Influence of the sintering temperature on morphology of alloy germanium-tin nanoparticles synthesized by spark discharge

A A Lizunova, V I Borisov, V V Ivanov

Moscow Institute of Physics and Technology, National Research University, Institutsky lane 9, Dolgoprudny, Moscow region, 141700, Russia.

Corresponding author’s e-mail: lizunova.aa@mipt.ru

Abstract. Alloy GeSn airborne nanoparticles (NP) with the rate of atomic content of Sn to Ge 30 % were produced by spark discharge during simultaneous erosion of germanium and tin electrodes in atmosphere of argon of purity 6.0. Then NP were moved by gas flow to a tube furnace, which were mounted directly after discharge chamber, and sintered at temperatures from 25 to 750 °C. The change of morphology, element composition and crystal structure of NP were investigated using transmission electron microscopy (TEM) with energy dispersive X-ray analysis (EDX), aerosol spectrometer and Fourier-transform infrared spectroscopy (FTIR). Agglomerates of predominantly amorphous primary NP with the mean size of 7 nm were obtained at low sintering temperatures of the tube furnace (25 and 200 °C). High temperature (550 and 750 °C) flow-through thermal sintering of NP agglomerates resulted in production of individual crystal NP with an average size of 28 nm with various crystal structures.

1. Introduction

Nowadays, GeSn is a promising material for different infra-red applications compatible with the existing silicon processing technology, such as quantum well infrared photodetectors [1], light emitting diodes [2] and lasers [3] which can operate at room temperature. The incorporation of Sn in Ge makes it possible to alter the electronic band system of germanium and, theoretically, manipulate band gap width of GeSn material from 0 to 0.65 eV [4] by changing the tin concentration. In this case, to obtain a material with photoluminescence in the mid-IR range (3–8 μm), it is necessary to obtain a GeSn alloy with a high tin content.

By increasing the tin concentration from 9 to 12.5 %, various researcher groups experimentally achieved the GeSn alloy with a direct bandgap and PL luminescence up to 2 μm [5, 6]. Disappointingly, the developing of GeSn films using molecular beam epitaxy with higher Sn content has turned out to be indeterminable due to a large lattice mismatch between Ge and Sn and limits of the preparation method [7].

On the other hand, the spark ablation technology was successfully applied for producing of binary, ternary and even senary alloy nanoparticles from immiscible metals [8, 9]. The preparation/synthesis of alloys during a simultaneous electrodes erosion from various materials in a gas-discharge aerosol generator was previously shown by a group of European scientists in 2010 using the example of metal alloys Ag-Cu, Au-Pt, Cu-W [10]. Also a spark discharge enables to fabricate pure metal [11, 12], semiconductor [13, 14] and oxide nanoparticles [15, 16]. Furthermore, it is an advanced technique for aerosol nanoparticle production for 3D aerosol printing [17] and preparation of platinum and tin oxide powders for developing inkjet inks for gas sensors [18, 19].

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd
It is known that temperature sintering can lead to dramatically change in morphology and physical-chemical properties of nanoparticles [20, 21]. It was found that additional thermal sintering of nanoparticles directly in gas flow leads to altering photo luminescent and absorption properties of Ge nanoparticles [20, 22]. As well as postdeposition thermal annealing is an efficient method to improve crystalline quality and strain relaxation of GeSn films [23].

Thus, the objective of this work was to investigate the size, element composition and morphology of germanium-tin nanoparticles, produced by the spark ablation of electrodes of two different materials (tin and germanium) in atmosphere of argon of purity 6.0, with additional in-flow sintering at temperatures from 25 to 750 °C.

2. Methods and Materials
In this work, GeSn nanoparticles were produced by a custom made spark discharge generator with simultaneous erosion and evaporation of germanium cathode and tin anode under the following conditions: argon flow (purity of 6.0) of 2.5 L/min, a capacitor 38 nF, an interelectrode gap voltage 3 kV, a pulse repetition rate 550 Hz, an electrical circuit provided current damping for one period by using a ballast resistor 5 Ω. Then the synthesized nanoparticles were moved by an argon carrier gas to the tube furnace with temperature in the range from 25 to 750 °C, after which they were deposited on a copper grid with a carbon film for transmission electron microscopy investigations. The schematic illustration of nanoparticles formation during evaporation of two different electrodes is shown on figure 1a.

![Figure 1.](image)

Figure 1. (a) Scheme of gas-phase synthesis of GeSn nanoparticles, (b) typical EDX spectrum of nanoparticles agglomerates produced at 25 °C and (c) average size of primary nanoparticles and their agglomerates vs. sintering temperature, measured by TEM and in-flow aerosol spectrometer analysis, correspondingly.

The dispersed composition (size distribution and concentration) of aerosol nanoparticles was measured in real-time using a TSI SMPS 3936 aerosol spectrometer. The size of the primary nanoparticles in the agglomerates, morphology, elemental composition and crystal structure of the obtained alloy NP were investigated by Jeol JEM-2100 (200 kV) transmission electron microscope with energy dispersive X-ray spectrometer X-MAX™ OXFORD Instruments. Chemical composition and existence of alloy oxides were studied by Fourier-transform infrared spectroscopy using Nicolet™ iS50 FTIR Spectrometer (Thermo Scientific).
3. Results and discussion
In-flow measurements of the agglomerates median diameter by the aerosol spectrometer showed a dramatically decrease in size from ~320 to ~75 nm while the sintering temperature growth from 25 to 750 °C (figure 1c), whereas the average size of primary nanoparticles obtained by TEM image analysis increased from 7 to 28 nm. Thus, the morphology and size of the GeSn airborne nanoparticles dramatically changed during the thermal sintering. TEM images show the change in particle morphology, which is caused by progressive melting of the primary nanoparticles in agglomerates, resulting in the formation of liquid drops and recrystallization.

Element composition of nanoparticles obtained by the energy dispersive X-ray analysis shows that the average ratio of Sn to Ge is equal to 0.3 for four samples of GeSn materials, prepared at different temperatures. The typical EDX spectrum obtained from agglomerates, synthesized at room temperature is presented at figure 1b. Agglomerate to agglomerate element composition is quite stable and varies a little for atomic ratio of Sn to Ge from 0.25 to 0.4. At low temperatures of 25 and 200 °C, particles contain a lot of oxygen about 35 Wt. %. With temperature growth the mass fraction of oxygen decreases to 26 and 15 % for 550 and 750 °C, respectively. The oxygen is present in the amorphous matrix of agglomerates, produced at 25 and 200 °C, and shells of the particles, which were prepared at high temperatures.

TEM images of GeSn nanoparticles sintered at different temperatures are presented on figure 2; they show different morphologies of the particle ensembles. Nanoparticles prepared at room temperature form large fractal-like structure agglomerates of primary particles, which are 3–14 nm in diameter with an average size of 7.1 ± 2.5 nm. A few big spherical crystal particles with diameter from 40 to 70 nm were found. The same particle morphology was observed for the sample, prepared at 200 °C with an average size of 7.4 ± 2.8 nm. According to selected area electron diffraction (SAED) pattern with weak ring reflexes and high-resolution TEM (HRTEM) images, morphology of nanoparticles prepared at low temperatures was agglomerates of probably Ge crystals with the sizes from 3.5 to 9 nm embedded in the GeSnO matrix.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** TEM images of GeSn nanoparticles synthesized at different sintering temperatures and corresponding electron diffraction patterns for (a) low-temperature and (b) high-temperature samples. The scale bar is 100 nm.
However, with a further increase in temperature up to 550 °C, the primary particle average size increases by four times to 28 nm, nanoparticles become individual with the sizes various from 13 to 94 nm, characterized by oval and spherical shape and predominantly crystalline structure. Typical SAED patterns are described by strong ring reflexes formed by big crystals of separate cubic germanium and β-tin materials and probably GeSn solid solution. The interplanar distance for (111) plane of cubic Ge and GeSn is closed to each other and was 0.33 nm. So, the difference of d-spacing between Ge and solid solution GeSn, unfortunately, could not be distinguished by HRTEM or SAED patterns. According to high-resolution TEM images (figure 3), most of the particles which were sintered at 550 and 750 °C have a core-shell structure with the heterogeneous core of two crystals: β-tin and cubic germanium with a crystal interface, and an amorphous shell of a complex oxide, presumably GeSnO.

![HRTEM images and EDX line profiles for Ge, Sn and O of GeSn nanoparticles produced at 750 °C](image)

Figure 3. HRTEM images and EDX line profiles for Ge, Sn and O of GeSn nanoparticles produced at 750 °C: (a) bicrystal NP with independent germanium and tin crystals with grain boundary, (b) core-shell nanoparticle with probably solid solution GeSn core and amorphous oxide shell. Represented EDX profiles and HRTEM images were obtained from different nanoparticles with the same crystal structure.

The EDX line profiles of GeSn nanoparticles confirm bicrystal formation of nanoparticles: one part of the particle contains only tin while the second part characterized by only germanium material with small amount of oxygen in both parts (figure 3a). According to EDX analysis, the tin content in the sample with sintering temperature 750 °C varies significantly from particle to particle. There are
particles in which the tin content is higher than germanium, and vice versa. Thus, the tin and germanium crystals sizes vary in a wide range from particle to particle. By EDX line scan element analysis it was found a few crystal particles with simultaneous existence of tin and germanium in the core of the particle (figure 3b). The measured d-spacing of the particles is 0.33 nm, that can be corresponded to Ge (111) or GeSn (111) plane distances. So, we suggested that these particles have a solid solution GeSn core, but at the same time it can be germanium crystal core with thick GeSn oxide shell.

According to FTIR absorption spectra the main absorption bands at 550 and 840 cm\(^{-1}\) were detected for two alloys prepared at 25 and 200 °C. None of these peaks was detected for nanoparticles which were sintered at high temperatures 550 and 750 °C. It is known that two intense Ge-O bands were detected at 570 and 820 cm\(^{-1}\) for germanium NP synthesized in spark discharge [20]. These peaks were attributed to the Ge-O-Ge bending vibration mode and to the stretching vibration mode of the same group, and tin oxide bands are located at 460 and 620 cm\(^{-1}\). Thus, we suggested that the amorphous matrix of agglomerates, prepared at 25 and 200 °C is related to complex GeSn oxide with a small tin content as in the paper [24]. Extreme heating above 550 °C of the nanoparticles in an inert atmosphere resulting in deoxidization of germanium-tin oxide to pure metal and semiconductor crystals.

In summary, mixed germanium-tin nanoparticles of various morphologies were obtained in a wide range of sizes from 3 to 94 nm using the spark discharge technology with an additional thermal sintering of particles at temperatures from 25 to 750 °C in an argon flow. The agglomerates of germanium crystals in amorphous complex probably GeSn oxide matrix with average size of primary nanoparticles about 7 nm were produced at low sintering temperatures 25 and 200 °C. The individual core-shell nanoparticles were prepared during an additional sintering at 550 and 750 °C and had four times larger mean sizes up to 28 nm. The core of mostly obtained nanoparticles was heterogeneous with cubic germanium and β-tin crystals, some of individual nanoparticles probably have solid solution GeSn crystal of the core. Thus, production of germanium-tin nanoparticles by the spark discharge technology with different sizes, morphologies and crustal structure can be controlled by the temperature of an additional thermal sintering. This is a perspective method for creating infrared devices based on semiconductor wafers using aerosol jet-printing technology [17,18].

**Acknowledgments**

This work was financially supported by Russian Science Foundation (project No. 19-79-00337).

**References**

[1] Lee K-C, Lin M-X, Li H, Cheng H-H, Sun G, Soref R, Hendrickson J R, Hung K-M, Scajev P and Medvids A 2020 *Appl. Phys. Lett.* **117** 012102

[2] Zhou Y, Dou W, Du W, Pham T, Ghetmimi S A, Al-Kabi S, Mosleh A, Alher M, Margetis J, Tolle J, Sun G, Soref R, Li B, Mortazavi M, Naseem H and Yu S-Q 2016 *Journal of Applied Physics* **120** 023102

[3] Soumava G, Mukhopadhyay B and Sen G 2020 *Semiconductors* **54** 77–84

[4] Marris-Morini D, Vakarin V, Ramirez J M, Liu Q, Ballabio A, Frigero J, Montesinos M, Alonso-Ramos C, Roux X L, Serna S, Benedikovic D, Chrastina D, Vivien L and Isella G 2018 *Nanophotonics* **7** 1781–93

[5] He G and Atwater H A 1997 *Phys. Rev. Lett.* **79** 1937–40

[6] Julsgaard B, Driesch N von den, Driesch N von den, Tidemand-Lichtenberg P, Pedersen C, Ikonick Z and Buca D 2020 *Photon. Res., PRJ* **8** 788–98

[7] Sadofyev Y, Martovitsky V, Bazalevsky M, Klekovkin A, Averyanov D and Vasil’evskii I 2015 *Semiconductors* **49** 124–9

[8] Tabrizi N S, Xu Q, Pers N M van der and Schmidt-Ott A 2010 *Journal of Nanoparticle Research* **12** 247–59

[9] Feng J, Chen D, Pikhitsa P V, Jung Y, Yang J and Choi M 2020 *Matter* **3** 1646–63

[10] Blomberg S, Gustafsson J, Martin N M, Messing M E, Deppert K, Liu Z, Chang R, Fernandes V R, Borg A, Grönbeck H and Lundgren E 2013 *Surface Science* **616** 186–91
[11] Tabrizi N S, Ullmann M, Vons V A, Lafont U and Schmidt-Ott A 2008 J Nanopart Res 11 315
[12] Borisov V I, Lizunova A A, Mazharenko A K, Malo D, Ramanenka A A, Shuklov I A and Ivanov V V 2020 J. Phys.: Conf. Ser. 1695 012021
[13] Mylnikov D A, Urzov M N, Efimov A A, Lizunova A A and Ivanov V V 2017 AIP Conference Proceedings 1858 040007
[14] Lizunova A A, Mylnikov D A, Efimov A A and Ivanov V V 2017 J. Phys.: Conf. Ser. 917 032031
[15] Efimov A A, Volkov I A, Ivanov V V, Vasiliev A A, Varfolomeev A E, Pislyakov A V, Lagutin A S and Maeder T 2016 Procedia Engineering 168 1036–9
[16] Ivanov V V, Efimov A A, Myl’nikov D A and Lizunova A A 2018 Russ. J. Phys. Chem. 92 607–12
[17] Kornyushin D V, Efimov A A, Khabarov K M and Ivanov V V 2020 J. Phys.: Conf. Ser. 1695 012032
[18] Volkov I A, Simonenko N P, Efimov A A, Simonenko T L, Vlasov I S, Borisov V I, Arsenov P V, Lebedinskii Y Y, Markeev A M, Lizunova A A, Mokrushin A S, Simonenko E P, Buslov V A, Varfolomeev A E, Liu Z, Vasiliev A A and Ivanov V V 2021 Applied Sciences 11 526
[19] Efimov A, Arsenov P, Kornyushin D, Lizunova A, Volkov I and Ivanov V 2020 Materials 13 730
[20] Lizunova A, Mazharenko A, Masnaviev B, Khramov E, Efimov A, Ramanenka A, Shuklov I and Ivanov V 2020 Materials (Basel) 13 4431
[21] Lizunova A A, Efimov A A, Arsenov P V and Ivanov V V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 307 012081
[22] Malo D, Lizunova A A, Ramanenka A A, Masnaviev B I, Solovey V R and Ivanov V V 2020 J. Phys.: Conf. Ser. 1695 012123
[23] Wang L, Zhang Y, Wu Y, Liu T, Miao Y, Meng L, Jiang Z and Hu H 2020 IEEE Transactions on Electron Devices 67 3229–34
[24] Lizunova A A, Borisov V I, Masnaviev B I, Solovey V R and Ivanov V V 2020 J. Phys.: Conf. Ser. 1695 012017