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Pulsed laser ablation of silicon nanowires and porous silicon in liquids

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Nowadays pulsed laser ablation of solid-state targets in different liquids and gases is a powerful tool to produce a variety of nanoparticles with desirable size, physical and chemical properties [1]. Silicon nanoparticles (Si-NPs) produced by this technique have potential in different biomedical applications [2, 3] due to high biocompatibility and biodegradability of this material [4].

In this work we present a novel two-stage technique of Si-NPs fabrication. At the first stage silicon nanowires (Si-NWs) arrays or porous silicon (por-Si) films are fabricated by the metal-assisted chemical etching [5] or electrochemical etching [3] technique, respectively. At the second stage the Si-NPs are produced by pulsed laser ablation of these targets in liquids (PLAL). The ablation was performed in distilled water, ethanol and liquid nitrogen under picosecond (1064 nm, 34 ps, 10Hz) and femtosecond (1250 nm, 125 fs, 10 Hz) laser irradiation.

Measurement of ablation thresholds for Si-NWs and por-Si samples in liquids revealed that they are several times less in comparison to the corresponding values for the crystalline silicon (Table I).

Table I. *Picosecond laser ablation thresholds of SiNWs, por-Si and crystalline Si in water and ethanol.*

Sample	Ablation threshold in water, J/cm^2	Ablation threshold in ethanol, J/cm^2
Si-NWs	0.32±0.01	0.10±0.02
por-Si	0.66±0.04	0.57±0.04
Si	1.26±0.11	1.18±0.09

The lower values are explained by a lower thermal conductivity of the porous matrix in contrast to bulk material and partial destruction of Si–Si bonds in the crystal lattice during chemical etching. As a result, in the process of subsequent laser irradiation of the Si-NW arrays or por-Si layers, the yield of ablation products and, respectively, the efficiency of agglomeration of the latter in the Si-NPs is several times higher in comparison to the case of using crystalline silicon [3].

Scanning electron and atomic-force microscopy techniques revealed polydisperse size distributions of the formed Si-NPs. The average size varies from 16 to 120 nm depending on the used buffer liquid and duration of laser pulses. Such sizes are substantially smaller than ones for Si-NPs prepared by traditional mechanical grinding of Si-NWs, por-Si and crystalline silicon, thus facilitating more effective administration of the Si-NPs into biological tissues. Therefore, PLAL technique has an additional advantage for biomedical applications.

Raman spectroscopy analysis of the Si-NPs fabricated via PLAL showed that the volume fraction of crystalline Si in them is higher than 87% for all types of the studied samples. The remainder is amorphous Si. This indicates that the optical properties of the Si-NPs are close to those for silicon nanocrystals with similar sizes.

Photoluminescence studies revealed a high fluorescence of all Si-NPs fabricated in ethanol and liquid nitrogen with fluorescence peaks in the range 600 – 900 nm for excitation wavelength of 532 nm. The initial Si-NWs arrays and por-Si films exhibit similar fluorescence. However, the lifetime for this process changes significantly before and after ablation at the microsecond scale. Fluorescence emission for the Si-NPs produced in water was not detected. We assume that the observed fluorescence efficiency depends on numerous defects in the studied nanocrystalline structures.

Spectrophotometry measurements of the ablated Si-NPs suspensions revealed that scattering coefficient reaches value ~ 1 mm^{-1} in the spectral range of 400 – 1000 nm indicating their potential as contrast agents in biomedical imaging. Optical coherence tomography imaging of the suspensions drops administered on agar gel surfaces confirmed this by providing the contrast of up to 30 dB.

Thus, PLAL of Si-NWs arrays and por-Si layers provide high yield fabrication of Si-NPs with relatively small size and high level of crystallinity, that are promising as fluorescence markers and scattering contrast agents in bioimaging.

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