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NANOSTRUCTURES

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Formation of nanostructures upon laser ablation of silver in liquids

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Abstract. **The formation of a dense array of nanospikes is studied upon ablation of a silver target immersed into water or ethanol by 350-ps pulses from a neodymium laser. The average height of nanospikes is 50 nm and their density amounts to 10^{10} cm^{-2}. The irradiated surface is studied by using reflection spectroscopy in the 200 – 600-nm range and an atomic force microscope. Small lateral dimensions of nanospikes confine plasmon oscillations of electrons, which is manifested in the colouring of the irradiated surface. The plasmon resonance of nanospikes is observed at 380 nm and shifts to the visible region upon oxidation in air. The initial spectrum of nanospikes is recovered after processing of their oxidised surface in an aqueous solution of ammonium. The use of nanospikes for observing surface enhanced Raman scattering is discussed.**

Keywords: *laser ablation, nanostructures, plasmon resonance*.

1. Introduction

Laser ablation of solids in liquids is one of the methods for producing nanoparticles. Unlike nanoparticles obtained by chemical synthesis methods, nanoparticles produced by laser ablation of solid targets in liquids can be in principle free of surfactants and foreign ions [1]. The properties of nanoparticles produced by laser ablation of solids in liquids depend on many parameters such as the laser radiation wavelength, the beam energy density on a target, the type of liquid, etc. Because the target substance is ejected to a liquid during ablation, a relief is formed on the target surface whose morphology depends both on the energy density and the total radiation dose absorbed at a given point on the surface.

Upon irradiation of a target by a fixed laser beam, a crater is formed in it, whereas upon irradiation of a target in a liquid by a scanning laser beam, periodic microcones are produced on the target surface, whose period virtually coincides with the laser-beam diameter on the target. Such periodic structures were observed in tungsten, copper, brass, and other materials upon their ablation in liquids [2]. The dependence of the period of these structures on the laser-beam diameter distinguishes them from periodic structures produced by laser ablation in vacuum or diluted gases [3]. The period of the latter is determined by the properties of the target-material melt and, as a rule, several periods fit the laser-beam diameter.

In this paper, we describe a new type of structures with characteristic dimensions of tens of nanometres. Unlike periodic structures produced due to the ejection of the target material to a liquid in the form of nanoparticles, nanostructures are formed from the initial roughness of the target under the action of the pressure of vapour of a liquid surrounding the target.

2. Experimental

We used 100 – 200-μm thick silver plates of the 99.99 % purity as targets. Before irradiation, the targets were mechanically polished or polished to obtain the required roughness level. The targets were located at the bottom of a glass cell which was filled with water or ethanol. The cell was mounted on a computer-controlled stage and could be moved at the given velocity being irradiated by a laser beam. A silver target was irradiated by 350-ps, 1.06-μm pulses from a Nd : YAG laser with a pulse repetition rate of 300 Hz. Laser radiation was focused on the target through a liquid layer of thickness several millimetres.

3. Results and discussion

Upon irradiation of targets at the fluence of 1 J cm^{-2}, silver nanoparticles were produced in the liquid and a cavity was formed on the target surface, which grew with the exposure time. The spectra of silver nanoparticles obtained under these conditions are as a whole similar to those observed when other lasers were used; in particular, they exhibit the maximum plasmon resonance at 400 nm. As the energy density was reduced, the generation rate of nanoparticles decreased and became negligible for the energy density 0.4 – 0.5 J cm^{-2}. In this case, the target itself became coloured, its surface being visually smooth. It is the irradiated sites of the target that changed to a distinct yellow colour. This is illustrated in Fig. 1 which shows the absorption spectra of the initial silver target and this target irradiated in water by a 0.4-J cm^{-2} laser beam. One can see that the maximum of the absorption spectrum of the irradiated surface is located in the region 370 – 380 nm. This maximum is absent in the spectrum of the initial target,

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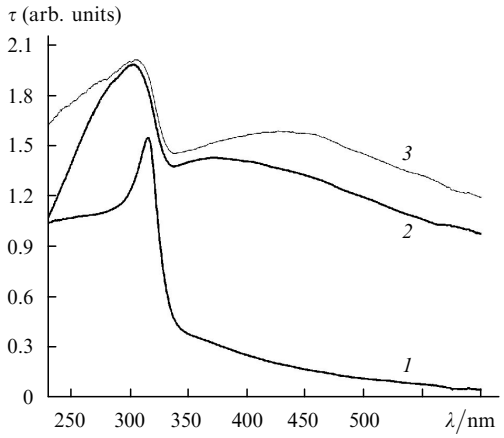

Figure 1. Absorption spectra of the initial silver surface (*1*) and this surface ablated in water for $W = 0.4$ J cm^{-2} (*2*), and of the ablated target after keeping it for several days in air (*3*). The reference sample is metal aluminium.

which exhibits only the typical absorption peak of silver at 315 nm. A similar absorption maximum is also observed upon ablation of silver in ethanol at close energy densities on the target. The ablation-induced absorption maximum shifts with time (for several days) to ~ 430 nm.

The appearance of the absorption maximum of the silver surface at 380 – 400 nm unambiguously indicates the formation of nanostructures on the target surface because plasmon oscillations of electrons in silver nanostructures correspond to this wavelength range [4]. The target irradiated in water was studied with an atomic force microscope in the tapping mode. The topology of a silver target surface after laser ablation in water is shown in Fig. 2. One can see that the silver target surface is strewn with nanospikes of height of 50 – 70 nm and the same lateral size. The formation of these nanostructures causes the change in the absorption spectrum of the target surface shown in Fig. 1. The density of nanospikes estimated from Fig. 2a is $\sim 10^{10}$ cm^{-2}. For the scanning rate of the laser beam equal to 300 μm s^{-1}, the time required to irradiate the target surface area of 1 cm^2 is only several minutes.

An interesting feature of the ablation process is the necessity of existence of microscopic irregularities on the silver surface for formation of nanostructures. Indeed, it was found that nanostructures were not formed on a polished silver surface with a root-mean-square roughness with amplitude ~ 10 nm (averaged over the 5×5-μm area) over the entire range of energy densities up to the beginning of the intense ablation of a silver target and the appearance of cavities on its surface, i.e. generation of silver nanoparticles at a high rate. On the contrary, on a surface with the root-mean-square roughness with amplitude ~ 100 nm, nanostructures are formed in a broad range of laser energy densities. In this case, the generation rate of nanoparticles in liquid is low and the optical density of the liquid near 400 nm almost does not change.

Nanostructures are predominantly formed near irregularities of the roughness of the initial target surface. This is illustrated in Fig. 2b showing the accumulation of nanospikes around a microscopic scratch on the target. The characteristic yellow colouring is also observed in the case of a much greater (with the amplitude of 2 – 4 μm) initial roughness of the target. Unfortunately, such a relief amplitude lies outside the dynamical range of probe microscopes.

The red shift of the absorption maximum of nanostructures with time suggests that they are oxidised by oxygen in air. In this case, nanospikes are covered with oxide having a higher refractive index [5], which results in the red shift of the plasmon resonance peak. It was found that the spectrum of a silver surface with nanostructures can be recovered by the chemical reduction of the oxidised surface in the 10 % aqueous solution of ammonia heated to 50 – 60 °C.

When laser pulses of longer durations, for example, 20 – 30 ns (a copper vapour laser) or 130 ns (a Nd : YAG laser) were used, the formation of nanostructures was not observed. Because to produce nanostructures, the irradiated surface should have a proper initial relief, we propose the following formation mechanism of nanostructures. Upon heating by a sufficiently short laser pulse with the beam energy density close to the melting threshold of the target material, the parts of the target that are in a poor thermal contact with a bulky substrate (protrusions, corners, etc.) melt first. When heat is transferred to the liquid surrounding the target, pressure near the target surface drastically increases due to liquid evaporation. The melted fragments of the microstructure are elongated under the action of a shock wave in liquid reflected from the target. This

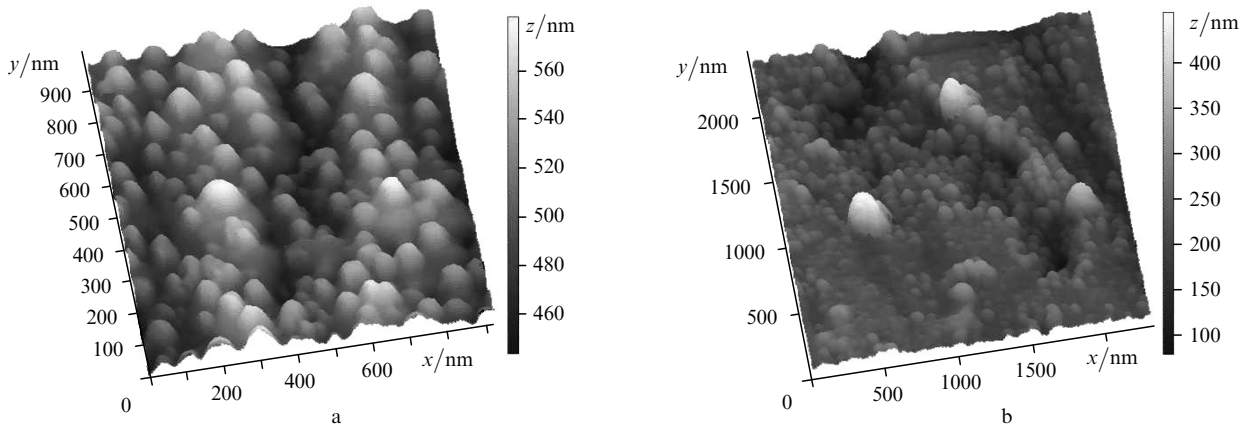

Figure 2. Nanostructures on the silver surface (a) and surface microscopic defects (b) after ablation in water for $W = 0.5$ (a) and 0.4 J cm^{-2} (b).

mechanism is indirectly confirmed by the absence of nanostructures on the silver surface upon ablation in air at comparable laser energy densities. Instead of nanostructures, a system of crossed periodic structures is observed, which are probably caused by the interference of the incident laser beam with a surface electromagnetic wave excited by the laser beam. The period of such structures is close to the laser wavelength (about 1 μm), which is typical for a surface electromagnetic wave.

The nanostructures produced in our experiments can be used to amplify Raman signal of molecules adsorbed on them due to surface-enhanced Raman scattering. The possibility of reducing the oxidised surface of nanostructures on silver demonstrated in the paper allows their application as re-usable substrates for the diagnostics of trace amounts of molecular compounds.

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