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Fabrication of nanogradient coatings for laser devices using the method of magnetron sputtering

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Abstract. **Significant advantages of the magnetron sputtering method for producing complex high-quality optical coatings for laser devices are shown. Technology aspects of efficient fabrication of such coatings are considered. The capabilities of the developed automated technological and control equipment are described.**

Keywords: *nanogradient coatings, magnetron deposition, thin film elements, optical coatings.*

1. Introduction

To obtain various thin film elements of electronic, optoelectronic and optical instruments and devices it is necessary to use vacuum setups, including systems of molecular vapour production, vapour condensation upon the substrates, and measurement of the parameters of deposited structures. Such vacuum facilities are equipped with complex electric supply schemes, high-precision mechatronic systems, and the means of optoelectronic control.

The nanogradient composite thin film element is a nanodimensional film composed of different materials, in which one of the physical parameters (dielectric constant, magnetic permeability, modulus of elasticity, etc.) demonstrates gradient variation in one, two, or three dimensions. The thickness d at which the variation of this parameter occurs is smaller than or of the order of 100 nm. This corresponds to the condition $d \ll \lambda$, or, at least, $d < \lambda$ for the wavelengths of UV, visible and near-IR radiation. The absence of multiple boundaries between the layers of different materials leads to the reduction of the radiation scattering and, as a consequence, of the optical losses in the coating [1].

For being used in laser systems, e.g., in ranging instruments, such coatings must meet the following basic requirements: simultaneous operation at several wavelengths, deep modulation of amplitude characteristics, high spectral resolution ($\Delta\lambda \leqslant 20$ Å, the transmission coefficient $T > 0.8$ in the region $0.5\ \mu\text{m} < \lambda_{\text{oper}} < 5\ \mu\text{m}$), small optical losses ($1 - T - R \leqslant 5 \times 10^{-5}$), high resistance to intense ($I > 10^9$ W cm^{-2}) radiation, and non-sensitivity of spectral characteristics to the variation in the coating parameters (temperature-dependent variation of layers thickness, 'aging' of the coating).

The developed technological and controlling equipment, as well as software, make the process of gradient film fabrication fully automated.

2. Magnetron sputtering

During the last decade the magnetron method is actively replacing the traditional methods of laser coating deposition, e.g., the electron-beam evaporation method. The main advantages of the magnetron method are the high rate of the coating growth, the possibility of precise control of the process, the high uniformity of the coating deposition onto large-diameter substrates, very dense structure of the coating with a minor number of defects, good adhesion, high-productivity sputtering of both metal and dielectric targets, as well as the possibility of preparing stoichiometric coatings.

Magnetron systems belong to the sputtering systems of the diode type, in which the sputtering of the material occurs as a result of bombarding the magnetron target surface by ions of the working gas, produced in the anomalous glow discharge plasma (Fig. 1). In these systems the electrons, emitted from the target under the action of the ion bombardment, are captured by the magnetic field and execute complex cycloidal motion along closed trajectories in the vicinity of the target surface. This motion will continue until a few ionising collisions with the working gas atoms occur, after which the electron will lose the energy, received from the electric field. Thus, the major part of the electron energy is consumed by the ioni-

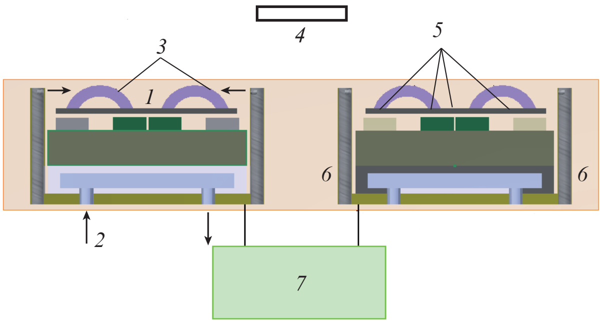

Figure 1. Schematic of a dual magnetron: (*1*) target; (*2*) cooling system; (*3*) plasma discharge; (*4*) substrate; (*5*) magnetic system; (*6*) gas system; (*7*) magnetron power supply.

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sation and excitation processes, which leads to the increase in the concentration of positive ions near the target surface. The magnetic field lines close up between the poles of the magnetic system.

Figure 1 shows the construction diagram of the dual magnetron, which is, in fact, two classical magnetrons having the mutual discharge gap. The simplest magnetron includes the disc target made of the material to be sputtered and the magnetic system. The water cooling, gas supply and magnetron electric supply systems are also provided. The substrate is located parallel to the magnetrons.

3. Technological aspects of magnetron sputtering

The nanocomposite material on the substrate is obtained by simultaneous deposition of two or more components using the pulsed reactive magnetron sputtering of the materials that form the composite. To obtain a nanogradient $1D_z$ composite film one has to provide an axial concentration gradient of the components. In the developed facility the system of several simultaneously acting magnetrons equipped with the optical-electronic control unit is used. The position of the substrate with respect to the magnetrons and the sputtering power of each magnetron determine the nanogradient composition of the thin film. Below we describe the basic technological processes that increase the deposition productivity and the quality of gradient coatings for laser devices.

Ion-plasma substrate cleaning. Preliminary cleaning of the substrate surface from contaminations and oxides plays an important role in coating deposition. Imperfections and soiling of the substrate surface change the conditions of condensation of metal atoms and the mobility of atoms, which affects the resulting film structure.

Among the classical methods of surface cleaning the chemical, galvanic, and ion methods are singled out. From these only the last ones completely satisfy the up-to-date quality requirements. In the ion methods an ion source produces a directed flux of inert gas ions, accelerated to a high energy. They bombard the substrate, causing its sputtering and thus providing its cleaning [3]. In the process of coating deposition the adhesion depends on the film material, the substrate surface purity, the rate of deposition, and the substrate temperature. The ion surface cleaning allows achievement of atomic purity of the surface, which provides an improvement of adhesion between the deposited coating and the substrate, and also activates the surface and promotes the formation of growth centres.

The process of preliminary cleaning of substrates by bombarding with ions of oxygen (or any other working gas) is implemented using a separately installed HF cleaning magnetron.

Ion-plasma cleaning of targets. To stabilise the process of sputtering the technological cycle also includes the stage of preliminary target cleaning from oxide films using the plasma of the intrinsic discharge of the magnetron [4, 5]. In order to prevent the sputtered material deposition on the substrates a special shutter is used.

Ion-plasma assistance. Providing efficient oxidation of the material deposited onto the substrate is one of the most important problems in the production of high-quality dielectric coatings.

The developed device for oxidation of the coating is an autonomous generator of oxygen ions, which is, in fact, a single-magnetron system. The pulsed MF or HF voltage is used for electric supply. The aim of this magnetron is to supply the active oxygen to the substrate both during the operation of the main magnetrons that sputter the material and after it.

The process of ion-plasma assistance allows an improvement of the mechanical properties of the obtained coatings, including the hardness and resistance to abrasion.

Laser assistance. The laser assistance is used to initiate and intensify the physical and chemical processes that facilitate the formation of coatings with high functional characteristics (the required chemical and phase composition, mechanical, thermal climatic, and radiation resistance, etc.).

The laser assistance unit used in the present system consists of the laser projector based on the UV solid-state laser, the radiation from which is directed onto the substrates through the chamber window, and the unit of optical control of the laser spot (video camera) and substrate temperature under the laser action. The projector includes the unit that provides focusing of the radiation onto the substrate and its scanning over the substrate surface.

The laser assistance facilitates the reduction of roughness of metal and dielectric films, produced using the magnetron sputtering.

Substrate heating. Before the film deposition, the substrates are heated using the IR radiation. The experiments have shown that the substrate temperature significantly affects the structure of the deposited film, first, of all, its homogeneity. The substrate heating also promotes the increase in the coating adhesion.

4. Equipment for nanogradient coating deposition

Working chamber and vacuum system. The working chamber contains a complete set of devices, necessary for solving different research and technological problems. The set includes four magnetron sources, the magnetron for plasma cleaning of substrates, the oxygen ion generator, the optical and electronic control *in situ*, the system for measuring the spectral characteristics of the coating and its physical thickness, the sample moving mechanism.

Argon and oxygen are used as working gases and can be supplied independently with the control of partial pressures. The flow of gases is automatically controlled using three-channel gas-flow control devices with stop valves. Decreasing the gas pressure in the chamber during the process facilitates the production of high-purity films. The control of the three-channel high-precision gas supply system is implemented in automatic regime following the technical programme.

When several layers of different materials are deposited in one cycle, the mechanism automatically places the substrate in front of the magnetron with the required material. The height and shift of each magnetron are chosen in a way that provides maximal uniformity of the coating and deposition rate.

Control system. By means of a spectrovisor and a laser thickness gauge the thickness, the refractive index, and the current spectral characteristics of the coating are measured *in situ*. Since the sputtering rate is kept constant during the process, the control of deposition time is also possible. The developed software allows complete control of the basic system parameters, i.e., the operation pressure, the gas consumption, the discharge current, the substrate position, etc., thus providing a fully automated technology that does not require human participation.

Magnetron power supply system. Various versions of the magnetron method are for a long time used in optical technologies, with DC, AC, pulsed MF or HF voltage applied to the magnetrons. The DC supply of magnetrons, when the constant negative potential with respect to the chamber is applied to the target, are now becoming rarely used because of numerous drawbacks, such as arc and microarc generation, the effect of 'electrode disappearance', and the low density of plasma near the substrate in reactive processes. In the case of MF supply used in our system, the pulsed or rectangular AC voltage is applied to the magnetrons with the frequency varying within the limits 20 – 100 kHz.

Two operation modes are possible, the unipolar and the dual one. The unipolar mode suffers from practically the same disadvantages as the DC supply, but to a smaller degree. In the dual mode the surface of the chamber walls does not take part in the discharge, due to which this mode is free of drawbacks mentioned above. As a result, the use of the MF range allows the solution of the 'disappearing anode' problem, and in the dual mode the productivity is increased, since the material sputtering occurs during both half-periods. The magnetron with a HF voltage supply is used for sputtering dielectric targets.

The analysis of the magnetron power supply systems shows that the use of dual magnetrons with MF supply has overwhelming advantages in all parameters of the most importance for the process [2, 6]. The developed supply system allows the variation of the mean discharge current in the plasma, the duty cycle and repetition rate of the pulses, and the stabilisation of the magnetron discharge with respect to current, voltage, or power. This provides the constant rate of material sputtering. The output voltage of the magnetron supply unit is sufficient to ensure discharge initiation in the plasma in the entire range of working pressures and its operation with any type of targets and reactive gases.

5. Experimental results

To produce the nanogradient coating the MF supply was used for magnetrons containing the silicon and tantalum targets. In the coating the low-refractive material is SiO_2, and the high-reflective is Ta_2O_5. The calculated specified dependence of the refractive index n of the nanogradient coating on its thickness d is presented in Fig. 2 [7]. In the process of the material sputtering the initial electric and gas operation modes of the magnetron sputtering system were not changed. Therefore, the required profile of the refractive index was obtained only as a result of implementation of the calculated law of the substrate movement.

Figure 3 presents the theoretical and experimental dependences of the nanogradient coating transmission on the wavelength that practically completely coincide in the region of maximal transmission.

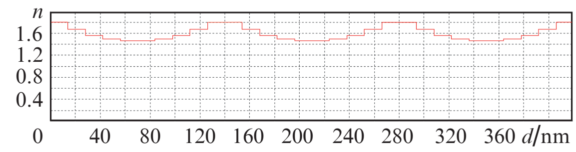

Figure 2. Dependence of the refractive index of nanogradient coating on its thickness.

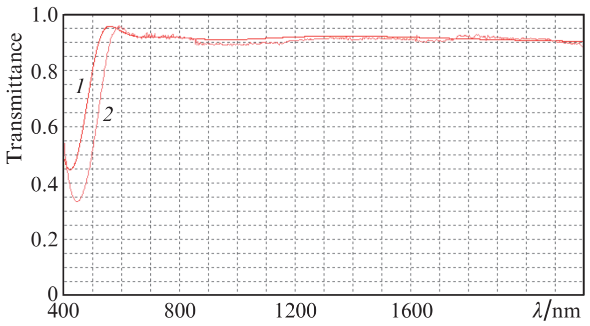

Figure 3. (*1*) Theoretical and (*2*) experimental dependences of the transmittance of the nanogradient coating on the wavelength.

In Fig. 4 the results of the measurement, performed at the National Research Technical University 'Moscow Institute of Steel and Alloys' using the method of X-ray reflectometry are presented that demonstrate the correspondence of the theoretical and experimental profiles. The density profile lies within the thickness range 0 – 140 nm.

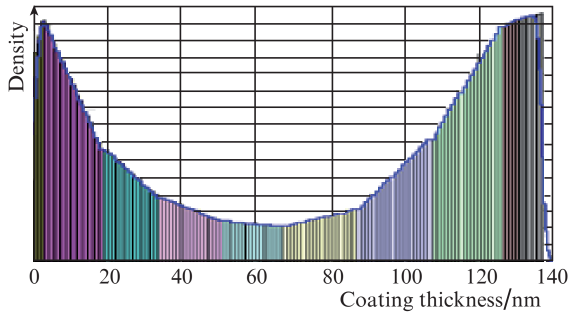

Figure 4. Experimental profile of the nanogradient coating obtained using the method of X-ray reflectometry.

The tests of the obtained coatings demonstrated their high resistance to severe environment conditions, including the temperature, mechanical, thermal climatic and radiation effects.

Thus, the used magnetron sputtering method for producing nanogradient coatings for laser devices possesses significant advantages over the analogous methods of deposition of complex optical coatings. The developed automated magnetron sputtering facility is promising for deposition of unique nanogradient composite coatings. High stability of the process, precise control of the sputtering parameters and the developed software allow production of high-quality coatings.

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