The thermal treatment at 700 ^oC leads to the detection of two additional weak lines in the spectrum of ZnO:Al at 2θ =54.4 and 55.6,

assigned to cubic ZnO_2. The highest annealing temperature results in good polycrystalline films with a wurtzite ZnO crystal phase. The average crystallite sizes are estimated according to Scherrer's formula (for peaks: 100, 002 and 101) and the results obtained are shown in the inset (figure 1) and table 1. The Al component influences the crystallization of the films, namely, the crystallite size significantly diminishes compared to that of ZnO films. The average crystallite size of ZnO is 32 nm, while the value for ZnO:Al is 20 nm. Table 1 presents also the calculated lattice parameters and the dislocation density of the films. Dislocations are imperfections in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. The dislocation density of the films is given by the Williamson and Smallman's relation ([9]): $\delta = n/d^2$ (1), where n is a factor equal to unity at the minimum dislocation density and d is the grain size. The dislocation densities decrease as the annealing temperature is raised, which indicates a lower concentration of lattice imperfections.

Table 1. Average crystallite size (d), dislocation density (δ) and lattice parameters.

Material	T, (^{o}C)	d, nm	$\delta \times 10^{-4}$ (1/nm^2)	a (Å)	c (Å)
ZnO	500	27.2	13.5	3.243	5.197
	600	30.9	10.5	3.243	5.193
	700	34.8	8.3	3.242	5.189
	800	36.2	7.6	3.241	5.185
ZnO:Al	500	10.3	94.3	3.244	5.192
	600	18.3	29.9	3.242	5.200
	700	22.9	19.1	3.242	5.196
	800	26.9	13.9	3.241	5.187
JCPDS 01-07-8070 card, wurtzite ZnO				3.2489	5.2049

The lattice parameters a, c of the two materials decrease slightly with the annealing temperature. The XRD study reveals that the degree of crystallization worsens with the addition of Al, resulting in crystallites of a smaller size. The finding that there is no indication of mixed Zn/Al oxide phases can imply that the Al atoms substitute for the zinc in the respective sites or are incorporated in the lattice [10].

FTIR spectroscopy was used as a supplement for revealing the structure of the films studied. FTIR analysis reveals that both the metal additive and the annealing procedures affect the vibrational properties of the films. The absorption bands due to metal-oxygen bonds are expected in the spectral range 350-1200 cm^{-1} (figure 2). The line around 1100 cm^{-1} observed in all spectra is due to Si-O bonding. For the ZnO:Al films, weak peaks at 665 and 681 cm^{-1} are observed, which might be assigned either to Zn-O [11] or to O-Al-O bonding [12]. However, a line at 667 cm^{-1} is also observed in the ZnO spectra. The main IR lines are located in the spectral range 390-425 cm^{-1} (see the insets).
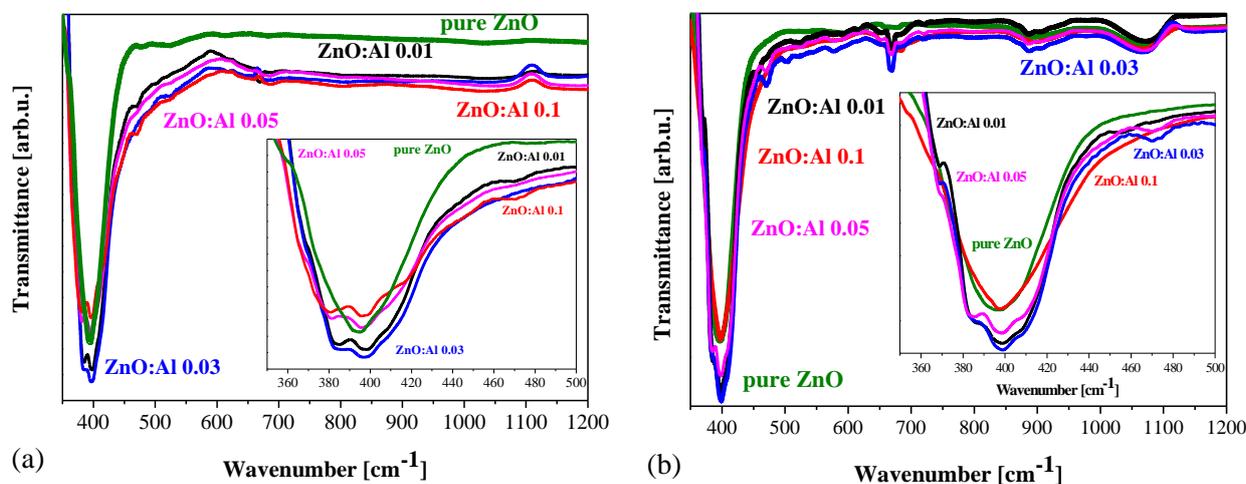

Figure 2. FTIR spectra of sol-gel ZnO and ZnO:Al films annealed at 600 (a) and 800 ^{o}C (b).

The Al component influences the shapes of the absorption bands. The bands are broader and with different intensities compared to the ZnO spectra. The IR spectra may be influenced by the crystallite's size, shape and degree of crystallinity and are often used to corroborate the XRD study. Upon addition of Al, the main absorption band shifts from 394 to 400 cm^{-1}. Clear shoulders of the main bands appear at 415 cm^{-1}. They are related to Zn-O stretching vibrations. It must be noted that there are no clearly identified absorption bands that are connected with vibrations of the Al-O bonds. This conclusion is in agreement with the XRD study, where the only detected crystalline phase is wurtzite ZnO.
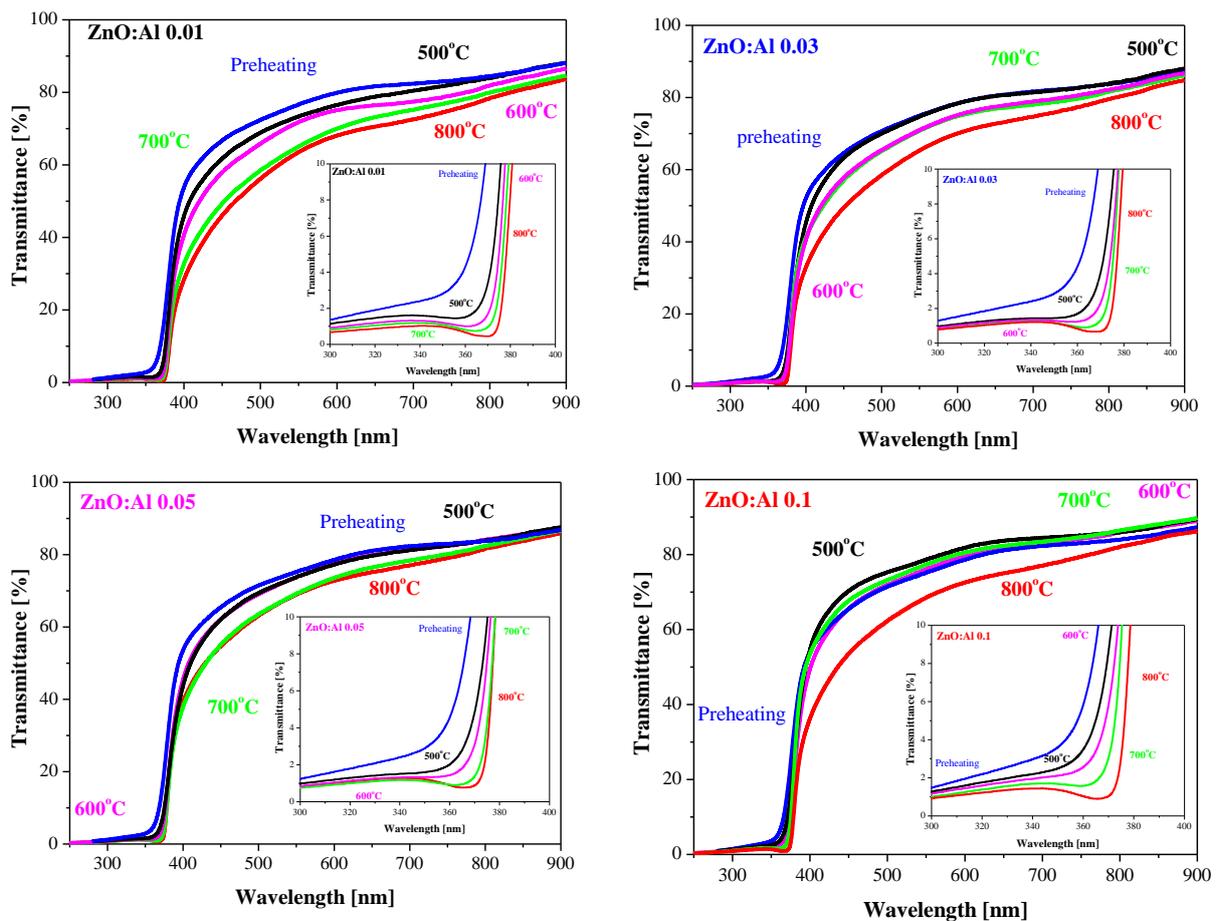

Figure 3. Transmittance spectra of sol-gel ZnO:Al films annealed at different temperatures.

The optical properties of the sol-gel ZnO and ZnO:Al films were also investigated; the transmittance spectra are presented in figure 3. The ZnO films possess a lower transparency compared to ZnO:Al films; their transmittance decreases as the annealing temperature is raised. The ZnO:Al films demonstrate the same tendency of decreasing the transmittance after higher temperature annealing.

Our previous study [13] showed that as a higher amount of the Al component was introduced to the sol solution, the films produced exhibited a significantly higher transparency in the visible spectral range. This effect is more clearly pronounced for ZnO:Al 0.05 and ZnO:Al 0.1, as can be seen in figure 4.

The specific bands in the optical spectra below the absorption edge are due to the excitonic absorption of ZnO (insets in figures 3 and 4). The bulk ZnO excitonic feature is located at 373 nm [14]. The appearance of an excitonic peak is a sign of the degree of ZnO crystallinity. Respectively,
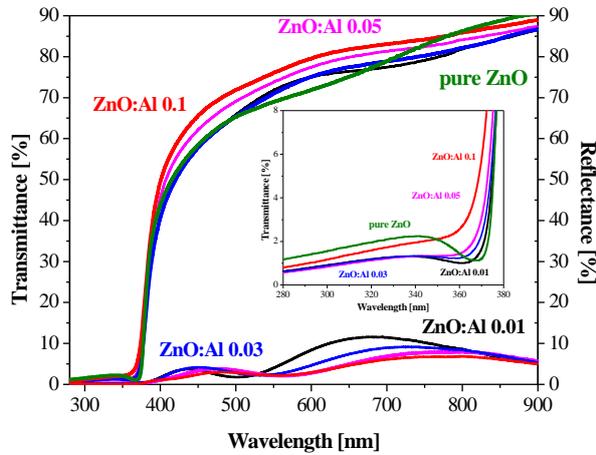
Figure 4. Comparison of transmittance and reflectance spectra of ZnO and ZnO:Al films annealed at 600°C.

the excitonic absorptions prove that the ZnO:Al films are less crystalline compared to the ZnO thin films, as it has been found by the XRD analysis.

The excitonic absorptions of ZnO are found to be in the range of 331 to 347 nm. The ZnO:Al films show excitonic absorptions only after annealing at 700 and 800°C. This is due to the smaller degree of crystallization of the ZnO:Al films annealed at lower temperatures, as has been proved by the XRD study.

Table 2 shows the values of the optical band gap E_g of ZnO; there is no clear trend of an increase or a decrease of the values observed after annealing at different temperatures. The optical band gap of ZnO:Al films decreases with the increase of

the annealing temperature. The results are close to those for ZnO films. It has been found earlier [15] that increasing the Al component results in a widening of E_g due to the lower degree of crystallization and/or formation of Zn-Al–O phases. The optical band gap values of the films studied by us agree with the data reported in [16]. On the other hand, the band gap values of all sol-gel ZnO and ZnO:Al films

Table 2. Optical band gap values [eV] determined from spectrophotometrical data.

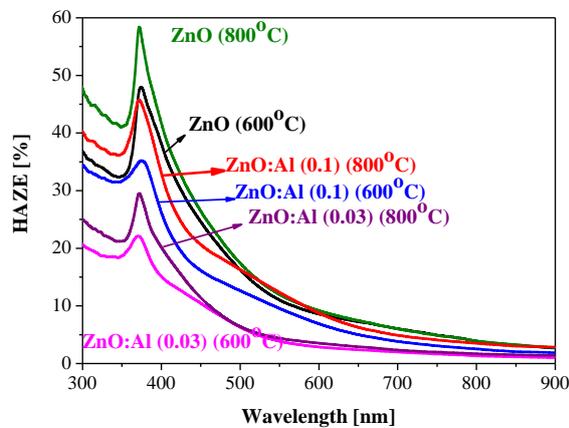|	ZnO	ZnO:Al 0.01	ZnO:Al 0.03	ZnO:Al 0.05	ZnO:Al 0.1
Preheating temperature	3.30	3.27	3.28	3.28	3.29
500°C	3.28	3.27	3.25	3.25	3.28
600°C	3.27	3.27	3.26	3.26	3.27
700°C	3.28	3.26	3.27	3.27	3.27
800°C	3.28	3.26	3.26	3.27	3.26

Figure 5. Haze of ZnO, ZnO: Al (0.03) and ZnO: Al (0.1) films annealed at 600 and 800 °C.

are smaller than the optical band gap of single crystalline ZnO (3.37 eV). It has also been reported that the lower values of the optical band gap could be due to the presence of growth stress, thermal expansion and mismatch stress.

Another interesting optical property is the haze value. The haze parameter serves as an indicator for the diffuse scattering of light by thin films. The haze parameter for transmitted light is defined as the ratio between the diffuse part of the transmitted light to the total transmitted light. Total and diffuse transmittance spectra were measured using an integral sphere attachment.

Figure 5 shows the haze parameter. It can be seen that the ZnO films exhibit higher values of

haze compared to ZnO:Al. It is interesting to note that the films with a higher content of Al reveal values higher than those of ZnO:Al (0.1). When the Al component amount is increased in the sol solution, the spectra of the direct and total transmittance are very similar, indicating that the films are very smooth and there is no light scattering.

4. Conclusions

In this work, a sol-gel technology was successfully applied to depositing transparent ZnO and ZnO:Al films. The XRD analysis reveals the existence of wurtzite ZnO and a decrease of the film crystallinity upon Al doping. The crystallite sizes of ZnO and ZnO:Al films differ, as those of the doped films are smaller. No Al containing phases are detected by XRD and FTIR analysis. The optical transmittance is improved for the ZnO:Al films in comparison with pure ZnO films. The optical study also reveals that the optical band gap is not significantly changed by Al addition and thermal treatments. The technological approach proposed for ZnO:Al film deposition is very promising.

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