Near-infrared photoluminescence and micro-Raman study of spark discharge germanium nanoparticles

D Malo1,2, A A Lizunova1, A A Ramanenka3, B I Masnaviev1, V R Solovey1 and V V Ivanov1

1 Phystech School of Electronics, Photonics and Molecular Physics, Moscow Institute of Physics and Technology, Dolgoprudny, 141701, Russia
2 Biomedical Engineering Department, Faculty of Mechanical and Electrical Engineering, Damascus University, Damascus, Syria
3 B.I. Stepanov Institute of Physics NASB, 220072 Minsk, Belarus

Abstract. We report the investigation of near-infrared (NIR) photoluminescent and structural properties of aerosol germanium nanoparticles, synthesized by spark discharge method followed by sintering in a tube furnace at different temperatures varying from 25 to 750 °C. We demonstrate a growth of mean primary particle size and change in morphology from agglomerates of germanium nanocrystals in amorphous matrix to individual pure crystal germanium nanoparticles with temperature increase. Pure germanium nanoparticles were prepared at temperatures above 600 °C and distinguished by absence of near-infrared photoluminescence. According to Raman spectroscopy the presence of amorphous germanium in the samples, sintered at 25 to 450 °C, leads to appearance of the luminescence in infrared region with intensity increase from 1100 to 1550 nm.

1. Introduction
Germanium nanoparticles (NPs) continue to be a subject of interest for achieving enhanced properties of light emitters in various quantum technologies especially for biomedical applications and optoelectronic devices due to its unique photoluminescent properties, in particular, the possibility of emission in wide range, from UV through the visible to the near-infrared (~ 1.7 mkm) [1]. Unique photoluminescent properties were discovered for germanium nanoparticles both for colloids [2] and metal-oxide-semiconductor structures based on embedding germanium nanoparticles in silicon structures [3, 4]. It is known, that by varying the size of nanoparticles from 2 to 5 nm it is possible to alter the PL of the germanium colloid particles in a wide range from 300 to 1600 nm [5, 6]. Nevertheless, the maxima of luminescence peaks are affected not only by the particles’ size, but also by size distribution width, structure, method of synthesis and surface properties [7]. Thus, the synthesis of NPs by spark discharge [8] is the most promising method for studying the photoluminescent characteristics of various materials, including nanoparticles of metals and semiconductors [9-11]. Since this method allows controlling the size, crystal structure, elemental composition and other physical properties of NPs depending on synthesis conditions [12, 13]. Moreover, this method can be used as a source of photoluminescent NPs in aerosol jet printing [14, 15] with the goal to form microstructures for biomedical and optoelectronic applications. Thus, the aim of our work is to study the size, structural properties and NIR luminescence of aerosol Ge NPs produced by spark discharge method.
2. Materials and methods

Germanium nanoparticles were synthesized using the aerosol spark discharge generator [8], which was supplemented by a tube furnace, that was located after spark-discharge chamber, and where nanoparticles were sintered at different temperatures directly in gas flow [16]. Five samples were produced at various temperatures of the furnace: 25, 300, 450, 600 and 750 °C. Cylindrical n-type germanium was used as electrodes for electrical erosion. Spark processing was performed in argon gas of 99,999 purity, the pressure was maintained at 1.5 bar. The frequency of the discharges and the capacitor voltage were 370 Hz and 1.5 kV, respectively. Aerosol NPs were collected on a cellulose filter and TEM copper grids with carbon film directly in the setup chamber.

Fluorescence measurements in the IR region were performed on the Fluorolog-3 spectrophotometer (Horiba Scientific) with laser excitation at 532 nm. Micro-Raman spectroscopy studies was carried out with a LabRAM HR Evolution (Horiba Scientific) using the 532 nm excitation wavelength of the He-Ne laser (0.1mW) directly on nanoparticles collected on the cellulose filter. The particle size properties and crystal structure of the samples were analyzed with the aid of transmission electron microscopy (TEM) Jeol JEM 2100 (200 kV).

3. Results and discussion

According to the analysis of TEM images, the mean size of primary nanoparticles increased with raising of sintering temperature from 6.8 ± 5.2 nm for 25 °C sample to 51.3 ± 31.8 nm for 750 °C, the width of the particle distribution by size and the proportion of large particles also increased. The particles sintered at temperatures from 25 to 450 °C formed agglomerates, at 750 °C individual Ge particles were observed (Figure 1). High resolution TEM images presented in Figure 2 show the typical agglomerate, obtained at low temperatures below 450 °C with small germanium crystals 4 – 11 nm in size embedded in an amorphous matrix. Only spherical germanium crystals without any shell were observed in the samples, sintered at the temperatures of the furnace above 600 °C. Electron diffraction patterns on inserts in Figure 1 show the presence of only germanium crystal with cubic lattice (Fd3m) with lattice constant 5.656 Å independently on the sintering temperature. As shown at Figure 3 the Raman spectrum of the as-synthesised Ge nanoparticles in spark discharge and with additional heat treating below 450 °C characterized by two broad peaks around 275 cm⁻¹ and 298 cm⁻¹. While for the samples sintered at high temperatures above 600 °C the presence of only one peak with maximum at position 298.3 cm⁻¹ was observed. 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, and position of the Raman peaks attributed to vibrations of amorphous Ge bonds has a diffuse frequency at 85, 190, 240 and 275 cm⁻¹ correspond to TA, LA, LO and TO modes, respectively [19, 20]. Thus, we demonstrated that mix of amorphous and crystalline germanium are produced in spark discharge with additional heat treating at low temperatures below 450 °C whereas the sintering above 600 °C, induces a crystallization of the amorphous phase, causes the increase of intensity of the phonon Ge-Ge peak at 298 cm⁻¹ and disappearance of amorphous phase.

It is known, that the width of Raman peak attributed to vibrations of the Ge-Ge bonds decreases as a function of increase size of germanium crystals [21] The full width at half maximum (FWHM) for obtained nanocrystalline germanium of Raman band Ge-Ge bond (298.3 cm⁻¹) decrease from 11.4 to 6.0 cm⁻¹ with the increase of sintering temperature from 25 to 750 °C. To calculate denoted FWHM values the shape of the obtained peaks for germanium nanoparticles sintered at temperatures below 450 °C was considered to be the sum of two broad Gaussian peaks with maximum at 298.3 and 275 cm⁻¹. According to the linear dependence of the Raman peak width on the reciprocal of germanium crystals’ sizes and the models and experiments presented in the works [21, 22], the sizes of nanocrystalline germanium calculated for the obtained particles increase from 5.3 to 11.4 nm depending on sintering temperature growth from 25 to 750 °C. The discrepancy of TEM and Raman spectroscopy results for primary particles sizes can be explained in the following manner: Firstly, with agreement to HRTEM images large individual nanoparticles obtained above 600 °C are polycrystalline, but we calculated the size of the whole particle not crystals so the sizes received from TEM images are higher than from Raman
spectroscopy. Secondly, the estimations [22] were developed for Ge nanoparticles embedded in SiO$_2$ matrix and have exceptions. Finally, the sizes of primary particles in agglomerates were measured including both the crystal core and amorphous shell.

**Figure 1 (a, b).** Typical TEM images and corresponding SAED patterns (on the insert) for (a) germanium nanoparticles agglomerates, formed during synthesis at low temperatures from 25 to 400 °C, (b) individual spherical nanoparticles obtained for samples with extra sintering at high temperatures above 600 °C.

**Figure 2 (a, b).** High resolution TEM images of germanium nanoparticles for samples sintered at: (a) 25 °C and (b) 750 °C.

Figure 3b represents the near-IR luminescence for obtained germanium nanoparticles. The photoluminescence intensity increased from 1100 to 1550 nm for Ge NPs prepared at 25, 300, 450 °C were observed. Herewith, the absence of near-IR luminescence for Ge NPs, sintered at 600, 750 °C were established. By comparing the data of Raman spectroscopy and NIR luminescence, it can be assumed that luminescence occurs either in amorphous Ge or on the interface of the crystal—amorphous germanium which occur only in agglomerates of nanoparticles, formed in spark discharge generator with additional low temperature sintering of nanoparticles in the tube furnace.
Figure 3 (a, b). (a) Raman spectra; (b) Near-IR luminescence of germanium nanoparticles, sintered at various temperatures.

In results, we have demonstrated that agglomerates of germanium nanoparticles synthesized in spark discharge generator with additional sintering in tube furnace at the temperatures below 450 ºC have the structure of small crystals embedded in amorphous matrix of germanium and show near-IR luminescence behaviour. While the sintering above 600 ºC, inducing a crystallization of the amorphous germanium phase, leads to disappearance of amorphous germanium and photoluminescence effect in infrared region.

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

References
[1] Vaughn D D and Schaak R E 2013 Chem. Soc. Rev. 42 2861
[2] Shirahata N, Hirakawa D, Masuda Y and Sakka Y 2013 Langmuir 29 7401
[3] Ou H, Ou Y, Liu C, Berg R W and Rottwitt K 2011 Opt. Mater. Express 1 4 643
[4] Seo M A, Kim D S, Kim H S, Choi D S and Jeoung S C 2006 Opt. Express 14 11 4908
[5] Lee D C, Pietryga J M, Robel I, Werder D J, Schaller R D and Klimov V I 2009 J Amer Chem Soc 131 10 3436
[6] Taylor B R, Kauzlarich S M, Lee H W H and Delgado G R 1998 Chemistry of Materials 10 1 22
[7] Carolan D 2017 Progress in materials science 90 128
[8] Ivanov V V, Efimov A A, Mylnikov D A, Lizunova A A, Bagazeev A V, Beketov I V and Shcherbinin S V 2016 Tech. Phys. Lett. 42 876
[9] Ivanov V V, Efimov A A, Myl'nikov D A and Lizunova A A 2018 Russ. J. Phys. Chem. 92 607
[10] Mylnikov D A, Lizunova A A, Efimov A A and Ivanov V V 2017 AIP Conf. Proc. 1858 040007
[11] Mylnikov D, Lizunova A, Borisov V, Paranin S and Ivanov V 2018 Orient J Chem 34 5
[12] Mylnikov D, Efimov A and Ivanov V 2019 Aerosol Science and Technology 53 1393–1403
[13] Arsenov P V, Efimov A A, Protas N V and Ivanov V V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 324 012016
[14] Efimov A, Arsenov P, Kornyushin D, Lizunova A, Volkov I and Ivanov V 2020 Materials 13 730
[15] Arsenov P V, Efimov A A and Ivanov V V 2020 Key Engineering Materials 834 10–15
[16] Lizunova A, Efimov A, Arsenov P and Ivanov V 2018 IOP Conf. Ser.: Mater. Sci. Eng. 307 012081
[17] Bermejo D and Cardona M 1979 Journal of Non-Crystalline Solids 32 979 405–419
[18] Peshko I 2012 Laser Pulses: Theory, Technology, and Applications (IntechOpen)
[19] Volodin V A, Krivyakin G K, Ivlev G D, Prokopyev S L, Gusakova S V and Popov A A 2019 Semiconductors 53 3 400–405
[20] Sasaki Y and Horie C 1993 Phys. Rev. B 47 3811
[21] Gouadec G and Colomban P 2007 Raman Spectroscopy of nanomaterials: How spectra relate to disorder, particle size and mechanical properties Progress in Crystal Growth and Characterization of Materials vol 53 (Elsevier) pp 1-56
[22] Milani P and Bottani C E 1999 Vibrational Spectroscopy of Mesoscopic structures Handbook of Nanostructured Materials and Nanotechnology vol 2 ed H S Nalwa (Academic Press) p 242