Transparent and Conducting ZnO:Al and ZnO:Ga Films Prepared by Magnetron Sputtering

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Abstract – Influence of magnetron sputtering regimes on characteristics of Al-doped and Ga-doped zinc oxide films was investigated. It is shown that the use of pulsed bipolar supply of magnetron leads to improvement of spatial uniformity of the coating properties. The use of an unbalanced magnetron sputtering system allows reducing the resistivity of the films deposited at low substrate temperature.

1. Introduction

Transparent conductive oxides (TCO) are widely used in the manufacture of flat panel displays, transparent electrodes and heating elements. Thin TCO films are also used as antistatic, antireflection and barrier coatings. Due to their transparency in the visible region and high reflectance in the infrared region, they can be used as low-emission coatings on architectural glass [1]. At present a multilayer system of transparent oxides and thin layers of silver are most often used as such coatings. Replacement of the above multilayer coatings with single-layer TCO films seems promising from the point of view of economy and technology.

Recently, tin and zinc oxides, whose electrophysical properties are improved by doping with various chemical elements, have been considered as an alternative to the expensive indium and tin-based oxide (ITO) coatings. Aluminium-doped zinc oxide (ZnO:Al or ZAO) and gallium-doped zinc oxide (ZnO:Ga or GZO) posses a lower resistivity and better optical properties than fluorine-doped tin oxide [2].

Magnetron sputtering is a promising technique of depositing TCOs on large-area substrates, which allows one to control change of the deposition conditions that determine electrophysical and structural characteristics of the coatings. It is a task of current interest to produce coatings with a high conductivity at low substrate temperatures and without subsequent annealing, for instance, in the manufacture of multilayer solar cells [3], since at a low temperature the processes of mutual diffusion of the layers decreasing the efficiency of the cell operation slow down. When ZAO or GZO are deposited on architectural glass, the substrate low temperature allows one to considerably simplify the technology.

The purpose of the present work was to obtain transparent and conductive films possessing a high reflectance in the infrared range, which can be produced at a low (up to 110 °C) substrate temperature. The ZAO films were deposited by means of reactive magnetron sputtering of a target from Zn alloy with a dopant concentration of 2 wt. % Al. The GZO films were prepared using a Ga_2O_3 doped ZnO ceramic target.

2. Experiment

Deposition of the ZAO films was conducted on a vacuum set up equipped with magnetron system. It has the cathode 85 mm in diameter and 400 mm long. The magnetron operated either from a DC power supply capable of functioning in the modes of stabilization of power, current and voltage or a pulse-DC power supply operating at a frequency of 25 kHz. Both power supplies have an arc-suppressing system ensuring a release of energy in the arc no more than 50 mJ.

The GZO films were produced by means of magnetron system equipped with the electromagnetic coil for creation of an unbalanced configuration of a magnetic field above the cathode surface. In this case was used flat highly conductive Ga_2O_3 doped (3.5%) ZnO ceramic target 95 mm in diameter.

The glass substrates were heated with a nichrome heater. The substrate temperature was controlled by a chromel-alumel thermocouple with an accuracy of ± 5 °C. The substrates were set parallel to the target surface at a distance of 50 or 100 mm. The substrate temperature was 90–110 °C. The part of samples has been prepared at the room temperature. The vacuum chamber 600×600×600 mm was evacuated with a turbomolecular pump up to a residual pressure of $8 \cdot 10^{-3}$ Pa. The flow of argon and oxygen was sustained by the mass flow rate controllers.

The operating pressure was 0.25–0.3 Pa. The optical properties of the obtained coatings were investigated in the visible region using a USB 2000-VIS-NIR spectrometer and in the infrared region with a spectrophotometer. The film thickness was measured with a microinterferometer. Measurements of charge carrier mobility and concentration were made using the van der Pauw method in a magnetic field of 0.61 T at room temperature. The sample dimension was 17×17 mm. The film surface morphology and the root-mean-square (RMS) value of the sample roughness were determined by means of the atomic-force microscope Solver P47.

The microstructure of the obtained films was studied with a Shimadzy XRD 6000 X-ray diffractometer using CuK_α radiation.

3. Results and discussion

In the case of reactive sputtering of metallic targets, the deposition rate, films stoichiomery and electrophisical properties are strongly depend on the oxygen content in the sputtering chamber.

Figure 1 shows the dependence of the concentration N and the Hall mobility of the carriers μ on the oxygen flow during the production of ZAO films under three sputtering regimes when a DC power supply is used. In the first regime, the discharge power was constant while the discharge voltage varied from 450 to 475 V when the oxygen flow changed. In the second and third regimes, the discharge voltage was kept constant while its power depended on the oxygen flow and varied within the range of 0.55 and 1.6–3.1 kW, respectively. All the regimes were characterized by a narrow range of oxygen flow (5–10 sccm), at which the highest values of N and μ and, correspondingly, the lowest values of the resistivity ρ are achieved. For the first regime of film deposition the minimum resistivity value was $\rho = 6 \cdot 10^{-4}\ \Omega \cdot$ cm. The least value of $\rho = 4.4 \cdot 10^{-4}\ \Omega \cdot$ cm was characteristic of the ZAO films produced under the second regime at a discharge voltage of 360 V and the target-substrate distance $L = 5$ cm. The film growth rate, in this case, was 110 nm/min, the transparency of 1-μm-thick films in the visible region was as high as 75% and the reflectance in the infrared region was 83–85%. The above parameters were achieved in the central spot of the substrate at the axis of symmetry.

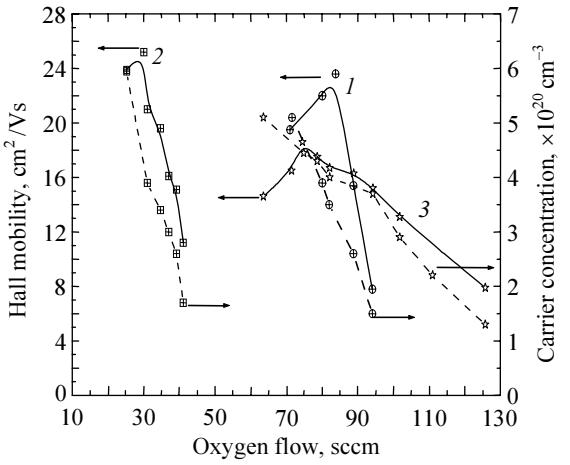

Fig. 1. Dependence of carrier concentration and Hall mobility of ZAO films on oxygen flow for 3 regimes: *1* – Ar flow of 109 sccm, DC power of 1.9 kW, target-substrate distance of 10 cm; *2* – Ar flow of 130 ccm, discharge voltage of 360 V, target-substrate distance 5 cm; *3* – Ar flow of 153 sccm, discharge voltage of 460 V, target-substrate distance of 10 m

The electrical properties of the ZAO films were significantly influenced by the position of the samples with respect to the target. In the region close to the erosion zone of the target, the values of N and μ decrease. The reason is an increased bombardment of the substrate regions located opposite the sputtering zone of the target with energetic oxygen atoms and negative oxygen ions. An excess quantity of the oxygen atoms and ions results in increasing the film resistivity [4, 5].

We investigated the possibility of improving the properties of the deposited film using the bipolar pulse-DC power supply [6]. Figure 2 shows the data on the resistivity distribution and reflectance in the infrared region ($\lambda = 9.8$ μm) of a coating obtained by magnetron sputtering using the pulse bipolar power supply.

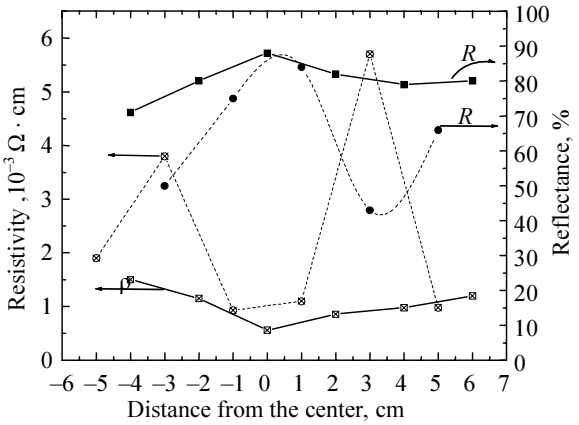

Fig. 2. Resistivity ρ and IR-reflectance R of ZAO films as a function of location on the substrate. The films are deposited by bipolar DC-pulsed mode (solid lines) and DC-mode (dotted line)

For comparison, we show similar characteristics of the films obtained using a DC power supply. As one can see, the resistivity and reflectance in the peripheral regions of the substrate are nearly the same in both cases, but in the films produced using the bipolar power supply, the uniformity of the coating property distribution is considerably higher.

The electrophysical characteristics of the coating are determined by its structure and morphology. Thus, the Hall mobility value depends on the grain size, the surface roughness, the microstress values and the presence of defects in the film. We have made the X-ray diffraction analysis of the ZAO films sputtered in two regimes of the magnetron power supply. The investigation showed the reflexes corresponding to the zincite structure in all the XRD patterns.

Estimation of the average grain size d in the ZAO film according to the Scherrer formula [7] showed that, practically, it does not depend on the mode of the magnetron power supply. The maximum values $d \sim 80$ nm were obtained on the coatings produced at the magnetron axis. At the substrate edges the grain size reduced to 10–40 nm.

The lattice parameter C for all samples was larger that the ASTM value of 5.2 Å bulk ZnO. On the basis of the derived C values we calculated the stresses in the ZAO films. The calculation was based on the biaxial strain model [7].

The strain $\varepsilon = [(C_{film} - C_{bulk})/C_{bulk}]$ in the direction of the c-axis was measured by the XRD. In order to

calculate the tensile stress along the *c*-axes σ_{film}, we used the relationship $\sigma_{film} = -233\varepsilon$ GPa [8].

The stress level in the ZAO films obtained using bipolar voltage was considerably lower than that in the central spot of the substrate and was 0.7 GPa. For constant voltage, this value was 2.03 GPa and in the projection region of the erosion zone onto the substrate it increased up to 3.58 GPa.

In the case of the bipolar pulse-DC power supply, the film structure becomes more uniform. The AFM images of the films in different parts of the substrate also supported the fact.

Improvement of the coating uniformity and structure in the case of the bipolar magnetron power supply is probably related to the energy effect on the growing film. Modulation of the operating voltage causes change in the magnetron discharge plasma parameters. It was noted in [9], that the bipolar-pulsed power supply increases the plasma concentration and the electron temperature in the substrate region.

The GZO films were deposited at the 130–150 W of the magnetron discharge power. Magnetron voltage was within 330–380 V depending on the electromagnetic coil current.

Use of the external coil allowed changing a magnetic field configuration of magnetron and a degree of the energy effect on the growing film.

At increase of a current in the electromagnetic coil considerable increase of the ion current density on a substrate, the most expressed on an axis of system is observed. The reason is the increasing of unbalance magnetic field degree, which limits cross section mobility electrons and force them to move on an axis of system.

Electrons move together with ions because of necessity of maintenance of a plasma electroneutrality.

As well as in case of the ZAO films deposition, the electrical properties of the GZO films were significantly influenced by the position of the samples with respect to the target.

The least value of $\rho = 4.6 \div 8.2 \cdot 10^{-4}\ \Omega \cdot$ cm was achieved on 6 cm distance from an axis of a magnetron target. This position located beyond the erosion zone of the target.

The substrate temperature is the major factor determining properties of the GZO films prepared by magnetron sputtering with ceramic target.

Figure 3 shows the resistivity of GZO films as a function of substrate temperatures. Target-substrate distance is 6 cm. The electromagnetic coil current $I_c = 0$ A.

Later on, the GZO films were deposited at substrate temperature $T = 90$ °C. Such temperature has been chosen to estimate the possibility of using the polymeric substrates.

Also the dependences of the GZO films resistivity on value of a magnetron coil current I_c have been received. These dependences for two substrate temperatures are shown in Fig. 4.

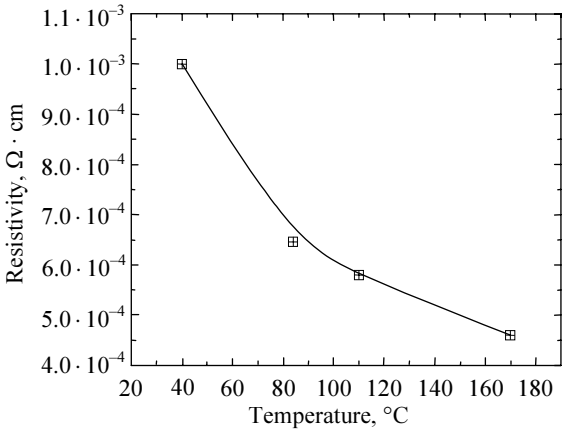

Fig. 3. Resistivity of GZO films as function of substrate temperature

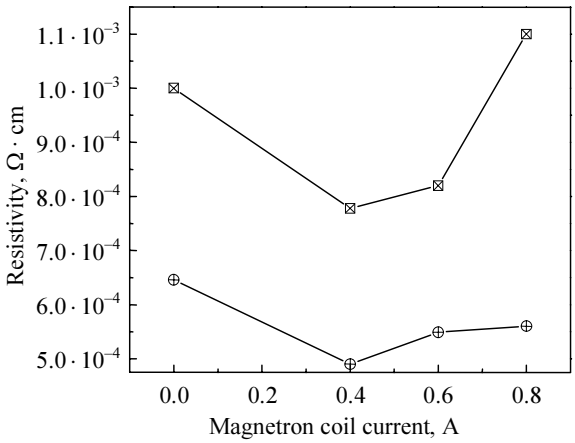

Fig. 4. Resistivity of the GZO films as function of the magnetron coil current. The films are deposited at room temperature (squares) and 90 °C (circles)

One can see that there is an optimum configuration of the magnetron magnetic field at which the least film resistivity was achieved. It corresponds to $I_c = 0.4$ A in the electromagnetic coil. This effect was more pronounced in case of the room temperature substrates.

Figure 5 shows the optical transmittance in the visible region versus the wavelength for the ZAO and GZO films. The absorption edge of the GZO films and ZAO films deposited by bipolar pulse DC shifts to the shorter wavelength region due to an increase of the charge carrier concentration in the film [10]. The use of the pulse DC power supply resulted in increasing the charge carrier concentration in the film from $2–4 \cdot 10^{20}$ cm^{-3} to $5–8 \cdot 10^{20}$ cm^{-3}.

4. Conclusions

Transparent conductive aluminium-doped and gallium-doped zinc oxide films were obtained by the method of magnetron sputtering on glass substrates heated up to 110 °C.

It is shown that the use of the bipolar pulse magnetron power supply allows one to considerably decrease the negative effect of the bombardment of the substrate with accelerated oxygen atoms and negative ions.

Simultaneously, the uniformity of the coating structure improves and the coating roughness decreases.

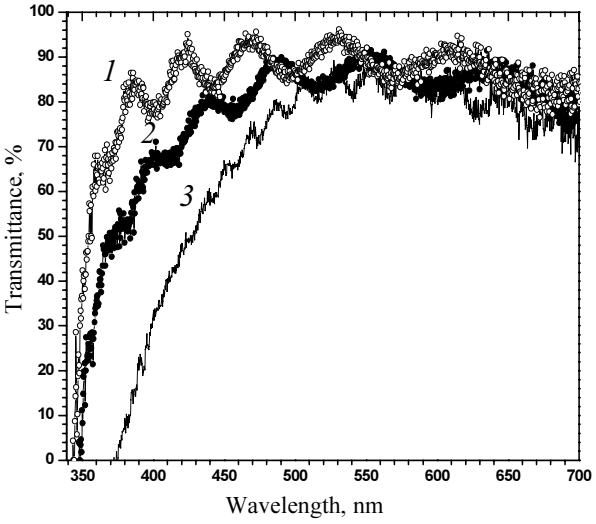

Fig. 5. Optical transmission spectra of ZAO and GZO films: *1* – GZO film; *2* – ZAO film deposited by bipolar DC-pulsed mode; *3* – ZAO film deposited by DC-mode

The use of an unbalanced magnetron sputtering system allows improving the electrophysical properties of the films deposited at low substrate temperatures.

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