doi: 10.15407/ujpe61.04.0325

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PACS 77.55.hf, 81.15.Cd, 61.05.cp

EFFECT OF ARGON DEPOSITION PRESSURE ON THE PROPERTIES OF ALUMINUM-DOPED ZnO FILMS DEPOSITED LAYER-BY-LAYER USING MAGNETRON SPUTTERING

ZnO:Al films are deposited layer-by-layer onto silicon and glass substrates, by using the radio-frequency magnetron sputtering method at various argon pressures from 0.5 to 2 Pa in a deposition chamber. The influence of this pressure on the structure and the optical and electrical properties of ZnO:Al films is studied. Higher argon pressures are found to reduce the electron mobility in transparent conductive ZnO:Al films and to worsen their conducting properties owing to the free electron scattering by grain boundaries. An increase in the free electron scattering at higher argon pressures reduces the transparency of ZnO:Al films in the visible spectral range.

Keywords: ZnO films, aluminum doping, argon pressure effect, X-ray diffraction analysis.

1. Introduction

Transparent conducting oxides are wide-band-gap semiconductors with a low specific resistance and a high transparency in the visible spectral range. They attract a keen interest because of their possibility to be widely used as transparent electrodes in displays, solar batteries, light-emitting diodes, sensors, and other devices [1, 2]. At present, indium-tin oxide (ITO) is the most used of them. However, this material has a number of serious shortcomings, such as its large and permanently growing cost, which is associated with limited indium resources on the Earth. Therefore, the intense efforts concerning the study of materials, which being cheaper than ITO have similar properties, were undertaken. Among those materials, a large attention is attracted by ZnO because of considerable resources of its initial components on the Earth, their low cost, and nontoxic character [3].

The main parameter that characterizes the efficiency of transparent electrodes is the Q-factor, which is defined as the transmittance times the conductivity,

$$Q = T\,\sigma = T/\rho. \tag{1}$$

The transparency of zinc oxide films up to 1 μm in thickness amounts to 90–95%, and the specific resistance is of an order of $10^{-1}\ \Omega\cdot$cm. In order to reduce the resistance, ZnO is doped with donor impurities. The latter are mainly elements of group 3 (Al, Ga, In). From the economical viewpoint, the most attractive is the application of aluminum as the doping impurity.

ZnO:Al films are grown up with the use of various technologies, such as molecular-beam epitaxy [4], spray pyrolysis [5], chemical deposition from the vapor phase [6], pulsed laser deposition [7], thermal evaporation [8], and magnetron sputtering (MS) [9, 10]. Among those technologies, the high-frequency MS is applied the most frequently owing to a high deposition rate and a high uniformity of the composition and properties of films obtained on large-size substrates. The most important MS parameters are the pressure and the composition of a gas mixture, substrate temperature, distance between the target and the substrate, and magnetron power. They determine the energy of particles sputtered from the target material and the deposition rate, which, in turn, affect the composition, structure, and properties of the films. Hence, by varying those parameters, it is possible to obtain films with prescribed electrical and optical properties [11]. Despite rather a considerable number of corresponding researches, the study of the influence of physical and technological sputtering parameters on the properties of ZnO:Al films is continued.

Recently, we have proposed a new procedure of MS for growing undoped zinc oxide films, the level-by-level deposition. ZnO films are grown in a number of stages, with breaks in between [12]. This procedure allowed us to improve the perfection of the undoped film structure. Therefore, it was also used to grow films doped with aluminum.

This work is aimed at studying the influence of the argon pressure on the structure and the optical and electrical properties of ZnO:Al films deposited level-by-level onto a substrate using the MS method.

2. Experimental Technique

In order to deposit ZnO:Al films on Si(100) and glass substrates within the high-frequency MS method, we used a vacuum system VS350 (Selmi, Ukraine). A zinc (99.99%) disk with aluminum (99.99 %) insertions was used as a target. The insertions occupied 1.4% of the area of the target erosion zone. In order to improve the optical and electrical characteristics of ZnO:Al films, the method of level-by-level deposition was applied. Al-doped ZnO films 80–145 nm in thickness were grown up in three stages. The breaks were made in every 2 min of the growing. The total film growth time amounted to 6 min. The deposition rate was 12–24 nm/min. In this work, the argon pressure at the film deposition was varied from 0.5 to 2 Pa. The other technological parameters remained fixed: an oxygen pressure of 0.05 Pa in a chamber, a magnetron power of 200 W, the substrate temperature $T_s = 300$ °C, a distance of 7 cm between the target and the substrate, and a sputtering time of 6 min.

The morphology of the ZnO:Al film surface was studied using the atomic-force microscopy (AFM) method on a scanning probe microscope Nanoscope III (Digital Instruments) with a silicon probe, in the tapping mode. The scanning region was $1\times1\ \mu\text{m}^2$. The AFM data were processed using the Gwyddion modular program in order to determine the grain size and the root-mean-square roughness.

The structural parameters were studied with the help of X-ray diffraction analysis (DRON-4), by using Cu-Kα radiation ($\lambda = 0.1542$ nm). The average diameter of coherent scattering regions (CSRs) was calculated, by using the peak halfwidth with the help of the Scherrer equation [14]

$$D = \frac{0.9\lambda}{W\cos\theta}, \tag{2}$$

where λ is the X-ray radiation wavelength, W the peak (002) halfwidth, and θ the angle of Bragg diffraction.

The element analysis of ZnO:Al films was carried out within the method of energy-dispersive X-ray spectroscopy on a scanning electron microscope ZEISS EVO 50 XVP SEM equipped with an analyzer INCA 450 (Oxford Instruments).

The transmittance of the films in the visible range of frequencies and their thickness were studied with the help of a spectrophotometer on the basis of a monochromator DMR-4. An incandescent lamp was used as a source with a continuous radiation spectrum, and a silicon photodiode as a photodetector.

The energy gap width was determined from the absorption curve plotted in the Tauc coordinates α^2 versus $(h\nu)^2$ [15]. The specific electrical resistance of the films was measured, by using the four-probe method.

3. Results and Discussion

The film thickness is an important factor that affects the optical and electrical properties of the film. Thin films are characterized by the enhanced transparency. They require a shorter deposition period and a less material amount [13]. At the same time, making the film narrower can result in the deterioration of its structure and the degradation of electrical properties [14].

The dependence of the film deposition rate on the argon pressure in a chamber at the deposition is shown in Fig. 1. The thickness of deposited ZnO:Al films amounted to 80–145 nm, depending on the argon pressure. The film deposition rate was found to decrease from 24 to 12 nm/min when the argon pressure in a deposition chamber was increased from 0.5 to 2 Pa, respectively. This phenomenon can be associated with the film sputtering by argon atoms in the course of the film growth, as well as with an increase of the scattering of sputtered atoms in the space between the target and the substrate.

With the help of AFM, we studied the surface morphology of ZnO:Al films deposited at various argon pressures in a deposition chamber. The corresponding results are shown in Fig. 2. The films are polycrystalline, with the crystal grain dimensions depending on this parameter. As is shown in Fig. 3, as the argon pressure grows from 0.5 to 2 Pa, the grain size decreases from 37 to 22 nm, respectively. At low growth rates taking place at high argon pressures (Fig. 1), the formed grains are smaller (Fig. 3). This result can be explained as follows. The growth of argon pressure increases the intensity of the ZnO:Al film bombardment with argon ions, which results in the re-evaporation of the film from the surface. The latter process gives rise to an increase in the number of crystallization centers on the film surface. As a result, the grain size in ZnO:Al films decreases. The root-mean-square roughness of the doped oxide films did not depend on the argon pressure, falling within an interval of 2–5.5 nm.

In Fig. 4, the X-ray diffraction patterns of ZnO:Al films deposited at various argon pressures are de-

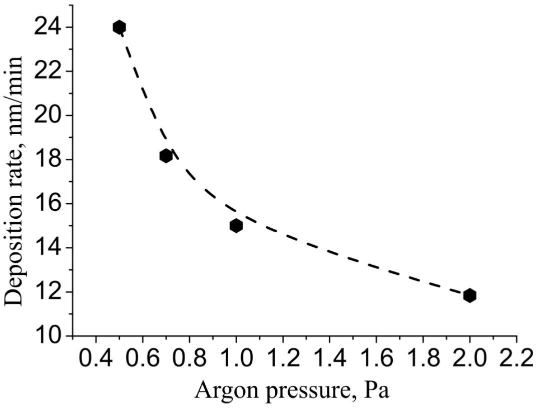

Fig. 1. Growth rates of ZnO:Al films at various argon deposition pressures

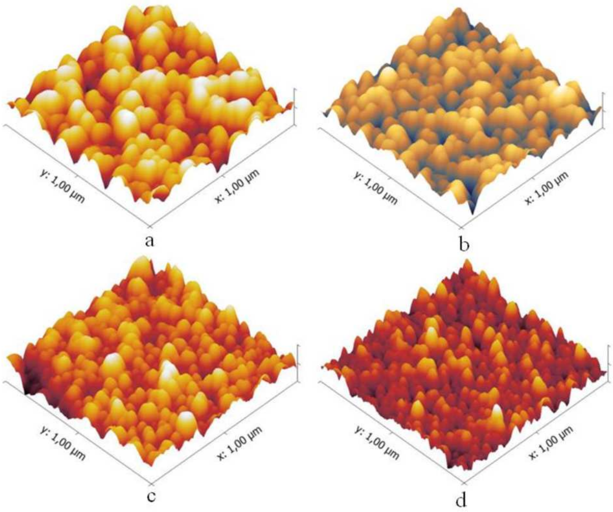

Fig. 2. Surface morphology of ZnO:Al films grown up at various argon deposition pressures

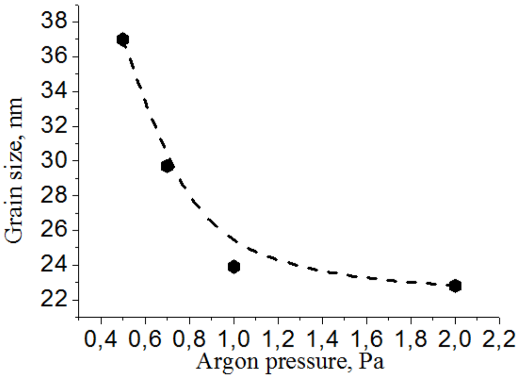

Fig. 3. Dependence of the average lateral size of grains in ZnO:Al films on the argon pressure

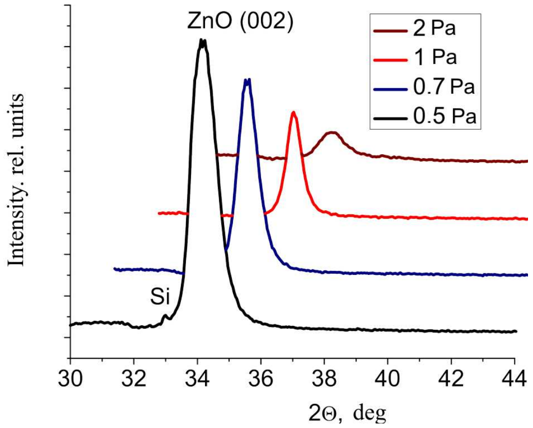

Fig. 4. X-ray diffraction patterns of ZnO:Al films deposited at various argon pressures

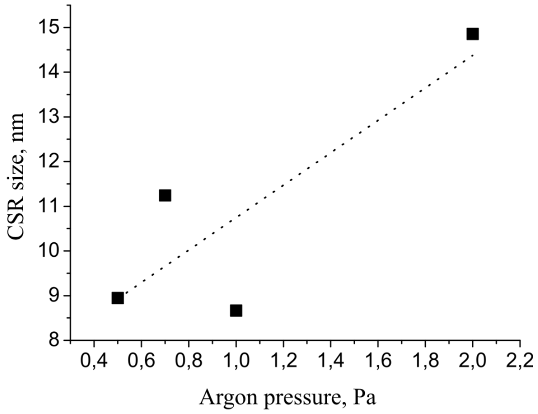

Fig. 5. Dependence of the coherent scattering region (CSR) size in ZnO:Al films on the argon pressure

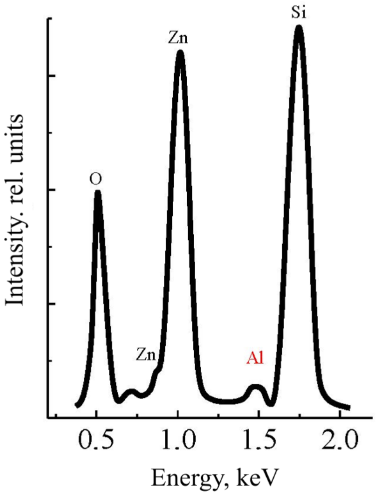

Fig. 6. Energy-dispersive X-ray spectrum of the ZnO:Al film deposited at an argon pressure of 1 Pa

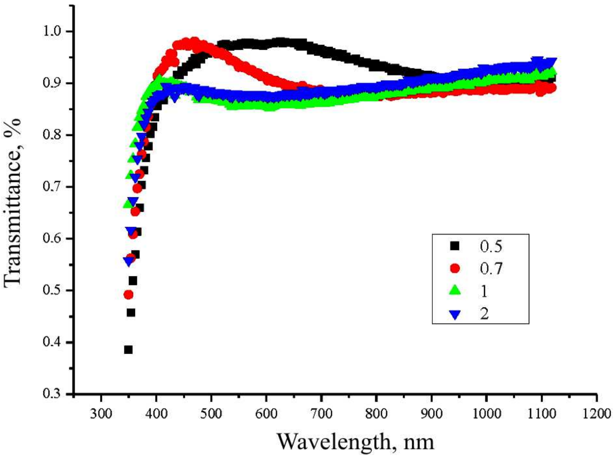

Fig. 7. Optical transmittance spectra of ZnO:Al films for various argon pressures

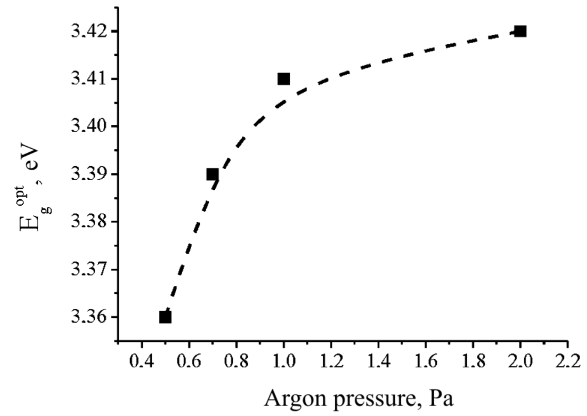

Fig. 8. Dependence of the optical energy gap width in ZnO:Al films on the argon pressure

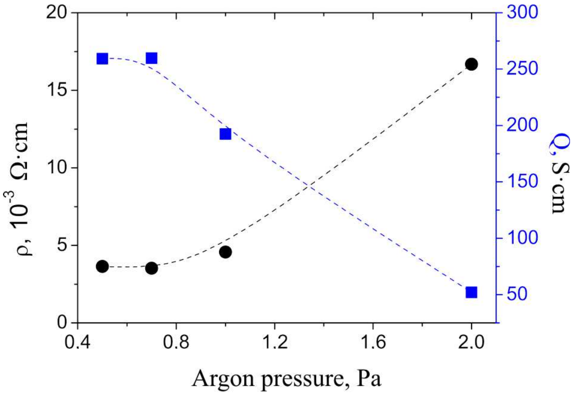

Fig. 9. Dependences of the specific resistance ρ and the Q-factor of ZnO:Al films on the argon pressure

picted. The well-pronounced peak (002) testifies that the films have the wurtzite structure. They are textured with the prevailing orientation of crystallites along the axis c, which is directed normally to the substrate.

In Fig. 5, the dependence of the average size of CSRs in ZnO:Al films on the argon pressure calculated by formula (2) is shown. A tendency of the CSR size to grow with the argon pressure in a deposition chamber testifies to a higher crystalline perfection of ZnO:Al films. This effect may possibly be explained by the fact that the more intense bombardment of the film surface with argon ions results in a reduction of the mean free path of adatoms, which gives rise to a relaxation on the growing surface and to an increase of the crystalline perfection of ZnO:Al films, i.e. to an increase of the CSR dimensions [16].

Figure 6 demonstrates a typical energy-dispersive X-ray spectrum of ZnO:Al specimens registered at an argon deposition pressure of 1 Pa. The following characteristic peaks are observed: the peak at 0.520 keV corresponds to oxygen, at 1.010 keV to Zn, and at 1.490 keV to Al. The aluminum content in ZnO:Al films amounted to 1 ± 0.2 at.% for all specimens.

The transmission spectra of ZnO:Al films measured at various argon pressures are exhibited in Fig. 7. All ZnO:Al films are highly transparent (at a level of 90–95%) in the visible spectral range of 400–700 nm. The transmission spectra reveal interference oscillations, which were used to determine the thickness of ZnO:Al films (80–145 nm). It was found that the argon pressure growth from 0.5 to 2 Pa resulted in a reduction of the ZnO:Al film transmittance from 94% to 87%, respectively, in the visible spectral range.

In Fig. 8, the dependence of the optical energy gap width on the argon pressure is shown. As the pressure grows, the optical energy gap width also grows. An increase of the energy gap width is induced by the Burstein–Moss shift ΔE_{BM}, which consists in a shift of the intrinsic absorption edge in heavily doped semiconductors owing to the filling of the conduction band by electrons or the valence band by holes [17]. In the constant effective mass approximation, the Burstein–Moss shift is defined as follows:

$$\Delta\, E_{\mathrm{BM}} = \left(\frac{h^2}{8\, m_d{}^*}\right)\left(\frac{3n}{\pi}\right)^{2/3}, \tag{3}$$

where m_d^* is the effective mass of the density of states, n the electron concentration, and h Planck's constant.

From formula (3), one can see that an increase of the energy gap width in ZnO:Al owing to a growth of the Burstein–Moss shift ΔE_{BM} testifies to an increase of the free charge carrier concentration in the doped oxide films with the argon pressure in a deposition chamber. The optical transmittance of the films depends on their thickness, morphology, and the scattering on free charge carriers. Therefore, a reduction of the optical transmittance through ZnO:Al films in the visible spectral range, which is observed, as the argon pressure increases, is associated with a more intensive scattering of light at free carriers.

Figure 9 demonstrates the influence of the argon pressure on the specific resistance ρ and the Q-factor of ZnO:Al films. The Q-factor of ZnO:Al films decreases by more than a factor of 5, when the argon pressure increases from 0.5 to 2.0 Pa. As was determined above, the electron concentration increases with the argon pressure. Therefore, a reduction of the Q-factor is explained by a growth of the specific film resistance because of a reduction in the mobility of charge carriers. The latter is caused by a growth of the scattering at grain boundaries, which is a consequence of the smaller grain size (Fig. 3).

4. Conclusions

The influence of the argon pressure on the structure and the optical and electrical properties of ZnO:Al films deposited level-by-level, by using the method of high-frequency magnetron sputtering has been studied. The film growth rate was found to become half as large, when the pressure increases from 0.5 to 2 Pa. We associate this decrease in the film growth rate with the more intensive scattering of sputtered zinc and aluminum atoms at argon ions in the region between the target and the substrate, as well as with the film re-evaporation owing to its more intense bombardment by argon atoms. The high intensity of the film surface bombardment by argon atoms increases the number of nucleation centers, which gives rise to a decrease in the average lateral dimensions of grains in ZnO:Al films. The transparency of ZnO:Al films deposited at a low argon pressure of 0.5–0.7 Pa was maximum owing to the lower light absorption by free charge carriers. The conductivity of ZnO:Al films was found to decrease, as the argon pressure at the deposition grows, which occurs because of an increase of the charge carrier scattering at grain boundaries. Hence, the regimes with low argon pressures of 0.5–0.7 Pa are optimal for the level-by-level deposition of transparent electrodes with a high Q-factor using the magnetron sputtering method.

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Received 05.09.15.
Translated from Ukrainian by O.I. Voitenko

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ВПЛИВ ТИСКУ АРГОНУ В КАМЕРІ ОСАДЖЕННЯ НА ВЛАСТИВОСТІ ЛЕГОВАНИХ АЛЮМІНІЄМ ПЛІВОК ZnO, ВИРОЩЕНИХ МЕТОДОМ ПОШАРОВОГО ОСАДЖЕННЯ ПРИ МАГНЕТРОННОМУ РОЗПИЛЕННІ

Резюме

Плівки ZnO:Al були осаджені на кремнієві та скляні підкладки методом пошарового осадження в високочастотному магнетронному розпиленні при зміні тиску аргону в камері осадження від 0,5 до 2 Па. Досліджено вплив тиску аргону в камері осадження на структуру, оптичні та електричні властивості плівок ZnO:Al. Встановлено, що збільшення тиску аргону призводить до зниження рухливості електронів у прозорих провідних плівках ZnO:Al та погіршення їх провідних властивостей за рахунок розсіяння на границях зерен. Показано, що збільшення поглинання вільними носіями зі збільшенням тиску аргону призводить до зниження прозорості плівок ZnO:Al у видимій області спектра випромінювання.