ELECTRIC ARC SYNTHESIS OF SILICON NANOSTRUCTURES

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Abstract. The paper proposes a method for the synthesis of silicon carbide of microscopic sizes and silicon Nano formations in the form of nanotubes and nanofilaments in an argon arc. Graphite electrodes with silicon inclusions were used as arc discharge electrodes. The electrodes were placed in a plasma reactor in an upright position at an argon pressure of 485 Torr. During the discharge, carbon and silicon atoms evaporated from the anode surface. As a result of the experiment, deposits of silicon carbide were formed on the surface of the graphite cathode, and carbon-silicon nanostructures were formed on the surface of the anode. The synthesized samples were analyzed on an electron microscope.

1. Introduction

Silicon nanostructures, such as silicon carbide (SiC), silicon nanofilaments, due to their exceptional hardness, wear resistance and chemical inertia, are widely used in the manufacture of turbine blades, diesel engines, light-emitting devices, field emission displays, nanosensors, as well as abrasive materials. Silicon carbide is mainly produced by the well-known Acheson method. Chemical vapor deposition (CVD) and pulsed laser ablation are also used for the synthesis of silicon nanostructures. These processes have some advantages, such as, for example, simplicity and the possibility of obtaining products in large volumes. But at the same time, there are some limitations, especially in terms of cost, processing time and purity of products. Plasma methods of synthesis of nanomaterials from silicon are proposed as alternative methods in [1-6]. Silicon carbides have already been successfully synthesized in various plasma sources, such as a DC arc embedded in a dielectric liquid [1,2].

In the article [1], for example, the synthesis of silicon carbide was carried out in an arc plasma immersed in fuel oil. Crystalline silicon was placed in a small depression in a graphite anode. In the arc discharge, carbon atoms were released from hydrocarbons and, simultaneously, silicon boiled in the graphite anode hole. Silicon carbide was deposited on the cathode of an electric arc sunk into fuel oil.

In [2], a similar synthesis method is presented with electrodes immersed in a dielectric liquid, but hydrocarbon liquids are taken as the medium. The authors carried out three types of experiments. In the first case, a prolonged spark discharge was ignited in liquid cyclohexane between a silicon anode and a graphite cathode, in the second case - in liquid cyclohexane between two silicon electrodes, in the third case - in liquid tetramethylsilane between two graphite electrodes or two tungsten electrodes. The authors of this work also studied the possibilities of synthesis of nanoscale silicon carbides in pulsed discharges. They managed to find modes in which nanoscale silicon carbides were synthesized. The
results obtained showed that pulsed discharges between Si - C and Si – Si electrodes in cyclohexane produce Si nanoparticles with a C shell, but not SIC nanoparticles. However, prolonged spark discharges in tetramethylsilane do produce SIC nanoparticles.

Coleman and co-authors [3] investigated the process of carbonation of silicon nanoparticles to SiC. Depending on the experimental conditions, either hollow or solid morphologies of SIC nanoparticles can be obtained. The authors found that the plasma first heats Si nanoparticles (with a C-shell) and initiates the diffusion of C into Si to generate SiC. Then energy is released (exothermic reaction), which additionally heats the particles, which leads to a complete structural transformation into SiC. This reaction takes about hundreds of milliseconds.

High-frequency induction and microwave plasmas are also worthy of attention for the synthesis of nanoscale silicon carbides.

Experiments with the production of silicon carbides in an argon arc with graphite electrodes were demonstrated in the work of V.I. Podgorny et al. [4]. The experiment was carried out under the following conditions: the discharge current is 60-75 A, the interelectrode gap is about 0.1-1 mm, the argon pressure is 100-300 Torr, burning time 20–30 minutes

The samples from the work [5] synthesized under conditions similar to those of the argon-arc discharge in the work of V.I. Podgorny et al., are carbon nanotubes and nanodiamonds. The elemental composition of the samples showed that they consist entirely of carbon. The authors suggest that Si acted as a catalyst for the formation of carbon structures, and silicon nanotubes and silicon carbide were transferred higher due to the high temperature and energy released during the synthesis of C-nanostructures.

In [6], the synthesis of ultrafine-grained nanoparticles of amorphous silicon carbide (a-SiC) was carried out by decomposition of hexamethyldisilane in an arc plasma based on a magnetically stabilized sliding arc discharge. The results showed that the synthesized products are a mixture of a-SiC nanoparticles and excess free carbon. The average size of the nanoparticles was about 9 nm, and there were many functional groups and oxidized coatings on the surface of the nanoparticles. Photoluminescent properties showed that a-SiC nanoparticles had strong blue-green radiation, when excited at a wavelength of 340-420 nm, which may be due to surface functional groups, oxidized upper layers and the effect of quantum limitation due to ultrathin dimensions. The correlation between the arc current and the crystal structure of the product showed that the low input energy contributes to the synthesis of a-SiC nanoparticles, while the high input energy contributed to the transition from an amorphous structure to b-SiC.

The electric arc method has its advantages over other methods of obtaining nano- and micro-sized structures of silicon and silicon carbide, due to the coexistence of regions with large temperature gradients. Near the arc column, the temperature can reach ten thousand degrees, and already at a distance of literally a few millimeters, the temperature will be about a thousand degrees. Effective synthesis of silicon nanostructures in an arc plasma does not require the presence of a catalyst, as for carbon nanostructures, and heating to a temperature at which the growth of formations begins occurs in a short period of time (about 100 ms). In this paper, an electric arc method is proposed for the synthesis of silicon nanostructures and the conditions under which some types of carbon-silicon and silicon structures differing in size by several orders of magnitude are created are described.

2. Experimental setup
The experimental setup for the synthesis of silicon nanostructures consisted of a vacuum chamber, power supply systems, vacuuming, and gas supply. Graphite rods with a thickness of about 14 mm were chosen as electrodes. The cathode was pointed at the end, and inclusions of crystalline silicon were placed on the anode. The cathode and anode had a vertical arrangement. During the experiment, it was possible to adjust the interelectrode distance. Before the experiment, the vacuum chamber was pumped out by a vacuum pump, and then purged and filled with argon to a pressure of 485 Torr. To initiate the arc, contact was briefly established between the electrodes and it was broken. At the same time, an arc was ignited.
between the electrodes. During the experiment, the voltage between the electrodes was maintained at about 26 V at a current of 45 A. The experiment lasted about 1 minute.

3. Experimental results

The samples obtained as a result of the experiment were studied using an electron microscope. Figure 1 shows images of silicon carbide. Their size is about 20-40 microns. Smaller formations of carbides are visible on the faces of some particles. The crystals have clear edges and smooth flat faces.

**Figure 1.** Silicon carbide crystals. An increase of 300 times.

Figure 2 shows images of nanoscale silicon carbide crystals with a size of about 200-500 nm. In the same figure, silicon nanowires are visible, the length of which reaches 10 microns.

**Figure 2.** Nanoscale silicon carbide crystals. An increase of 5000 times.
Figure 3 shows silicon nanowires synthesized during the same experiment at a magnification of 5000 times. The diameters of these filaments are about 50-100 nm, and the length is about 10 nm. There are also growths on the surface of the formed filaments, most likely from silicon oxide. The average length of surface neoplasms is approximately 10 nm.

![Silicon nanowires. An increase of 5000 times.](image)

The nanowires are indirect, arranged randomly, while filling the entire volume as much as possible. There are many oxidized coatings on the surface of nanowires. The elemental composition of this sample showed, in addition to silicon, the presence of oxygen.

4. Conclusion
In an argon arc at a pressure of 485 Torr, it was possible to synthesize silicon carbide of microscopic dimensions and silicon nanofilaments coated with multiple oxidized nanostructures. Low-temperature plasma can be used for the synthesis of various nanostructures and is well suited for the modification of various surfaces. This is shown in many works [7-10].

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