Synthesis of semiconductor nanostructures in an argon arc

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Abstract. In this paper, the synthesis of semiconductor spherical nanostructures is carried out by the plasma-chemical method. The sizes of the obtained nanospheres range from 100 nm to 1 mm. These structures are open on one side, have thin walls with a thickness of several nanometers, which end with "tentacles" with a diameter of several nanometers. Since the synthesis involved three elements of the fourth group of the periodic table (germanium, silicon, carbon), it has not yet been possible to determine the crystal structure of the obtained samples. All three elements are present on the surface of the sample in atomic percentages Ge-2.5%, Si-8%, C-55%. In addition to these elements, oxygen is also present in the spectrum.

1. Introduction
Non-equilibrium gas-discharge plasma [1,2] has found wide application in the synthesis of nanostructures. The synthesis of germanium and silicon nanostructures is usually carried out by the CVD method. However, as was shown in [3,4], the synthesis of germanium nanostructures can also be carried out in an argon arc. In [3], germanium nanotubes with a thickness of about 900 nm were synthesized in an argon microarc discharge. The catalytic properties of germanium to accelerate the reactions of diamond formation from graphite were used in [4,5]. In [2], the synthesis of diamonds was carried out by the HPHT method for 60 hours, and in [4] – by the plasma chemical method for several seconds. The method of electric arc synthesis of silicon nanotubes is demonstrated in [6]. In this paper, the method of electric arc synthesis in an argon medium is used to synthesize nanostructures from a mixture of elements of the fourth group of the periodic table. Such nanostructures are interesting primarily from the point of view of creating a developed surface and therefore can find application in the anode elements of lithium-ion batteries.

The experimental setup for the synthesis of semiconductor nanostructures consisted of a vacuum chamber with water-cooled walls, an electric power source, a vacuum and gas supply system, and measuring instruments. The vacuum chamber had an observation window for observing the course of the experiment, as well as a special device that allows you to change the distance between the electrodes.

The main difference between this work and all the previous ones is that the anode of the electric arc installation was a graphite rod, in which there was a small recess on the end part filled with a mixture of germanium powder with silicon. The discharge was ignited in an argon medium at a pressure of 500 Torr between the graphite anode and the molybdenum cathode. Ignition and stationary combustion of arc occurred at currents of 25-35 A. The voltage of the order of 30-35 V was supplied through the ballast resistance. The discharge was ignited by directly closing the cathode with the
anode. After the arc was formed, the electrodes were removed to a distance of about two mm. at the same time, a stable arc burned, the anode was heated to red, and intense evaporation of all available elements occurred. Carbon, germanium, and silicon vapors were deposited on the substrate surface and on the surface of the molybdenum cathode. These depositions were analyzed using an electron microscope. Figure 1 shows the image of the cathode surface after the experiment. We see a developed nanostructured surface at a magnification of 1500 times. This surface is mainly composed of nanoballs and oblong structures.

In the following figure (Fig. 2), at a magnification of 4000 times, we can see clusters of spherical formations of different diameters.

Figure 1. Images of nanostructures on the cathode surface with a magnification of 1500 times.
Figure 2. Images of germanium nanostructures on the cathode surface with a magnification of 4000 times.

Figure 3 and Figure 4 show individual plots magnified in 30,000 times and 50,000 times.

Figure 3. Images of nanostructures of germanium on the cathode surface with magnification of 30000 times.

Figure 4. Images of germanium nanostructures on the cathode surface with a magnification of 50000 times.

2. Discussion
From these figures, it can be seen that the nanostructures have the form of truncated spheres with a diameter from 100 nm to 1 µm. The wall thicknesses are on the order of a few nanometers. The nanospheres have a regular geometric shape and are quite close to each other. Some nanospheres have fused together. These structures are open on one side, have thin walls with a thickness of several
nanometers, which end with "tentacles" with a diameter of several nanometers. Since the synthesis involved three elements of the fourth group of the periodic table (germanium, silicon, carbon), it has not yet been possible to determine the crystal structure of the obtained samples. All three elements are present on the surface of the sample in atomic percentages Ge-2.5%, Si-8%, C-55%. It is possible that in carbon nanostructures some carbon atoms are replaced by silicon and germanium atoms. In the case of a more accurate selection of the composition of the powder mixture, it is possible to achieve a more uniform distribution of elements on the surface. In addition to these elements, oxygen is also present in the spectrum.

Based on the analysis of the appearance of the truncated nanospheres, it can be assumed that they acquired their shape as a result of an explosion. After the formation of the sphere is complete, the gases remaining inside heat up and tear the surface of the sphere. Subsequently, a new formation in the form of oblong nanostructures with a thickness of about 10 nm and a length of about 100 nm is localized at the boundary of the surface rupture. The resulting nanospheres will be useful for creating a developed surface of lithium-ion batteries.

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References
[3] Saifutdinov A.I., Timerkaev B.A. & Ibragimov A.R., Numerical Simulation of Temperature Fields in a Direct-Current Plasma Torch. Tech. Phys. Lett.2018. 44, 164–166.
[4] Saifutdinov, A.I., Timerkaev, B.A., Saifutdinova A.A. Features of Transient Processes in DC Microdischarges in Molecular Gases: From a Glow Discharge to an Arc Discharge with a Unfree or Free Cathode Regime. Jetp Lett.2020. 112. 405–412.
[3] Timerkaev B. A., Kaleeva A. A., Timerkaeva D. B., and Saifutdinov A. I.. Synthesizing Germanium Nanotubes in an Electric Arc Plasma. Russian Journal of Physical Chemistry A, Vol. 94, No. 3, pp. 613–617., 2020. Russian Text Zhurnal Fizicheskoi Khimii, 2020, Vol. 94, No. 3, pp. 448–452.
[4] Palyanov Yu.N., Kupriyanov I.N., Borzdev Yu.M., Surovtsev N.V.. Scientific Reports. 2015. V. 5. P. 14789.
[5] Timerkaev B.A., Kaleeva A.A., Timerkaeva D.B., Saifutdinov A.I.. High Energy Chemistry, 53 (2019), pp. 390-395.
[6] Timerkaev B. A., Shakirov B.R, Timerkaeva D.B. Creation of Silicon Nanostructures in Electric Arc Discharge. High Energy Chemistry 53 (2), 162-166. 2019.