Deposition of AL-doped Zinc Oxide on PET Substrates by Reactive Magnetron Sputtering[1]

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Abstract – Highly transparent conducting Al-doped Zinc oxide films (ZAO) with low resistivity have been prepared on polymer (PET) substrates by DC magnetron sputtering. The ZAO films were obtained with resistivity of $5.8 \cdot 10^{-4}$ Ω cm, carrier concentration more than $2.7 \cdot 10^{20}$ cm^{-3} and Hall mobility of 13 cm^2/V s. The maximal transmittance of the films is 80 % in the wavelength range of the visible spectrum.

1. Introduction

At present time, transparent conducting oxide films at polymeric substrates find application in production of flexible electrooptic devices, organic electroluminescent devices with plastic LCD displays. They are used as well as the transparent films screening electromagnetic radiation [1]. High transparency in the visible range and high reflection in the IR-range of the conducting oxides allows their application for production of low-E coatings [2]. Substitution of a glass substrate by a polymeric one makes possible creation of unbreakable heat reflecting mirrors that can be mounted in a usual window for a heating season. The advantage of such mirrors is their low weight and simplicity of using. Application of roll materials as substrates allows essentially increasing the area of the coating deposited during a technological cycle and cutting down the production cost price.

Recently, much attention is given to transparent conducting tin and zinc oxides. To improve the electric properties of oxide films, their doping with different chemical elements is widely used. Al-doped zinc oxide (ZAO) has relatively low resistivity and high transparency.

The most promising method of obtaining conducting oxides is the magnetron sputtering one. This method allows controlled change of the film deposition conditions that determine in many respects the electrophysical and structural properties of a coating. The advantage of the method is possibility to deposit coatings onto large-area substrates.

The aim of the work was to obtain Al-doped zinc oxide at the PET substrates by the reactive magnetron sputtering method and to investigate their properties.

2. Experimental

The experiments were carried out at a vacuum setup equipped with an unbalanced magnetron system with a cylindrical cathode. The cathode material was Zn:Al alloy (98:2 wt.%). The magnetron supply was realized from a dc source capable of working in the modes of current stabilization or discharge voltage. PET films of the 130×130 mm^2 dimension were fastened at a glass substrate holder. A nichrome heater was placed behind the substrate holder. The substrate temperature during the process of coating deposition was controlled by a chromel-alumel thermocouple with the accuracy of ±5 °C. A vacuum chamber of dimensions 600×600×600 mm^3 was pumped out to the residual pressure of the order of $8 \cdot 10^{-3}$ Pa by means of a turbo-molecular pump 01 АБ-1500-004. Necessary consumption of argon and oxygen was sustained by means of the mass flow controllers РРГ-9. The gases were preliminary mixed and then supplied into the chamber along the sputterable part of the target. The target-to-substrate distance was 6 cm. Other sputtering parameters are shown in Table I.

Table I. Ranges of sputtering parameters

Sputtering parameters	Ranges
DC-power, kW	0,7–0,8
Magnetron voltage, V	385–420
Working pressure, Pa	0,25–0,3
Oxygen flow rate, sccm	24–36
Substrate temperature, °C	70–85
Growth rate, nm/min	65–80

Optical properties of the obtained coatings were investigated in the visible range by means of the spectral interferometer USB 2000 (Ocean Optics Inc, USA). The coating reflection coefficient in the IR-range was measured by means of the spectrophotometer ИКС-29. 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.

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3. Results and Discussion.

The films obtained under optimum conditions were physically stable and had good adherence to the substrates.

Hall effect measurements show that the ZAO films are a degenerately doped n-type semiconductor with resistivities in the range of $5,25\cdot10^{-3}$ Ω cm to $5,8\cdot10^{-4}$ Ω cm, with carrier densities more than $2,7\cdot10^{20}$ cm^{-3} and Hall mobilities between 4.35 and 13 cm^2/V s for the films deposited on PET substrate.

The resistivities of the ZAO films deposited on the PET substrate as a function of oxygen flow are shown in Fig. 1. As the oxygen flow rate increases from 24 sccm to 36 sccm, the resistivities increase from to $5.8\cdot10^{-4}$ Ω cm to $3\cdot10^{-3}$ Ω cm. At the oxygen flow rate reduction to the values less than 22 sccm, the obtained zinc oxide films had low transparency in the visible range.

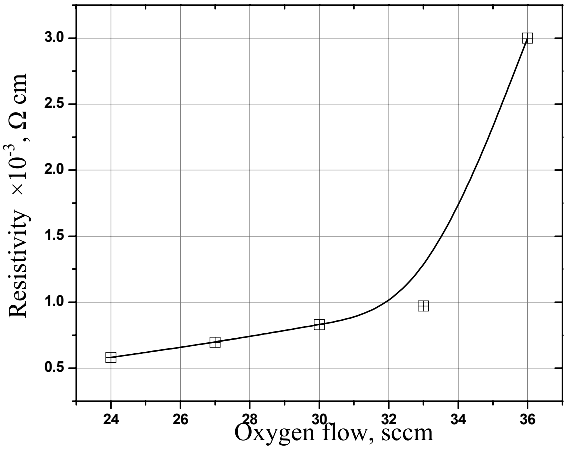

Fig. 1. Resistivity of ZAO films as a function of oxygen flow rate

The Fig.1. presents the resistivity values measured in the central part of the substrate at the magnetron symmetry axis. It is well known that ZAO films always attain the lowest resistivity at their location on the substrate near the center of the target, regardless of the sputtering conditions [3]. High-energy oxygen bombardment of the surface of the growing film is responsible for the nonuniformity spatial distribution of resistivity [4, 5]. The increase in resistivity on the substrate location opposite the erosion area of the target has been attributed to the decrease in crystallinity and to excess oxidation resulting from bombardment by high-energy oxygen. Increase in substrate temperature helps to improve the crystallinity of ZAO films deposited on the substrate location opposite the erosion area of the target, also the reduction of the number of native donors and imperfections, as well as the desorption of the oxygen atoms on the grain boundary, that would improve the spatial distribution of resistivity [6]. Resistivity distribution over the substrate surface becomes practically uniform at the substrate temperatures of 250–300 °C. However, such temperature values essentially exceed the PET film softening temperature (×150 °C). In our experiments, the substrate temperature was not higher than 85 °C, and spatial distribution of resistivity was considerably nonuniform. Hall effect measurements in the substrate location corresponding to the erosion area of the target have shown that the least resistivity value was $1.5\cdot10^{-3}$ Ω cm, Hall mobility value was not higher than 8 cm^2/Vs. Fig. 2 shows the AFM images of the ZAO coating sample obtained at the substrate temperature of 80 °C. Fig. 2, *a*) presents the coating structure in the central part of the substrate. Fig. 2, *b*) presents the substrate location corresponding to the erosion area of the target.

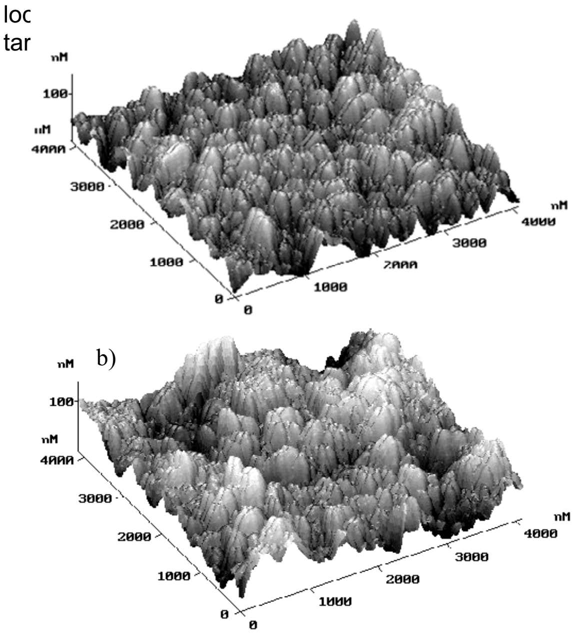

Fig. 2. AFM images for ZAO film sample prepared at Ts=80 °C: a) central part of the substrate; b) substrate location corresponding to the erosion

It can be seen that the films deposited on various substrate locations show different surface roughness. The surface roughness (δ_{RMS}) of a thin film measured in the central part of the substrate makes up 18.16 nm. Influence of the target erosion area reveals itself in the surface roughness increase up to 25.23 nm in the substrate areas located opposite to the erosion area. Decrease in the surface roughness of the films increases the effective thickness of a conducting path in the film and then decreases the electrical resistivity [7].

The coating reflection in the IR-range is related to its resistivity ρ by the ratio [9]:

$$R = 1 - \frac{4\varepsilon_o c\rho}{d}, \qquad (1)$$

where ε_o is the permittivity of a free space, c is the velocity of light, d is the film thickness.

Fig. 3 shows the optical transmittance versus the wavelength for the ZAO film measured for two substrate regions. The ZAO films obtained in the central substrate part have higher transparency in the visible range and higher reflection R in the IR-range (λ=9.8 μm). Optical transmittance and resistivity are two important factors that can characterize the quality of the heat reflecting mirror.

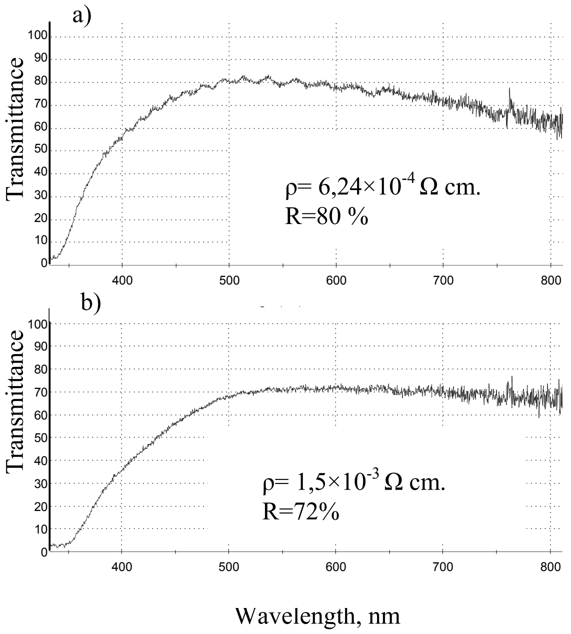

Fig. 3. Optical transmittance versus wavelength for the ZAO film: a) central part of the substrate, *d* –1500 nm; b) substrate location corresponding to the erosion area of the target, *d* – 1200 nm

4. Conclusions

Resulting from the work fulfilled, principal possibility to deposit transparent low-E coatings on PET films was shown. ZAO films obtained at the magnetron symmetry axis have high transparency in the visible range and high (up to 80 %) reflection in the IR-range. However, high transparency in the visible range and high reflection in the IR-range of ZAO films is reached in the central part of a fixed substrate. In order to obtain a qualitative heat reflecting mirror at polymeric roll materials, it is necessary to decrease the bombardment influence of the substrate regions located opposite the target sputtering zone by energetic atoms and negative oxygen ions

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