Optimization of ZnO:Al Film Deposition Process by Reactive Magnetron Sputtering of Zn:Al Target[1]

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Abstract – The paper presents experimental results on film deposition of the zinc oxide doped with aluminum on the preliminary heated glass substrates. Film deposition was made by a reactive magnetron sputtering method. Oxygen flow rate effect on discharge characteristics and film growth rate was investigated. Spectral characteristics of the obtained films in the visible and IR spectra were investigated as well. The coating reflection coefficient in the IR wavelength achieves 86% at a 90% transparency in the visible wavelength. Results of the film surface structure investigations carried out by means of an atomic power microscope are presented. The obtained films are shown to be promising for application as low-E coatings on architectural glasses.

1. Introduction

One of the well-known industrial applications of the thin-film technologies are low-E coatings deposition on architectural glass. Low-E glass has the transparency up to 85% in the visible wavelength (400–700 nm) and emission coefficient no more than 0.2 in the IR wavelength range (5–50 μm). For nontransparent bodies, the emission coefficient ε is related to the reflection coefficient *R* by the ratio $\varepsilon = 1 - R$. At present, world-wide make quantity of this glass considerably exceeds 200 million m^2 per year [1]. It is well known that the weakeast point in the thermal protection of buildings are windows: they occupy about 20% of area of filler structures but about half of the whole heat consumption is lost through the windows [2]. Rapid development of these technologies in west-European countries was stimulated by fuel and energy crises at the end of the seventies of the last century. The housing and communal service reform that is going on now has made this problem actual in Russia as well.

At present, two main types of heat-reflecting glass are produced industrially that are conditionally called as glasses with “soft” and “hard” selective coatings [3]. The “soft” selective coating is deposited on glass by methods of magnetron sputtering in vacuum. The merit of this glass is low emissivity factor (less than 0.1) and its drawback is low film durability. By its composition, the “soft” selective coating presents a layer structure with the general formula: oxide – metal – oxide. A 10–20-nm thick metal (usually silver) film having the property of spectral selectivity is of main importance here and just destruction of this film namely at mechanical forcing, in chemical reactions condition low resistance of the whole coating [4].

The “hard” selective coating is deposited by a pyrolytic method directly in the process of glass manufacturing. The merit of glass with the “hard” coating is high chemical and abrasive resistance and its drawback is more high emission coefficient (0.15–0.2). Moreover, the “hard” coating manufacturing process isn’t an environmentally appropriate technology. The “hard” selective coatings by their composition are conducting metal oxides. In industrial scales, tin oxide doped with fluorine is used more often [5].

The drawbacks inherent to these two methods of low-E coating deposition make actual prolongation of works on creation of alternative technologies. One of possible ways to solve this problem is development of technologies of vacuum ion-plasma deposition of selective coatings on the bases of conducting metal oxides. The main demands made to this type of technology are: high transparency of deposited coatings in the visible wavelength, high reflection coefficient in the IR wavelength, high chemical and abrasive resistance of a coating, ecological cleanliness and low prices for technological process.

This paper investigates the prospects of using zinc oxide film doped with aluminum (ZnO:Al) deposited by the method of reactive sputtering of the Zn:Al target as a low-E coating. The coatings of this composition are considered to be promising for application as transparent current conducting coatings on displays and therefore they are investigated enough actively [6–8].

2. Materials and Experimental Technique

The experiments were carried out at a setup presented chematically in Fig. 1 A vacuum chamber 1 has the dimensions of 600×600×600 mm^3 and is pumped out with a diffusion pump of the type АВДМ-250. The

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setup is equipped with a two-channel gas-filling system based on the gas-flow controller of the RRG-9 type. A substrate holder with a heater connected to a power supply is placed in the chamber. A cylindrical magnetron sputtering system cathode 6 is made in the form of a tube with the external diameter of 90 mm and the length of 400 mm. The cathode material is metal zinc with aluminum content of 2 weight % [6]. Magnetron magnetic system is placed inside the cathode and forms a 350-mm long sputtering zone on its surface. The coatings were deposited to the preliminary heated glass substrates with the dimensions of 100×100 mm^2. The distance from the substrate to the magnetron was of 50 mm.

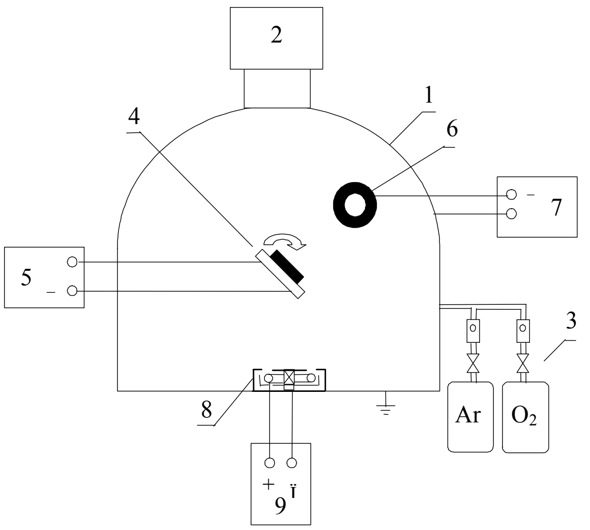


Fig. 1. Experimental setup: 1 – vacuum chamber, 2 – diffusion pump, 3 – gas-filling system, 4 – substrate holder with heater, 5 – heater power supply, 6 – magnetron, 7 – magnetron power supply, 8 – closed electron drift ion source, 9 – ion source power supply

In order to increase the coating adhesion to the substrates, the preliminary surface cleaning by means of the closed electron drift ion source *8* was used. The coating deposition was carried out in the argon-oxygen mixture. The main varying parameters were argon and oxygen flow rate, substrate temperature, coating deposition time.

Optical properties of the obtained coatings were investigated in the visible and IR wavelengths by means of spectrophotometers. Film thickness was measured with the microinterpherometer of the MII-4 type. Structural analysis of the films was carried out with the atomic power microscope Solver P47, their hardness was measured with the nanoindenter NanoTest 100. Surface resistance of the films was measured by a four-probe method.

3. Results and Their Discussion

Figure 2 presents discharge voltage and film growth rate versus oxygen flow rate at the constant argon flow rate. The discharge voltage dependence (curve 1) has the form characteristic of reactive magnetron sputtering process. The left part of the dependence corresponds to the magnetron operation in a “metal” mode characterized by high discharge voltage and oxygen deficit in the growing film that determines its low transparency in the visible wavelength. The right part of the dependence corresponds to the magnetron operation in the “oxide” mode characterized by the rapid discharge voltage drop due to the oxide film formation on the target surface. The central part of the dependence corresponds to the optimum deposition regime at which the transparent and conducting coatings are formed. As it is seen from Fig. 2, the width of this optimum zone is sufficiently large (about 15%) that is important from the technological point of view. For the experimental conditions, the range of the optimum oxygen flow rate made up 52–60 sscm. However, it should be noted that oxygen flow rate increase is accompanied by monotonous decrease of the film growth rate (curve 2) including the one in the field of oxygen flow rate being optimum from the point of view of the coating composition.

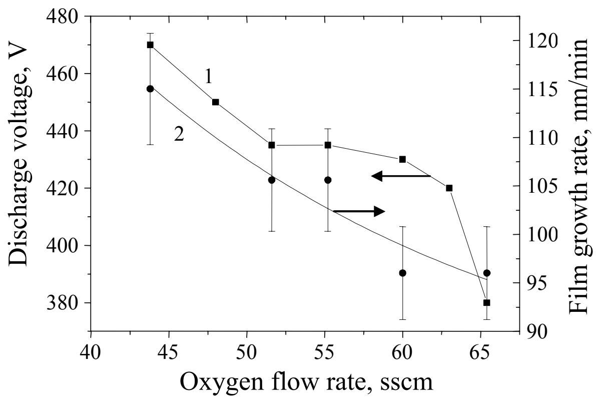


Fig. 2. Discharge voltage (1) and ZnO:Al film growth rate (2) versus oxygen flow rate at argon flow rate f_{Ar}= 100 sscm and substrate temperature of 110 °C

According to Vien displacement law, wavelength λ_m, having maximum radiation energy of the heated body is in inverse proportion to the absolute temperature T:

$$\lambda_m = b / T, \text{ where } b = 2.898\cdot10^{-3}\ \text{m}\cdot\hat{\text{E}}.$$

For the bodies at room temperature, this maximum has the wavelength of 9.8 μm. So, one of the main indexes of the low-E coating quality is a reflection coefficient at this wavelength. Fig. 3 presents the reflection coefficient of the films obtained at different substrate temperatures at the wavelength of 9.8 μm versus oxygen flow rate. The substrate temperature increase on the whole results in the reflection coefficient increase and expansion of the optimum oxygen flow rate zones. But it should be noted that the films obtained at a relatively low temperature (80 °C) have sufficiently high reflection coefficient as well.

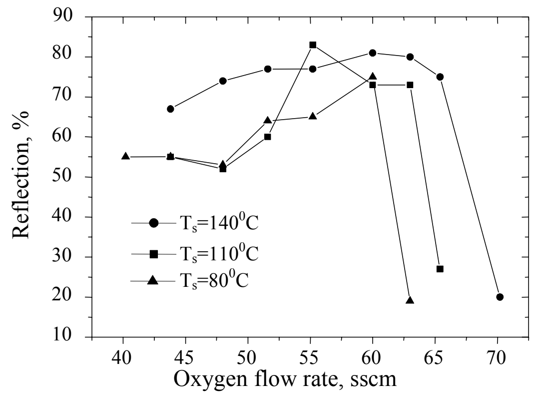
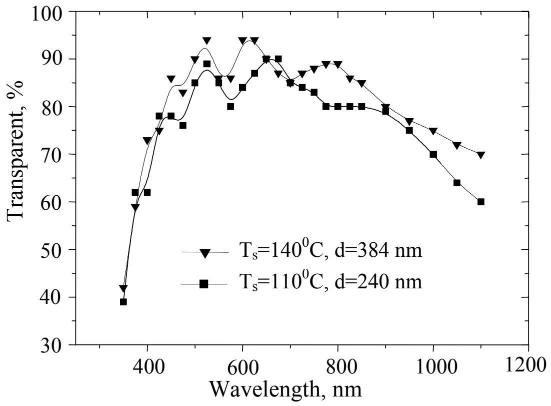


Fig. 3. ZnO:Al film reflection coefficient at the wavelength of 9.8 μm versus oxygen flow rate, at argon flow rate f_{Ar} = 100 cm^3/min



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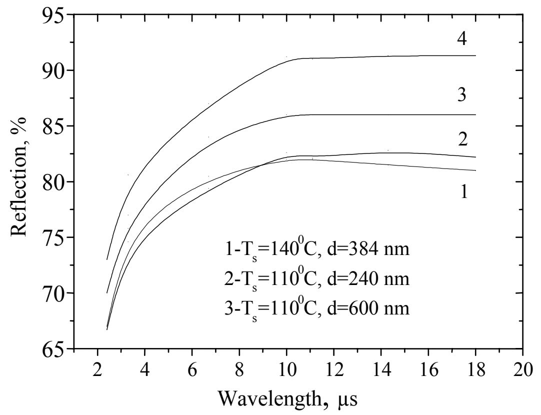

b

Fig. 4. Spectral characteristics of ZnO:Al films at oxygen and argon flow rate f_{O2} = 55.2 sscm and f_{Ar} = 100 sscm, respectively. a – transparency in visible wavelength, b – reflection coefficient of ZnO:Al films in IR wavelength (curves 1, 2 and 3) and silver-based low-E coating (curve 4) [9]

Figures 4, a and b present spectral characteristics of the films obtained at two substrate temperatures in the visible and IR wavelengths. For comparison, Fig. 4, b presents the spectral dependence in cm^3/min of reflection coefficient of the "soft" low-E silver-based coating obtained by technology of Ref. [9]. The substrate temperature rise from 110 to 140 °C at the constant oxygen flow rate (f_{O2} = 55.2 sscm) results in the film transparency increase from 80–85% to 85–90%, the specific surface resistance of the film being increased (from $7.0 \cdot 10^{-4}\,\Omega \cdot$cm to $1.28 \cdot 10^{-3}\,\Omega \cdot$cm). However, a reflection coefficient in the IR wavelength is changed insignificantly. It is seen from Fig. 4b that reflection of the coating with the silver functional layer in the IR wavelength is by 7–10% higher than of the obtaned ZnO:Al films.

The measured hardness of ZnO:Al films made up 900 kg/mm^2 that is comparable with the glass hardness and in complex with good adhesion it gives possibility to say that mechanical strength of ZnO:Al coating is higher than that of the films with the silver functional layer.

Figure 5 presents the pictures of the surface relief and surface friction forces of the coatings depending on the oxygen flow rate at the substrate temperature of 110 °C obtained by means of an atomic force microscope. The oxygen flow rate increase results in the sharp decrease of grain sizes beginning from 55.2 sscm, and at the flow rate of 65.4 sscm the coating structure becomes practically amorphous.

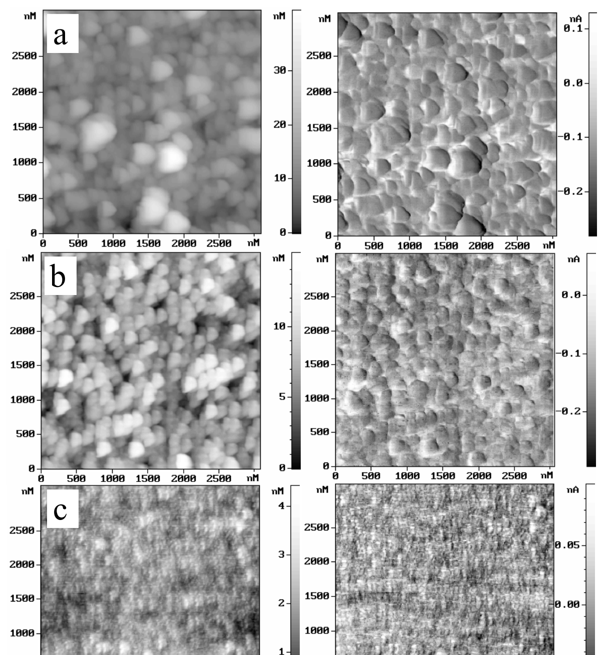

Fig. 5. Influence of oxygen flow rate on the surface relief (left) and surface friction force (right) at the substrate temperature of 110 °C and argon flow rate f_{Ar} = 100 sscm. a) f_{O2} = 43.8 sscm, b) f_{O2} = 55.2 sscm, c) f_{O2} = 65.4 sscm

Comparative tests for the coating resistance to the external influence were carried out as well. For this purpose, the samples with ZnO:Al films and silver-based films were placed into a 5% sodium chloride solution [10]. The results have shown that the silver-based coating was destructed completely during

24 hours while characteristics of ZnO:Al film had no changes.

Further experiments were directed to improvement of optical properties of sputtering films as well as to the decrease of dimensions of sputtering samples.

Resulting from the works on optimization of the sputtering conditions that were carried out, the samples have been obtained having the dimensions of 250×250 mm with the reflection coefficient in the IR wavelength of 86% at the transparency in the visible wavelength being higher than 90%. The film thickness was equal to 600 nm.

4. Conclusions

Investigations that were carried out have shown that it is possible to apply films of the zinc oxide doped with aluminum as low-E coatings. ZnO:Al films have good optical properties (transparency in the visible wavelength of 90%, reflection in the IR wavelength of 86%), resistance to mechanical and chemical influence. Minimum specific surface resistance was of $7 \cdot 10^{-4}\ \Omega$ cm.

4. References

[1] G. Bruer, Surface and Coatings Technology **112**, 365–385 (1999).

[2] M.A. Aizen, Rus. Construction Materials **7**, 7–9 (1998).

[3] V.I. Chairev, M.A. Kharchenko, A.V. Spiridonov, *in: Proc. Electrovacuum Technique and Technology*, 1999, pp. 137–142 .

[4] E. Ando, M. Miyazaki, Thin Solid Films **351**, 308–312 (1999).

[5] J.-M. Laurent, A. Smith, D.S. Smith et al., Thin Solid Films **292**, 145–149 (1997).

[6] B. Szyszka, Thin Solid Films **351**, 164–169 (1999).

[7] K. Ellmer, R. Wendt, Surface and Coatings Technology **93**, 21–26 (1997).

[8] O. Kluth, B. Rech, L. Houben et al., Thin Solid Films **351**, 247–253 (1999).

[9] S.P. Bugaev, N.S. Sochugov, Surface and Coatings Technology **131**, 474–480 (2000).

[10] C. Schaefer, G. Bruer, J. Szczyrbowski, Surface and Coatings Technology **93**, 37–45 (1997).