Fabrication of alloyed silicon-based nanocrystals by plasma and laser-induced chemistry in solution

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Abstract: The capabilities of the liquid assisted electrical discharge and laser ablation techniques with additional laser irradiation of suspension for synthesis of binary SiGe, SiSn and SiC nanocrystals have been studied. The results of the characterization of inner structure, phase composition and morphology performed by means of HRTEM, SAED, Raman and FTIR techniques proved the formation of near-spherical SiGe, SiSn and SiC nanocrystals under the found optimized experimental conditions.

Keywords: electrical discharge in liquid, alloyed nanocrystals, laser induced modification.

1. Introduction

In this paper we discuss the properties of binary compound nanoparticles (NPs) synthesized by electrical discharge and laser ablation techniques in liquids followed by laser annealing of the resulting particles with the second harmonic of a YAG: Nd^{3+} laser (532 nm). Set of the discharge conditions were determined to be effective to produce SiC, SiGe and SiSn nanocrystals (NCs), perspective for the high power, high temperature electronic devices as well as for biomedical applications.

The growing interest to this kind of nanostructures is based on the possibility of varying the bandgap as well as adjustment of the direct/indirect bandgap of the semiconductor. However, the synthesis of Si-alloys with control over their properties is still challenging because of the low solubility of the alloying elements (Sn, Ge) in silicon. Nevertheless, the formation of Si–based alloys becomes more favourable at the nanoscale. In addition, if –non-equilibrium processes are used for the preparation of nanoscale Si-based alloys, the solubility of the elements may be increased, as it was demonstrated in several works [1-3].

Among the NPs synthesis methods utilizing non-equilibrium conditions of the particles formation, the plasma-assisted techniques in liquids are now anticipated as a powerful tool for nanofabrication due to the combination of high production rates and versatility with the possibility of control over the size, size distribution, composition and surface state of the formed NPs during the synthesis process. Plasma-based processes favour initiation of the high temperature chemical reactions that allow the formation of particles with composition, surface properties and morphology important for their practical applications including a possibility of metastable phases synthesis that are difficult to produce using other methods.

Plasma-assisted approaches based electrical discharges and laser ablation developed in this work for the synthesis of silicon-based NPs enable both gas-phase and liquid-phase chemistries not available through other synthesis methods offering the control over the synthesis process to achieve desired NPs properties. Furthermore, electrical discharges in liquids at atmospheric pressure are low-cost and offer clear advantages over the other methods demonstrating great capabilities for fabrication of quality Si-based alloyed NCs to meet demanding application requirements.

The composition and morphology of the NPs formed were found to be dependent on the parameters of the discharges, laser irradiation and chemical composition of the solutions. Synthesis conditions were optimized by controlling the plasma parameters such as temperature and concentration of the plasma components that are significant factors influencing the nature of plasma-chemical processes in the solution. The formed NPs were studied by absorption spectroscopy, electron microscopy, Raman and FTIR techniques, and XRD analysis.

2. Results and discussion

2.1 Synthesis of Si-Sn NPs

For the synthesis of Si–Sn NCs we used electrical discharge processing of a stoichiometric mixture of Si and Sn micropowders followed by laser annealing of the resulting particles with the second harmonic of a YAG: Nd^{3+} laser (532 nm). Schematic diagram of the setups used for the NPs preparation is presented in Fig. 1.

For the discharge processing a special design of a discharge chamber consisted of a funnel-shaped plastic cell with two coaxial vertically oriented electrodes made of a refractory metal was developed. A conical shape of the cell prevented removal of particles from the discharge zone providing plasma processing of particles during a necessary time interval.

Silicon and tin powders were weighed and preliminarily mechanically mixed together in the stoichiometric ratio. The obtained mixture was loaded into the reaction vessel and then some (50 ml) pure ethanol (99.9%) was added to the mixture. The presence of the suspended particles in the conical cell allowed discharge burning at the expanded inter-electrode distances (up to 5 mm).

The discharge was initiated by applying a high-frequency voltage of 8.5 kV. The power supply provided an alternating current (ac) spark discharge with the repetition rate of 100 Hz. The electric circuit with a relaxation time pulse generator provided a typical oscillating discharge current with high peak (10-12 A) intensity and with duration of a single discharge pulse of 2-5 μs. The oscillations were damped quickly with a decay time of 40-50 μs. The formed colloids were additionally irradiated with the unfocused laser beam of the second harmonic (λ=532 nm) of the Nd^{3+}:YAG laser

(pulse duration 10 ns, repetition rate 10 Hz) with fluences in the range of 230 – 400 mJ/cm^2.

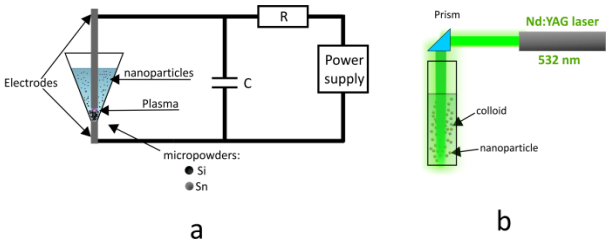

Fig. 1. Schematic diagram representing the techniques used for Si-Sn NPs preparation.

Primary analysis of the products formed was carried out by recording their Raman and absorption spectra. The absorption spectra were measured using a Cary 500 Scan spectrophotometer (Varian, USA) in the spectral range 200 – 2000 nm using quartz 5 mm cuvette. Raman spectra of SiSn alloy NPs deposited onto aluminium foil were investigated with the scanning probe confocal microscope\spectrometer «NanoFlex» (Solar LS, Belarus).

The absorbance spectra of the colloidal SiSn-NCs prepared in ethanol are presented in Fig.2. Absorbance measurements were carried out to estimate the energy bandgap of the synthesized SiSn-NCs and compared with the absorption of Si-NCs. The absorption peak is identified for SiSn-NCs at 1448 nm corresponding to energy at 0.85 eV.

This absorption peak was found to be shifted to longer wavelength compared to Si-NCs that display a peak at 351 nm (3.52 eV) [3]. The optical bandgap was estimated using Tauc plot for a direct bandgap semiconducting material, plotting $(\alpha h\nu)^2$ versus $h\nu$ in eV, where α is the absorption coefficient, h is the Planck constant, and ν is the frequency of light.

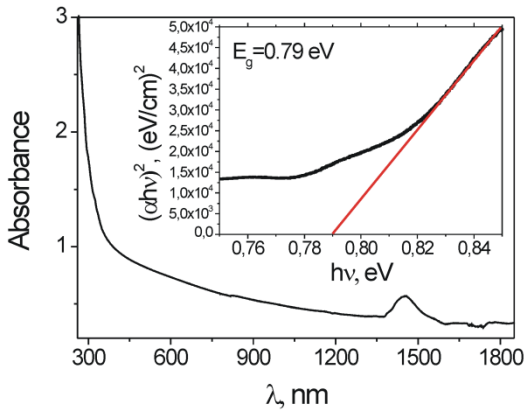

Fig. 2. Absorption spectrum and optical bandgap of silicon-tin nanocrystals fabricated by electrical discharge processing of a stoichiometric mixture of Si and Sn micropowders in ethanol.

The optical bandgap for SiSn-NCs was estimated to be 0.8 eV (Fig. 2), which is much lower than the optical bandgap for Si-NCs formed by electrical discharge between silicon electrodes in ethanol estimated to be about 1.3 eV [4], although the both nanocrystals were about the same average size. The estimated value of the optical bandgap is in agreement with the calculations of the SiSn electronic band structure where a direct bandgap was found to be about 0.79 eV [3].

To investigate the type of chemical bonding of the surface of nanocrystals Fourier transform infrared spectroscopy (FTIR) measurements were performed. Fig. 3 presents the FTIR spectra of the prepared NCs before and after laser irradiation that appeared to be rather similar. All the samples contained OH, C-H, C=O surface groups. Besides, the spectra contained the bands corresponding to the stretching vibrations of silicon bonded with oxygen, carbon and hydrogen in the range 700 cm^{-1} - 1300 cm^{-1} [3]. The band at 1090 cm^{-1} can be attributed to the vibrations of Si-O and Si-O-C bonds, while the one at 1150 cm^{-1} - to the Si-O-Si stretching modes [3]. The intensive broad band at around 600 cm^{-1} attributable to Sn-O--Sn stretching vibration was also identified in all the samples. But intensities of the similar bands are significantly lower in FTIR spectra of laser-irradiated samples. It can be indicated reducing the surface oxidation of NPs after laser irradiation.

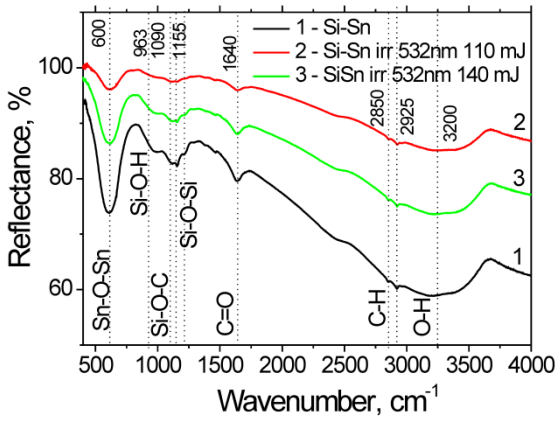

Fig.3. FTIR spectra of the synthesized SiSn nanocrystals deposited on the Al foil

Raman spectroscopy is one of the most powerful and non-destructive tools to characterize the structure, bonding, level of disorder, as well as the modification of silicon-based materials. Fig. 4 shows the corresponding normalized Raman spectra of the SiSn-NCs samples as-prepared and after additional laser irradiadion together with that of a crystalline Si wafer. The Raman spectrum of the bulk silicon contains the intensive peak at 521 cm^{-1} characteristic to the crystalline silicon and attributable to longitudinal optical (LO) phonon vibrations of the Si-Si bonds. If the alloying with Sn occurs, this Si-Si peak should shift to the low-frequency side that was observed

in the samples after plasma and combined plasma plus laser treatment (Fig. 3).

Raman spectra are characterized by two distinct peaks at 509 cm^{-1} and near 620 cm^{-1} presented in both spectra. The feature near 400 cm^{-1} attributed to Si–Sn vibrations [5] was not observed in the spectra.

The position of the Si-Si characteristic Raman peak is in agreement to the literature reports on the SiSn nanoalloys: in [6] it is reported that the presence of silicon nanocrystals in the structure of silicon films doped with tin is accompanied by a peak at 508 cm^{-1} in the Raman spectrum. So peak at 509 cm^{-1} can be attributed to SiSn nanocrystals formed during electrical discharge treatment of mixture of Si and Sn micropowders. However, it should be noted that the shift of the Si-Si Raman band generally depends on Sn content and stress created in the layer. Therefore, lowering of the size of the crystals up to nanoscale would also shift the silicon Raman peak to a lower frequency. For example, in our previous work Raman peak of Si NCs was observed at 517 cm^{-1} [4] compared to the Raman peak of bulk silicon situated at 521 cm^{-1}. Thus, it is difficult to conclude unequivocally about the fact of SiSn alloying on the base only the Raman spectra interpretation in case of nanocrystals. As for peaks near 620 cm^{-1} they can be attributed to SnO_2 formation and is in agreement with FTIR results discussed previously [7].

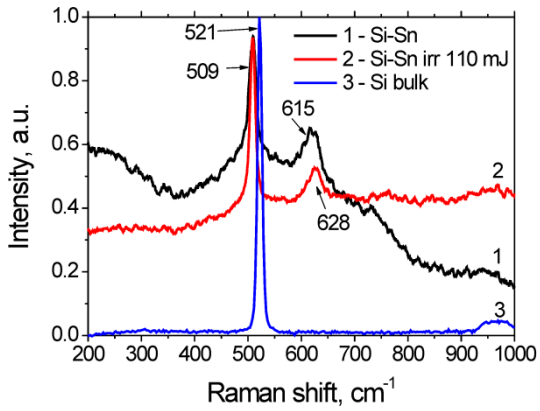

Fig. 4. Raman spectra of the SiSn NPs synthesised by electrical discharge treatment before (spectrum 1) and after (spectrum 2) additional laser irradiation in comparison to the bulk silicon (spectrum 3)

The additional confirmation of the formation of SiSn alloyed NCs can be found from the elemental analysis of the prepared samples. For example, the LIBS analysis of the NPs deposited onto the Al foil indicated the presence of both Si and Sn that allows assuming that the elements constitute the same NPs. The content of Sn in the laser treated sample increases that is also the indication of more efficient incorporation of Sn atoms into Si structure under the laser induced modification.

2.2 Properties of SiC NCs

Silicon carbide (SiC) is known as a chemically inert, extremely hard, key material for high power, high frequency and high temperature electronic devices and it is recognized as a candidate for next generation photonics and electronics.

To synthesize SiC NPs an ac electrical discharge between Si and C electrodes immersed in ethanol was used. The details concerning the parameters of the experimental reactor and procedure of NPs synthesis by electrical discharge in liquids can be found in our previous publications [4].

As can be concluded from the results of TEM studies, the electrical discharge between Si and C electrodes in ethanol results in the formation of near-spherical NPs with a two-peak size distribution. Indeed, because of their agglomeration, the particles of two types were formed – small well-separated ones with average diameter about 4 nm and narrow size distribution and aggregates with average diameter of about 11 nm. HRTEM analysis of the selected particle revealed lattice spacing close to 0.25 nm that belong to the (111) planes of 3C-SiC with a cubic unit cell parameter of 0.43591 nm [8It is known that SiC exhibits strong polytypism with several crystalline structures and varying stacking sequences, the most widespread and important of them result from cubic (β) stacking (3C-SiC) and hexagonal (α) stacking (specifically, 4H-SiC and 6H-SiC) [9]. Among all the structures, the β-SiC phase is known to be the most stable.

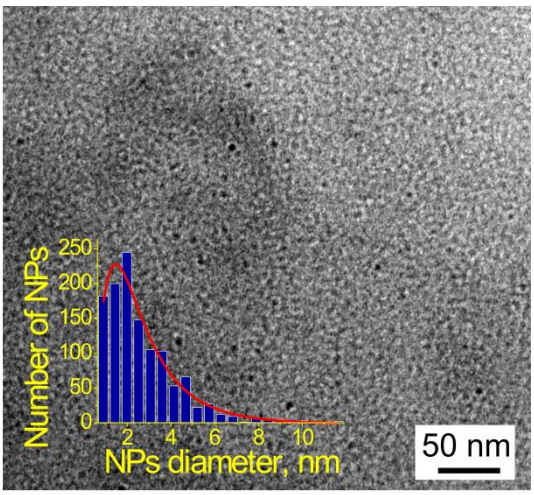

Fig. 5. TEM image of the SiC NPs prepared by electrical discharge in ethanol after 532 nm ns laser irradiation with fluence 560 mJ/cm^2, inset – size distribution of the NPs.

The determined lattice spacing values and plane assignments were confirmed by fast Fourier transform analysis (FFT) of the corresponding high resolution images. The observations support the assignment of the cubic crystal structure as more probable and stable than

the hexagonal one. It should be noted that minor reflections corresponding to cubic Si and carbon with graphite-like structure were also observed in the prepared sample.

Additional laser treatment resulted in the transformation of the size distribution as can be concluded from Fig. 5. Most probably, large aggregates undergo fragmentation in result of the absorption of laser pulses that results in the second peak disappearing in the size distribution and reduction of the average particles diameter up to 2.3±0.1 nm.

The cubic crystalline structure of the formed SiC NCs was also confirmed by X-ray diffraction patterns. Further evidence of the composition and purity of the synthesized SiC NPs was obtained by FTIR and XPS results that supported the TEM analysis suggesting the formation of SiC NPs. Indeed, the peak at around 796 cm^{-1} can be attributed to the stretching vibrations of the Si-C bonds.

2.3. Synthesis of the alloyed SiGe NCs

Nanostructures based on the Si_xGe_{1-x} alloys are interesting due to the possibility of adjusting the lattice parameters and the width of the band gap, changing the mobility of charge carriers.

For the alloyed SiGe NPs synthesis a two-step technique was developed based on the laser ablation of a germanium target immersed in a cell filled with the preliminarily prepared Si colloid suspension in ethanol followed by the subsequent laser irradiation of the formed colloid. For the ablation the Nd^{3+}:YAG laser (LOTIS TII, LS 2134D) operating in a double-pulse mode (1064 nm, energy 80 mJ/pulse, repetition rate 10 Hz, pulse duration 10 ns, interpulse delay τ = 10 μs) was used.

Fig. 6 presents the results of the SiGe nanocrystals studies of by transmission electron microscopy (TEM).

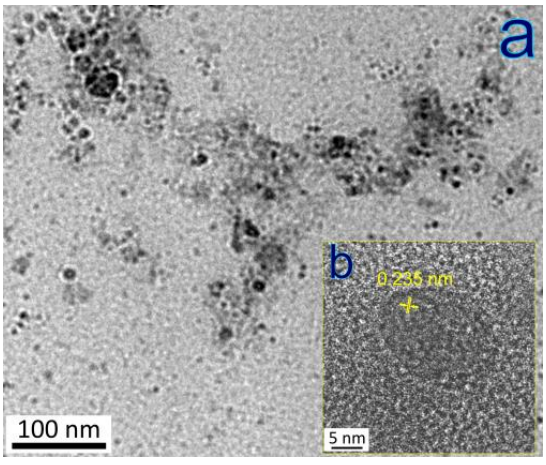

Fig. 6. - TEM images of NPs formed by laser ablation of Ge in a colloidal Si solution. The inset shows images of nanocrystals obtained with high resolution.

Laser ablation of Ge in a colloidal solution of Si leads to the formation of two types of particles: small particles and larger agglomerated particles. It should be noted that the observed weak agglomeration of NPs may be the result of their collection on the grid and not necessarily an indicator of the agglomeration of the original NPs. The results of electron diffraction confirm the crystallinity of the obtained particles.

Laser treatment did not result in a significant change of sizes of large particles (Fig. 6b). High-resolution TEM results indicated that the particles remain crystalline after laser treatment. Detailed analysis of single NPs using high-resolution TEM showed that in addition to particles consisting of silicon and germanium, there are also NPs having the interplanar distances of 0.24 nm and ~ 0.23 nm and can be attributed to the (200) and (101) planes of the tetragonal SiGe phase, respectively, (International Center for Diffraction Data, Map No. 04-005-9292). This result confirms alloying of the silicon and germanium particles. It should be noted that areas with an interplanar distance of 0.25 nm were also found on the surface of the particles, which may indicate the formation of silicon carbide as a result of interaction with the solvent and its decomposition products. Thus, to obtain particles of uniform composition consisting only of the SiGe phase, further optimization of the synthesis process is required.

Conclusion

Thus, synthesis of binary SiGe, SiSn and SiC nanocrystals has been demonstrated both with atmospheric pressure electrical discharge plasmas as well as with laser-produced plasmas in liquids. Si-based alloyed NCs have great potential for many applications due to their wide range of tunable properties and environmental safety.

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