Research of silicon and silver nanoparticles obtained by laser ablation in liquid

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Abstract. Laser ablations of silicon and silver in ethanol were made and the nanoparticles obtained were studied. It was shown that silver nanoparticles had both monocristal and polycrystalline structures and cubic and hexagonal structures. It was cleared the amorphous silicon nanoparticles included a little quantity of the monocristalline silicon nanoparticles.

1. Introduction
Laser ablation refers to the method of evaporation of a substance from a surface by a laser pulse. During laser ablation of solids in liquids, the high density of the buffer liquid prevents the laser plume from expanding, the vapor-plasma cloud escaping from the target quickly cools with the formation of small particles, the nanoparticles remain in the liquid volume, forming a colloidal solution.

Pulse laser ablation of substances in a liquid is applicable both for all types of solids [1, 2]. Ablation of solids in a liquid allows obtaining nanosuspensions and eliminates the presence of residual reagents in the final product and additional purification, in contrast to the chemical synthesis of nanoparticles in a liquid.

For a nanosecond laser, most of the laser energy comes to the target after the formation of a vapor layer. Target melting occurs after a boiling crisis (complete coating of the target surface with a vapor film). Ablation of the material following melting occurs in the atmosphere vapor of liquid (which subsequently forms cavitation bubbles above the target surface) [3].

2. Experimental
For ablation we used an ytterbium pulsed fiber laser YLP (Russia). The laser emitted periodic pulses with a wavelength of 1064 nm, pulse duration of 100 ns, pulse energy of 1 mJ and a peak pulse power of up to 10 kW. [4]

Ingots of Ag and Si were used as targets and an ethanol solution was used as dispersion medium. The silver has low chemical activity, therefore, pure metal particles are formed in ethanol.

The laser radiation was focused by a collecting lens onto a target sample, which was placed at the bottom of the liquid container. The sample was scanned at a speed of 0.3-1 mm / s using a motorized biaxial linear translator 8MTF (Lithuania) and a CNC USB TB6560 controller (China). Multiple scanning of a given surface of the sample was carried out within 10-30 minutes. The use of the scanning system made it possible to uniformly evaporate the material from the target, thereby increasing the ablation efficiency during prolonged irradiation and narrowing the size spread of the nanoparticles obtained.
Colloidal solutions were studied using a SALD-7500nano laser particle size analyzer (Japan). At a power density in the pulse of $8 \times 10^7$ W/cm$^2$ and a pulse frequency of 40 kHz, the average particle size in the solution was 50 nm for Ag and 14 μm for agglomerates of coagulated Si particles. After processing a colloidal Si solution in an ultrasonic bath with a frequency of 40 kHz and a power of 30 W, the average particle size of Si in the solution was 35 nm.

3. Results and analysis

The colloidal solutions obtained were investigated by transmission electron microscopy (TEM) (Figure 1). It indicates diffraction lines of the crystal structure. The interplanar distances $d$ are shown of double light segments. Ag nanoparticles have two structures. The first is a polycrystalline correspond to the cubic structure (interplanar distances of 0.236 nm or 0.205 nm) or the hexagonal structure (interplanar distances of 0.227 nm) (Figure 1a). The second is a monocrystal structure which corresponds to a hexagonal close packed structure (interplanar distance of 0.48 nm) [5] (Figure 1b).

Silicon nanoparticles are mainly amorphous, but there are also monocrystal structures (Figure 1c) with an interplanar distance of 0.19 nm (cubic diamond structure).

![Figure 1](image1.png)

**Figure 1.** TEM images of nanoparticles: (a) TEM image of Ag polycrystalline nanoparticle; (b) TEM image of Ag single-crystal nanoparticle; (c) TEM image of Si single-crystal nanoparticle.

TEM image shows that Ag nanoparticles have a shape which is close to spherical in size 24×30 nm$^2$ (Figure 1a) and 20×22 nm$^2$ (Figure 1b), and crystalline Si nanoparticles have an oblong shape of 2×8 nm$^2$ (Figure 1c). X-ray phase analysis confirmed the presence of crystalline silicon. Figure 2 shows X-ray diffraction patterns for silver and silicon nanoparticles. X-ray diffraction pattern (Figure 2a) shows the interplanar spacings of the crystal lattice for Ag nanoparticles to be 2.360 Å, 2.047 Å, 1.445 Å, 1.231 Å and (Figure 2b) for Si: 3.141 Å, 1.922 Å, 1.636 Å, 1.246 Å.

![Figure 2](image2.png)

**Figure 2.** X-ray diffraction patterns of particles: (a) for Ag; (b) for Si.
4. Conclusions
Thus, colloidal solutions of silicon and silver nanoparticles with shape close to spherical with an average diameter of 35 nm and 50 nm, respectively, were obtained. Silver nanoparticles have both monocystal and polycrystalline structures and exist in two polymorphic structures, cubic and hexagonal. Along with amorphous silicon nanoparticles, oblong 8 nm monocryalline silicon nanoparticles are also present.

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