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Aluminum doped zinc oxide layers by atomic layer deposition and magnetron sputtering: formation and comparison of optoelectronic properties

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Thin films of aluminum-doped zinc oxide (AZO) were prepared using magnetron sputtering and atomic layer deposition (ALD) techniques. Atomic force microscopy (AFM) studies of AZO films surface morphology show that the surface of produced by ALDfilms is a smoother in comparison with films formed by magnetron sputtering.According to comparative analysis of optical transmittance spectra in the visible range of 300 - 800 nm, films formed by ALD technique demonstrates 10% higher transparency than those that obtained by magnetron sputtering. Investigation of samples electrical properties show that the conductivity of AZO films obtained by ALD technique actually two orders of magnitude higher than analogues obtained by magnetron sputtering.

Key words: zinc oxide, thin films, morphology, optical properties, electrical properties.
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1 Introduction

Al-doped Zinc oxide thin films have gained much attention due to their high light transmission and potential applications in the field of sensors [1], photovoltaics [2], electronics [3], biomedicine [4], as alternative for indium-tin oxide (ITO)[5]. There are several basic physical [6-8] and chemical [9, 10] methods of obtaining AZO, each of which has its advantages and disadvantages. One of the most novel and effective methods thin semiconductor films formation is an atomic layer deposition [11]. Another, widespread and well-known technique for producing semiconductor thin films with different elemental composition is a magnetron sputtering method [12, 13]. The main objectives of this work were a comparison of the AZO growth techniques such as atomic layer deposition and magnetron sputtering, study optical and electrical properties of obtained films and compare results.

2 Experimental details

The first group of test AZO samples prepared by atomic layer deposition, based on the sequential use of cyclic gas - solid-state transition reactions. ALD is a modified type of chemical vapor deposition (CVD) which enables very homogeneous film thicknesses on complex 3D geometries. The process of film growth in an ALD reactor is self-limited and based on surface reactions, which makes it possible to control the deposition at the atomic level. Keeping precursors separate from each other throughout the deposition process allows controlling the growth of atomic thickness of the film and obtaining the most accurate result for the atomic / molecular monolayer.

In all our experiments we used as a substrates laboratory borosilicate glass and p-type (100) monocrystalline silicon wafers with a specific resistivity of 10 Ω*cm. The native silicon oxide removal carried out by a 1 min dip in 2% HF.Deposition of films was performed by thermal ALD with a deposited doping of 1:10, 1:20, 1:30 and none doping in a commercial ALD reactor (OpAl, Oxford Instruments). Range of deposition temperature was 150°C to 300°C. Trim ethylaluminum (TMA), diethyl zinc (DEZ) and deionized water (H_2O) used as precursors of reactions. In the Fig.1,one can see a cycle repetition scheme of ALD- reactor according to the selected mode: complete film deposition cycle consists of alternating cycles of deposition of oxides of zinc and aluminum. The layers alternated in following mode: 20 cycles of ZnO and 1 cycle

of Al_2O_3 deposition. Total cycle consisted of 21 monolayer deposition cycle and repeated 120 times, resulting in an AZO layer consisted of 2520 ALD deposition cycles. The scheme also shows the data for the duration of each constituent processes. The average thickness of resulting AZO films was 400 ± 20 nm. The deposition was conducted at 2 m Torr pressure in the reactor chamber.

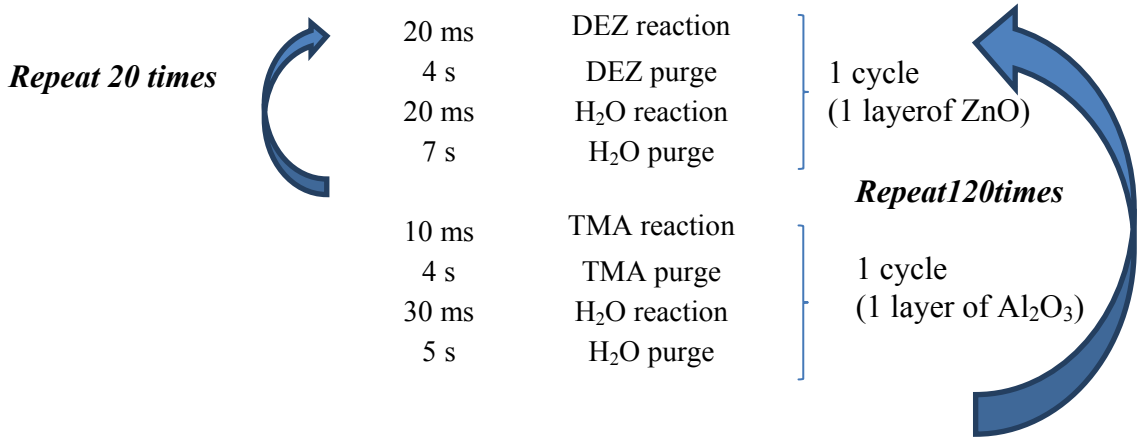

Figure 1 –Schematic representation of AZO thin film deposition experimental mode in the ALD reactor

The second group of experimental samples of AZO films obtained by the method of magnetron sputtering (VUP 5 deposition setup). In this deposition setup, the principle of targets cathode sputtering in magnetron discharge plasma is used. In our experiments as targets, we used Zn and Al mixed targets with different variations of the Al atoms concentration.AZO thin films deposited also on the surface of laboratory glass and p-type monocrystalline silicon wafers (100) with a specific resistivity of 10 Ω*cm at a temperature of 230°C and pressure of 5mTorr. The surface density of the discharge power ranged between 0.07 - 0 21 W/cm^2. The process conducted in Ar_2:O_2 mixture medium and the ratio of gases were 1:1.The average thickness of obtained AZO films was 400 ± 20 nm .

3 Results and discussion

The surface morphology of the AZO films was investigated by atomic force microscopy (AFM). In AFM images of AZO, obtained by atomic layer deposition, it is clearly seen that the surface is sufficiently smooth but contains irregularities in the form of needles of about 15-20 nm as shows in Fig. 2. The surface of AZO films with the presence of spherical features obtained by magnetron sputtering, is also quite homogeneous, but is looser than the surface of the films prepared by ALD technique as presented in Fig. 3. The averages size of the roughness in magnetron sputtered films was 35-40 nm. Data analysis of the surface morphology of the films obtained by two methods indicates that the use of ALD technology allow to obtain layers with more uniform and smooth surface.

One of the important characteristics for different optoelectronic application of investigated semiconductor material is an optical transparency. Optical parameters of samples were studied by means of spectrophotometry through measuring and analysis of transmission spectra in the optical range between 300 nm and 800 nm (Lambda 35, Perkin Elmer). In the Fig. 4the transmission spectra of the AZO films, obtained by ALD and magnetron sputtering are presented. There are shown transmission spectra of the AZO films deposited by both methods at the following aluminum and zinc ratios: 1:10, 1:20 and 1:30. Also, for the comparison of our experimental results, we added the spectrum of undoped ZnO film. The absorption edge of the undoped zinc oxide film is marked by dotted lines at the wavelength of 375 nm with a maximum of transmittance above 600 nm.

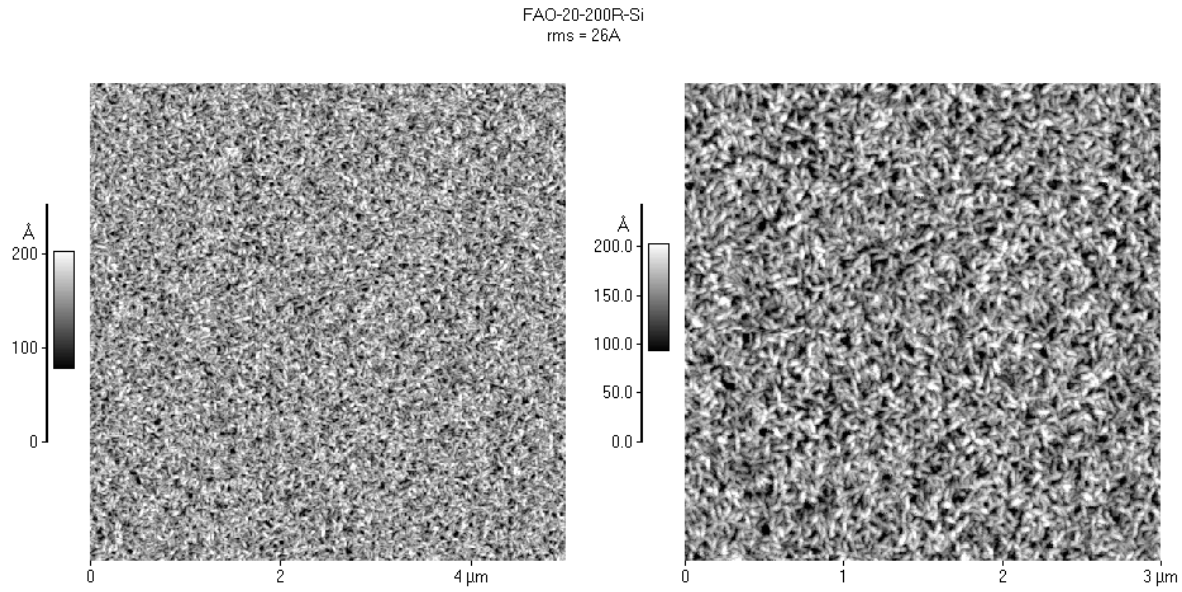

Figure 2 – AFM images of AZO film growth by atomic layer deposition method

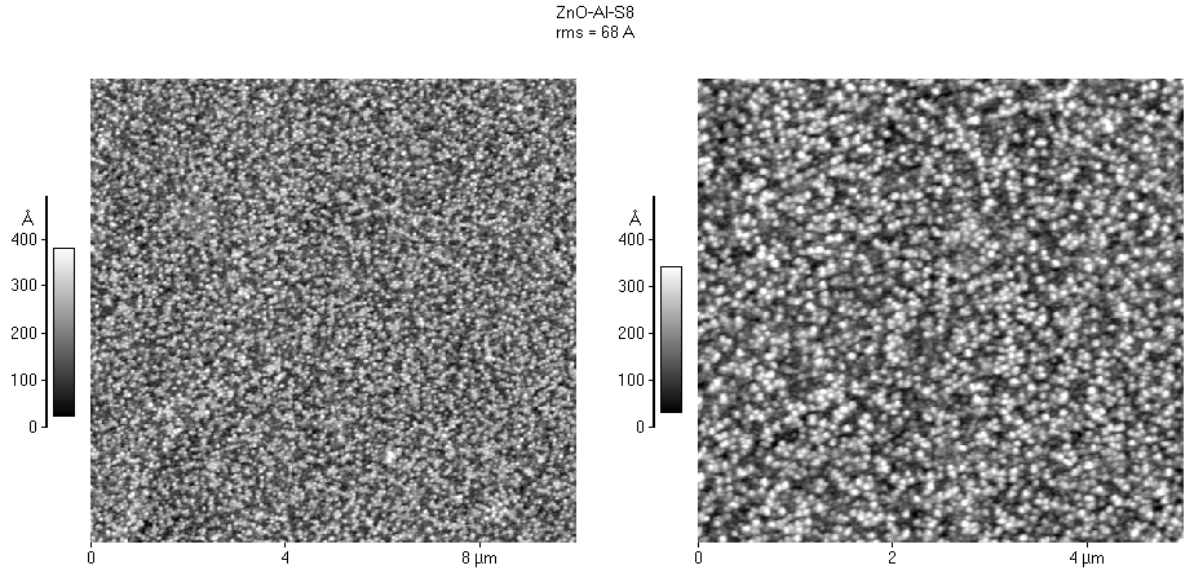

Figure 3 – AFM images of AZO film growth by magnetron sputtering deposition method

According to analysis of the spectra shown in the Fig. 4a, it follows that in the visible range of 400 nm - 800 nm transmittance of all samples, obtained by ALD, exceeds 90%. By all ALD AZO layers the transmittance is 10-20% higher in the 400-600 nm range. The maximum value of the transmittance reaches 99.4% for the sample obtained at the Al/Zn ratio of 1:10. The transmission spectra maxima occurs in the interval of 500 -550 nm. As concentration of dopant (Aluminum) increase transmission maxima shifted to shorter wavelengths area. The transmittance reduced to 70% in the area of the material's absorption edge, for which a blue shift is also observed. This result is very good indeed, because a high transparency rate of these films could become one of the key parameters for their application in photovoltaics and electronics related areas.

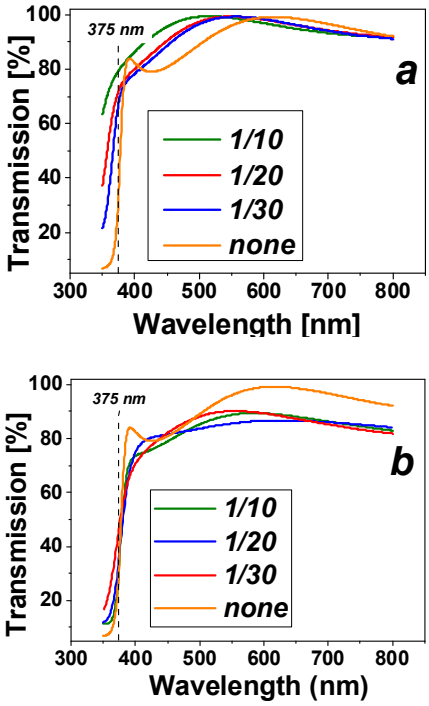

Figure 4 – The transmission spectra of AZO films growth by: (a) atomic layer deposition and (b) magnetron sputtering deposition method

The transmission spectra of AZO samples, produced by magnetron sputtering deposition are presented in the Fig. 4b. The spectra show that such AZO films also have a quite high transmittance in full visible range of 400-800 nm. The spectra of all examined samples there is a maximum transmission in the wavelength region of 500-550 nm. However, the maximum transmission does not exceed 90%. The similar transmittance to undoped ZnO layer was obtained for magnetron sputtered layer in the range between 400 up to 520 nm. The lower transmittance (10-15%) in comparison to undoped ZnO layer was obtained in the range between 520 up to 800 nm. Our results suggest that transparency of AZO films, produced by magnetron sputtering deposition is about 10-15% lowerin comparison of analogous layers produced by ALD method. Similar to AZO films, obtained by ALD, blue shifts of the transmission maximum and the absorption edge of the layer with increasing of dopant concentration obtained in transmission spectra of thin layers produced by magnetron sputtering deposition.

Another important criterion in the selection of materials for different technical applications is its electrical conductivity. Therefore, we measured the specific electrical resistivity of AZO layers, obtained at different concentrations of aluminum atoms and deposition temperatures. Resistivity of all AZO films was measured by four point method.Figure 5 represents a dependence of the r specific electrical esistivity average value on deposition temperature for ALD AZO films with different doping levels. The analysis of this study results that the minimum value of AZO films resistivity was obtained at the deposition temperature of 250°C for doped and undoped samples of zinc oxide layers. For all doped and undoped layers, there is observed almost the same behavior, thus with increasing deposition temperature resistivity of the material sharply decreases at first, then gradually. The lowest resistivity is 1.2 * 10^{-3} Ω*cm and respects to the sample obtained at 1:20 Al/Zn ratio.

For undoped zinc oxide layer the specific electrical resistivity minimum is almost observed at the deposition temperature of 250^0C and equal to 5.9*10^{-3} Ω*cm, hence, AZO films with doping ratio of 1:20 improves its conductivity almost for 5 times. As it shown in the Fig. 5 in the deposition temperature range of 250-300^0C resistivity of all samples increases. This phenomenon is presumably because of at high temperatures atomic layer deposition process does not occur uniformly and too high kinetic energy of aluminum atoms results to their irregular deposition on the zinc oxide surface, thus conductivity of the output material suffers.

In order to compare the ALD AZO electrical characteristics with magnetron sputtered AZO layers the specific electrical resistivity was also measured for magnetron sputtered AZO films. Unfortunately, the electrical parameters of these films were very weak. The minimum value of the resistivity was 0.22 Ω*cm for sample obtained from the dopant concentration ratio Al/Zn of 1:20. Thus, the comparative analysis of the samples resistivity indicates that the conductivity of AZO films obtained by atomic layer deposition actually two orders of magnitude higher in comparison to the thin films obtained by magnetron sputtering.

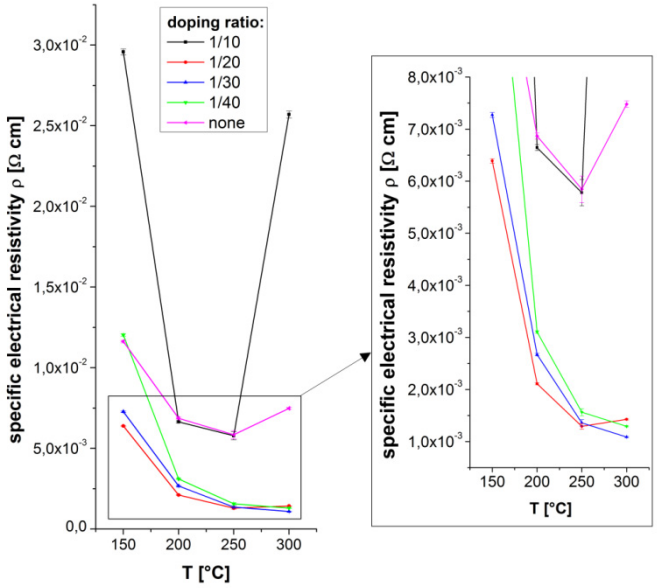

Figure 5 –Specific electrical resistivity of aluminum doped ZnO depending on deposition temperature and deposited doping ratio

4 Conclusions

We have performed experiments on formation of AZO films by atomic layer deposition and magnetron sputtering techniques. It is experimentally shown that the surface of produced by ALD AZO films is more smoother in comparison with those obtained by magnetron sputtering. According to comparative analysis of optical transmittance spectra in the visible range of 300 - 800 nm, layers formed by ALD technique demonstrates 10-15% higher transparency than those that obtained by magnetron sputtering or undoped ZnO layer. Investigation of samples electrical properties show that the specific electrical resistivity of AZO films obtained by ALD technique actually two orders of magnitude lower than analogues obtained by magnetron sputtering. Following the findings based on presented experimental results, we concluded that the most optimal characteristics have AZO films produced by ALD. Besides, ALD allows to obtain a high quality AZO layers with optimal optoelectronic properties at comparatively low deposition temperatures that opens a new technological opportunities for using temperature sensitive surfaces, such as flexible polymers, as a substrate.

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