Synthesis and Properties of Al-doped ZnO Thin Films for Photovoltaics

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***Abstract*— Polycrystalline undoped and Al-doped ZnO thin films were deposited by spray pyrolysis using oxygen and argon atmospheres. The influence of postdeposition vacuum annealing on the structure, morphology and optical properties was studied by X-ray diffraction, atomic force microscopy and UV–VIS spectroscopy. The thermal vacuum annealing induces structural and morphological changes, especially in Al-doped ZnO thin films synthetized in oxygen atmosphere. Further on, the electrical conductivity in dependence of the nature of gas atmosphere and Al concentration is discussed.**

Keywords—ZnO thin films, spray pyrolysis, Al doping, XRD analysis, electro-optical properties.

I. Introduction

The search for a cost-effective alternative material to TCO oxides have stimulated in the past decades research efforts in the field of ZnO transparent conductive oxide thin films. ZnO is environment friendly. ZnO films are used as transparent layers in the visible and infrared region of the spectrum as photo-electrodes and buffer layers in photovoltaics and recorders information [1-4]. Zinc oxide is a II–VI wide gap semiconductor with bandgap of 3.37 eV at room temperature [5]. Since, the exciton binding energy is close to 60 meV [6] and the biexiton formation energy is 15 meV [6] are several times higher than in GaN, ZnO is considered to be the more promising material for new exiton-related devices. Zinc oxide films have good piezoelectric and electroluminescent characteristics and can be used as functional layers in acoustic devices [7,8], ultraviolet and infrared radiation sources and detectors, and in linear optical elements [9-12]. The several physical and chemical techniques have been employed to obtain ZnO films which are more or less sophisticated and costly. Among these methods, the simple and inexpensive spray pyrolysis method allows easy control over deposition parameters, as well as, reproducibility. The doping of zinc oxide with group III elements, such as barium, aluminum, gallium and indium, allows to be obtained ZnO thin films with a relatively low resistivity [13-16]. However, exactly how gas atmosphere affect the physical properties of Al-doped ZnO films has seldom been studied. Therefore, in this paper, the systematic investigation of the effect of Ar and O_2 atmospheres on the structure, optical and electrical properties of spray deposited Al-doped ZnO films are investigated for its application in photovoltaics. Moreover, the effect of vacuum annealing in the same condition on the structural, optical and electrical properties will be discussed.

II. Experimental Detailes

A. Synthesis of ZnO thin films from solution

For the synthesis of ZnO thin films, zinc acetate ($Zn(CH_3COO)_2 \cdot 2(H_2O)$) with a concentration of 0.2 M dissolved in acetic acid-methanol-water solution in the ratio 10:25:65 was used. As the dopant source, aluminum nitrate was used. The concentration of Al was varied between 1% and 5% in the initial solution. Al-doped ZnO thin films were deposited on glass substrates by spray pyrolysis technique. Details of the deposition system and method are described in paper [17]. The equipment allows the deposition of ZnO layers on the area up to 80 cm^2. The furnace temperature is kept constant at an accuracy of ± 5°C. The oxygen and argon gases were used as the carrier gas. Spray rate of the solution was 30 ml/min. The temperature of the substrate and the carrier gas pressure were 410°C and 2 bar, respectively. The distance between the substrate and solution source was 30 cm. Glass substrates were, preventively, cleaned in toluene, isopropyl alcohol, corroded in + 5% Br methanol solution for 10 min and then dried in isopropyl alcohol vapors. First set of Al-doped ZnO films was synthetized in O_2 atmosphere and then vacuum annealed at 430°C for one hour in the deposition chamber, under a pressure of $4.0 \cdot 10^{-5}$ mbar. A second set of Al-doped thin films was synthetized in Ar atmosphere and then annealed in the same condition like the first set.

B. Characterization techniques

The crystal structure was determined by high-resolution Ultima IV X-ray diffractometer in the θ–2θ configuration with a copper target (CuKα λ=1.5406 Å, 40 mA, 40 kV). The grain size was calculated from the XRD patterns according to the well-known Scherrer equation:

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$$D = K\lambda/\beta\cos\theta \quad (1)$$

where β is the diffraction half-height peak width, K is the Scherer constant, λ is the wavelength of X-ray radiation, and θ is the diffraction angle. The surface morphology was investigated using an SPI 3800 atomic force microscope operated in tapping mode. A Jasco V-670 double-beam recording spectrophotometer was used to record transmission and reflectance spectra in the 200–800 nm wavelength range. Electrical properties of the samples were studied by Four point probe technique.

III. Results and Discassion

A. Structure and Morphology

The diffraction patterns for the first set of the as-deposited undoped and Al-doped ZnO thin films synthetized in O_2 atmosphere are shown in Fig. 1. As can be seen in Fig. 1, the films' peak intensities of (100), (101) and other planes of diffraction are very small in comparison with the intensity of (002) plane. The all films exhibited a preferred (002) orientation.

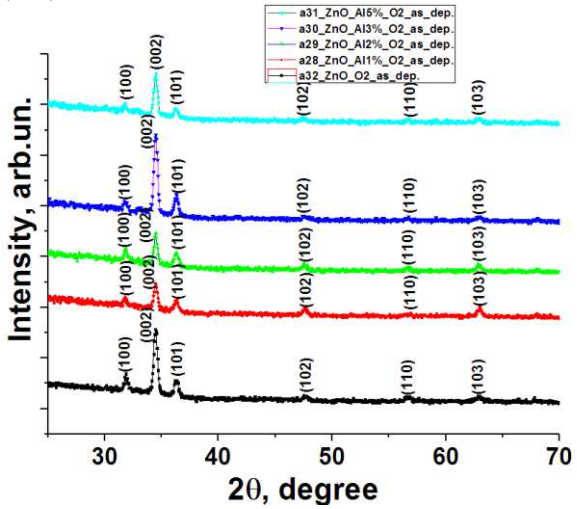


Fig. 1. The XRD patterns of the as deposited undoped and Al-doped ZnO thin films in O_2 atmosphere

Therefore, the interplanar distance (*d*) value of the all ZnO films indicated in the table 1 is presented only for the most intensive position peak situated at about 2θ = 34.5° that corresponds to the (002) crystallographic diffraction plane. The intensity of this peak slightly decreases with increasing the Al concentration up to 3 %. At this concentration it`s observed the highest intensity of the 2θ = 34.5° peak. This suggests good crystalline quality of Al3 % ZnO film in comparison with the undoped sample. However, the (002) peak intensity decreases with further increase of Al content up to 5% in the film. The diffractograms of the second set of the as-deposited undoped and Al-doped ZnO thin films synthetized in Ar atmosphere are shown in Fig. 2.The diffractograms show another type of behavior for the most intensive peak situated at 2θ = 34.5°. The intensity of (100), (101) and (002) planes for the as deposited undoped thin film are about the same. The most intensive peak is depicted for the 1% Al-doped ZnO film. The average strain and crystal grain sizes of (002) crystal plane for this set of ZnO thin films are presented in Table 2. The value of grains size of the as-deposited Al-ZnO thin films in Ar atmosphere reveal that the crystalline quality with Al doping is weakened less in comparison with of that synthetized in oxygen atmosphere (See tables 1 and 2 for comparison). For the sample obtained in Ar atmosphere with Al-doping concentration of 1 at%, grains tend to increase in size because of the lower strain of the crystal lattice in the film in comparison with the undoped ZnO thin film. However, when Al-doping concentration is 2 at%, and 3 at%, grains size decrease because of greater strain of the crystal lattice.

TABLE 1. STRUCTURAL PARAMETERS OF AS DEPOSITED Al-ZnO THIN FILMS OBTAINED IN O_2 ATMOSPHERE

O_2 atm.	**Nr.**	**2θ (deg)**	**d (ang)**	**FWHM (rad)**	**D (ang)**	**ε (lattice strain) x10^{-3}**
As-dep. Al-ZnO thin films	undoped	34.46	2.6015	0.0057	281.99	4.61
	1%	34.48	2.6004	0.0053	301.60	4.31
	2%	34.48	2.6003	0.0052	312.23	4.16
	3%	34.49	2.5998	0.0056	289.07	4.5
	5%	34.48	2.6003	0,0056	286.88	4.53

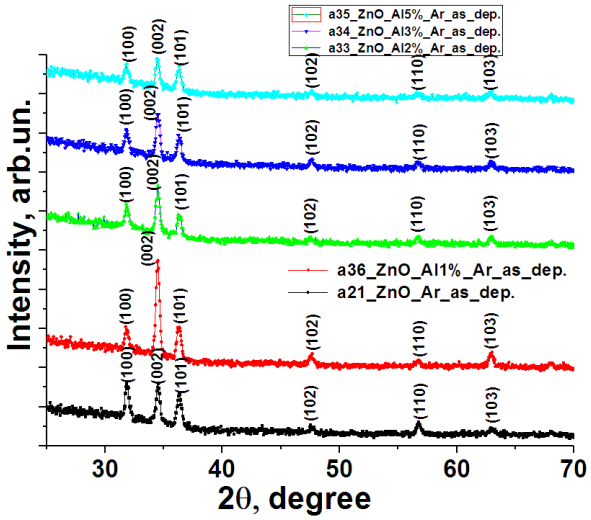


Fig. 2 The XRD patterns of the as deposited undoped and Al-doped ZnO thin films in Ar atmosphere

TABLE 2. STRUCTURAL PARAMETERS OF AS-DEPOSITED Al-ZnO THIN FILMS IN Ar ATMOSPHERE

Ar atm.	**Nr.**	**2θ (deg)**	**d (ang)**	**FWHM (rad)**	**D (ang)**	**ε (lattice strain) x10^{-3}**
As-dep. Al-ZnO thin films	undoped	34.49	2.5996	0.0055	292.56	4.44
	1%	34.48	2.6002	0.0055	294.46	4.42
	2%	34.49	2.5999	0,0057	284.27	4.57
	3%	34.50	2.5990	0,0055	291.08	4.44
	5%	34.47	2.6011	0.0053	305.58	4.26

In the case of higher doping 5 at%, the grains size increase due to lower strain, leading to better crystallinity. Other is the situation with the Al-doped ZnO thin films obtained in the O_2 atmosphere. The biggest grain size for 2 at% Al-doped ZnO film, but the smallest grain size for the higher

doped 5 at% Al film are observed. This illustrates that the crystalline structure is influenced by the nature of gas atmosphere in which the films are synthetized.

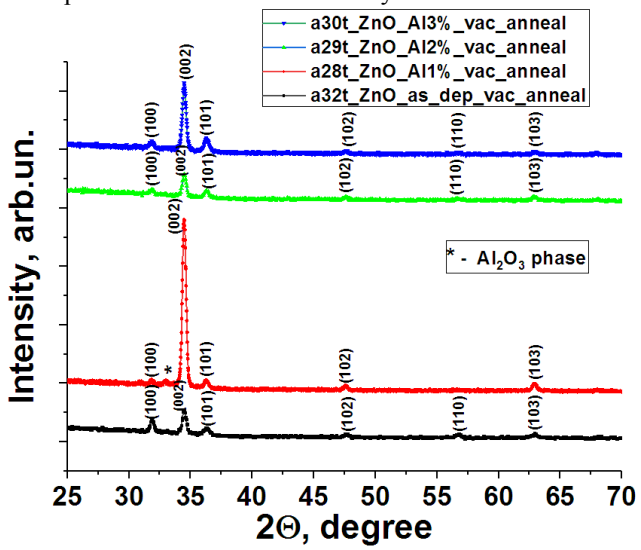


Fig. 3. The XRD patterns of the vacuum annealed undoped and Al-doped ZnO thin films in O_2 atmosphere

TABLE 3. STRUCTURAL PARAMETERS OF VACUUM ANNEALED Al-ZnO THIN FILMS IN O_2 ATMOSPHERE

O_2 atm.	Nr.	2θ (deg)	d (ang)	FWHM (rad)	D (ang)	ε x10^{-3}
Vacuum anneal. Al-doped ZnO thin films	undoped	34.47	2.6008	0.00551	292.6	4.4
	1%	34.48	2.6003	0.0052	308.2	4.2
	2%	34.49	2.5996	0.00553	291.7	4.5
	3%	34.48	2.6004	0.00541	298.3	4.4

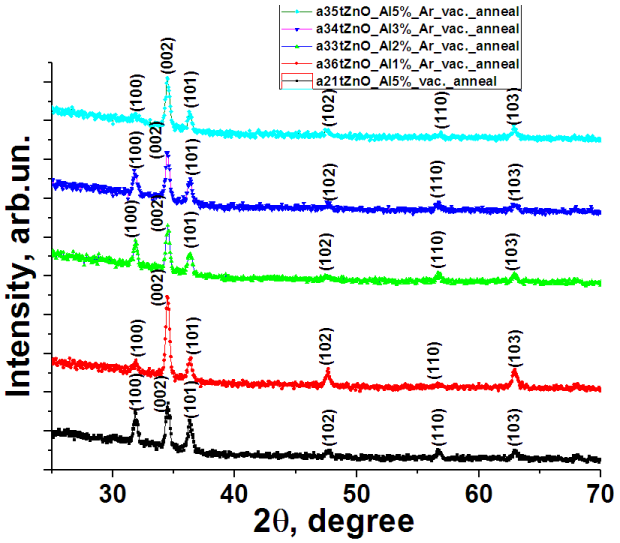


Fig. 4. The XRD patterns of the vacuum annealed undoped and Al-doped ZnO thin films in Ar atmosphere

The slightly shifting of the position of the peaks in comparison with tabular data [18] indicates the presence in them of various kinds of defects. The values of 2θ for the diffraction peaks are very close to that of the standard ZnO crystal [19]. Other researchers [20–22] observed the similar results. The effect of thermal annealing in the vacuum on the structural properties of Al-doped ZnO thin films is investigated. Figures 3 and 4 show the XRD spectra of the thermal annealed undoped ZnO and Al-doped thin films in O_2 and Ar atmospheres. The structural parameters of (002) crystal diffraction plane for the set of thermal annealed undoped and Al-doped ZnO thin films obtained in O2 and Ar atmospheres are presented in Tables 3 and 4.

After annealing at 430◦C, the broad band covering the whole spectrum in all samples obtained in O_2 atmosphere disappears, but in the samples obtained in Ar are kept. This indicate an overall improvement of the crystal quality of the Al-doped synthetized in O_2 atmosphere. The XRD patterns for the thermal annealed 1 at% Al- and 2 at% Al-doped ZnO thin films synthetized in O_2 atmosphere reveal a very lowest intensity peak situated at 2θ = 32.95° that corresponds to Al_2O_3 phase, oxidized from the Al in the ZnO films. According to the structural parameters presented in the tables 3 and 4, for the undoped ZnO film obtained in Ar atmosphere the lattice strain increases after annealing, but for those obtained in O_2 decreases. The value of grains size for all Al concentrations in ZnO films obtained in Ar atmosphere after annealing decreases with the increases of the Al concentration. Generally the Al-doped ZnO obtained by spray pyrolysis in the present paper show growth of the films oriented along the (002) plane as in the most publications [5, 14-15, 20-23, 28]. The crystalline quality of the Al-doped ZnO films enhances after thermal annealing irrespective of the Al doping and it is in good agreement with results obtained by research teams [15, 29-31].

TABLE 4. STRUCTURAL PARAMETERS OF VACUUM ANNEALED Al-ZnO THIN FILMS IN Ar ATMOSPHERE

Ar atm.	Nr.	2θ (deg)	d (ang)	FWHM (rad)	D (ang)	ε (lattice strain) x10^{-3}
Vacuum anneal. Al-doped ZnO thin films	as dep.	34.49	2,5997	0.00565	285.6	4.55
	1%	34.49	2.5994	0.00525	307.3	4.23
	2%	34.50	2.5986	0.00529	304.8	4.26
	3%	34.48	2.6003	0.00545	296.1	4.39
	5%	34.48	2.6002	0.00571	282.6	4.6

The AFM study of the samples allows us to determine more accurately the surface roughness and skewness.

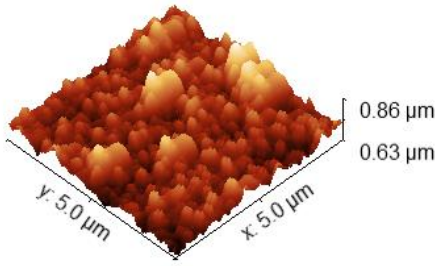


Fig. 5. AFM image of as-deposited 2%Al-doped ZnO synthetized in Ar atmosphere.

For the comparison, Fig.5 shows the surface topography (as shown by the AFM imagistic) of the as-deposited 2 at% Al ZnO film synthetized in Ar atmosphere, while Fig.6 and Fig.7 show the AFM images of vacuum annealed at 420 °C for 1 hour of 2 at% Al doped ZnO thin films synthetized in Ar and O_2 atmospheres. Generally, the roughness of as deposited Al-doped thin films is less than 30 nm, which indicates that the films fabricated by spray pyrolysis are relatively smooth. It was found, also that after annealing the roughness of Al-doped ZnO thin films is large, close to 40 nm. For example, see the table 5 for the comparison for the as deposited and annealed 2 at % Al-doped ZnO thin film.

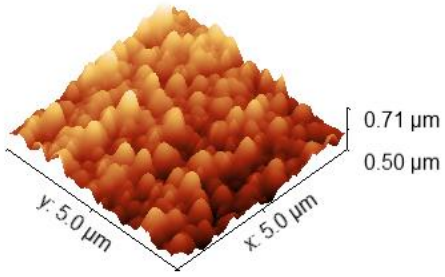


Fig. 6. AFM image of vacuum annealed 2%Al-doped ZnO synthetized in Ar atmosphere.

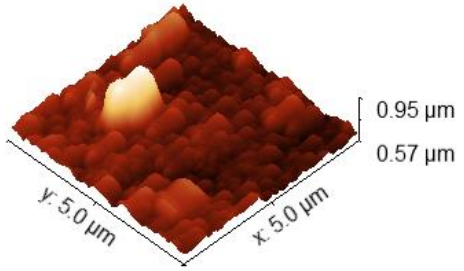


Fig.7. AFM image of vacuum annealed 2%Al-doped ZnO synthetized in O_2 atmosphere.

TABLE 5 ROOT MEAN SQUARE ROUGHNESS (R_{MS}) AND SKEWNESS (R_{SKEW}) OF THE FILMS

	As deposited Al2%-doped ZnO in O_2	**As deposited Al2%-doped ZnO in Ar**	**Vacuum Annealed Al2%-doped ZnO in O_2**	**Vacuum Annealed Al2%-doped ZnO in Ar**
R_{ms}, nm	38.26	29.48	30.75	37..37
R_{skew}, nm	0.88	0.46	0.21	0.87

It is evident an increase of film roughness after vacuum annealing for films obtained in both atmospheres in comparison with as deposited

B. Optical Properties

The transmission and reflectance spectra for the first set of the as-deposited undoped and Al-doped ZnO thin films synthetized in O_2 are presented in Figure 8. For the undoped ZnO thin film the highest transmittance is observed. Doping with Al slightly decrease the optical transmittance of the as deposited films, and the transmittance in the visible region is still higher than 80% which is important for the applications in the field of photovoltaics. The film thickness is estimated from cross-sectional view of SEM and is 292 nm for undoped and 305 nm for Al-doped ZnO films. The estimated E_g values of both undoped and doped with different concentration of Al ZnO films in O_2 atmosphere show a slight decrease of the band gap, within the experimental errors (0.02 eV).

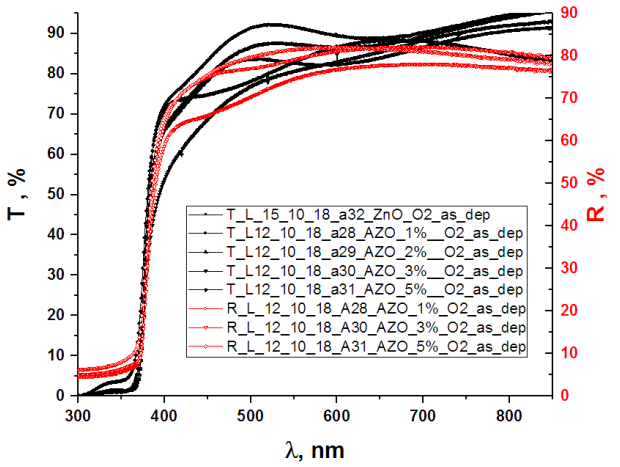


Fig. 8. The transmission and reflectance spectra for the as deposited undoped and Al-doped ZnO thin films synthetized in O_2 atmosphere

From the Figure 9 can be observed that the transmittance of the all thermal annealed Al-doped ZnO layers obtained in the O_2 atmosphere varies between 70% - 90%, the maximum of 90% being reached at longer wavelength for the 5 at% Al-doped ZnO layer. The lowest transmittance shows the 2 at% Al-doped ZnO thin film.

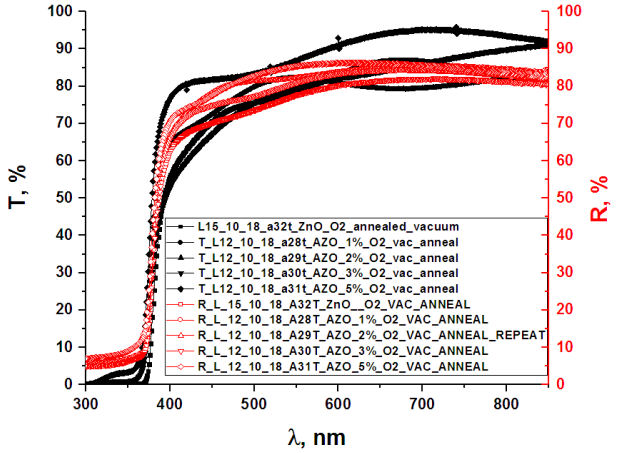


Fig. 9. The transmission and reflectance spectra for the thermal annealed undoped and Al-doped ZnO thin films in O_2 atmosphere

With the increasing concentration of Al, the value of band gap (E_g) slightly varied and displays a growing trend with

the increasing concentration of Al from 3.25 eV for undoped and to 3.32 eV for 5 at% Al-doped ZnO thin films.

The estimated values of the band gap agree well with the data literature values for Al-doped ZnO thin films [23-25]. Also, all spectra of as deposited and thermal annealed ZnO thin films show a decrease of transmission near the fundamental absorption, which identifies a good crystallinity of the obtained layers. Figure 10 illustrates the transmission and reflectance spectra for the second set of the as-deposited undoped and Al-doped ZnO thin films synthetized in Ar atmosphere. The transmittance of as deposited undoped and Al-doped ZnO thin films in Ar atmosphere in the visible region is slightly higher in comparison with of as deposited undoped and Al-doped ZnO thin films in O_2 atmosphere.

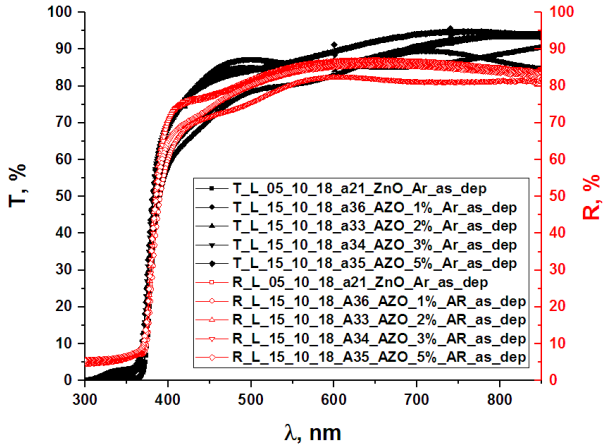


Fig. 10. The transmission and reflectance spectra for the as deposited undoped and Al-doped ZnO thin films in Ar atmosphere

The value of E_g for all ZnO thin films synthetized in Ar atmosphere reaches the same values as in the case of the set of ZnO thin films synthetized in O_2 atmosphere. The transmittance and reflectance of thermal annealed undoped and Al-doped ZnO thin films in Ar atmosphere are presented in Figure 11.

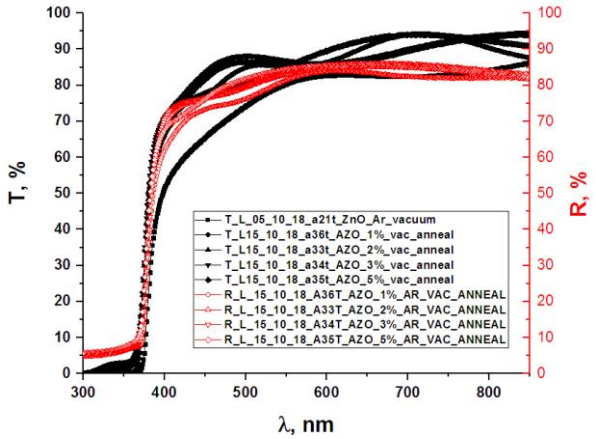


Fig. 11. The transmission and reflectance spectra for the thermal annealed undoped and Al-doped ZnO thin films in Ar atmosphere

The thermal annealed undoped ZnO thin films show the lowest transmittance. The transmittance of the all thermal annealed Al-doped ZnO thin films in the visible region are higher than 85% and it is modified in the limit of 10%. The E_g for the undoped film is 3.26 ev, while for the Al-doped ZnO thin films reaches the value of 3.29 eV and it vary in the limit within the experimental errors (0.03 eV). The value of the reflectivity over measured wavelengths for both sets of ZnO thin films vary from about 80% to about 85%.

C. Electrical Properties

For photovoltaic application of transparent conducting oxide thin films, not only high transparency over the visible light region is essential, but also high conductivity is required. The resistivity of as deposited Al-doped ZnO thin films, for both sets synthetized in O_2 and Ar atmospheres, measured at room temperature is highly and does not present interest for photovoltaic applications.

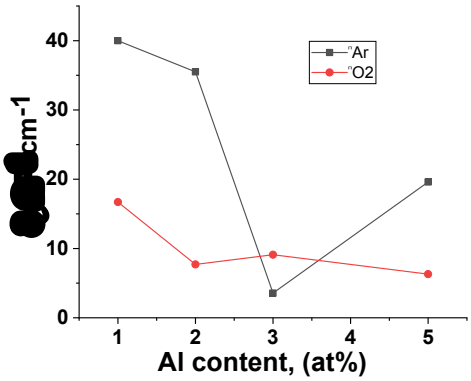


Fig.12. The conductivity vs. Al content of ZnO thin films synthetized in Ar atmosphere

The ZnO films conductivity vs. Al content show that by increasing the Al concentration the conductivity decreases in differently trends, in function of the synthetized gaseous atmosphere. Probably, the conductivity is reduced with increasing of the Al concentration due to distortion of the ZnO lattice and formation of the defects or neutral complexes [26, 27]. The Al-doped ZnO thin films in the O_2 atmosphere showed increased resistivity in comparison with those obtained in Ar gas atmosphere. The 1.0 at % Al – doped ZnO thin film synthetized in Ar atmosphere exhibit the highest value of conductivity. The origin of the increasing conductivity is the generation of free charge carriers which are influenced by the oxygen vacancies and Zn interstitials, that in our case is influenced by the nature of gas atmosphere. Both structural defects provide extra electrons as free charge carriers.

CONCLUSION

In this study have been investigated structure, optical and electrical properties of Al-doped ZnO thin films synthetized by spray pyrolysis in Ar and O_2 atmospheres. The XRD analysis shows that regardless of the nature of the carrier gas used in the preparation, the undoped and Al-doped ZnO films are polycrystalline and show the [002] preferred crystallite orientation. In addition, it is observed that higher structural distortion can be related to lower crystallite size. After thermal annealing both sets of Al-doped ZnO films exhibit a better crystallization, however the XRD patterns of the thermal annealed 1 at% - and 2 at% Al-doped ZnO thin

films synthetized in O_2 atmosphere reveal the formation of Al_2O_3 phase. For all Al-doped ZnO thin films deposited in both atmospheres an increase of film roughness after vacuum annealing is noted. The transmittance of the as deposited and thermal annealed first set of ZnO thin films deposited in Ar atmosphere in the visible region is slightly higher in comparison with of second set synthetized in O_2 atmosphere, but still higher than 75%, which is important for the applications in the field of photovoltaics. The band gap values of ZnO films synthetized in Ar atmosphere show a slight decrease of the band gap values (within the experimental errors (0.02-0.03 eV)) compared with that synthetized in O_2 atmosphere. The best conductivity is noted for the thermal vacuum annealed 1.0 % Al-doped ZnO thin films synthetized in Ar atmosphere with the presence of the strong (002) reflection in the XRD patterns, as reported in the many references. The nature of the carrier gas does not modify the trend of changes in Al-doped ZnO properties, but it influences the reduction of trace oxygen from ZnO films. The more oxygen-deficient film exhibits a higher conductivity.

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