Structural, Optical and Electrical Properties of ZnO: Al Thin Films Synthesized by Sol-gel Method

A. Rogachev[1], A. Semchenko[1], V. Sidsky[1], V. Gaishun[1], D. Kovalenko[1],
V. Gremenok[2], H. Zaretskaya[2], and L. Sudnik[3]

[1] Francisk Skorina Gomel State University, Gomel, Belarus
[2] Scientific-Practical Materials Research Centre of the National Academy of Sciences of Belarus, Minsk, Belarus
[3] State Scientific Institutions Powder Metallurgy Institute, Minsk, Belarus

Abstract— **The possibility of synthesis of active layers for solar cells by sol-gel method has been shown. The structural features of the surface (AFM), crystallization behavior (XRD) during the heating and properties of synthesized films are discussed. Achieved parameters suggest the possibility of using synthesized ZnO layers in solar cells. The perturbation imposed by Al atom incorporation leads to the atomic relaxation, which is computed and discussed in detail.**

Keywords— **sol-gel method, semiconductors, surface structure, crystallization, solar cells.**

I. Introduction

Zinc oxide ZnO is widely used in a number of optoelectronic devices such as solar cells [1-2]. ZnO films can be prepared by various methods. Of particular the opportunities to obtain ZnO films with controlled physical properties by sol-gel synthesis is very attractive. This method combines the simplicity of the process and the lower cost of used equipment and materials. In this paper, the structural and optical properties of ZnO:Al films formed by sol-gel method has been discussed

II. Material and Methods

The required amount of zinc acetate filled into absolute isopropyl alcohol and stirredin order to manufacture the ZnO/Al layer from the precursor (sol). Then sol was stirred for 30 minutes. Sol was kept at the room temperature (22±2)° C for 2-3 days. Monoetalamin was selected as the catalyst because reduced the exposure time to two days and ensure their stability during the month. After applying the sol onto the surface of glass, single crystal silicon etc., the samples were placed in the furnace and were heated stepwise at intervals of 20 °C to the temperature of 350 0C for 10 minutes. The process of applying and drying had been repeated until the desired thickness of the ZnO/Al layer was achieved.

X-ray phase analysis was performed by ARL X'tradiffractometer (Thermo Ficher Scientific, Switzerland), using Bragg-Brentano geometry and reflected Cu Kα1-and Kα1-radiation. To reduce reflections from the substrate small incidence angles was used. Angular 2θ-range was selected from 10º to 60º.

Diffraction peaks identification was performed using database JCPDS (with software Search Match). Diffractograms were processed using JANA 2006 software. The electrical resistivity ρ was measured at room temperature by four-probe method.

III. Results and Discussion

A. Structural Properties of ZnO: Al Sol-gel Films

The ZnO:Al film synthesized by sol-gel method was investigated with AFM (Figure 1) wich confirmed the high

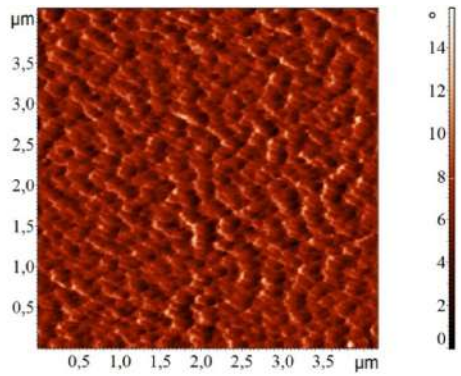


Fig. 1 AFM of ZnO:Al sol-gel films

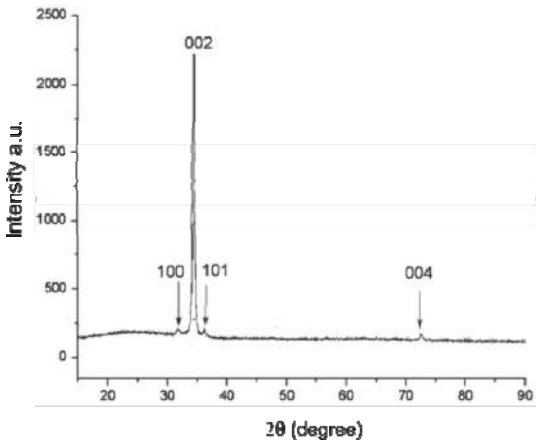


Fig. 2 XRD spectrum of ZnO:Al sol-gel films

V. Sontea and I. Tiginyanu (eds.), *3rd International Conference on Nanotechnologies and Biomedical Engineering*,
IFMBE Proceedings 55,
DOI: 10.1007/978-981-287-736-9_26

homogeneity of the films. According to the XRD ZnO:Al films are polycrystalline, single-phase and have a hexagonal wurtzite structure (Figure 2). The angular position of the peaks is consistent with the JCPDS-data for nominally pure zinc oxide (JCPDS, № 36-1451). The Al^{3+} ions do not violate the hexagonal wurtzite structure ZnO.

B. Optical Properties of ZnO: Al Sol-gel Filmsnsent

Figure 3 shows the transmission spectra as a function of wavelength for samples of zinc oxide obtained at different aluminum content (0.6-1.4 wt.%). Studies of the optical characteristics of the films ZnO: Al showed that zinc oxide films have a high transmittance T (λ) = 80 – 94%, indicating that this material is acceptable for use as a window layer and for tandem solar elements.

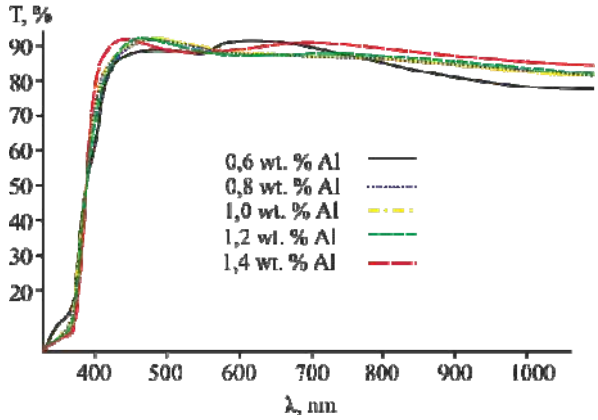


Fig. 3 Transmission of ZnO films depending on the concentration of aluminum

Research of Raman spectra (RS) of obtained ZnO:Al sol-gel films is in good agreement with XRD data. According to the theory of groups for ZnO, which is crystallized in hexagonal wurtzite structure with spatial symmetry C_{6V}, there are a set of phonon modes: $1A_{1\ (TO)} + 1A_{1(LO)} + 2B_1 + 1E_{1(TO)} + 1E_{1(LO)} + 2E_2$ [3]. Phonon modes are observed in ZnO at the following frequencies: $E_{2(low)}$ (low frequency) = 101 cm^{-1}, $E_{2(high)}$ (high-frequency) = 437 cm^{-1}, $A_{1(TO)}$ = 380 cm^{-1}, $A_{1(LO)}$ = 574 cm^{-1}, $E_{1(TO)}$ = 407 cm^{-1} and $E_{1(LO)}$ = 583 cm^{-1}, respectively (LO - longitudinal optical, TO - transverse optical modes). Among these $2B_1$ modes are not Raman activity [4]. In the fall of the beam is strictly normal to the surface of the ZnO layer are observed only $A_{1(LO)}$ and E_2 modes, while the other modes are prohibited under the rules of selection. It is known that the intensity and frequency position of $E_{2\ (high)}$ mode largely depends on the crystal lattice stress ZnO [4]. On the other hand, the study of spectral characteristics of oscillation $A_{1(LO)}$ provides the opportunity to get information not only on the chemical composition of the resultant ZnO: Al films, and about the presence of foreign phases and areas with locally ordered lattice. According to the data [3] all the bands observed in the Raman spectra of the resulting coatings (Fig. 4) can be attributed to scattering by phonons of zinc oxide. In the low-frequency Raman spectra of sol-gel ZnO:Al films (Series № 1-3) are observed mode $E_{2\ (low)}$ at 330 cm^{-1}, high-frequency mode $E_{2(high)}$ in the range of 427 - 439 cm^{-1} and mode $A_{1\ (LO)}$ in the range of 575-582 cm^{-1}. Mode at 330 cm^{-1} is a second-order oscillation mode phonon $E_{2\ (high)}$ and is due, mainly, the vibrations of atoms Zn [5]. Fixed high-$E_{2\ (high)}$ and $A_{1\ (LO)}$ mode are associated with the fluctuations of the oxygen atoms in a perfect crystal ZnO and local vibration of intrinsic lattice defects such as oxygen vacancies, intermediate cations [5].

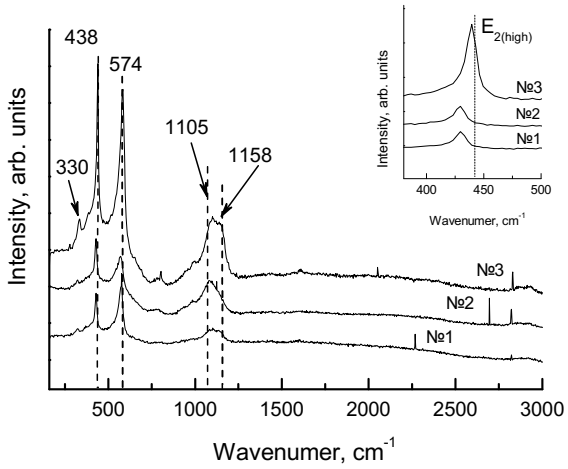
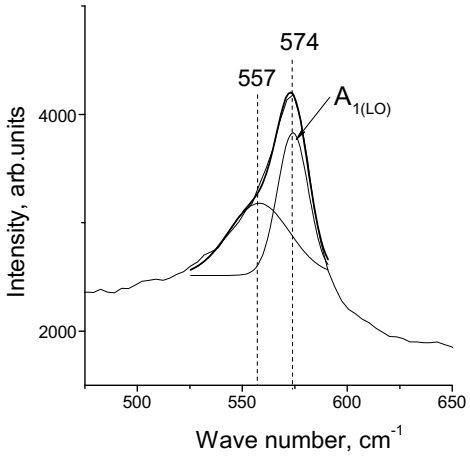


Fig. 4 Raman spectra of ZnO:Al films produced by sol-gel deposition of solutions based on: №1 -2-methoxyethanol - isopropylalcohol;№2 - dimethylformamide; №3 -isopropylalcohol.

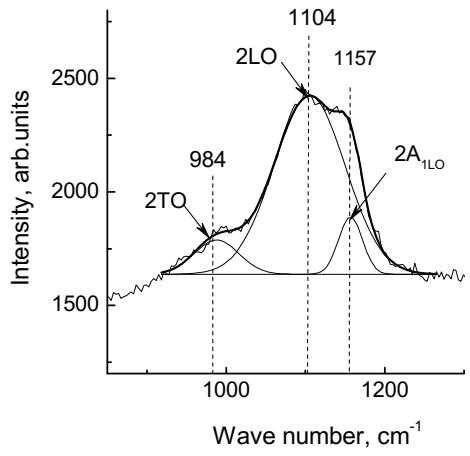
The spectral position, intensity and half-width (FWHM) of $E_{2\ (high)}$ and $A_{1\ (LO)}$ oscillations are significantly different for the ZnO:Al coatings obtained from different starting compounds. Relatively to the standard ZnO, mode $E_{2(high)}$ and $A_{1(LO)}$ which are observed for specimens series № 1-2, are shifted to lower frequencies. A significant red shift of $E_{2\ (high)}$ mode ($\Delta\nu \approx$ 8 cm-1) is associated with the disordering influence of the crystal lattice, a nonuniform distribution of Al impurities and indicates the presence of the coatings compressive stresses. With the improvement of the quality of the crystalline coating ZnO: Al modes $E_{2\ (high)}$ and $A_{1(LO)}$ are shifted to higher frequencies. Simultaneously, the intensity of these oscillations and their half-width (FWHM) are reduced (for mode $E_{2(high)}$ up to 8 cm^{-1} and for mode $A_{1\ (LO)}$ up to 10 cm^{-1}, respectively). Reflex from fluctuations $E_{2\ (high)}$ on the Raman spectra of the films ZnO: Al Series №3 is symmetrical (Figure 3). That fact is indicate the process of ordering the

crystal lattice [6]. For the series of ZnO:Al films, obtained from isopropyl alcohol and monoetalamina (№3), oscillation position of $E_{2\ (high)}$ and $A_{1(LO)}$ is shifted to the standard ZnO. This means that the films of this series have no stress.

The fact that the mode $E_{2(high)}$, due to vibrations of oxygen atoms in the crystal lattice of ZnO, is subject of more obtaining conditions than mode $E_{2(low)}$, attributed to fluctuations sublattice Zn, suggests that defects in the oxygen sublattice are dominant. Increase of the intensity of mode $E_{2\ (high)}$ with the improving of crystal quality of the filmss indicates on the ordering of oxygen anion sublattice formed in layers with optimal choice of reactants and deposition conditions.



a)



b)

Fig. 5.Raman spectra of ZnO: Alcoatingsproducedusing sol-gel precipitation from solutions based on isopropyl alcohol: a) the area of frequency-phonon mode A1 (LO); b) the frequency range of the phonon mode 2_{LO}

C. *Electrical Properties of Properties of ZnO: Al Sol-gel Filmss*

It should be noted that the mode $A_{1\ (LO)}$ of the resulting film at 574 cm^{-1} in the Raman spectra is asymmetric (Figure 4a). According to [7, 8] asymmetry of $A_{1(LO)}$ mode, observed in doped aluminum and gallium ZnO films, is attributed to local disordering of the crystal lattice, and created by oxygen vacancies. Therefore, we can conclude that the increase of the intensity fluctuations at 557sm^{-1} in the Raman spectra of the samples in the series №3 is due to the higher concentration of aluminum Al^{3+} in these films. Fig. 6 depicts the variation of resistivity (ρ), carrier concentration (n) and mobility (μ) of Al doped ZnO films with doping concentration. The resistivity first decrease with increasing current and a lowest resistivity (6.5 ohm cm) is obtained at a current $0{,}8*10^{-4}$ further increase in current the resistivity value started to increase significantly.

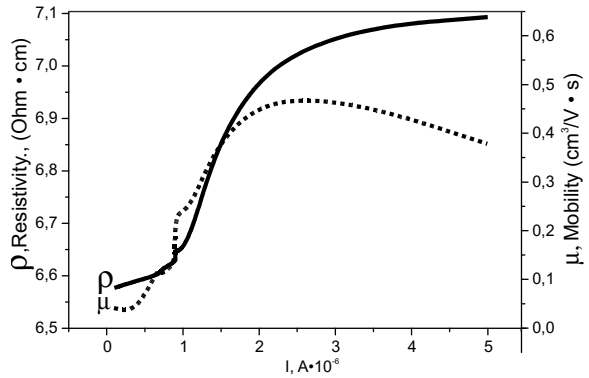


Fig. 6 The dependence of the resistivity of the charge mobility of the current ZnO: Al-film obtained by a sol-gel method

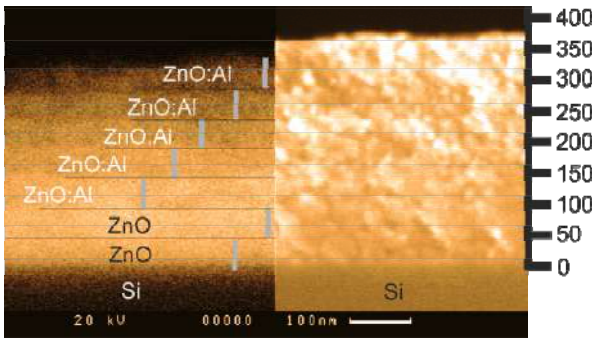


Fig. 7 SEM image ZnO:Al-Si film annealed at 550 ° C for 1 hour in an atmosphere of oxygen

Figure 7 depict the SEM micrographs of the surface of Al doped ZnO thin film with (0,4 at.%). The surface morphology of the deposited films is observed to be smooth and

plane without crack. From the figure we find that the microstructure of the films consisted of many round shaped crystalline particles. The microstructure formed is found to uniform and compact interconnected grains. The average grain size of the ZnO thin films is around 20 nm.

IV. CONCLUSIONS

It has been shown that the use of sol-gel method allows to synthesize the functional nanostructured materials semiconductors (ZnO)) for electronic devices with required properties.

ACKNOWLEDGMENT

This research was partially conducted in the framework by the Belarusian Foundation for Basic Research, project T15MLD-033.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Sci J, Technol., Suwanboon, Songklanakarin et al. (2008) Fabrication and properties of nanocrystalline zinc oxide thin film prepared by sol-gel method, 30 (1), , pp. 65-69.
2. Mat. J, Today, L. Shmidt-Mende and J. L. MacManus–Driscoll. (2007) ZnO – nanostructures, defects, and devices, 10 (5), pp. 40-48.
3. Damen T., Porto S., Tell B., (1966) Phys. Rev. 570:142
4. Cuscó R, Alarcón-Lladó E, et al. (2007) Phys. Rev**.,** 165202: B **75**
5. Serrano J, Manjon F. J et al. (2003) Phys. Rev. Lett., 055510:90
6. Arguello C.A,. Rousseau D.L, (1969) S.P.S. Porto, Phys. Rev. 1351:181
7. Lorite I., Villaseca L. et al. (2013)Thin Solid Films, 657:548.
8. Cusćo R, Alarćon-Lladó E, et al. (2007) Phys. Rev., 165202:B 75

Author: A.V. Rogachev
Institute: Francisk Skorina Gomel State University
Street: Sovetskaya 104
City: Gomel
Country: Belarus