Synthesis of mixed germanium tin nanoparticles by spark-discharge

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Abstract. The paper represents the investigations of dimensional and structural properties of nanoparticles produced by pulsed-periodic spark discharge by simultaneous electrical erosion of germanium and tin electrodes in inert atmosphere. Two alloys of GeSn nanoparticles with different mass fractions of tin were obtained by altering the polarity of the electrodes. The nanoparticles' sizes from 4 to 45 nm were observed. It was shown that the samples consist of core-shell nanoparticles agglomerates, where both β-tin crystals and cubic germanium ones presence as a core; the shell is a mixed germanium tin oxide. Furthermore, a shift of a maximum of Raman peak by 3.5 cm$^{-1}$ to lower wave numbers with an increase in relative fraction of tin was detected.

1. Introduction

The increased interest in GeSn compounds in recent years is associated with the possibility of regulating the width band gap in the range 0 - 0.65 eV to obtain direct-gap materials which can be base for creating solar cells, quantum-cascade lasers and photodetectors operating in the IR region (from 1 to 8 mkm) at room temperature [1]. The transition from the indirect-gap structure of the Ge1-xSnx semiconductor to the direct-gap can occur according to calculations in the range of tin fraction x from 2 to 20 %. Experimentally, pseudomorphic heterostructures were formed with a direct forbidden zone with a concentration tin more than 9 %. Nanostructured films of GeSn alloys with a tin concentration of up to 12.6%, with a band gap above ~ 0.57 eV [2], were obtained. At the same time, it is necessary to obtain a material with a high tin content for the transition to the middle IR range, which is problematic due to the large difference in the periods of tin and germanium periodic lattices, as well as technological problems of growing crystal layers by molecular beam epitaxy [3]. In this case, theoretical studies were carried out, which showed the possibility of generating radiation in semiconductors of GeSn structures with a direct bandgap to create group IV lasers with optical pumping in the wavelength range from 3 to 7 μm, integrated into silicon [4].

The basic method for growing semiconductor GeSn alloys is low-temperature molecular beam epitaxy, more rarely, gas-beam epitaxy, which has a number of limitations with the growth of germanium structures with a high tin composition. An alternative technology for creating compounds from immiscible materials is the method of a pulse-periodic spark discharge [5, 6]. Aerosol nanoparticles of the Ag – Cu, Au – Pt, Cu – W [7], Co – Cr [8], and InSn [9] alloys were obtained by this method. The theoretical models presented in [10] and supported by experiments on Au-Pt describe the possibility of controlling the elemental composition of the alloys by varying the parameters of the current pulse and its polarity. The work on the synthesis of nanoparticles of pure germanium and silicon semiconductors by the method of gas discharge synthesis in an inert atmosphere showed the
possibility of producing germanium and silicon crystals in an amorphous matrix of the corresponding oxides [11, 12]. Moreover, this method can be used as a source of nanoparticles in aerosol jet printing [13, 14] with the goal to form microstructures for electronic and optoelectronic applications. Thus, the task of synthesizing mixed germanium tin nanoparticles by spark discharge and investigation its dimensional and structural properties is a future-oriented goal for material science.

2. Materials and Methods
Two samples of aerosol nanoparticles were produced in the pulsed-periodic spark discharge generator [15] under the following synthesis conditions: frequency of the discharges was 370 Hz, the battery voltage was 1.5 kV, pressure in the chamber - 1.5 atm, to synthesis the first alloy (Sample 1) a cylindrical tin electrode was used as a cathode while germanium electrode was an anode, to get the second sample (Sample 2) inversely the cathode was germanium and tin acted as an anode. The particles are generated under an inert atmosphere (Ar, 99.999%), and collected on a cellulose filter fixed with TEM carbon coated Cu grid. Micro-Raman spectroscopy studies was carried out with a LabRAM HR Evolution (Horiba Scientific) using the 632.8 nm excitation wavelength of the He-Ne laser. Transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) were performed on the collected particles to study their size, morphology, composition and structure using the Jeol JEM 2100 (200 kV) microscope with energy dispersive X-ray spectrometer X-MAXN Oxford Instruments. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet™ iS50 FTIR Spectrometer (Thermo Scientific) directly from the alloy nanoparticles on a cellulose filter.

3. Results and Discussion
A typical TEM image of primary nanoparticles in large agglomerate, and the corresponding electron diffraction pattern are presented on Figure 1. The primary nanoparticles in the two samples are characterized by a spherical shape, with close values of mean sizes 23.4 ± 10.1 and 21.6 ± 9.3 nm and lognormal particle size distribution for the Sample 1 and Sample 2, correspondingly. The particle size distributions shows (Figure 2) that the most of the particles’ sizes are detected to be from 4 to 45 nm, a few single particles with sizes of 50-75 nm were observed. Pursuant to high-resolution TEM images, we had concluded that all particles had a core-shell structure with a crystalline core and an amorphous shell. Herewith, small crystals with sizes of 2-7 nm were found to be diamond-like germanium (Figure 1d), while large particles with the sizes above 12 nm were detected to be β-Sn crystals (Figure 1c). Selected area electron diffraction (SAED) pattern collected from agglomerate (Figure 1b) includes weak diffuse ring close to the central beam which is corresponds to germanium (111) lattice plane and two intensive side by side rings consisting of bright spots from β-Sn planes (200) and (101) with close interplane distances 2.91 and 2.79 Å, correspondingly.

![Figure 1(a-d). (a) Typical TEM image; (b) SAED pattern; (c) HRTEM of Sn crystal; (d) Ge crystal.](image)

According to the energy dispersive elemental spectra obtained from different nanoparticles and areas of agglomerates from sample 1 (Sn - cathode), the mean atomic fractions of elements is the
following: Ge – 7.4 ± 3.2 at.%, Sn – 31.5 ± 4.6 at.%, O – 61.1 ± 4.9 at.%; for Sample 2: Ge – 8.8 ± 3.4 at.%, Sn – 22.5 ± 4.1 at.%, O – 68.7 ± 6.3 at.%. That is the average percentage of mass fractions of tin to germanium was 4.3 which is equal to alloy Ge_{0.19}Sn_{0.81}. When germanium electrode was a cathode (sample 2) the ratio of atomic fraction of tin to germanium in the nanoparticles was found to be 2.6, in other words if not counting the presence of oxygen Ge_{0.28}Sn_{0.72} alloy was produced. In the spark-discharge generator, to form a current pulse, the high voltage source charges the capacitor to the breakdown voltage of the inter-electrode gap, and periodic damped oscillations occur in the electric circuit. As estimated in our circuit 55% of the stored energy is released at the cathode [16]. Thus, as the coefficient of ablation material depends on discharge energy and physical properties of the material, we found out in case the material acts as the cathode its relative mass fraction in nanoparticles alloy is higher than in the case this material is an anode. That is, altering the polarity of electrodes produced from different materials we can manage the alloy composition.

Further compositional analysis was conducted by EDX spectroscopy elemental mapping of agglomerate (Figure 3a), which demonstrates the uniform distribution of germanium, tin and oxygen within the agglomerate. Figure 3b shows the elemental profile scanning along of diameters of two nanoparticles: β-Sn crystal 50 nm in diameter, in which the intensity of oxygen and germanium are constant for the whole particle only with small increase in the boarders (shell of the particle), and nanoparticle 20 nm in size probably of complex oxide GeSnO. Figure 3c presented nanoparticle 30 nm in diameter that is likely to be solid solution of GeSn with germanium atoms embedded in tin crystal structure, in which the intensity of germanium increase with the increase of tin content. According to FTIR absorption spectra the main absorption bands at 525 and 780 cm⁻¹ were detected for two alloys. While germanium oxide FTIR peaks it is known to be at 570 and 850 cm⁻¹, and for tin oxide bands are located at 460 and 620 cm⁻¹. Reference core-shell particles of germanium-germanium oxide and tin-tin oxide, produced by spark-discharge at the study were described by similar FTIR peaks positions as mentioned above. Consequently, it was assumed that nanoparticles’ shell consist of the amorphous mixed germanium - tin oxide.

The Raman spectroscopy spectra presented at Figure 4 showed the presence of one intense peak at the 279.5 and 283 cm⁻¹ positions for the first (Sn-cathode) and second (Ge - cathode) samples, respectively. Concordantly to different works [17-18] the peak assigned to Ge-Ge optical mode in crystalline bulk germanium is located at position around 300 cm⁻¹, correctly it is disposed from 298 to 301 cm⁻¹. It is also known that Raman frequency attributed to vibrations of the Ge-Ge bonds decrease as a function of increase Sn-concentration [19]. Position of the Raman peak attributed to vibrations of Sn-Ge bonds has a frequency about 260 cm⁻¹ [20]. The shape of the peaks is considered to be the sum

![Figure 2](image-url)
of several broad Gaussian peaks at positions near 280 and 260 cm$^{-1}$. As a result we suppose that the obtained Raman peak is a superposition of two vibrations modes of intense Ge-Ge and weak Ge-Sn bonds. As the wavenumber of Ge-Ge bond in the sample 1 is lower than for sample 2, we conclude that the sample 2 includes more Sn-content. This conclusion confirms well the results of EDX analysis.

![Figure 3](attachment:image.png)

**Figure 3 (a-c).** Composition analysis by energy dispersive x-ray spectroscopy. (a) Elemental mapping images by scanning TEM image of GeSn agglomerate; EDX line scanning along (b) the core-shell Sn nanoparticle, (c) probably homogeneous alloy of GeSn in oxide matrix.

![Figure 4](attachment:image.png)

**Figure 4.** Raman spectra of two samples of GeSn alloy nanoparticles prepared at spark discharge generator during simultaneous erosion of Sn-cathode and Ge-anode (black curve) and Ge-cathode and Sn-anode (red curve).
For a more detailed analysis of produced GeSn alloys turn to investigation described at [19, 21] which defined the models that with increase of tin content Raman peak shifted to low wave numbers as like line functions. Referring to this models and experimental results obtained samples of alloys with Raman peaks 279.5 and 283 cm\(^{-1}\) corresponds to Ge\(_{1-x}\)Sn\(_x\) alloy with \(x\) in the range from 0.20 to 0.28. Heterostructures based on a GeSn layers with such tin content can be used to create lasers operating at a temperature of 270 K in the infrared region from 3 to 4 μm [22]. The discrepancy of Sn to Ge concentration ratio obtained by EDX and Raman spectroscopy is most likely due to the fact that EDX is a local analysis and the agglomerates includes the mix of tin particles and solid solution alloy GeSn particles with amorphous oxide tin-germanium shell.

In summary, we have demonstrated that mixed GeSn nanoparticles with average diameter about 22 nm with different mass fractions of tin were obtained by altering the polarity of tin and germanium electrodes in spark discharge generator. When the germanium electrode was the cathode the ratio of atomic fraction of Ge to Sn in alloy was 1.7 times higher that when the tin electrode was the cathode. Raman peak position shift by 3.5 cm\(^{-1}\) to lower wave numbers (279.5 cm\(^{-1}\)) with an increase in relative fraction of tin was detected. Thus, the obtained alloy Ge\(_{1-x}\)Sn\(_x\) nanoparticles with proposed Sn content \(x\) from 0.20 to 0.28 potentially can have photoluminescence in the infrared region above 2 μm and find wide applications for creating devices operating in the infrared region.

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