Journal of Engineering Physics and Thermophysics, Vol. 75, No. 5, 2002

TECHNOLOGY OF SPUTTERING HIGH-REFLECTION COATINGS ON ABS-PLASTIC ARTICLES

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UDC 537.525

A technology of magnetron sputtering of metal high-reflection coatings on ABS-plastics (acrylonitryl-butadienestyrol plastics) [M. Yu. Katsnel'son and G. A. Balaev, Plastics: Handbook *[in Russian], Leningrad (1978)] for the automative industry has been developed. The influence of the working gas pressure in the tube and of the magnetic field induction on the operating parameters of the magnetron and the characteristics of obtained films on ABS-plastic are considered.*

Production of high-quality thin films of metals and their alloys, semiconductors and dielectrics is an urgent problem in upgrading the quality and improving the reliability and longevity of products of machine-building, radioelectronics, and optics. With the advent of magnetron sprayers the possibility of obtaining thin-film coatings has greatly increased [2]. The operation of magnetron systems is based on the use of an abnormal glow discharge in crossed electric and magnetic fields localizing plasma in the cathode region. As a result of multiple collisions of electrons with atoms of the working gas, the degree of ionization of plasma sharply increases and the ion current density increases by two orders of magnitude compared to diode sprayers without magnetic fields. This makes it possible to considerably (by a factor of 50–100) [3] increase the sputtering rate of the target material.

Varying the parameters of the technological process (cathode voltage, working gas pressure, magnetic field induction), one can sputter coatings with a different density, adhesion, and microstructure. This leads to the necessity of investigating the process of magnetron sputtering in obtaining new coatings. The present paper is devoted to the development of a technology of sputtering high-reflection coatings on ABS-plastic substrates for the automotive industry. As materials for sputtering, we chose aluminum and titanium, since they feature a reflection complying with ECE standard No. 46 for rear-view mirrors of automobiles.

We used a vacuum assembly of the UVN 3.279 type, which was modified for solving the formulated problem. As an operating element, two identical planar magnetrons located in the vacuum chamber were used. To increase the evacuation rate of the vacuum system, a two-rotor DVN-50 pump was additionally installed. A system of photometric control making it possible to control the thickness of deposited layers in the process of sputtering coatings was mounted.

The vacuum chamber is made of stainless steel (12Kh18N10T) and is a horizontal cylinder with an internal diameter of 700 mm and a length of 700 mm. The vacuum chamber has two side doors. On one of them two planar magnetrons are fixed and on the other a substrate-rotating mechanism and a viewing window permitting viewing of the sputtering process are located. Due to the presence of two identical magnetrons with identical cathodes, it is possible to sputter coatings at a high rate and sputter complex multilayer coatings in one working cycle when the magnetron cathodes are made of different materials. The cathode of each magnetron is a $495 \times 140 \times 8$ mm Al or Ti plate. The magnetic system of the magnetron consists of permanent magnets, some of which are located along the plate perimeter and others, having opposite directions of magnetic field lines, are located in the center. The magnetic system forms a closed spatial configuration of the magnetic field in the form of an oval. The magnet and the whole of the rear surface of the cathodes are intensively cooled by water. The choice of the cathode materials was determined by the problem of developing a technology of sputtering highly reflecting coatings on ABS-plastic substrates.

The supply voltage was applied to the magnetrons through the ballast resistor $R_b = 9\ \Omega$, which served to ensure stable discharge glow. The second electrode is the housing of the facility.

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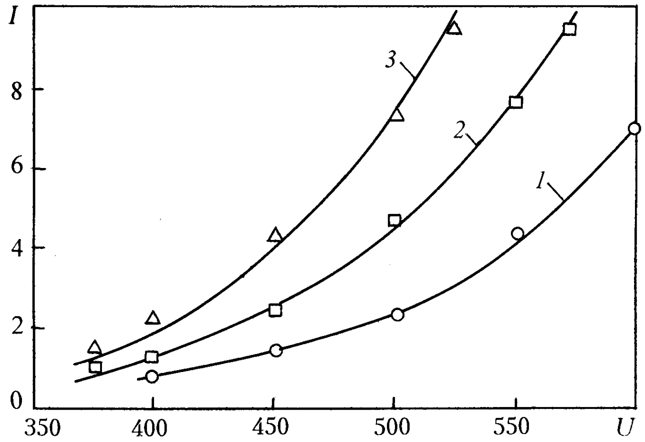

Fig. 1. Volt-ampere characteristics of the magnetron at various pressures of argon p: [1) p = 0.1 Pa, 2) 0.25, 3) 0.3]. I, A; U, V.

The magnetron cathode voltage was measured by an M-24 voltmeter of an accuracy class of 1.5 and the temperature was measured by a KSP-1 instrument with a chromel-copel thermocouple. The discharge current strength was measured by an M-906 ammeter of an accuracy class of 1.5 and the pressure in the vacuum chamber was measured by a VIT-3 vacuum gauge with PMI-2 and PMT-2 manometric converters.

The photometric control system consists of a light source with a stabilized power supply, a modulator (f = 400 Hz), a narrow-band light filter λ_{lf} = 0.55 μm, a silicon photodetector (FD-7K), a resonance amplifier, and a recorder (ShCh-1413). The optical thicknesses of sputtered layers were controlled by the change in the intensity of light reflected from the control sample located in the plane of working articles. As soon as the maximum reflection is attained the sputtering process terminates. The geometric thickness of the sputtered films was determined by an MII-4 Linnik interferometer. The measurement error was ±0.03 μm.

The magnetron spraying system is characterized by the cathode voltage, the discharge current, the current density on the target, the value of the magnetic field induction, and the working gas pressure. The geometry and value of the magnetic field induction are invariable for the given magnetron.

The influence of the working gas pressure in the chamber on the characteristics of obtained films and the operating parameters of the magnetron were investigated under the following conditions: the cathode voltage U was varied between 200 and 600 V, the argon pressure in the chamber was maintained at p = 0.13–1.3 Pa, and the sputtering time t was varied from 120 to 1500 sec.

On the basis of the data obtained volt-ampere characteristics (VAC) were constructed for various pressures p of argon and a constant value of the magnetic field induction B = 0.06 T. As seen from Fig. 1, with decreasing pressure p the VACs are shifted into the region of larger operating voltages. An increase in voltage with decreasing pressure is a characteristic feature of the discharge in the magnetron. Comparison of the curves shows that even a slight change in the pressure produces a strong effect on the discharge voltage, which in turn affects the regimes and rate of target sputtering. The experimental curves are approximated by an equation of the form

$$I = K\,(U - U_{\mathrm{in}})^2 \tag{1}$$

and permit judging the ionization efficiency in the discharge system. As the working gas pressure decreases, the voltage markedly increases. Such a change in the voltage is due to the fact that electrons leave the magnetic trap without noticeable ionization because of the small amount of ions created, on average, by each primary electron before it leaves the system.

The steady-state regime of the existence of a discharge in the magnetron sputtering system is characterized by the following conditions:

$$\omega_{\mathrm{e}} t_{\mathrm{e}} >> 1\,;\quad \omega_{\mathrm{i}} t_{\mathrm{i}} < 1\,;\quad r_{\mathrm{i}} > l > r_{\mathrm{e}}\,;\quad \lambda_{\mathrm{i}} > l\,. \tag{2}$$

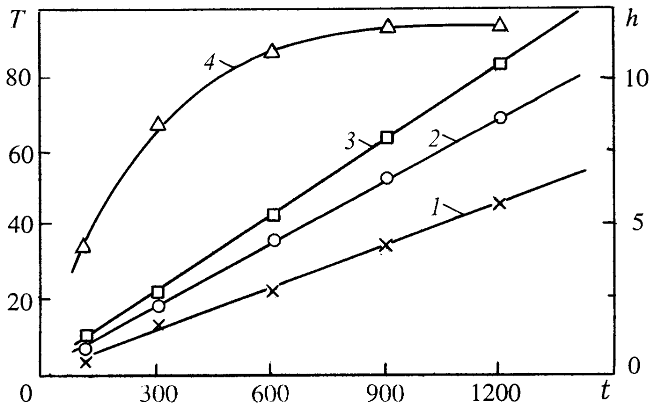

Fig. 2. Coating thickness *h* (lines 1, 2, and 3 correspond to regimes 1, 2, and 3) and substrate temperatures *T* (curve 4) as a function of the sputtering time *t*. *T*, ^{o}C; *h*, μm; *t*, sec.

In the magnetron system, the magnetic field increases the mechanical trajectory of electrons in the interelectrode gap; consequently, there is also an increase in the number of collisions with the working gas atoms. It may be assumed that the superposition of the magnetic field is equivalent to the increase in the working gas pressure. The equivalent pressure in the presence of the magnetic field has the form [4]

$$p_{\mathrm{eq}} = p_0\,[1 + (\omega_{\mathrm{e}} t_{\mathrm{e}})^2]^{1/2}\,. \tag{3}$$

The product $\omega_{\mathrm{e}} t_{\mathrm{e}}$ characterizing the degree of magnetization of electrons is called the Hall parameter. From expression (3) it is seen that the influence of the magnetic field is effective at high values of the Hall parameter when the condition $\omega_{\mathrm{e}} t_{\mathrm{e}} >> 1$ is met.

Since

$$\omega_{\mathrm{e}} = eB/m\,, \tag{4}$$

$$t_{\mathrm{e}} = \lambda_0/p_0\,\{2\,(e/m)\,U\}^{1/2}\,, \tag{5}$$

we have

$$\omega_{\mathrm{e}} t_{\mathrm{e}} = \{\lambda_0 B\,(e/m)^{1/2}\}/\{2^{1/2} p_0 U^{1/2}\}\,. \tag{6}$$

Consequently, the equivalent pressure in the presence of the magnetic field can be given by the expression

$$p_{\mathrm{eq}} = p_0\left[1 + \left[\{\lambda_0 B\,(e/m)^{1/2}\}/\{2^{1/2} p_0 U^{1/2}\}\right]^2\right]^{1/2}\,. \tag{7}$$

As a result of the magnetic field superposition, the discharge exists at lower pressures of the working gas *p*.

To investigate the influence of the value of the magnetic field and the distance from the target to the substrate on the rate of sputtering coatings, we chose three regimes of sputtering: 1) $B = 0.03$ T, $l = 0.6$ m; 2) $B = 0.04$ T, $l = 0.6$ m; and 3) $B = 0.064$ T, $l = 0.4$ m.

As is seen from Fig. 2, the obtained dependences of the change in the coating thickness on the sputtering time are linear for all the above regimes of sputtering. With increasing magnetic field induction the sputtering rate increases, which points to an increase in the efficiency of the target sputtering process. The mean sputtering rates in different regimes of sputtering are $v_1 = 4.8$ nm/sec, $v_2 = 7.0$ nm/sec, and $v_3 = 9.0$ nm/sec, respectively. High deposition rates have been obtained due to (a) the simultaneous switch of two identical magnetrons; (b) the large area of the cathode surface being sputtered; (c) the fairly high magnetic field induction B; (d) the presence of erosion of the target surface; and (e) the relatively high pressure of the working gas p = 0.3 Pa.

The results of the investigations point to a strong influence of the discharge parameters on the film deposition rate in magnetron sprayers [5]. The deposition rate is determined by the sputtering rate (v_s), the value of the magnetic field induction, the system geometry, including the distance to the substrate (l), and the operating pressure. Under the assumption of a uniform current distribution of the cathode surface the sputtering rate v_s can be expressed for the planar magnetron in the form [6]

$$v_s \approx q/(\rho t)\ . \tag{8}$$

In sputtering in argon

$$q = (j_+/e)\ \delta t\ (A/N)\ ; \tag{9}$$

then

$$v_s = (j_+/e)\ \delta\ (A/N\rho)\ . \tag{10}$$

The ion current density is related to the thickness of the dark cathode space (DCS) d and the drop of potential U in the DCS by the Langmuir–Child law and to the electron density in the plasma and the temperature — by the Bohm equation [6]

$$j_+ = 8.6{\cdot}10^{-9}\ (40/M)^{1/2}\ (U^{3/2}/d^2) + 1.48{\cdot}10^{-16} n_e\ (40T_e/M)^{1/2}\ . \tag{11}$$

Thus, one of the major technological parameters of the sprayer (film deposition rate) is directly associated with the parameters of the glow discharge in the magnetic field of the magnetron device.

In sputtering coatings, the substrate surface was heated. This was due to the bombardment of the surface by electrons and neutral particles, as well as to the radiation heating. The temperature dependence of substrate heating on time in the first regime of sputtering is shown in Fig. 2 by curve 4. From Fig. 2 it is seen that in the sputtering process the values of the substrate temperature increase, asymptotically tending to the limit determined by the system parameters. The choice of the sputtering regime corresponding to a low deposition rate is explained by the fact that in this case the substrate temperature can be maintained at a level not higher than T = 100^{o}C without additional cooling, which is important in sputtering on substrates from a low-thermostability material, for example, on plastics [7]. Particular consideration in sputtering metal coatings by the magnetron technique on plastic substrates was given to the surface pretreatment for obtaining a good adhesion. Samples treated with glycidol for τ = 60 min feature a good adhesion and insignificant residual stresses in the coating.

An organic-silicon (hexamethyldixyloxane) layer deposited on the substrate improves the adhesion of a metal coating compared to the substrate surface treated with glycidol. This is corroborated by the tests for separating the film by the Scotch tape. The same layer applied over a metal coating protects it from damage. On the basis of the experimental results, we chose the following technology of sputtering high-reflection coatings on ABS-plastic products: preliminarily degreased substrates were placed in a vacuum chamber, in which forevacuum was created. To improve the adhesion, an organic-silicon layer was sputtered for three minutes. Further evacuation of air was carried out until a pressure of p_{res} = 6.6·10^{-3} Pa was attained. The next step was to bleed in argon up to a pressure of p = 0.26 Pa. The substrates were covered with a shutter and a magnetron discharge was initiated. During the first five minutes of discharge glow the oxide film was removed from the target surface. The shutter was removed and a reflecting coating was deposited. The cathode voltage was U = 340 V. The argon pressure in the chamber was maintained at p = 0.26 Pa. The sputtering time was five minutes. A protective organic-silicon layer was sputtered for 15 min on the reflecting layer, which has high mechanical properties and protects the metal layer against damage.

The tests carried out have shown that the obtained samples of coatings belong to the zeroth group of mechanical strength according to the OST3-1901-85 standard and to the first group of moisture resistance. The moisture-resistance tests were carried out under the conditions of 98% humidity and T = +(38–40)^{o}C for 10 days [8].

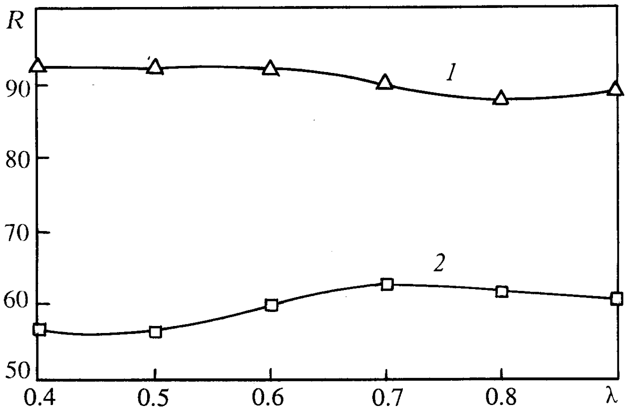

Fig. 3. Spectral dependence of the reflection coefficient R, %, of high-reflection coatings from Al (curve 1) and Ti (curve 2) in the visible region of the spectrum on the wavelength λ, μm. R, %; λ, μm.

By the developed technology, high-reflection metal coatings (Al, Ti) on ABS-plastic substrates have been produced. In particular, mirror coatings on substrates of a complex form have been obtained. The Al coatings deposited by a magnetron sputtering technique have a high reflection coefficient of 92% (Fig. 3, curve 1), which decreases at a wavelength $\lambda = 0.8$ μm down to 87%. Coatings from Ti deposited by the same technique do not have such a high reflection coefficient. The spectral dependence of their reflection coefficient is given in Fig. 3 by curve 2.

The magnetron sputtering technique has been used to apply coatings on ABS-plastic products. The proposed sputtering technique provides a low temperature of the substrate in depositing high-reflection coatings on low-thermostability plastics. Coatings obtained by the proposed technology exhibit a high adhesion due to the introduction of an organic-silicon layer. Their optical characteristics are as good as in coatings obtained by the thermal sputtering technique in a high vacuum. These samples of coatings do not lose their properties under the conditions of severe field operation. Investigations of the influence of the working gas pressure, the magnetic field strength, and the distance from the target to the substrates on the coating deposition rate have been carried out. High deposition rates have been obtained.

NOTATION

R_b, ballast resistance; f, modulator frequency; λ_{lf}, transmission wavelength of a narrow-band light filter; U, cathode voltage; p, pressure in the vacuum chamber; t, sputtering time; B, magnetic field induction of the magnetron; I, discharge current; K, proportionality coefficient; U_{in}, discharge initiation voltage; ω_e, cyclotron frequency of an electron; t_e, time between electron collisions with the working gas atoms; ω_i, cyclotron frequency of an ion; t_i, time between collisions of ions; r_e and r_i, cyclotron radii of the electron and ion, respectively; l, distance from the source of ions to the substrate; λ_i, mean free path of the ion; p_{eq}, equivalent pressure; p, gas pressure without magnetic field; e, electron discharge; m, electron mass; $e/m = 1.76 \cdot 10^{11}$ C/kg, specific electron charge; λ_0, mean free path of the ion without magnetic field; h, coating thickness; T, substrate temperature; v_1, v_2, v_3, mean sputtering rates in different regimes of deposition; v_p, target sputtering rate; q, density of the material sputtered from a unit area of the cathode; ρ, film density, j_+, ion current density on the cathode; δ, sputtering ratio; A, atomic mass of the material being sputtered; N, Avogadro number; d, thickness of the dark cathode space (DCS); M, molecular mass of the ion; n_e, concentration of electrons; T_e, temperature of electrons; τ, time of treatment of samples; p_{res}, residual pressure; λ, electromagnetic wave- length. Subscripts: b, ballast; lf, light filter, in, initiation; e, electron; i, ion; eq, equivalent; s, sputtering; res, residual.

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