Laser synthesis of hybrids Si-Au complex

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Abstract The paper demonstrates that the laser ablation approach can be used for synthesis (with average nanoparticle size control) of silicon nanoparticles supporting strong resonant optical responses in the visible spectral range. Porous and monolithic crystalline silicon targets are considered. The generated colloidal solutions have been used for the formation of one-layered covering composed of silicon nanoparticles. The obtained results may be used for the realization of many functional metasurfaces consisting of randomly distributed resonant nanoparticles.

1. Introduction
A huge spectra of photonic applications require silicon nanoparticles [1, 2]. Its optical properties, including resonant responses, are considerably dependent on the size, shape, and crystallization degree [3]. The development of fabrication techniques with controlled nanoparticle parameters is very important. The methods of laser ablation in liquid [3, 4] allow to control the average size and shape of the obtained particles choosing suitable irradiation conditions (pulse duration, energy density etc.). The order deposition of such particles in thin films allows to create metasurfaces for controllable manipulation of the reflection and transmission properties [6,7].

The paper presents results of the silicon nanoparticle synthesis by the continuous laser irradiation of the thin silicon target placed in ethanol. Porous and monolithic silicon targets are considered.

2. The obtaining of colloidal particles

For obtaining of silicon nanoparticles the method of CW-laser ablation was used [8, 9]. Application of the CW-laser radiation source with moderate intensity provided the possibility to obtain nanoparticle with a small deviation of the average size [4, 10]. In our experiments the targets of crystalline monolithic and porous silicon were used. To avoid the oxidation of nanoparticles we realized the laser ablation experiment in the 99% ethanol [3].

The laser beam (diameter 100 μm) was focused on the surface of the target (using the long focal-length lens with the focal length of 100 mm). The power variation was in the diapason of 10 – 100 W, which was resulted in the radiation intensity of 105 – 106 W/cm². As the conventional time of laser irradiation may be calculated by \( \tau = \frac{d}{v} \) (\( v \) – scanning speed), the laser beam diameter and scanning speed variations resulted in the irradiation time in the interval from 1 s up to 10 s (the mechanized table moving speed 10 μm/s – 100 μm/s). The whole irradiation time was 60 minutes.
The laser irradiation of the porous target resulted in a wider distribution function of nanoparticle sizes as compared with crystalline target (fig. 1). In the both cases spherical nanoparticles with average diameter of 100 nm were obtained (fig. 2).

Fig. 1. The histogram of the particle diameters distribution in colloidal system, which was obtained using laser irradiation (intensity $10^6$ W/cm$^2$, scanning speed 100 μm/s) of the monolithic target (a) and porous (b).

Fig. 2. REM-images of spray-jet deposited colloidal particles, obtained during the ablation of the porous (a) and monolithic (b) targets.

3. The colloidal particles deposition

Images of the particles shown in fig. 2 correspond to the evaporation process of the ethanol colloidal drop with nanoparticles inside. The experiment was carried out in a temperature controlled chamber with the temperature of 20 C. As it can be seen from fig. 2 there are uniformly deposited particles on the base area of the drop after its evaporation.

To control the deposition of the nanoparticles from a small colloidal drop we have used the methods described in [8, 10, 11]. We have deposited silicon nanoparticles using the sputtering small colloidal drops technology on the surface of the transparent substrate.

Colloidal systems have been sprayed through a capillary with a diameter of 100 μm (see fig. 3).
The system was pressurized by the pneumatic pump, and the pressure was about 5 bar. The capillary was positioned perpendicular to the surface of the substrate at a distance of 100 mm. The glass substrate was fixed on the surface of thermostabilized one-coordinate table with a temperature of 20 °C. The table movement speed ($V_s$) was ranged from 0.1 mm/s to 1 mm/s. The deposited droplets took a spherical shape, because of the Bond condition

$$B_o = \frac{g(\rho-\rho_m)d^2}{\sigma} \ll 1,$$

where $g$ – the gravity acceleration index, $\rho$ – the density of the drop material, $\rho_m$ – the density of the volume, in which is a drop, $\sigma$ – the surface tension, $d$ – the droplet diameter.

In this case the drop evaporation may be calculated using Maxwell diffuse model. Then the changing of the drop profile and height in time may be described by following equation:

$$h(r,t) = \frac{\left(\frac{h(0,t)^2+R^2}{2h(0,t)}\right)^2 - r^2}{2h(0,t)} - \frac{R^2-h(0,t)^2}{2h(0,t)},$$

where $h(0,t)$ – the height of drop in center, $R$ – the drop base radius.

4. **The measurement of the optical properties of the particles using a dark-field microscopy**

The measurements of nanoparticle optical properties were carried out using dark field microscope [5], where only scattered light is collected. As we can see from fig. 4a nanoparticles fabricated from the crystalline Si targets can resonantly scatter light of different frequencies.

![Fig. 4 A dark-field (scattered light) image of the deposited colloidal systems of monolithic (a) and porous (b) silicon.](image)

It is also important that in the case of the irradiation of the porous silicon target a large amount of nanoparticles does not support the resonant optical response in the visible range fig. 4b, because of their low refractive index. The different color presentation of the dark-filed images of the nanoparticles in fig. 4a is connected with excitation of electric and magnetic multipole resonances. Depending on the nanoparticle size these resonances are realized at different spectral points. The larger nanoparticle the large resonant wavelength [4,11]. Q-factors of the multipole resonances are decreased with decreasing of the nanoparticle dielectric permittivity as a result dark-filed images of nanoparticles with low refractive index are presented by white color like in fig. 4b.

5. **Conclusion**

It has been experimentally demonstrated that the cw-laser ablation can be applied for synthesis of silicon nanoparticles supporting resonant optical responses in the visible spectral range. Crystalline and porous silicon targets have been considered. The proposed method allows the silicon nanoparticles with an average size of 100 nm, the dispersion of the sizes used depends on the target structure. In the latter case resulting porous nanoparticles had relatively low refractive index and did not show strong resonances. In the case of crystalline nanoparticles, the strong electric and magnetic multipole resonances have been demonstrated. These obtained results have important implications to the realization of optical metasurfaces, with many functional properties, in the visible spectral range.
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