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Nanosized gold films formation under conditions of multiple autoirradiation with ion-beam deposition

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Uniform gold films with a thickness of several tens of nanometers were obtained for the first time on silicon and quartz substrates by ion-beam deposition−sputtering. It is shown that the predominant lateral growth of nanoscale metal layers along the substrate surface occurs under exposure to the high-energy component of the sputtered atoms flux. The decisive role in the nanometer gold film formation is played by elastic collisions of sputtered metal atoms with atoms of the substrate and growing film. The application of the multiple deposition−sputtering operation allows suppressing the grain formation process and obtaining gold films with better characteristics than those with a single deposition.

Keywords: ion-beam sputtering-deposition, nanosized gold film, electric resistance, surface roughness, autoirradiation

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Obtaining nanoscale materials having properties characteristic of lump samples is a fundamental research and technological issue. In solving it, it is possible to better understand, on the one hand, the substance behavior in an extremal state when the influence of quantum effects is strong, and, on the other hand, e.g., interaction of magnetic and optical phenomena; it is also possible to solve a number of relevant practical tasks. The possibility of efficiently control light by affecting the medium optical properties with external magnetic fields is restricted by the weakness of magnetooptical effects [1]. One of the ways of their enhancement is using materials whose required optical characteristics are reached by fitting not the structure chemical composition but geometric parameters. For instance, creation of periodic structures in the form of metal grids on dielectric substrates [1] enables localization of the electromagnetic field energy on the metal/dielectric interface by exciting surface electromagnetic waves (surface plasmon-polaritons) and, hence, intensification of light−matter interaction. The most intense excitation of plasmon-polaritons is observed when nanoscale films of noble metals, e.g., gold, are used [1–3]. However, formation of magnetoplasmonic structures [1,3–5] needs highly uniform ultrathin films.

There is a great number of studies [6–8] where gold films tens and hundreds of nanometers in thickness were synthesized by various methods [6], e.g., ion-beam deposition, thermal evaporation, molecular beam epitaxy, and cathode, ion-plasma and magnetron sputtering. All these studies failed to solve the problem of obtaining continuous uniform gold films because of unsatisfactory metal/substrate adhesion and also because of grain formation in the film itself. The latter is caused by chemical intertness of gold to materials of other nature, due to which interaction of gold atoms with each other prevails over interaction with the substrate atoms [6].

The goal of this work is to synthesize continuous uniform gold films several tens of nanometers thick on silicon and quartz substrates by vacuum deposition with ion beam sputtering [2,9].

Prior to the gold layer deposition, the silicon and quartz substrates were cleaned from foreign surface impurities for 120 s with an oxygen ion beam with the energy of below 0.3 keV and ion beam current density of $0.1-0.15\,\mathrm{mA/cm^2}$. The deposition was performed at a setup for twofold ion beam deposition-sputtering equipped with a wide-aperture ion source [10]. Gold was applied on the preliminary prepared substrate by sputtering a golden target with 1−1.3 keV argon ions with the ion beam current density of $0.1-0.25\,\mathrm{mA/cm^2}$. During the film deposition, the operating pressure did not exceed 10^{-2} Pa, the residual pressure in the operating chamber was 10^{-3} Pa. To get the necessary vacuum, an oil diffusion pump was used. The gold deposition time was 5 min. In the case of multiply repeating the deposition-sputtering operation, the metal layer was applied under the same conditions for 60 s, and then sputtering with argon ions of the same energy was performed for 30 s. To ensure better adhesion, the first metal layers were sputtered fully until total loss of metal conductivity. The deposition-sputtering cycle was repeated 10 times.

Surfaces and cross sections of the gold films were analyzed with scanning electron-ion microscope SEIM Helios NanoLab 600 produced by FEI Company, USA. The surface morphology was studied by atomic force microscopy using scanning probe microscope NanoEducator (produced by NT-MDT, RF). Optical reflection and transmission spectra

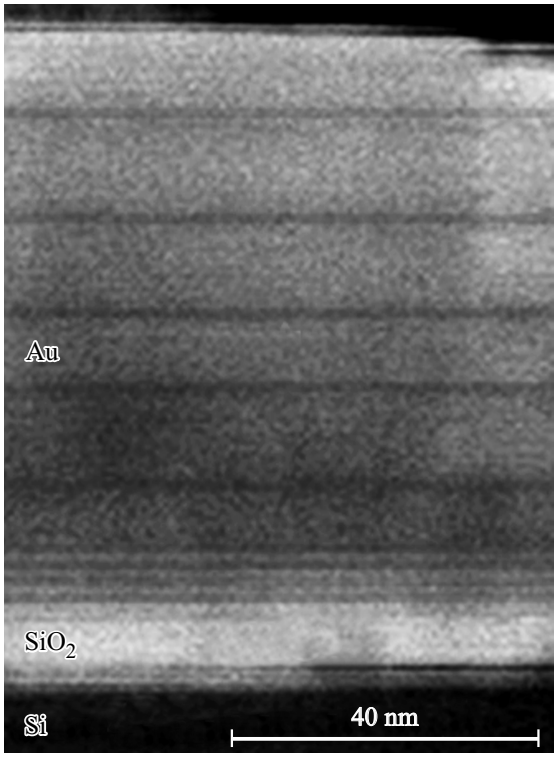

Figure 1. SEM image of the cross section of gold film 90 nm thick on silicon in the case of multiple deposition.

of gold films on quartz substrates were measured using spectrophotometer Cary-500 (produced by Agilent Technologies, USA) in the wavelength range of 400 to 800 nm.

Fig. 1 clearly demonstrates a laminar structure formed due to the action of gold atoms first upon the substrate and then upon the metal film in the process of its growing on the substrate. On the cross section in the vicinity of the film/substrate interface, no delamination is observed, while the interface itself remains a continuous even boundary, which evidences the absence of chemical interaction between the film and substrate. After each act of deposition, mainly lateral growth of the metal layer along the surface takes place, when the absorbed atoms attach to the growing layer until its total overgrowth. This proves the enhancement of the metal atom–substrate atom interaction and, hence, improvement of the gold adhesion to the substrate.

To explain formation of a high-quality continuous gold layer on the substrate surface, it is necessary to take into account that the spectrum of energy distribution of sputtered metal atoms is continuous till the maximum energy $E_{\max}$ [11] that depends on the energy of ions performing sputtering. From the flux of sputtered substance atoms, two components may be conditionally distinguished: the main one and the high-energy one [2]. The main component consists of atoms with medium energy approximately equal to sublimation energy U (~ 3.8 eV/atom for gold [12]), while the high-energy component contains atoms with energies an order of magnitude higher than U [11].

As per estimates obtained using code SRIM (www.srim.org, [13]), the major part of sputtered gold atoms having energies of up to 10 eV penetrates into the silicon or quartz substrate by the depth of no more than 0.8 nm. They condense on the substrate surface thus forming the metal layer.

At the initial stage of deposition, high-energy (up to 300 eV) gold atoms are able to implant into the near-surface layer by the depth of up to seven lattice constants (up to 2.8 nm [14]) and form point defects in this region. However, fast decrease in the number of sputtered atoms with increasing energy due to the distribution function asymmetry allows limiting to the maximum energies of up to 20 eV (atoms of such energies penetrate into the substrate by 1 nm). Indeed, the number of particles with energies above 20 eV is essentially lower than 0.01%, while that for energies above 100 eV is lower than 10^{-6}%. This is why the major part of point defects will arise in the substrate near-surface layer at the depth of no more than two lattice constants, namely, 1 nm.

Specific features of the sputtering processes and, hence, of formation of thin films of the deposited substance, are governed by kinetics of collisions [15,16] taking place both on the substrate surface with participation of the metal and substrate atoms and on the surface of the growing metal film with participation of only the metal atoms. All the atom–atom collision processes belong to a range between two limiting cases of the kinetic energy transfer: absolutely elastic and absolutely inelastic collisions. In the latter case, variations occur in the atom internal state that may be ignored.

In the case of a central collision, the maximal portion γ of the transferred energy is determined by the ratio between masses M_1 and M_2 of the projectile and stationary atom, respectively: $\gamma = 4M_1M_2/(M_1 + M_2)^2$ [16]. Interaction between gold atoms and lighter silicon and oxygen atoms is accompanied by transferring to them energy portions equal to $\gamma = 0.44$ and 0.22, respectively. Moving in the initial direction, they stop at a certain depth in the near-surface substrate regions and form point defects. When gold atoms interact with each other in the process of autoirradiation of the growing film, total transfer of kinetic energy takes place ($\gamma = 1$). In the case of the central collision, this results in the energy exchange between the metal atoms. The metal layer is much thicker than the gold atom implantation depth, especially in the process of the second and subsequent depositions; according to the SRIM data, the implantation depth does not exceed 0.6 nm for the highest energy (300 eV) of atoms of the sputtered substance flux and 0.3 nm for the 20 eV atoms. In this case, the increase in the number of point defects in the substrate near-surface regions beneath the metal layer may be explained by the mechanism of either direct or cascade knocking the gold atoms out of the layer into the substrate during absolutely elastic collisions with the same high-energy atoms.

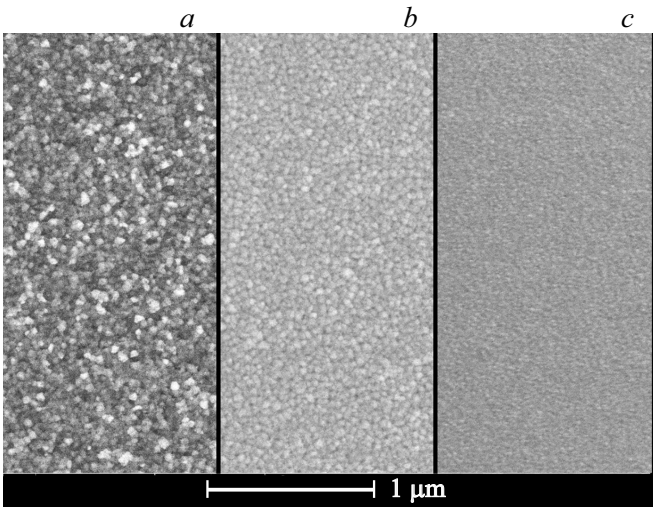

Figure 2. SEM image of the gold film surfaces in the case of single (*a*), twofold (*b*) and multiple (*c*) deposition on the initial silicon surface.

The second deposition of the metal layer under the above conditions enables at least twofold increase of the number of atoms implanted into the substrate near-surface regions. The point defects being added to the already existing ones (implanted during the previous deposition) lead to adhesion improvement [2] due to formation of extra physical bonds between the implanted and deposited gold atoms. This ensures formation on the substrate of a continuous gold layer several monoatomic layers thick and subsequent application on its surface of the nanoscale film of the same metal.

All the above mentioned leads to improvement of the surface morphology due to transition to the mode of multiple growing film exposure to the high-energy component of the sputtered ion beam flux. Comparison of the results of studying with the atomic force microscopy the gold films obtained on silicon substrates has shown that the mean-square roughness R_q of the thin gold film surfaces is 1.2 nm after the single deposition, 0.8 nm after the second deposition, and 0.3 nm after multiple deposition. According to the results of studying with scanning electron microscopy (SEM), the mean grain size decreases in transition to the multiple deposition mode (Fig. 2). In the last case, almost total suppression of grain formation in the gold film occurs due to the increase in the nuclei density resulting from autoirradiation with high-energy gold atoms, which leads to improvement of the film uniformity and continuity. This promotes improvement of the film-to-substrate adhesion [17].

Optical properties of the gold films on quartz substrates in the wavelength range of 400 to 800 nm do not worsen after the multiple deposition (Fig. 3). Sharp increase in the reflection factor in the wavelength range of 520–550 nm, as well as the presence of a peak in the transmission curve, evidences suppression of the localized plasmon resonance [3] conventionally observed in this spectrum range.

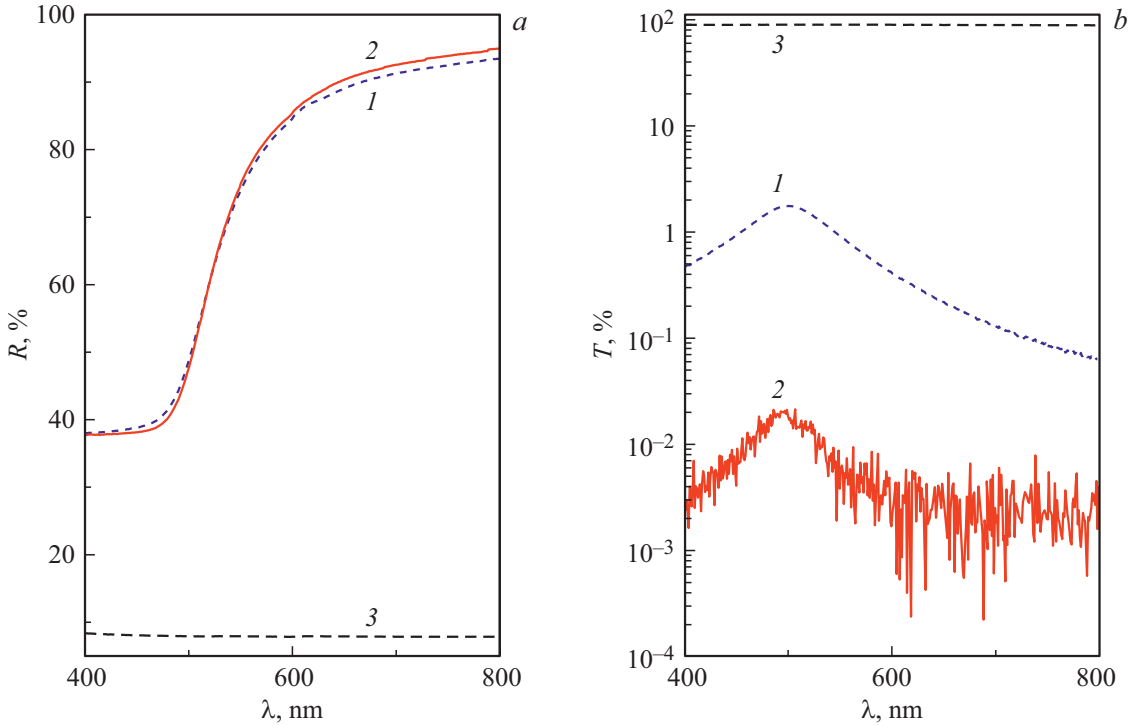

Figure 3. Reflection (*a*) and transmission (*b*) spectra of the gold films on quartz obtained by single deposition (*1*) and by multiple deposition-sputtering (*2*). *3* —relevant quartz spectra.

Thus, a new approach has been demonstrated to formation of continuous uniform nanoscale gold films with predominantly lateral growth due to self-stimulating the forming layer with a flux of inherent adatoms. The method of multiple deposition-sputtering allows the high-energy part of the deposited atoms flux to multiply act upon the forming film. This leads to suppressing the grain formation, ensuring high adhesion between the metal layer and substrate, and obtaining high-quality nanoscale gold films. The paper shows that a simple model of absolutely elastic pair collisions is able to qualitatively describe the initial stage of the uniform gold film formation.

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Conflict of interests

The authors declare that they have no conflict of interests.

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