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SYNTHESIS OF THIN FILMS WITH CONTROLLED ABSORPTION USING A JET HIGH-FREQUENCY INDUCTION PLASMATRON

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The authors investigate SiO_x *and* TiO_x $(0 < x < 2)$ *thin-film coatings with controlled absorption which are produced using a jet high-frequency plasma under conditions of dynamic vacuum.*

Thin-film coatings came to enjoy wide application in various fields of modern instrument engineering. They are used in radiation detectors, protective insulation coatings, high-ohmic resistors, elements of the microelectronics industry, and interference equipment. The problem of microminiaturization of many optical and electronic devices necessitates the production of thin-film coatings from different materials with prescribed physical properties. The demand for stable films with predictable optical properties of quasicontinuous film structures has stimulated the development of methods for manufacturing films with controlled absorption.

The method of production of thin-film coatings using a jet high-frequency induction plasmatron under conditions of dynamic vacuum makes it possible to combine the process of evaporation of material with the ionization and excitation of atoms and also to form the ordered flux of particles and transport them to the substrate surface. The presence of an extended transport portion enables one to control the physicochemical processes and the composition of the deposited substance.

The aim of this work is to synthesize and implement technically the coatings with controlled absorption using a high-frequency induction plasma under dynamic-vacuum conditions in order to attain a prescribed high-frequency dielectric permittivity in the visible spectrum. This makes it possible to create interference systems with the required spectral characteristics based on two layers. The advantage of the method proposed is shown using nonreflective neutral optical filters as an example.

Procedure and Equipment of Experimental Investigations. Thin-film optical coatings were applied using a plasma unit (Fig. 1), which includes a high-frequency oscillator [1] and a high-frequency induction plasmatron [2], systems of evacuation pumping and supply of the working (process) gas, diagnostic equipment, and a device for displacement of workpieces. The high-frequency inductor plasmatron consists of an induction and a discharge chamber with water cooling and is fixed in the opening of the base plate.

To apply coatings use was made of a plasma jet of a high-frequency induction discharge with variation of the parameters within the following limits: power consumption — from 2 to 10 kW, working pressure — from 50 to 500 Pa, flow rate of the plasma-forming gas — from 0.04 to 0.1 $g \cdot sec^{-1}$, and oscillator frequency 1.76 MHz; Ar was used as the working gas. This corresponds to a change in the internal characteristics of the plasma jet: $n_e = 10^{15}–10^{19}\ m^{-3}$, $P_{disch} = 0.1$ to 4 kW, $j_i = 15–25\ A \cdot m^{-2}$, $W_i = 10–30$ eV, and $Q = 5 \cdot 10^2–5 \cdot 10^3\ W \cdot m^{-2}$.

The optical coatings were applied on substrates of K-8 glass 20 mm in diameter and 2–3 mm thick which were installed in the holder. The vacuum chamber was evacuated to a pressure of 0.1 Pa. A plasma-

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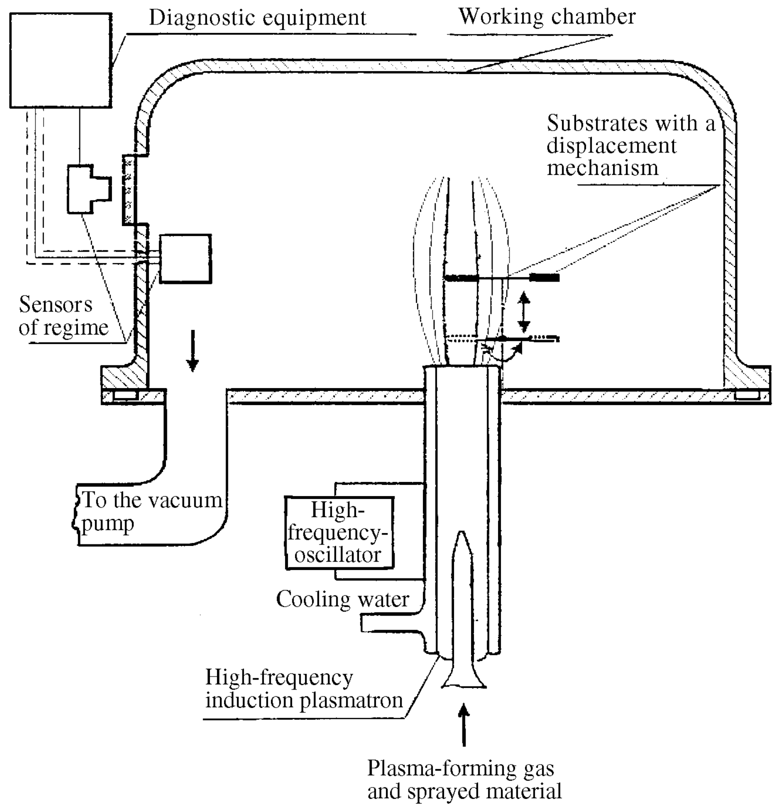

Fig. 1. Block diagram of a high-frequency induction plasma unit for spraying of films.

forming gas was supplied, which, being heated to the plasma state, heated the substrates in the inductor region. The required temperature (623–673 K) was obtained by increasing the power contributed to the discharge; this power was 2.4 kW. The evaporated substances SiO_2 and TiO_2 in the form of a bar 4–6 mm in diameter were axially introduced into the plasmoid. Owing to a low thermal conductivity, high-melting materials heated and evaporated to the maximum on the bar end, which enabled us to perform the process of evaporation for a long time. Plasma heating provided the possibility of transferring the material to a vaporous state. The vapor of the evaporated substance was transported to the substrates by a plasma jet and deposited on them. The composition of the film was varied by changing the distance from the evaporated substance to the substrate. After completion of spraying, the evaporated substance was removed from the plasmoid and the power of the discharge was decreased to its decay.

Results and Discussion. The process of evaporation significantly changes the qualitative composition of the plasma spectra. The investigation results showed that the composition of the vapor phase is variable along the length of the transport portion. The plasma spectra were taken by a spectrograph above the upper coil of the inductor (z = 0.015 m), where the condensation of the vapor on the chamber walls is absent, and in the vacuum volume (z = 0.2 m). The change in the radiation intensity of the plasma component was governed by the concentration of the vapor in the flow, the flow rate of argon, and the power in the discharge. The composition of the oxide films produced also changed as a function of the distance to the vaporization point. An increase of 300 to 650 K in the substrate temperature had a much smaller effect on the composition of the film than a change in the length of the transport portion. At distances less than 0.05–0.07 m, the composition of the film included mainly pure Si and Ti and also lower oxides. The fraction of the oxidized phase increased with distance from the inductor region, and for a distance of z = 0.18–0.25 m the composition of the film corresponded to the composition of the initial material [3]. The existence of a correlation between

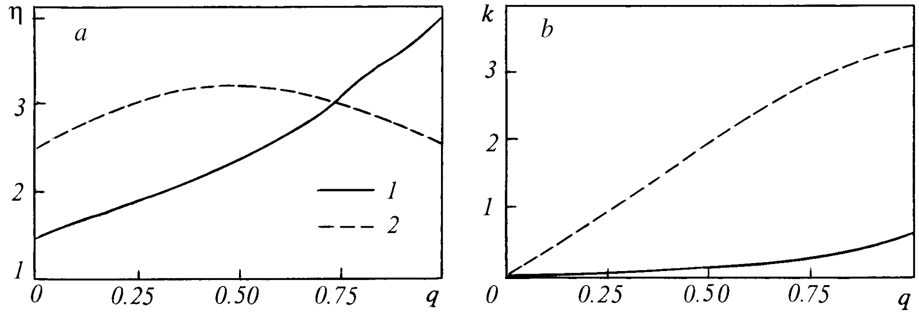

Fig. 2. Dependence of the refractive indices (a) and the absorption coefficients (b) of films on the filling factor (q) (degree of oxidation): 1) SiO_x; 2) TiO_x.

the composition of the vapor phase and the composition of the condensate provides the possibility of controlling the absorption of the coating.

According to the model of a macroscopic mixture (MM) — (random mixture model), SiO_x (TiO_x) films are a mixture of the clusters Si and SiO_2 (Ti and TiO_2) that are immersed in suboxides (unsaturated oxides) consisting of $SiO_\nu Si_{\nu-x}$ ($TiO_\nu Ti_{\nu-x}$), $\nu = 1, 2, 3$ [4]. The configurations $SiOSi_3$ and SiO_3Si (TiO_3Ti and $TiOTi_3$) appear in the macroscopic-mixture model owing to the presence of the transition layer between the clusters Si and SiO_2 (Ti and TiO_2).

The optical properties of the films are characterized by a complex refractive index, dependent on the wavelength λ, $(n/\lambda) = \eta(\lambda) - ik(\lambda)$. The latter is related to the complex dielectric permittivity ε by the following relation:

$$\varepsilon = \varepsilon_1 - i\varepsilon_2 = n^2 , \tag{1}$$

where ε_1 and ε_2 are the real and imaginary parts of the complex dielectric permittivity respectively.

The macroscopic-mixture model enables us to calculate n as a function of the composition of a coating. The degree of oxidation of synthesized films is described by the filling factor $q = 4\pi Na^3/3$, i.e., by the part of the volume which is occupied by the absorbing clusters. Fairly small colloidal particles of a semiconductor (metal) with a permittivity ε impregnated into a dielectric with a permittivity ε_d can be considered as dipoles. The expression for the complex dielectric permittivity of the mixture ε_m is given by the Maxwell–Garnett relation [5]

$$\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon} = q\frac{\varepsilon - \varepsilon_d}{\varepsilon + 2\varepsilon_d} . \tag{2}$$

Relation (2) primarily yields that the dielectric constant of the mixture ε_m depends on the optical characteristics of the substances and on the filling factor q. This provides the possibility of controlling the absorption of SiO_x (TiO_x) films as a function of the degree of oxidation. The optical constants of the SiO_x (TiO_x) layers were calculated within the framework of the Garnett model. The absorbing coating is represented in the form of a volumetric colloid that contains a great number of absorbing islets in the dielectric matrix. Taking into account the dipole moments induced in the absorbing sphere by a periodic electric field and the interaction of neighboring dipoles, we obtain the expressions for the refractive index and the absorption coefficient of the medium that contains N randomly distributed homogeneous absorbing spheres in unit volume; the radius of the spheres is much smaller than the exciting-radiation wavelength. The degree of oxidation of the synthesized films is described by the filling factor q. The numerical solutions of the Garnett equation (2) for the refractive index and the absorption coefficient of SiO_x (TiO_x) at a wavelength of λ =

0.55 μm are presented in Fig. 2. (Here, we used the following optical constants: $\eta = 2.54$ and $k = 3.43$ for Ti; $\eta = 4.02$ and $k = 0.62$ for Si; $\eta = 2.4$ and $k = 0$ for TiO_2; $\eta = 1.45$ and $k = 0$ for SiO_2 [6]).

The spectral characteristics of multilayer interference systems were calculated based on the matrix method [7]. When the composition of the films (i.e., the number of layers and their thicknesses and refractive indices) are prescribed, the spectral characteristics are relatively easy to calculate. The inverse problem (synthesis of films) where the spectral characteristics of the film are prescribed and it is necessary to determine such a composition of it for which it would have these prescribed characteristics is more difficult. Here the exact solution does not necessarily exist, and in the case of an approximate solution it becomes difficult to select its optimum variant. We can say that the solution in general form does not exist. It is usually sought for a concrete particular problem.

To evaluate the proximity of the spectral characteristics of the coating produced to the required characteristics, we introduce the estimating functional [8]

$$F = \int_{\lambda_1}^{\lambda_2} \nu_R (\lambda) \, [R_{\mathrm{m}} (\lambda) - R (\lambda)]^2 \, d\lambda + \int_{\lambda_1}^{\lambda_2} \nu_T (\lambda) \, [T_{\mathrm{m}} (\lambda) - T (\lambda)]^2 \, d\lambda \, , \tag{3}$$

where $[\lambda_1, \lambda_2]$ is the range of wavelengths in which the synthesis is carried out, $R_{\mathrm{m}}(\lambda)$ and $T_{\mathrm{m}}(\lambda)$ are the calculated energy coefficients of reflection and transmission respectively, and $\nu_R(\lambda)$ and $\nu_T(\lambda)$ are weight factors. In this case, $\lambda_1 = 0.4$ μm, $\lambda_2 = 0.7$ μm, $R(\lambda) = 0$, and $T(\lambda) = 0.1$. Weight functions were selected to be equal to unity. This followed from the conditions of the formulated problem where the values of reflection and transmission are equally important throughout the entire prescribed spectrum range. The problem of synthesis is considered in a variational formulation and is reduced to the minimization of the functional by the size of the thicknesses of the layers and by the value of the complex refractive index of the absorbing upper layer. As an initial approximation we seek the solution of $R(d_1, n_2, d_2) = 0.1$ and $T(d_1, n_2, d_2) = 0.1$ at one central spectral point $\lambda = 0.55$ μm and find the required values of the thicknesses d_1 and d_2 of the coatings, which satisfy the prescribed reflection and transmission coefficients at this point for the obtained complex refractive index of the absorbing layer n_2. The composition of the required antireflecting coating is determined from relation (2) in terms of the filling factor q. Then with account taken of the dispersion properties of the coatings the solution is refined by minimizing the estimating functional (3).

In creating nonreflecting neutral optical filters with a transmission coefficient of about 10% in the visible region of the spectrum 0.4–0.7 μm, the traditional synthesis approach, namely, sorting of metal and dielectric layers with subsequent optimization, leads to an interference system made up of nine layers of three different film-forming materials (Ni, SiO_2, and TiO_2). This structure ensures an average value of reflection in the visible region of the spectrum of about 2% [8].

The proposed method of manufacture of coatings using a jet high-frequency induction plasmatron makes it possible to implement the required spectral characteristics based on the two-layer structure Ti–TiO_x. Bringing the absorption in the TiO_x film to $k_2 = 0.2$–0.22 ensures an integral reflection coefficient of less than 1% in the region 0.4–0.7 μm. We implemented such a filter on the basis of the calculations performed.

Thus, the use of a jet high-frequency induction plasmatron of low pressure simplifies the problem of synthesis of interference systems, decreases the number of film-forming materials, and reduces the number of layers to two while ensuring the required spectral characteristics.

NOTATION

P_{disch}, power of the discharge; n_{e}, concentration of the electrons; j_{i}, density of the ionic current arriving at the surface; W_{i}, energy of the ions; Q, heat-flux density; λ, wavelength; $n(\lambda)$, complex refractive index;

$\eta(\lambda)$ and $k(\lambda)$, real (refractive index) and imaginary (absorption coefficient) parts of the complex refractive index; i, imaginary unit; ε, complex dielectric permittivity; ε_d, dielectric permittivity of the dielectric; ε_m, complex dielectric permittivity of the mixture; q, filling factor; N, number of homogeneous metallic spheres of radius a randomly distributed in unit volume; F, estimating functional; d_1 and d_2, geometric thicknesses of the metallic and antireflecting coatings; z, distance from the upper end of the sprayed material; HF, high-frequency (radio-frequency); HFI, high-frequency induction.

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