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# Analysis of the surface layer of the platinum film grown by the ion-plasma deposition method on Si (001) and MgO (001) substrates

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Platinum films deposited by a method of ion-plasma (cathode) sputtering at a constant current on a (001) cut of single-crystal silicon and magnesium oxide substrates. The angular dependence of the reflection coefficients of the E and H optical modes of laser radiation with a wavelength of 632.8 nm was measured. It is shown that, within the measurement error, it is not enough to use the formulas for reflection with the optical parameters of platinum, and it is necessary to additionally introduce an effective anisotropic layer related to surface heterogeneity.

**Keywords:** Ion-plasma sputtering, platinum film, relief surface, effective layer.

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Platinum is highly chemically stable, so it is often used as electrodes or sublayers for the subsequent deposition of film structures, and due to its high reflectivity, platinum thin film coatings are used as mirrors. Technological peculiarities of film deposition on the surface lead to the formation of a relief, the characteristic dimensions of which significantly exceed the topological features of the initially smooth surface on which the metal is deposited. The formation of surface relief leads in interaction with light to the appearance of some transient surface layer, the properties of which differ from those of the bulk, which must be taken into account when studying the optical properties of [1–4]. If the coating is used as an electrode bordering a ferroelectric, the surface topography leads to an increase in the intermediate layer (dead layer) that degrades the ferroelectric performance [5]. In the present work, the parameters of the effective surface layer were determined based on the results of measuring the angular dependence of the laser reflectance.

Platinum films with a thickness of 200 nm were deposited on the polished (001) surfaces of $p$--type magnesium oxide and silicon oxide single-crystal substrates (KDB-12) by cathodic (ion-plasma) sputtering at direct current in a residual gas atmosphere. The initial temperature of silicon substrate was 300°C, MgO substrate — 400°C, target distance – substrate 18– 20 mm, $P_{atm} = 0.007$ Torr. The applied voltage from the high voltage source ranged from 7 to 9 kV. The discharge current was set at 70–120 mA. Spraying time 5 min. Analysis of $\theta - 2\theta$ X-ray diffraction patterns showed the presence of $(00l)$ and (111) platinum reflexes, indicating that the film is polycrystalline. Optical measurements of the angular dependence of the reflectance intensity of the films were performed on a [6] bench using a helium-neon laser with a wavelength of 632.8 nm as a source of monochromatic polarized (TE- and TM-modes) probing radiation.

The obtained angular dependences of the reflection intensity are not normalized. To determine the normalized reflectances and refraction index, the measured dependencies were processed as follows. Since the probing laser beam is not a perfect plane-parallel beam, it diverges weakly. This has the effect of weakening the intensity of the beam. In addition, the beam propagates in a weakly scattering medium (air), which in addition to attenuation of intensity leads to the appearance of a weak background. Due to these distortions, which we will call hardware distortions, each angular dependence of the reflectance can be represented in the form

$$exp(\theta) = NR(\theta) + S, \quad (1)$$

where $\theta$ — angle of incidence; $exp(\theta)$ — experimental value of reflected beam intensity for angle $\theta$; $R(\theta)$ — true reflectance; $N$ — scaling factor; $S$ — bias background value. In the absence of losses, the value of $N$ is equal to the inverse of the incident beam intensity. To get rid of the hardware values $N$ and $S$ when processing the experimental curves, the spectra were transformed to the following form:

$$\frac{exp(\theta) - exp(\theta_{shift})}{exp(\theta_{norm}) - exp(\theta_{shift})} = \frac{R(\theta) - R(\theta_{shift})}{R(\theta_{norm}) - R(\theta_{shift})}, \quad (2)$$

where $\theta_{norm}$, $\theta_{shift}$ — the angles of accretion, $\theta_{norm} \neq \theta_{shift}$. The angles $\theta_{norm}$, $\theta_{shift}$ introduced in (2) are not fitting parameters. These are, generally speaking, arbitrary angles taken from a set of experimental data. In (2) there are no hardware parameters from formula (1), the left part contains only experimental values, the right part includes only the reflectance with parameters to be determined.

Determination of the value of the complex refraction index from the angular dependence of the reflection spectra was performed by the least-square method using formula (2). The following were used as the angles of conversion in formula (2): $\theta^{\mathrm{H}}_{shift} = 75°$, $\theta^{\mathrm{H}}_{norm} = 35°$, $\theta^{\mathrm{E}}_{shift} = 20°$,

$\theta^{\mathrm{E}}_{norm} = 75^\circ$ for TM- and TE-waves, respectively (more precise angle values are determined from the experimental data set near these values). After finding the refraction index, the parameters $N$ and $S$ were determined using the least-square method to compare the obtained angular dependence with the experimental data using formula (1).

In processing the measurement results, we found the following problems. First of all, according to literature data, there are two significantly different refraction indices of platinum for the optical wavelength range. For example, in [7] for a wavelength 632.8 nm, the complex refraction index is given as $n + ik = 2.32 + i \cdot 4.16$. According to [8], at the same wavelength, the refraction index is $n + ik = 0.53 + i \cdot 6.12$. When using the formulae for the reflectance from the semi-infinite platinum layer [9] the latter values give a more satisfactory agreement with our experimental data. Therefore, for further calculations, we adopted the values from the paper [8] for the refraction index of platinum: $n = 0.53$, $k = 6.12$. The penetration depth of the electromagnetic wave is determined by the multiplier $\exp(-2\pi kz/\lambda)$. At a wavelength of 632.8 nm at a film thickness of 200 nm and a value of the complex part of the refraction index of $k = 6.12$, we obtain a value of the multiplier $5.27 \cdot 10^{-6}$, i.e., the electromagnetic wave practically does not penetrate to a depth of 200 nm. Therefore, we consider the platinum layer to be semi-infinite.

The processing of experimental values with this refraction index gives a RMS error of about 5%, which exceeds the accuracy of the measurement. Therefore, for better agreement between theory and experiment, we introduced an effective surface layer with a thickness to be determined. Since the surface has natural anisotropy, the effective layer is introduced with refraction index isotropic in the film plane ($n_{2o} = n_o + ik_o$) and different along the normal to the film plane ($n_{2e} = n_e + ik_e$). The approximation of the angular dependence of the reflection curves taking into account the effective surface layer was performed using the formulas for the reflectance $R$ from an anisotropic plane-parallel film lying on a semi-infinite layer:

$$R = rr^*, \quad r = \frac{r_{12} + r_{23}\exp(2i\beta)}{1 + r_{12}r_{23}\exp(2i\beta)},$$

Where for the TE mod $n_2 = n_{2o}$,

$$r_{12} = \frac{n_1\cos(\theta_1) - n_2\cos(\theta_2)}{n_1\cos(\theta_1) + n_2\cos(\theta_2)},$$

$$r_{23} = \frac{n_2\cos(\theta_2) - n_3\cos(\theta_3)}{n_2\cos(\theta_2) + n_3\cos(\theta_3)},$$

for TM mods

$$n_2 = \sqrt{n_{2e}^2 n_{2o}^2 + n_1^2\sin(\theta_1)^2(n_{2e}^2 - n_{2o}^2)}/n_{2e}^2,$$

$$r_{12} = \frac{n_{2o}^2\cos(\theta_1) - n_1 n_2\cos(\theta_2)}{n_{2o}^2\cos(\theta_1) + n_1 n_2\cos(\theta_2)},$$

$$r_{23} = \frac{n_2 n_3\cos(\theta_2) - n_{2o}^2\cos(\theta_3)}{n_2 n_3\cos(\theta_2) + n_{2o}^2\cos(\theta_3)}.$$

Here, everywhere

$$\theta_2 = \arcsin(\sin(\theta_1)n_1/n_2),$$

$$\theta_3 = \arcsin(\sin(\theta_1)n_1/n_3),$$

$$\beta = 2\pi n_2\cos(\theta_2)h/\lambda.$$

For semi-infinite layer of platinum, the refraction index $n_3$ is taken from the work [8], the refraction index of air $n_1 = 1$. In TE-mod (TM -mod), the electric (magnetic) field vector is normal to the plane of incidence. The film parameters were found by minimizing the square of the difference between the left and right parts of expression (2) summed over all experimental points of the angular dependence. Minimized total amount for TE- and TM-mod. The following parameters for the effective layers ($\sigma$ — standard deviation, $h$ — effective thickness of the surface layer) are obtained from the results of the calculations: on MgO substrate ($\sigma_{\mathrm{H}} = 0.001\%$, $\sigma_{\mathrm{E}} = 0.6\%$)

$h = 11$ nm, $n_o = -0.21$, $k_o = 5.26$, $n_e = 1.62$, $k_e = 4.99$, on the substrate Si ($\sigma_{\mathrm{H}} = 0.003\%$, $\sigma_{\mathrm{E}} = 0.6\%$) $h = 27$ nm, $n_o = -0.03$, $k_o = 4.06$, $n_e = -0.002$, $k_e = 4.98$. The results of the calculations are presented in Fig. 1, where symbols show the experimental values. As can be seen from the figure, the reflectances for TE-modes for both samples do not differ within the measurement error (0.1%). However, the difference in reflectances for TM-modes is noticeably beyond the measurement error.

To realistically estimate the thickness of the surface layer, measurements of the surface topography of the obtained samples were made on the INTEGRA atomic force microscope of NT-MDT. Images of the surface topography of the films are shown in Fig. 2. Statistical analysis of the

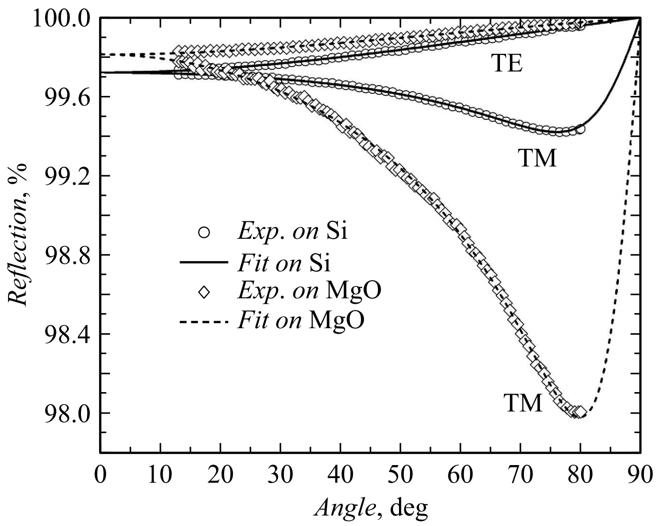


**Figure 1.** Angular dependence of the reflectances of TE- and TM -modes at wavelength $\lambda = 632.8$ nm from a thin film of platinum deposited on a silicon (circles) and magnesium oxide (rhombuses) substrate. TM -modes have a minimum at 75.9 and 79.8° for films on silicon and magnesium oxide substrates, respectively.

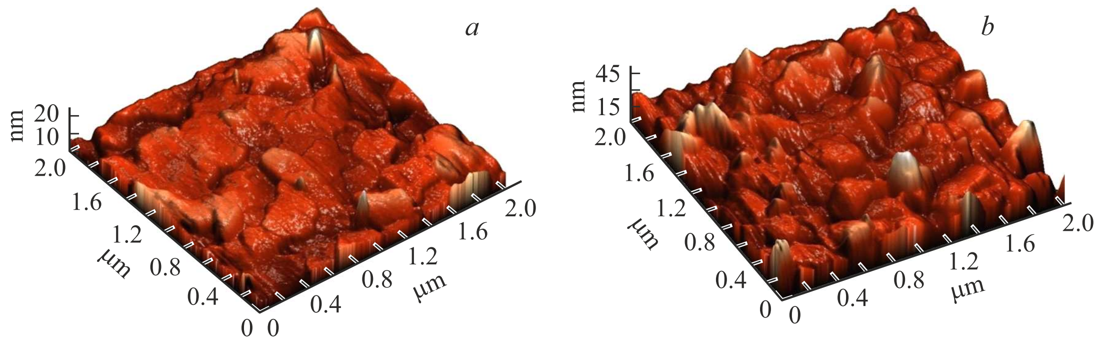


**Figure 2.** 3D surface images of a platinum film deposited on the polished surface (001) of a slice of a magnesium oxide (*a*) and silicon (*b*) single-crystal substrate

surface yields a histogram in the form of a peak similar to a Gaussian distribution. The width of this peak at half height characterizes the average thickness of the surface layer. Such an analysis for a film of platinum deposited on the surface of MgO gives a value of 12 nm. For a film on a silicon surface, this analysis gives a layer thickness equal to 22 nm. These values are close to the effective layer sizes (11 and 27 nm) obtained from the optical measurements performed. A non-ideally smooth surface layer for electromagnetic radiation with wavelengths significantly exceeding the characteristic dimensions of the surface topography can be represented as a layer with an inhomogeneous refraction index varying from the value of the refraction index of the film material at the lower boundary to the value of the refraction index of air at the upper boundary. The representation of such a surface layer by introducing an effective layer, isotropic in the plane and with anisotropy along the normal, satisfactorily describes the reflection of TM- and TE-waves from the platinum surface.

Thus, for the optical characterization of platinum films deposited on the substrate, mathematical processing of the results of measurements of the angular dependence of the reflectance of laser radiation of two polarizations (E and H) has been performed. The agreement between experiment and theory is achieved by introducing a thin surface layer into the calculation algorithm. It is shown that, within the limits of measurement error, it is not sufficient to use traditional reflection [9] formulas with the optical parameters of platinum, but it is necessary to introduce additionally an effective anisotropic layer related to the surface inhomogeneity.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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