Electric arc method for synthesis of silicon nanotubes

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Abstract. This paper proposes a method for creating silicon nanotubes in electric arc plasma, by evaporating the anode material and collecting it on the cathode. During the experiments, various types of power sources were tested. Silicon nanotubes of complex configuration in the form of a straight stem with cylindrical branch and single-wall curved nanotubes were obtained. The obtained nanotubes will be able to find further application in light-emitting diodes, lithium-ion batteries, and photovoltaics.

1. Creating silicon nanostructures

1D silicon nanostructures, such as nanowires and nanotubes attract much attention, on the one hand, as objects for scientific research, and on the other hand, as objects for technological applications. Today, silicon nanowires are widely studied precisely because of the ease of their synthesis and the prospects for use in light-emitting diodes, lithium-ion batteries, and photovoltaics. 1D silicon nanostructures are created using CVD method, thermal evaporation, reactive ion milling, etc. However, the samples obtained do not yet meet the requirements that are necessary for their practical application. And what's more, there is very little information in the publications about successes in the synthesis of silicon nanotubes. In recent years, several publications have appeared on the progress achieved in the synthesis of silicon nanostructures, in which they report on the methods of synthesis of silicon nanotubes in argon plasma [1-7].

Creating reliable conditions for growing silicon nanostructures of various shapes and achieving an understanding of the behavior of individual silicon atoms in the process of growing nanomaterials is extremely important today.

This paper proposes a method for creating silicon nanotubes in electric arc plasma, by evaporating the anode material and collecting it on the cathode. Silicon semiconductors have a very high electrical resistance at room temperature, and therefore spend only small currents. Their sharp heating leads to cracking and structural destruction. Therefore, in this work, an attempt was made to gradually heat the silicon by passing small currents within less than 100 mA. With gradual heating, the temperature of silicon can be raised to large values at which the conduction of silicon increases tenfold.

The experimental setup consisted of a evacuation chamber, a gas-supply system, electric power sources, water supply, and measuring instruments. For the formation of silicon nanostructures, it turned out that a tungsten rod with a well-polished butt is very well suited. The tungsten rod served as the cathode, silicon as the anode.

In the course of the experiments, various types of power sources were tried out: electric arc direct current source, electric arc AC generator, high-voltage source with ballast resistor.
1.1 Creating silicon nanostructures using electric arc direct current source

The evacuation chamber was filled with argon to a pressure of 500 Torr. The silicon anode was heated for 5 minutes using an additional source. Then the electrodes were switched to an arc source and a steady arc discharge was ignited. During the experiments, the arc current was limited by the ballast resistance within 15-25 A.

![Image of silicon nanotubes obtained with an electron microscope.](image)

Figure 1 and figure 2 shows electron microscopic images obtained during the experiments of the samples.

Silicon nanotubes have the shape of a cone with a closed end, their diameters range from 20 to 50 nm, and lengths from 0.5 to 0.8 μm. Their growth begins with another conical base material with a length of about 2 microns and a diameter of about 30-100 nm. A certain pattern of nanotube arrangement has been observed. They look like a pine trunk with knots. At the same time, the “knots” are true vertical to the “trunk” and are also strictly linearly arranged along the “trunk” line. The number of growth directions of nanotubes from the «trunk» is six, and these directions are strictly separated from each other at an angle of 60 degrees.

The value of the results obtained is that silicon nanotubes are a certain set of interconnected nano-objects. Therefore, such structures can be directly used as anodes of lithium-ion elements, since the surface area of the anode of such nanosilicon materials increases by orders of magnitude. At the same time, the strength of these nanotubes is very high. There are no broken nanotubes on electron microscopic images.
1.2. Creating silicon nanostructures using an electric arc AC generator

The electric arc AC generator is designed to operate at a pressure of at least 400 Torr and has two circuits: a low voltage arc power supply circuit (220 V) and arc ignition circuit with high-frequency high-voltage spark discharge of low power (activator circuit). In the arc mode, the beginning of the arc burning process and its subsequent maintenance in each half-period of the supply voltage is provided by a high voltage (40 kV) of increased frequency supplied from an activator (low-power spark generator).

The arc, activated by high-frequency current, is maintained fairly stably. In the course of the experiment, the average current was maintained between 2.5 and 3 A.

To increase the temperature of the electrodes, before connecting AG-2 (arc generator), we replaced the power supply with a high-voltage, low-current one and maintained a glow discharge with a voltage of 400 V and a current of 0.05 A for 2 minutes. Then, the power source was quickly switched to AG-2, which gave an average amperage of about 3 A. In this embodiment, the arc discharge started and the deposition of silicon onto the tungsten cathode began. The surfaces of the cathode were subsequently thoroughly studied with a scanning electron microscope. The pictures show a large number of formations in the form of curly cylinders with diameters from 30 to 40 nm, which are closely intertwined with each other.

Silicon nanostructures, which are very different from the previous forms of silicon nanomaterials, were grown in a high-voltage electric arc discharge.
Figure 3. The result obtained in the process of growing silicone nanotubes using a high-voltage power source with a ballast resist.

1.3. Creating of silicon nanostructures using a high-voltage power source with a ballast resist
The evacuation chamber was filled with argon to a pressure of 500 Torr. A voltage of about 80 V was applied to the electrodes. Ballast resist was connected to the discharge circuit to ensure the discharge stability. For ignition of the arc several times for a short time closed and opened the contacts. At the same time, the silicon anode gradually warmed up. The procedure was repeated until the formation of the arc. In this case, a discharge ignited with a current of the order of 8A and silicon nanostructures was growing on the cathode.
These silicon nanostructures were studied on a scanning electron microscope, the results of which are presented in figure 3 and figure 4.
These silicon nanostructures were studied on a scanning electron microscope. From these figures it can be seen that if nanoobject have the form of nanotubes, their cross sections are similar to an ellipse. The nature of the location of the nanotubes on the body is also different from the results of previous experiments. They have a maximum of only two directions on their bodies. They look like ribs on the vertebra of the animal. At the same time, these “edges” are true vertical to the “trunk” and are also strictly linearly arranged along the line of the “trunk”. The lengths of nanotubes vary within 5–7 microns. Such structures will also be useful for use as anodes of lithium-ion elements.

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