Technological peculiarities of deposition anti-reflective layers in low-e coatings

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Abstract. This article reports on the investigation of technological features magnetron sputtering for deposition anti-reflection layers in low-emission (low-e) coatings. The three-layer TiO_2-Cu-TiO_2 films were deposited by dual and planar magnetron sputtering systems (MS) on glass substrate. Studies of the current-voltage characteristics (CVC) and the hysteresis effect show that deposition of anti-reflection layers is possible in the transition mode with higher rates. For planar magnetron, the stability of electrical discharge parameters is achieved at 60 % O_2 content in mixture. The calculations optical band gap E_g show that anti-reflective films have a rutile or anatase phases that depending on the content O_2 in gas mixture. The optimum deposition conditions of TiO_2 films were determined for all modifications of magnetrons. Anti-reflective layers, which are deposited by balanced dual MS, improve the transparency of low-e coatings (integral T_{VIS} increase in 15%).

1. Introduction

At present, low-e coatings are widely used to reduce heat loss in residential buildings [1]. The simplest structure of such multilayer film composition is dielectric-metal-dielectric having the following properties: a high transmittance T_{VIS} in the visible region (approximately 0.8), and high reflection R_{IR} in the infrared range (0.85-0.9) [2]. The main functional layer is a semi-transparent metal (Cu, Ag). The translucence of low-e coating is achieved by deposition anti-reflection layers. Predominantly, such films are oxides metals (TiO_2, SnO_2, ZnO).

The main problem of heat-reflective coating is in the deposition of high-quality anti-reflective layers on account of variability of process parameters in the reactive process. Magnetron sputtering, preferably used for deposition optical coatings, is associated with the following disadvantages: no stability of electrical discharge parameters, poisoning target, electric breakdowns on target [3]. Therefore, the main purposes of this study are to determine the technological features of the magnetron in case of reactive process and investigate the effect of plasma source to the properties of the low-e films. In this work, we used Cu as a model metal material, anti-reflective layer - TiO_2.

2. Experimental work

The low-e coatings were deposited on glass substrate (75x25x1 mm^3) by an ion-plasma installation «Yashma», which is based on diffusion pump AVP-250. The vacuum chamber was pumped down to a

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base pressure p_0 (10^{-2} Pa). For cleaning surface, substrates were treated by means of an ion source with closed electron drift. TiO_2 films were reactively prepared by dual and planar magnetron sputtering systems in Ar + O_2 mixture at the constant total pressure 0.12 Pa. The deposition of functional layer (Cu film) was occurred by planar magnetron sputtering systems in Ar at the total pressure $8 \cdot 10^{-2}$ Pa. The technical features of magnetrons are shown in table 1.

To provide the uniformity of the film thickness, substrates moved under plasma sources. For this reason, for evaluation a deposition rate we use such technological term as «nm/pass», which means the thickness of the deposited material in one pass under plasma source. Measurements and control of deposition rate ensured by means of a quartz gauge «Micron-5». The investigations of transparency were by a spectrophotometer SF-2000 in the visible region (400-750 nm). The determination of refraction spectra was produced by the ellipsometer Ellipse-1891. The structure of the TiO_2 films was characterized by X-ray diffraction using Shimadzu XRD-7000S in the Bragg-Brentano configuration.

Table 1. The configuration of magnetrons.

magnetron	power supply	impulse form	repetition frequency, kHz	target size, mm^2	magnetic field
planar	unipolar	rectangle	166	100x700	balanced
dual	bipolar	trapezium	66	94x200	balanced, unbalanced

3. Results and discussion

3.1. The deposition Cu layer

It is well known that high quality low-e coatings reflect infrared radiation (R_{IR}) and transmit in the visible light region (T_{VIS}). Therefore, the thickness of functional layer determined based on the comparison of the R_{IR} and T_{VIS}. According to [1], the formation of a continuous Cu film takes place at least a 9 nm thickness. For deposition Cu layer, work mode of planar magnetron (U=360 V, I=3 A, W=1.1 kW, v_{Cu}=9 nm/pass) was used.

3.2. Peculiarities of deposition TiO_2 films

Magnetron sputtering in a reactive atmosphere is difficult due to a problem of «disappearing anode», a hysteresis of discharge parameters, a drop in the deposition rate. It leads to change of structure films and their optical characteristics. Thence, deposition mode of TiO_2 films determined by the stability of discharge parameters and maximum deposition rate (v_{TiO2}) throughout the reactive process.

The current-voltage characteristics (figure 1) and hysteresis of the electrical discharge parameters were studied (figure 2). For reactive deposition of TiO_2 films, S-shaped current-voltage characteristic is a typical. In the experiment, CVC is essentially linear for three modifications of magnetrons. Moreover, a region of negative dynamic resistance of the discharge (negative slope of the curve) is missing. Such peculiarities were associated with the maintenance of a constant total pressure by gradually reducing the Ar flow in proportion to addition the O_2 flow. This leads to what is we forcedly oxidizes target by reducing intensity of Ar^+ bombardment.

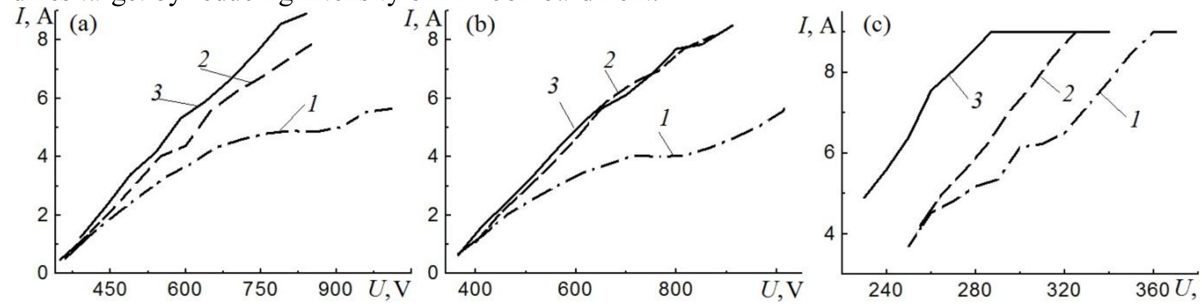

Figure 1. CVC of the discharge: a - balanced dual MS, b - unbalanced dual MS, c - planar MS, 1 - 5% O_2 in a mixture, 2 - 20% O_2 in a mixture, 3 - 60% O_2 in a mixture.

The differences in current and voltage values of CVC for various O_2 content in mixture determined by the degree of target oxidation [4]. For unbalanced dual magnetron, the proximity of the electrical discharge parameters is due to increasing ion current on target. This behavior of the discharge leads to expand of transient region mode. It is presented in more detail in [5]. For planar magnetron, the strong dependence CVC on the O_2 content is specified by a small area of transition mode.

In the experiment, it was found that hysteresis of discharge parameters is completely absent for deposition TiO_2 films by means of the balanced dual magnetron, for other types – hysteresis loop areas are more. It is important to note that the peculiar sharp changes of voltage for planar magnetron aren't observed. This allows for the deposition of stoichiometric TiO_2 films in the transition region of the discharge.

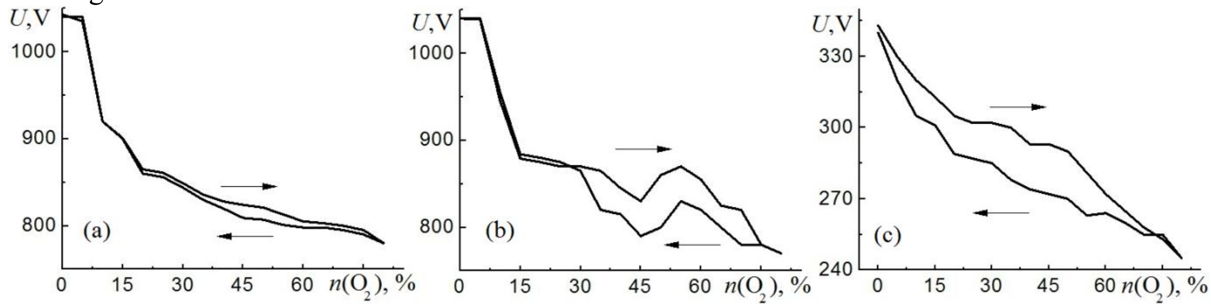

Figure 2. Hysteresis of the operating discharge parameters: a - balanced dual MS, b - unbalanced dual MS, c - planar MS. Arrows indicate the direction of changes in the inlet gas stream O_2.

3.3. Optimal deposition modes TiO_2 layers

For extended periods, attempts to stabilize the operation parameters of planar magnetron in transition mode failed. Magnetron inevitably changed over to sputter fully oxidized target that doesn't occur in the case of using dual magnetrons. As a result, the deposition TiO_2 films by planar magnetron is possible in case of high content O_2 in gas mixture (60%). Therefore, optimal modes were determined by the achievement of maximum deposition rate (table 2). For unbalanced dual magnetron the deposition rate is higher owing to increasing ion current on target.

Table 2. The optimal deposition modes TiO_2 layers.

	Balanced dual MS	Unbalanced dual MS	Planar MS
U, V	830	890	340
I, A	7.5	8	9
W, kW	4.4	5	2.8
v_{TiO2}, nm/pass	3.1	3.8	0,7
$v_{TiO2}/(S_{target}\cdot W)$, nm/(pass·W·cm^2)	$3.75\cdot10^{-6}$	$4.04\cdot10^{-6}$	$3.57\cdot10^{-7}$

Significant numerical differences in the discharge parameters for dual and planar magnetrons are due to their geometric dimensions. Furthermore, the discrepancy of measurements of the electrical characteristics of the dual MS is due to the complex shape of the current impulse. Thence, calculations of deposition rate on power density show that dual magnetrons are more profitable.

The thickness of anti-reflection layers TiO_2 films was determined by means of mathematical modeling of three-layer film in the program IMD [6]. The best translucence is reached at 50 nm for the upper and lower layers. This result correlates with [1].

3.4. Characterization of low-e coating

Transmission spectra of low-e coatings TiO_2 (50 nm)-Cu (9nm)-TiO_2 (50 nm) are shown in figure 3. The lowest transmittance (T_{VIS}) in case using planar MS is associated with lower refractive index n of anti-reflective layers in the visible region. For dual MS, the higher values of T_{VIS} are due to changing film microstructure.

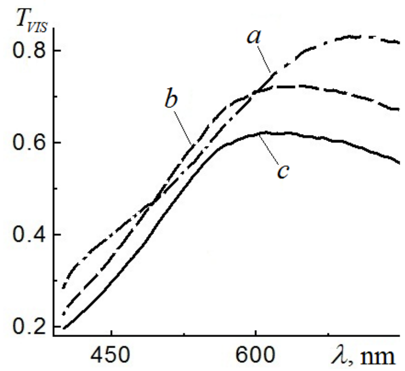

Figure 3. The transmission spectra of low-e coating: a - balanced dual MS, b - unbalanced dual MS, c - planar MS.

According results of XRD, TiO_2 films are X-ray amorphous. For this reason, the investigation microstructure is based on refractive indexes *n* and optical band gap E_g of TiO_2 films. The E_g calculations were carried out by J. Tauc method, described in [7]. According to table 3, properties of anti-reflective films differ for planar and dual MS due to the selected deposition mode.

It is well known that TiO_2 films, which are reactively prepared at low O_2 content (transition mode), have a rutile phase, for high O_2 content (oxide mode) - an anatase phase. Thus, we assume that anti-reflective films, deposited by dual MS, are more similar to rutile phase, deposited by planar MS - to anatase phase.

Table 3. Characterization TiO_2 films.

	planar MS	dual MS	
		balanced	unbalanced
n at 632.8 nm	1.95	2.22	2.34
E_g, eV	3.52	3.41	3.33

The deposition TiO_2 films with different structure provide a distinction of integral transmittance of low-e coatings. For unbalanced dual MS, the reduction integral T_{VIS} apparently associated with structural changes at the boundary between Cu and upper TiO_2 layers. This aspect requires more detailed study.

4. Conclusions

Main results of our investigation can be summarized as follows:

- the stabilization of electrical discharge parameters of dual MS is possible even in transient mode;
- unbalanced dual MS have a higher width of transient mode;
- dual MS provide higher deposition rates of TiO_2 films concerning planar MS;
- TiO_2 films, which reactively deposited at low O_2 content, have higher *n* and E_g that associated with content of rutile phase;
- anti-reflective layers, which are deposited by balanced dual MS, improve the transparency of low-e coatings: integral T_{VIS} increase in 15%.

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