Magnetron Sputtering of AL-doped Zinc Oxide: DC and Bipolar DC-Pulsed Modes[1]

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Abstract – Influence of magnetron sputtering regimes on electrophysical properties of Al-doped zinc oxide films was investigated. Oxide deposition was realized using DC and bipolar DC-pulsed sputtering. Zinc oxide films with resistivity ρ=4.4·10⁻⁴ Ω cm were obtained. Distribution of the coating parameters at a substrate as well as the coating morphology and structure for both sputtering modes were obtained. Increase of distribution uniformity of the coating parameters at a fixed substrate using a bipolar mode allows obtaining a qualitative coating in a dynamic deposition mode at large-area substrates

1. Introduction

Transparent conducting oxides have a wide application in producing flat displays, transparent electrodes and heating elements. They are widely used as antistatic, antireflection, and barrier coatings. Transparency in the visible range and high reflection in the infrared range allows their application for low-E glass production [1]. At present, a multilayer system of transparent oxides and a thin silver layer is used as a low-E coating on architectural glass. Replacement of such coating by the one-layer conducting oxide one is desirable both from economical and technological viewpoints. Al-doped zinc oxide (ZAO) can be used for this purpose. One of the promising methods of ZAO-film deposition on the large-area substrates is a magnetron sputtering method. Magnetron sputtering techniques developed by now provide obtaining low-resistivity ZAO films at the substrate temperatures exceeding 200 °C. High substrate temperatures are necessary to improve distribution uniformity of the coating parameters on a substrate. The nonuniform distribution of electrophysical coating parameters on a substrate is the result of the bombardment of the substrate regions situated opposite the target erosion zone by energetic atoms and negative oxygen ions [2, 3].

The aim of the work was obtaining transparent conducting Al-doped zinc oxide films with high reflection in the infra-red (IR) range at a low substrate temperature. Influence of the film deposition regimes on their electrophysical and structural properties as well as on the uniformity of the obtained coatings was investigated.

Film deposition was made by the reactive magnetron sputtering method using DC and bipolar DC-pulsed modes.

2. Experimental

The experiments were carried out at a vacuum setup equipped with an unbalanced magnetron system with cylindrical cathode [4]. The target material was Zn:Al alloy (98:2 wt.%). The magnetron was supplied either from a DC power supply capable to work in the modes of power, current, and voltage stabilization or from a bipolar DC-pulsed supply operating at the frequency of 25 kHz. The typical oscillograms of discharge voltage U and current I are shown in fig. 1.

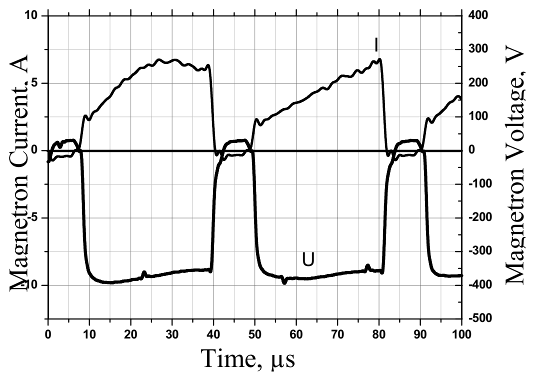

Fig. 1. Plots of the discharge voltage, U, and the current, I, waveforms (bipolar DC-pulsed mode)

The glass substrates of 130×130 mm² were used. Prior to deposition, substrates were ultrasonically cleaned in ethyl alcohol. The ZAO films were deposited at substrate temperature 110±10 °C.

A vacuum chamber of dimensions 600×600×600 mm³ was evacuated by a turbo-molecular pump 01 АБ-1500-004 providing residual pressure of 8×10⁻³ Pa. The argon and oxygen flow rates were maintained by the mass flow controllers РРГ-9. The sputtering gas pressure was in the range 0.25–0.3 Pa.

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Optical properties of ZAO films were determined using the spectrophotometers СФ-46 in the visible range and ИКС-29 in IR range. The thickness of the deposited coatings was measured by a МИИ-4 interferometer. Hall measurements were carried out at room temperature using van der Pauw method in a magnetic field 0.61 T. The film surface morphology and the surface roughness of the sample were determined using the atomic-force microscope Solver P47. The microstructure of the obtained films was studied by means of the X-ray diffractometer Shimadzu XRD 6000 with CuK_{α} source.

3. Results and Discussions

One of the main requirements made to a low-E coating is its high (>80 %) reflection in the infrared range. For this purpose the coating should have low resistivity. The film resistivity is a direct result of the carrier concentration and the Hall mobility of the free carriers in the films.

Fig. 2. presents carrier concentrations N and Hall mobility μ as function oxygen flow for three sputtering regimes using DC power supply.

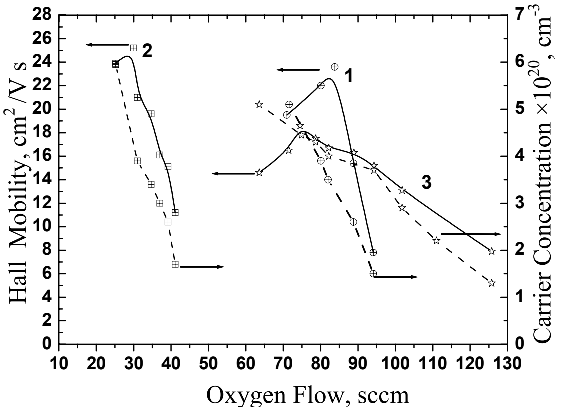

Fig.2. Dependence of carrier concentration and Hall mobility of ZAO films on oxygen flow for 3 regimes: 1 – Ar flow of 109 sccm; DC power of 1,9 kW; target-substrate distance of 10 cm. 2 – Ar flow of 130 sccm; discharge voltage of 360 V; target-substrate distance 5 cm. 3 – Ar flow of 153 sccm; discharge voltage of 460 V; target-substrate distance of 10 cm

In the first regime, the discharge power was constant, the discharge voltage varied in the range 450–475 V at the oxygen flow change. In the second and third regimes, the discharge voltage was maintained constant while the power depended on the oxygen flow and varied in the range 0.55–0.75 kW and 1.6–3.1 kW, respectively. Measurement samples were cut out from the substrate central part situated at the symmetry axis of the magnetron target. All the regimes are characterized by the narrow range of the oxygen flow (5–10 sccm) at which high values of N and м are achieved. Minimum resistivity values were as follows: ρ=6·10^{-4} Ω cm for the first regime and ρ=6.7·10^{-4} Ω cm for the third regime. The minimum resistivity ρ=4.4·10^{-4} Ω cm had the samples of ZAO films obtained in the second regime at the discharge voltage of 360 V and the target-substrate distance L=5 cm. The growth rate of the coating for this regime was about 110 nm/min. The transparency in the visible range of the 1 μm-thick film was of 75 % and the reflection in the infrared range was of 83 – 85 %.

Distribution of film characteristics at a substrate is characterized by essential non-uniformity. One of the tasks of this work was to investigate the distribution of the coating parameters at a substrate and to search ways for improving its uniformity.

Fig. 3 presents measurement results on distribution of parameters of the coating deposited to a fixed substrate. The sample was obtained at the temperature of 110 °C in the second regime at the 5-cm target-substrate distance.

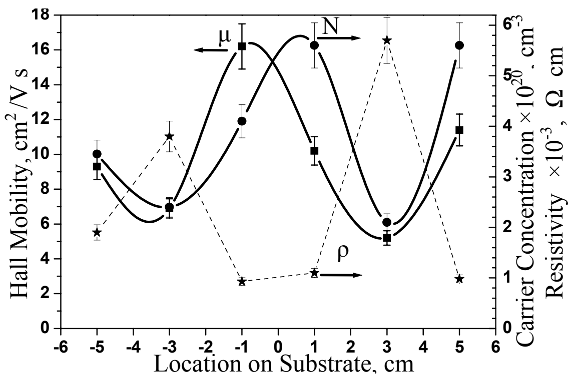

Fig. 3. Resistivity (ρ), Hall mobility (μ), and carrier concentration (N) as function of location on the substrate of a ZAO film (DC- mode)

Maximum values of Hall mobility and carrier concentration are observed in the central part of the substrate. Plasma concentration in this region is maximum in front of the substrate and bombardment by energetic ions and oxygen atoms is practically absent. Values of N and μ decrease in the substrate regions, opposite to the target erosion zones, and increase at the substrate edges. One of the ways to decrease the energetic oxygen flow negative influence is to increase the substrate temperature up to 250–300 °C, though that limits the range of potential application of the films. In Ref. [1] a dual magnetron (Leybold TwinMag®) was used for deposition of ZAO films. The substrate temperature was 200 °C. The authors of the work mention no essential influence of the target erosion zones on the film structure and properties. Structural, electrical, and optical properties of the films deposited in the dynamic mode (V=1 mm/s) were comparable with those of the films obtained in our experiments in the central zone of the fixed substrate.

It is well known that when using a dual magnetron, the sputtering process is characterized by bombardment of a growing film by the low-energy ion flow. The ion current density can exceed in 10 times the ion current values of the magnetron operating at a DC mode [5]. Ion distribution by energies has its maximum in the region of 50 eV [6].

Previously, we have developed bipolar pulsed power supplies for magnetrons. The main destination of such supplies is prevention of arcing at the cathode but using of such power supplies also allows essentially changing characteristics of the deposited coatings [7]. Experiments on ZAO film deposition using a power supply of this type were carried out in the given work.

Fig. 4 presents measurement results of resistivity c and reflection R in the IR (λ=9,8 μm) distributions of the coating obtained by means of the bipolar pulse magnetron sputtering method. Similar characteristics of the films obtained by DC magnetron sputtering are presented in the same figure for comparison. It can be seen that the values of resistivity and reflection in the central and periphery parts of the substrate are approximately the same for both deposition methods but in the films deposited by the bipolar pulse magnetron sputtering method the uniformity of the coating properties is essentially higher.

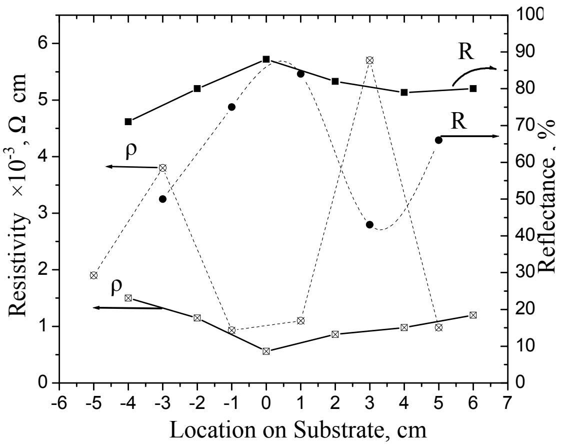

Fig. 4. Resistivity (ρ) and IR-reflectance (R) as function of location on the substrate of a ZAO films. The films are deposited by bipolar DC-pulsed mode (solid lines) and DC-mode (dotted line)

Electrophysical properties of a coating are determined by its structure and morphology. Investigation of the coating samples by the X-ray spectroscopy method was carried out. Reflexes corresponding to the zincite structure were observed in all X-ray pictures. The diffraction angle 2θ was equal to 33.9°–34.27° for all DC samples and to 34.04°–34.36° for all coatings obtained with using bipolar DC-pulsed mode. Deterioration of the crystallinity of the coating in the regions located opposite the target erosion zones was discovered at the samples obtained by DC sputtering. Shift of the reflex position from the angle of 34.42° (ZnO) allows making a conclusion concerning a higher level of internal residual stress in the DC deposited films.The Scherrer formula was used to evaluate the average grain size d in ZAO film [8]. The average grain size was practically independent on the mode of magnetron power supply. Maximum values of d ~80 nm had the coatings obtained at the magnetron axis. The grain size at the substrate edges decreased to 10–40 nm.

The images of the surfaces of the ZAO-film obtained by the atomic-force microscope at different location on the substrate using both DC and bipolar DC-pulsed mode testified to more uniformity coating structure in the second case. The surface roughness of films achieved 25 nm for DC coating samples. The surface roughness of the coating in the pulsed mode is essentially less and makes up about 7 nm. The roughness increase is observed in the substrate location corresponding to the target erosion zones for both cases.

Improvement of the coating uniformity and structure in the bipolar DC-pulsed mode is probably related to energetic influence on the growing film just like in case of a dual magnetron. The operating voltage modulation results in the change of parameters of the magnetron discharge plasma. In Ref. [9] it is noted that the pulsed bipolar mode increases plasma concentration and electron temperature in the substrate region. The flow of energetic particles to the substrate increases. There is well-defined population of ions with the energies of 20–50 eV related to a positive pulse. In such a way conditions for obtaining qualitative conducting ZAO films at the low substrate temperatures are created. It is noted in the review paper [10] that energy of the particles bombarding the film should not exceed 50 eV. Higher energy bombardment results in defects of a crystalline structure and deterioration of the coating quality. One more factor influencing the improvement of the coating quality is that using of mode allows obtaining transparent conducting coatings at lower partial pressures of oxygen. This also results in decrease of the negative oxygen ion flow to the substrate. Presence of a positive pulse can decrease the energy of the oxygen ions bombarding the substrate surface.

4. Conclusions

Transparent conducting films of Al-doped zinc oxide have been prepared by the reactive magnetron sputtering method at the substrate temperatures of 110 Co. It is shown that using of a bipolar DC-pulsed mode allows essentially decreasing the negative influence of bombarding the substrate regions situated opposite the target erosion zones by energetic atoms and negative oxygen ions. Uniformity of the coating structure is improved and its roughness is decreased. Low substrate temperature during the coating deposition process as well as obtained spectral characteristics make promising application of such coatings as low-emissive ones, including those on transparent polymer films.

References

[1] R.J. Hong, X. Jiang, B. Szyszka et.al., Journal of Crystal Growth 253, 117 (2003).

[2] K. Tominaga, T. Yuasa, M. Kume and O.Tada, Jpn. J. Appl. Phys. 24, 944 (1985).

[3] T. Minami, T. Miyata, T. Yamamoto, H.Toda, J. Vac. Sci. Technol. A 18, 1584 (2000).

[4] S.P. Bugaev, N.S. Sochugov, K.V. Oskomov et.al. Laser and particle beams 21, 279 (2003).

[5] J. Sczyrbowski, G. Brauer, M. Ruske et.al. Journal of Non-crystalline Solids 218, 262 (1997).

[6] G. Brauer, J. Sczyrbowski, G. Teschner, Journal of Non-crystalline Solids 218, 19 (1997).

[7] I.R. Arslanov, V.G. Podkovyrov, N.S. Sochugov, in Proc. of the 6th Int. Conf. on Modification of Materials with Particle Beams and Plasma Flows, 2002, pp.186–189.

[8] N.H. Kim, H.W. Kim, Materials Letters 58, 938 (2004).

[9] J.W. Bradley, S.K. Karkari and A. Avetushka, Plasma Sources Sci. Technol. 13, 189 (2004).

[10] K. Ellmer, J. Phys. D: Appl. Phys. 33, R17 (2000).