Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

Silicon and germanium nanostructures formed by spark discharge plasma

To cite this article: V G Yakunin *et al* 2019 *J. Phys.: Conf. Ser.* **1238** 012052

Silicon and germanium nanostructures formed by spark discharge plasma

V G Yakunin [1], D E Presnov [1,2], M V Stepikhova [3,4], A N Yablonskiy[3,4], R B Assilbaeva [5], T Yu Grevtseva[6], Z Zh Zhanabaev[6], V P Savinov[1] and V Yu Timoshenko [1,7,8]

[1] Lomonosov Moscow State University, Faculty of Physics, Moscow, 119991, Russia
[2] Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University, Moscow, 119991, Russia
[3] Institute for Physics of Microstructures of RAS, 603087 Nizhniy Novgorod, Russia
[4] Lobachevsky State University, 603950 Nizhny Novgorod, Russia
[5] Satpayev Kazakh National Technical University, 050013, Almaty, Kazakhstan
[6] al-Farabi Kazakh National University, Almaty, Kazakhstan
[7] National Research Nuclear University "MEPhI", Phys-Bio Institute, 115409 Moscow, Russia
[8] Lebedev Physical Institute of RAS, 119333 Moscow, Russia

E-mail: vtimoshe@gmail.com

Abstract. Formation of semiconductor nanostructures on the surface of single crystalline silicon and germanium wafers by spark discharge plasma in air was investigated. The prepared nanostructures were analyzed by means of the scanning and transmission electron microscopy and optical spectroscopy of the photoluminescence and Raman scattering. The formed nanostructures exhibit a fractal-like morphology with interconnected nanocrystals of 2-200 nm sizes that is explained by repeated processes of spark ablation and subsequent condensation. While the size and morphology of the nanostructure depend on power sources of the spark discharge, short interaction times of spark discharge plasma and target determine a relatively low efficiency of the chemical oxidation of germanium and silicon, as well as low ionic temperatures of the plasma.

Keywords: spark discharge, plasma, ablation, nanocrystals, fractals, Raman scattering, photoluminescence

1. Introduction

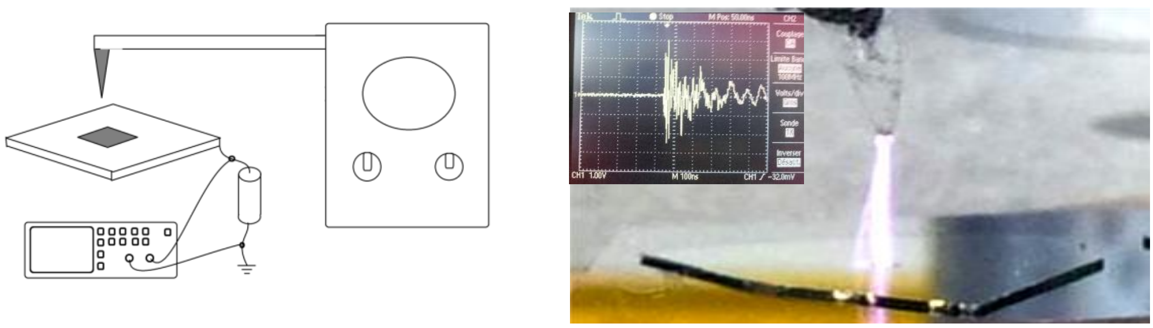
Different types of spark discharge were used to produce nanoparticles of semiconductors and metals [1-4]. Spark ablation represents a process in which the substance is removed from the electrodes due to the spark plasma excitation and then it is deposited in the form of nanoparticles or nanoclusters. If the electrodes, which are usually a tip and substrate, are made of the same material, it is possible to obtain nanoparticles without external impurities, since the reaction rate and the conditions of the ablation process exclude the possibility of interaction of evaporated particles with the environment. The size and type of the nanostructure obtained by ablation are determined by the concentration of particles in the gas cloud of the evaporated substance, since it is the concentration that regulates the process of coagulation and condensation of particles. Reducing the concentration of ablated material in gas phase or liquids makes it possible to reduce the size of deposited nanoparticles of conventional semiconductors, metals and metal oxides [1, 2. 5].

IOP Conf. Series: Journal of Physics: Conf. Series **1238** (2019) 012052 doi:10.1088/1742-6596/1238/1/012052

Silicon (Si) nanocrystals obtained during spark ablation were found to exhibit photoluminescence (PL) in the visible range [3]. Spark-discharge treatment of crystalline germanium (c-Ge) in air resulted in formation of strongly oxidized Ge nanostructures with PL properties, which were attributed to the radiative transitions between defect levels [4]. Our recent work is devoted to study the formation of nanostructures on the surface of c-Si and c-Ge wafers during their processing by spark discharge in air ambient.

2. Experimental

Experiments were carried out with one-side polished low doped c-Si and c-Ge wafers, which were subjected to spark discharge processing by using different power sources. The power supply unit of ILGA-503 type nitrogen laser was used in the first source, and self-made generators based on the high – voltage ignition coil, e.g. model 27.3705, and so-called Tesla spark discharge generator were also used. In all experiments, the total duration of radio pulse did not exceed 1 μs, the repetition rate of high – frequency pulses was about 100 ns, and the repetition rate of pulse series was about 10 Hz. The average current in the first source was in the range of 1-10 mA. In the self-made sources the average current was always less than 1 mA, so the power of spark discharge was much less. The experiments were carried out at atmospheric pressure in air. Exposure time was varied from 1 to 40 min. A scheme of the experimental set-up and the photographic image of the spark processing of a semiconductor plate are shown in Figure1.

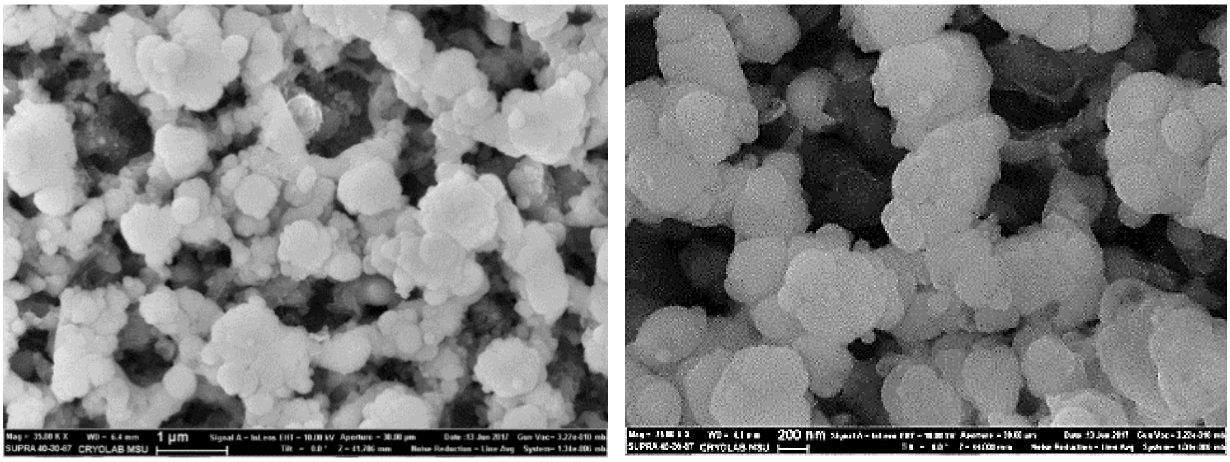


(a) (b)

Figure 1. Scheme of the experimental set-up (a) and a photograph of the spark processing of a semiconductor wafer (b). Inset in panel (b) shows a typical transient (scale bar 100 ns) of the electrical current under spark discharge.

3. Results and Discussion

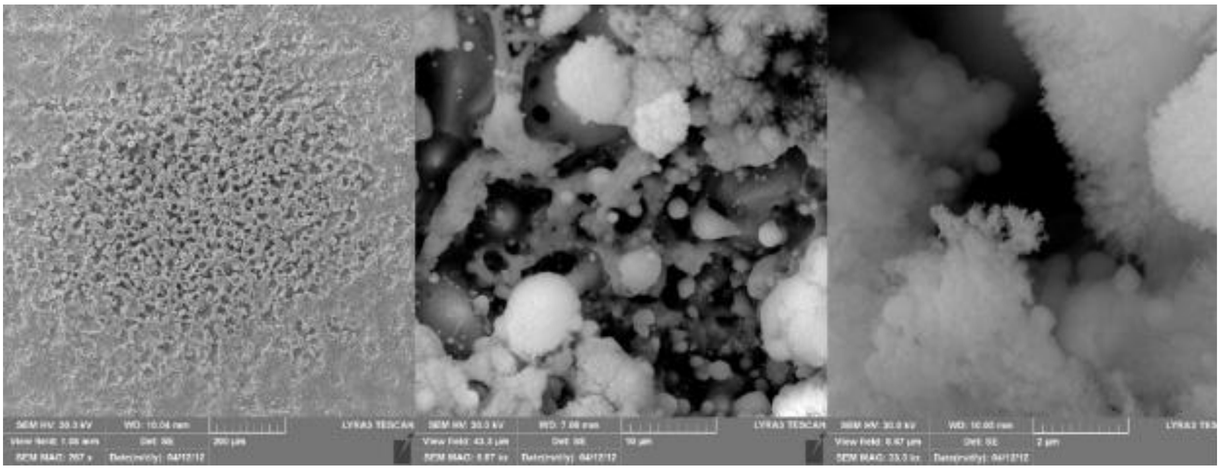
Figure 2 shows typical scanning electron microscopy (SEM) images of a c-Si wafer after spark-processing by high and medium power supplies for 30 min. The images reveal the presence of nanoparticles with sizes from about 10 nm up to 500 nm. Using the approach developed in Refs.[6,7], we analyzed the SEM c-Si plates after prolonged treatment in spark discharge (Fig. 2), which gave the value of the fractal dimension of 1.8 - 1.9 of the spark ablated nanostructures. The latter value is close to 2D dimensionality that indicates the role of internal surface of the formed nanostructeres.



(a) (b)

Figure 2. SEM images with smaller (a) and larger (b) magnification of the surface of c-Si wafers after prolonged treatment with high power spark discharge.

Experiments have shown that structures of bound nanoparticles of different sizes are formed on the surface of c-Ge plates after long treatment with a spark discharge of low power (see Figure3), reminiscent of the fractal structure of silicon, discussed above.

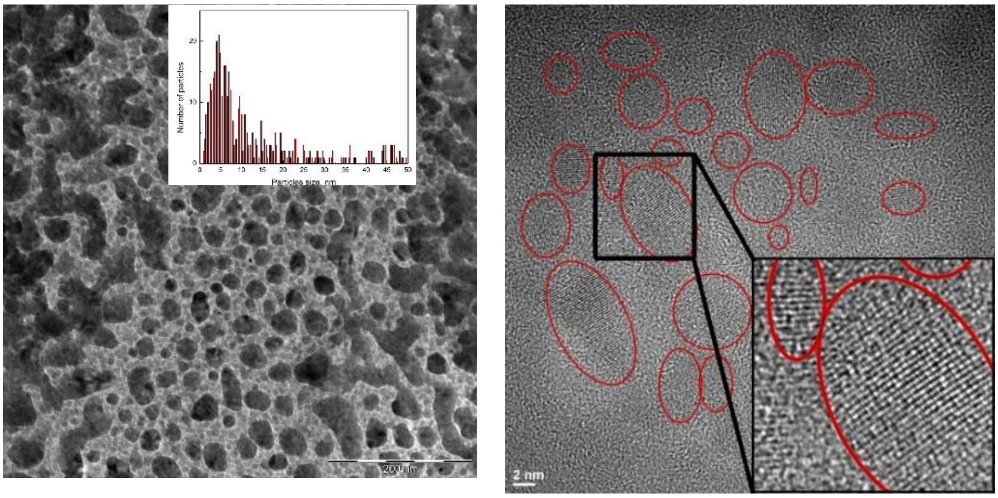


(a) (b) (c)

Figure 3. SEM image of the surface of c-Ge wafer after treatment with a low-power spark discharge for 20 min. The scale bars in panels (a), (b) and (c) are 200, 20 and 2 μm, respectively.

It was found that the nanoparticles formed by spark discharge near the surface of c-Ge are mainly Ge nanocrystals with fractal morphology (Figure 3). Individual Ge nanocrystals with sizes of about several nanometers are observed in TEM pictures (Figure 4). At the same time, the maximum distribution lies in the region of 5-7 nm, but there are also nanoparticles with dimensions of more than 10 nm (see inset in Figure 4a) Study of the nanostructures obtained by means of the high resolution TEM allowed us to identify an individual isolated nanocrystals with sizes from 5 to 20 nm (see Figure 4b).

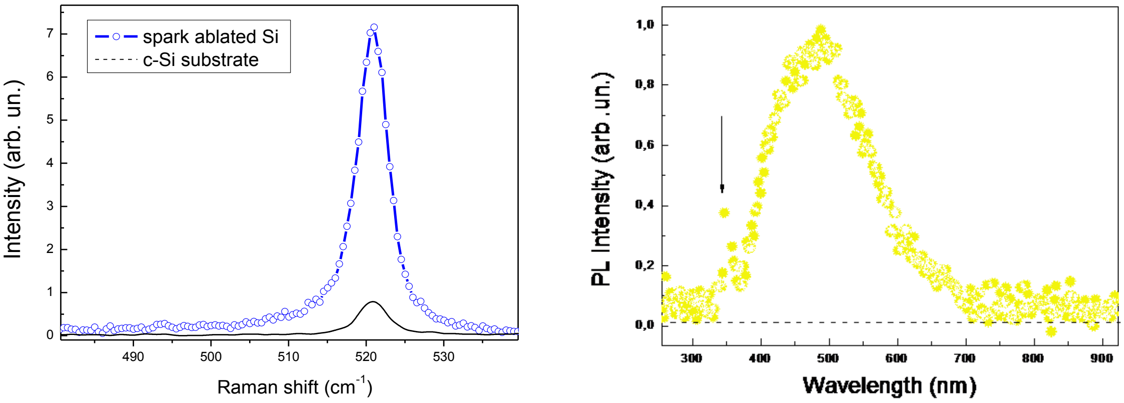
IOP Conf. Series: Journal of Physics: Conf. Series **1238** (2019) 012052 doi:10.1088/1742-6596/1238/1/012052



(a) (b)

Figure 4. TEM images of nanoparticles obtained by processing a low-power c-Ge spark discharge for 20 min at a scale of 600x600 nm^2 (a) and high resolution TEM (b). Insert in panel (a) shows the size distribution of nanoparticles. Panel (b) shows the boundaries of nanocrystals with red oval lines, and the black straight lines and box indicate a separate Si nanocrystal.

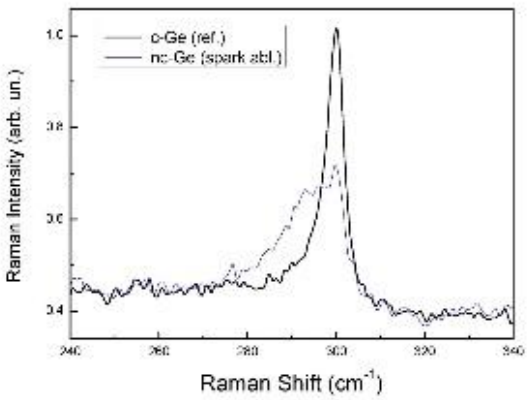
Figure 5 shows Raman and PL spectra of a c-Si wafer after treatment with a spark discharge of high power. It is seen that for the treated part of the wafer, the spark discharge causes a multiple increase in the Raman scattering intensity, which can be explained by multiple elastic scattering of the excitation radiation in randomly located Si nanostructures, similar to that observed in layers of silicon nanowires [8,9]. The Raman line shape of the resulting nanostructures was close to that of initial c-Si wafer that indicate a negligible effect of the phonon confinement [10] (see Fig. 5a). This fact is also in good agreement with the observed SEM images, which revealed nanoparticles with sizes above 10 nm. At the same time, the PL spectra of silicon nanostructures formed by spark discharge exhibit a weak PL band in the region of 400-600 nm (see Fig. 5b), which can be associated with radiative transitions in the oxide layer on the surface of Si nanocrystals with dimensions large enough to realize the quantum confinement effect [11-13].



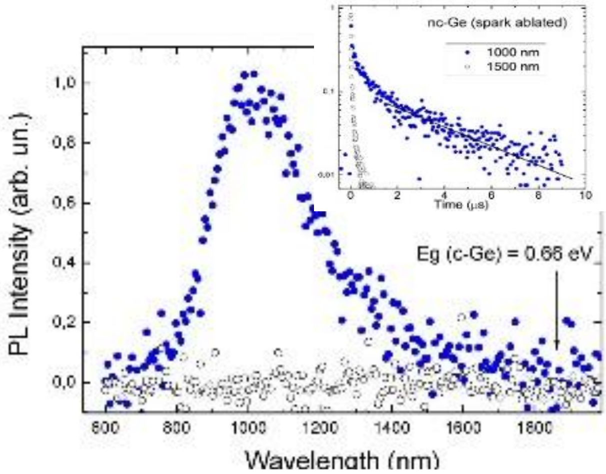
(a) (b)

Figure 5. Raman (a) and PL (b) spectra of c-Si surface after spark discharge treatment. The lower curve in part (b) shows the Raman spectrum for c-Si reference plate. Vertical arrow in part (a) indicates excitation wavelength.

Small nanoparticles with sizes less than 10 nm were observed on the surface of c-Ge wafers after treatment with a low-power spark discharge (Tesla generator) and more powerful sources. As can be seen from Figure 6a, in such nanostructures there is a modification of the Raman spectrum, which indicates an effect of the spatial confinements for phonons in good agreement with the generally accepted model [10]. The experiments showed that the spark-discharge generated Ge nanostructures have a maximum of the PL spectrum near 1 μm and lifetime of about 1 μs (see Fig.6 b). These PL properties are in good agreement with the literature data known for Ge nanocrystals with sizes of about 8-10 nm [13,14].



(a)



(b)

Figure 6. Raman (a) and PL spectra (b) of c-Ge surface before and after spark discharge treatment. Vertical arrow in section (a) indicates the band gap of c-Ge, and the inset shows decay curves of the PL intensity for different wavelengths after pulsed laser excitation.

4. Conclusions

The experiments demonstrated the possibility of formation of small silicon and germanium nanocrystals in the process of spark ablation of the corresponding c-Si and c-Ge wafers in air ambient. The nanocrystal formation is explained by the short time of interaction of spark discharge plasma with the surface of a solid target. Fractal-like morphology of the formed nanostructures is probably caused by repeated processes of the spark ablation and subsequent condensation of the ablated materials. While the short interaction time of spark discharge plasma and target determines a relatively low probability of the oxidation of germanium and silicon, the formed nanostructures possess nanocrystalline origin. The mean nanocrystal sizes were found to be larger than 10 nm and about 5-10 nm for Si and Ge structures, respectively. The spark-ablated Ge nanocrystals exhibit photoluminescence in the near infrared spectral region, which can be attributed to the radiative recombination of excitons in Ge nanocrystals. This fact indicates a low density of the structure defects in the prepared Ge nanocrystals. The observed formation of rather small Si and Ge nanocrystals by using the spark-discharge in air with low power sources can be a good alternative for the laser-ablative synthesis of ultrapure nanoparticles for biomedical applications in both therapy and diagnostics (theranostics) [15]. The spark-discharge synthesis seems to be cheap and simple method to prepare luminescent nanoparticles of Si and Ge, which can be used in bioimaging of cancer cells under excitation with visible and near-infrared radiation sources. While our results confirm the possibility to prepare a small amount of the nanoparticles, the spark processing can be scalable and optimized to obtain required amount of the nanoparticles for biomedical purposes.

Acknowledgments

The authors thank A. Ermishin, A. Fedorenko and D. Petrov for their assistance in the preparation of samples, measurements of TEM and SEM, respectively. The work was partially supported by the

Russian Foundation for Basic Research (project 16-02-00668) and by the Ministry of Education and Science of the Russian Federation (state project 16.2969.2017/4.6). SEM measurements were partially carried out by using the equipment of the "Educational and Methodical Center of Lithography and Microscopy," M.V. Lomonosov Moscow State University Research Facilities Sharing Centre.

References

[1] Berkowitz A E, Walter J L 1987 Spark erosion: A method for producing rapidly quenched fine powders *J. Mater. Res.* **2** 277–288

[2] Ivanov A V, Nikiforov V N, Shevchenko S V, Timoshenko V Y, Pryadun V V, Bulychev N A, Bychenko A B, Kazaryan M A 2017 Properties of metal oxide nanoparticles prepared by plasma discharge in water with ultrasonic cavitation *Int. J. Nanotech.* **14** (7-8) 618-626

[3] Saunders W A, Sercel P C, Lee R B, Atwater H A 1993 Synthesis of luminescent silicon clusters by spark ablation *Appl. Phys. Lett.* 63 (11) 1549 – 1551

[4] Chang S-S, Choi G J, Hummel R E 2000 Optical properties of spark-processed Ge 2000 *Materials Science and Engineering B* **76** 237-240

[5] Vons V A, Anastasopol A, Legerstee W, Mulder F, Eijt S, Schmidt-Ott A 2011 Low-temperature hydrogen desorption and the structural properties of spark discharge generated Mg nanoparticles *Acta Mater*. **59** 3070

[6] Zhanabaev Z Zh, Grevtseva T Yu 2014 Physical fractal phenomena in nanostructured semiconductors *Rev. Theor. Sci.* **2** (3) 211-259

[7] Zhanabaev Z Zh, Grevtseva T Yu, Ibraimov M K 2016 Morphology and electrical properties of silicon films with vertical nanowires *J. Computat. & Theor. Nanosci.* **13** 615-618

[8] Osminkina L A, Gonchar K A, Marshov V S, Bunkov K V, Petrov D V, Golovan L A, Talkenberg F, Sivakov V A, Timoshenko V Yu 2012 Optical properties of silicon nanowire arrays formed by metal-assisted chemical etching: evidences for light localization effect. *Nanosc. Reseach Lett.* ***7*** (1) 524

[9] Gonchar K A, Osminkina L A, Sivakov V, Lysenko V, Timoshenko V Y 2014 Optical properties of nanowire structures produced by the metal-assisted chemical etching of lightly doped silicon crystal wafers *Semiconductors* **48** (12) 1613-1618

[10] Richter H, Wang Z P, Ley L 1981 The one phonon Raman spectrum in microcrystalline silicon *Sol. Stat. Comm.* **39** 625 – 629

[11] Kovalev D, Heckler H, Polisski G, Koch F 1999 Optical properties of Si nanocrystals *Phys. Stat. Sol. (b)* **215** 871-932

[12] Saunders W A, Sercel P C, Lee R B, Atwater H A 1993 Synthesis of luminescent silicon clusters by spark ablation. *Appl. Phys. Lett.* **63**. (11) 1549 – 1551

[13] Chang S S, Choi G J, Hummel R E 2000 Optical properties of spark-processed Ge. *Mat. Sci. & Eng. B* **76** 237-240

[14] Niquet Y M, Allan G, Delerue C, Lannoo M 2000 Quantum confinement in germanium nanocrystals *Appl. Phys. Lett*. **77** (8) 1182-1184.

[15] Kabashin A V, Timoshenko V Y 2016 What theranostic applications could ultrapure laser-synthesized Si nanoparticles have in cancer? *Nanomedicine* **11** (17) 2247-2250.