Micro-arc method for the synthesis of silicon nanostructures

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Abstract. This paper presents the results of plasma synthesis of silicon nanostructures in an air-argon medium. The synthesis of silicon nanostructures was carried out in a vacuum chamber at a gas mixture pressure of 500 Torr, with partial pressures of argon and air in the ratio of 4:1. Molybdenum and silicon embedded in a copper tube were used as electrodes. Current and voltage were maintained in the range of 8-25 A and 30-50 V, corresponding. As a result of experiments, silicon nanostructures were deposited on the surface of the electrodes. Nanostructures were studied by optical and electron microscopes. Forms of silicon nanostructures were mainly in the form of nanotubes. Their diameters range from 200 nm to 500 nm, and their length reaches 1 mm. On the surface of these nanotubes, nanovilli with a diameter of about 5 nm and a length of 100 nm are observed.

1. Introduction
Nanostructures based on silicon and silicon dioxide: nanopowders, nanotubes and nanofilaments, nanocomposites have the prospect of wide application in nanoelectronics, optoelectronics and solar energy. Replacing a monolithic material with a substance in a nanostructured state allows several times to improve the necessary technical characteristics of the devices in which they are used. In particular, replacing the graphite anode element in lithium-ion batteries with nanostructured silicon will increase the battery capacity several times [1, 2].

Nanostructured materials can be synthesized using chemical and physical methods. For example, by chemical reactions of reduction, disproportionation and etching with subsequent heat treatment, or dissociation of silane due to heating by CO\textsubscript{2} laser radiation, by chemical vapor deposition and thermal evaporation using a catalyst (Au), etc. One of the promising physical methods for the synthesis of nanostructures is the use of various types of gas discharges [3,4]. The glow discharge in relation to the synthesis of nanostructures was studied in [5-8]. The same authors used a glow discharge for the synthesis of fullerenes [9].

For the synthesis of silicon and silicon dioxide nanostructures, we used an electric arc discharge. In the plasma of an arc discharge, due to high temperatures, the material decomposes either to an atomic or molecular state, and then these atoms can combine into nanostructures. The efficiency of the synthesis of silicon nanostructures in arc plasma was shown in [10].

To obtain silicon nanostructures, an experimental setup was assembled, which consists of a water-cooled vacuum chamber, vacuum and gas supply systems, a current source, a ballast rheostat, a rectifier unit, and measuring devices. In the experiments, monocrystalline silicon and molybdenum were used as electrodes. A molybdenum rod with a length of about 6 cm and a diameter of 1 cm with a polished end served as a cathode, and a piece of silicon embedded in a copper tube served as an...
The electrodes were initially fixed at a distance of 1 cm from each other and with the help of distance regulators were movable along the vertical axis.

A number of experiments were carried out on the synthesis of silicon dioxide nanostructures in an arc discharge plasma, with changes in such parameters as current, voltage, chamber pressure and discharge time. To obtain silicon dioxide nanostructures, a mixture of oxygen and argon gases was used in the experimental chamber in a ratio of approximately 1:4, respectively. Therefore, before the experiment, the vacuum chamber was pumped to a pressure of 100 Torr, and then filled with an inert gas-argon to a pressure of about 500 Torr. The pressure in the chamber was monitored using a mercury pressure gauge. The anode, consisting of single-crystal silicon, at room temperatures has a very large electrical resistance, which reaches several thousand ohms*cm. But with an increase in the temperature of silicon, it decreases exponentially and at 500 K it already becomes on the order of several ohms*cm, this is enough to ignite an electric arc. To warm up the electrodes before starting the experiment, they were closed and opened several times for a few seconds. When the electrodes are closed, a current flows through them, the silicon heats up, and its conductivity increases. Then the contacts are opened, and an arc discharge is formed. We conducted several experiments with different values of currents from 8 A to 25 A. The voltage varied from 30 to 50 V. Due to possible overheating and melting of the silicon cathode, the discharge time was limited to 30 seconds.

As a result of experiments, deposits appeared on the surface of the electrodes, which were later studied using optical and electron microscopes (Fig. 1-5).

2. Discussion
Samples for the study were taken from the side surface of the anode. When observing the samples with an optical microscope, it can be seen that millimeter-long processes are visible at the edges of the sample (Fig. 1).

Photos taken with an electron microscope show many multilayer nanostructures with spherical closed ends (Fig. 2-4). The nanotubes have a conical shape. Unlike germanium nanotubes synthesized under similar conditions [9], the spherical ends of silicon nanotubes are located on the side of the thicker end, while in germanium nanotubes, the spherical ends are located on the side of the nanotube with a smaller diameter. If germanium nanotubes ended their growth with a spherical end, then silicon nanotubes begin to grow from the spherical end. Part of the silicon nanotubes has a wave-like shape. They are intertwined. Both types of nanostructures can have either a smooth surface or be covered with many small nanofibers or nanotubes, whose diameters are only a few nanometers at a length of about 100 nm. The shape of some nanostructures can include both configurations, namely, first these
nanotubes were formed with a smooth surface, and then the shape turned into a wave-like shape and the surface was overgrown with smaller nanostructures, as, for example, in Fig. 4 and Fig. 5. The diameters of nanotubes range from 200 to 500 nm, and the length of some can reach up to 1 mm.

Figure 3. Image of nanostructures obtained by the arc method: magnification of 1500 times.

Figure 4. Snapshot of silicon dioxide nanostructures: magnification 5000 times.

Figure 5. Hollow nanostructures, sample magnification 15000 times.

| Element | Weight % | Atomic% |
|---------|----------|---------|
| C K     | 4.37     | 6.78    |
| O K     | 59.93    | 69.70   |
| Si K    | 35.37    | 23.43   |
| Cu L    | 0.32     | 0.09    |
The resulting nanostructures are hollow and their walls have a thickness of about 50 nm (Fig.). In addition to the studied surface morphology of the obtained samples, elemental analysis was carried out, which showed that there is a high concentration of oxygen on the surface of the nanotubes. Either the oxidation of the nanotubes occurred during the experiment and the resulting nanostructures are silicon dioxide nanostructures, or the surface of the nanotubes was simply oxidized after the experiment was completed. The elemental composition of the obtained sample is presented in Table.1 (fig. 6), which shows that silicon dioxide is present in the samples.

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