

# Synthesis of 6H-SiC Single-Crystal Nanowires in a Flow of Carbon–Silicon High-Frequency Arc Plasma

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**Abstract**—Silicon carbide 6H-SiC nanoparticles and nanowires were obtained in carbon–silicon high-frequency arc plasma in a helium atmosphere at a pressure of 0.1–0.6 MPa. It was shown that 6H-SiC nanowires grow from the arc plasma, as well as from the vapor, according to the known mechanism of vapor–solid condensation on a cold surface covered with single-crystal silicon carbide nuclei. The content of silicon carbide nanowires in the condensate reached 60 wt %. The obtained single-crystal silicon 6H-SiC nanowires had the diameter of 15–18 nm and length of 200–600 nm.

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## 1. INTRODUCTION

Silicon carbide (SiC) exhibits unique properties such as mechanical strength, chemical stability, and capability of withstanding high temperatures. SiC is a nanostructured layered semiconductor whose macroscopic properties depend on the mutual arrangement of layered, i.e., on the sequence of their alternation and repetition period [1]. Nowadays, the properties and possibilities of application of SiC in the form of nanoparticles, nanorods, and nanowires are under active study [2–4]. It is expected that nanorods and nanowires will be used for solving problems of nanoelectronics [5, 6] and problems in which the materials must combine various unique properties, i.e., be multifunctional. Nanowires can be used as substrates for catalysts [7]. In [8, 9], it was reported that the plasticity and strength of SiC in the form of nanorods increase as compared to bulk SiC. A decrease in the crystal size leads to an increase in the hardness and elastic modulus due to the progressing influence of intercrystalline boundaries, which play the role of barriers for the propagation of dislocations and cracks. The results obtained in [10, 11] evidence not only an increase in the photoluminescence but also a change in the luminescence wavelength with variations in the size and shape of SiC nanorods.

Nowadays, the basic methods for producing nanodisperse SiC are laser ablation, high-frequency induction heating, vapor phase deposition, physical evaporation, and hydrothermal methods [12–19]. These methods are commonly used for producing nanowires

of cubic SiC with a diameter of 30–150 nm. For solving problems of optoelectronics [20] and for producing radiation-proof equipment [21] and substrates, hexagonal SiC of polytype 6H is used.

The basic nanowire growth mechanisms are the vapor–liquid–solid (VLS) [22–25], vapor–solid (VS) [26, 27], and solid–liquid–solid (SLS) [28, 29] mechanisms. Methods for producing SiC nanowires according to the VLS mechanism require the use of catalysts such as Fe, Ni, and NiO. Nanowires obtained by this method are polluted with the catalyst material, which restricts their further application. In [30, 31], the authors described the VS mechanism and presented the results of the study of SiC nanowires grown by the interaction of SiO and CO vapors. An increase in the O<sub>2</sub> flow rate led to a decrease in the nanowire formation rate, and the structure transformed from single-crystalline to polycrystalline.

In this work, we present the results of studies of SiC nanoparticles and nanowires and consider the mechanism of their formation during cooling of carbon–silicon high-frequency arc plasma in a helium atmosphere.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Nanodisperse SiC was produced by arc evaporation of graphite electrodes in the form of rods whose axial hole was filled with a silicon powder (with a Si content of 99.2 wt % and a particle size of 1–2 mm). The Si

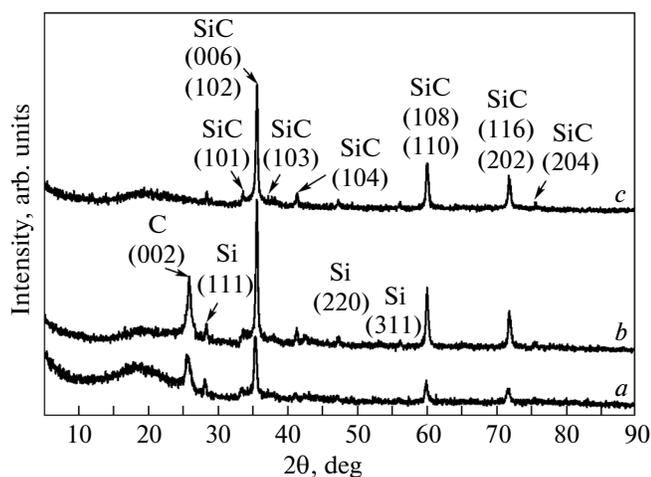


Fig. 1. X-ray diffraction patterns of sample (a) no. 1, (b), no. 2, and (c) no. 3.

content in the graphite rods amounted to 35–40 wt % of the total a electrodes. The graphite rods were evaporated by a high-frequency (44 kHz) arc discharge in a helium atmosphere. The synthesis was performed by two methods at a helium pressure of 0.1–0.6 MPa in the chamber. In the first method (A), the arc was excited by two symmetrically placed graphite electrodes [32] and, in the second method (B), between the evaporated graphite rod and the unevaporated electrode (graphite tube) [33]. The temperature of the carbon–silicon arc plasma near the graphite rod was 5000–5500 K [34]. The graphite tube (at a temperature of 1800–2000 K) also played the role of a substrate on which the nanowires were grown. The main difference between these methods is that, in the first method, the carbon–silicon plasma is cooled in the helium atmosphere with the formation of nanodisperse particles, whereas in the second method, it is cooled also due to the contact between the surface of the external electrode with the formation of nanowires.

The maximum content of nanowires in the carbon–silicon condensate (60 wt %) synthesized by method B was obtained at a helium pressure of 0.4 MPa (sample no. 1). The extraction of SiC nanowires from carbon–silicon condensate was performed by boiling in nitric acid followed by washing off in water (sample no. 2) and annealing at a temperature of 850°C for 45 min in air flow (sample no. 3).

The X-ray phase analysis (XPA) of the carbon–silicon condensate was performed on a DRON-4 powder diffractometer using  $\text{CuK}_\alpha$  radiation. The elemental composition of samples was determined by X-ray fluorescence spectral analysis (XFSA) on a Bruker Pioneer S4 spectrometer. Images of the sample surfaces were obtained by scanning electron microscopy (SEM) on a Hitachi S5500 scanning electron microscope. The structure of the products obtained was

determined by transmission electron microscopy (TEM) on a JEOL JEM-2100 high-resolution transmission electron microscope.

### 3. RESULTS AND DISCUSSION

#### 3.1. Structure and Morphology

The synthesis on the evaporation of silicon-containing graphite electrodes by method A made it possible to obtain spherical nanoparticles of hexagonal SiC. The analysis of carbon–silicon condensate collected from the chamber walls has shown that an increase in the helium pressure in the chamber led to an increase in the average particle diameter; nanowires were not detected in this case.

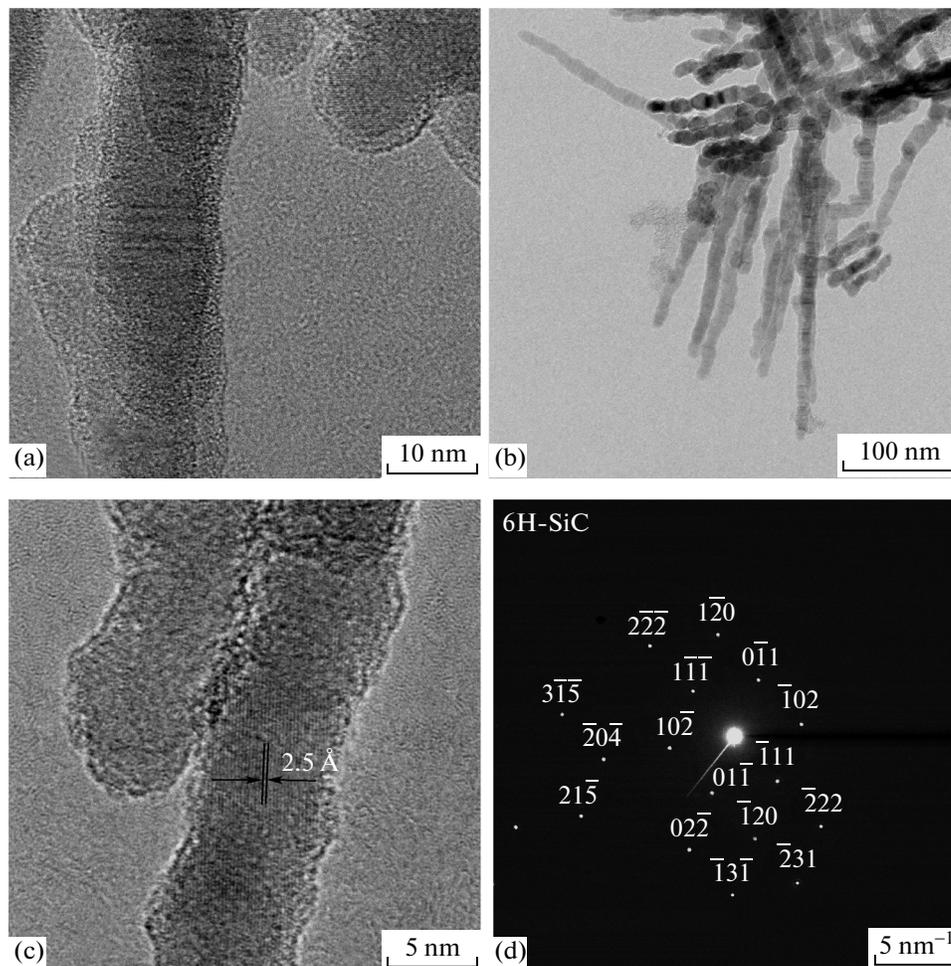
The X-ray diffraction pattern of carbon–silicon condensate obtained by method B (Fig. 1a) is characterized by the presence of the amorphous component ( $2\theta = 5^\circ\text{--}25^\circ$ ) and crystal phases of graphite ( $2\theta = 26.4^\circ, 42.2^\circ, 44.4^\circ, 50.5^\circ, 54.6^\circ$ , etc.), silicon ( $2\theta = 28.4^\circ, 47.3^\circ, 56.1^\circ, 69.2^\circ, 76.4^\circ$ , and  $88.0^\circ$ ), and silicon carbide ( $2\theta = 34.1^\circ, 35.7^\circ, 38.2^\circ, 41.4^\circ, 45.3^\circ$ , etc.). The diffraction peaks characterizing SiC correspond to the rhombohedral structure of 6H-SiC with the following crystal lattice parameters: space group  $P6_3mc$ ,  $a = 3.0806 \text{ \AA}$ ,  $c = 15.1174 \text{ \AA}$ ,  $c/a = 4.9072$ ,  $V = 124.25 \text{ \AA}^3$ ,  $Z = 6$  (PDF Card no. 04-007-1548). The presence of several crystal phases in the condensate obtained is caused by different cooling rates of local regions of plasma. According to the XPSA, the silicon content in sample no. 1 was 26.7 wt %.

The TEM images of the carbon–silicon condensate demonstrate the presence in sample no. 1 of both nanoparticles (with a diameter of 10–15 nm) and nanowires (with a diameter of 15–18 nm and length of 200–600 nm) of carbide silicon (Figs. 2a, 2b).

Figure 2c shows an image of a separate 6H-SiC nanowire having a single-crystal structure. The observed interplanar distance (Fig. 2c) is  $\sim 2.5 \text{ \AA}$  and corresponds to 6H-SiC ( $d_{102} = 2.52 \text{ \AA}$ ). The electron-diffraction pattern (Fig. 2d) obtained by nanodiffraction of a separate nanowire corresponds to 6H-SiC (PDF Card no. 04-007-1548) with the orientation [211].

#### 3.2. Cleaning of SiC Nanowires

The XPA of sample no. 2 has shown that boiling in nitric acid made it possible to decrease the amorphous component of carbon–silicon condensate and increase the fraction of crystal phases: 6H-SiC, graphite, and Si (Fig. 1b). According to the SEM and XPA data, the high-temperature annealing in an air flow (sample no. 3) made it possible to remove graphite that was present in sample no. 2. In the SEM image of sample no. 3, the high (95%) concentration of single-crystal 6H-SiC nanowires is observed and separate carbon



**Fig. 2.** TEM images of sample no. 1: (a) SiC particle and SiC nanowire, (b) bunch of SiC nanowires, (c) SiC nanowire with the interplanar distance shown, and (d) electron diffraction pattern of a single SiC nanowire.

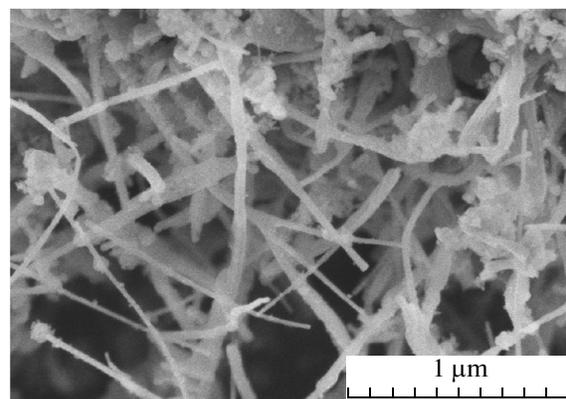
agglomerates are absent (Fig. 3). In the X-ray diffraction patterns of sample no. 3, graphite reflexes and amorphous halo are also absent (Fig. 1c). Thus, the maximum content of nanowires (60 wt %) in carbon–silicon condensate was obtained at a helium pressure in the chamber of 0.4 MPa.

### 3.3. Growth Mechanism

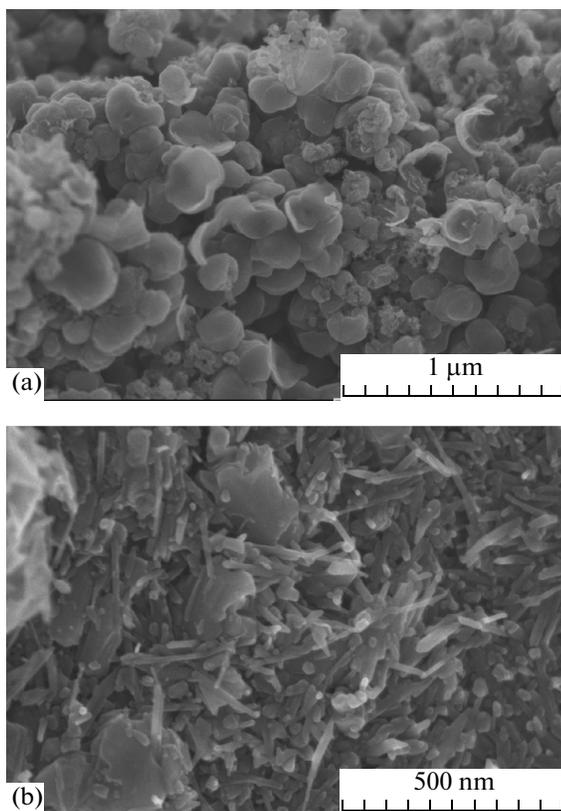
The analysis of SiC nanostructures obtained by method *A* has shown that they appear only in the form of nanoparticles. The mechanism of nanoparticle formation in a HF arc plasma jet is explained by the nucleation of silicon on carbon nuclei simultaneously with silicon carbide formation.

The analysis of SiC nanostructures obtained by method *B* has shown that they appear both in the form of nanoparticles and in the form of nanowires. The temperature of the unevaporated electrode—the graphite tube—in the process of synthesis is substantially lower than the plasma temperature. The contact of the carbon–silicon plasma with the electrode sur-

face results in the formation of single-crystal SiC nuclei, on which the nanowire growth takes place. The constant arrival of silicon and carbon vapors to the end of a growing nanowire generated its further growth. After that, the nanowires formed are carried away by



**Fig. 3.** Micrograph of the surface of sample no. 3.



**Fig. 4.** SEM images of the graphite tube surface after the synthesis of carbon–silicon condensate in the HF arc plasma: (a) SiC nanoparticle and (b) SiC nanowire.

the helium flow from the interelectrode gap to the chamber. This explains the fact that, on the surface of the graphite tube, there are nuclei in the form of silicon carbide particles and nanowires (Fig. 4). The above-described mechanism of SiC nanowire growth corresponds to the known VS mechanism of condensation on a cold surface covered with single-crystal silicon carbide nuclei [26, 27].

#### 4. CONCLUSIONS

In this work, we have shown that, in the carbon–silicon high-frequency arc plasma in a helium atmosphere at a pressure of 0.1–0.6 MPa, both nanoparticles and nanowires of silicon carbide 6H-SiC are formed. The synthesis was performed by two methods. In the first method, the arc was excited between two electrodes made in the form of graphite rods with axial holes filled with silicon powder. In the second method, the arc was excited between the unevaporated electrode and the graphite rod with the axial hole containing silicon powder. In the first case, both electrodes were evaporated and the carbon condensate contained silicon carbide nanoparticles. In the second case, the carbon condensate, in addition to nanoparticles, contained 6H-SiC nanowires. The synthesis at a helium

pressure in the chamber (0.4 MPa) made it possible to increase the content of nanowires in the silicon carbide condensate to 60 wt %. Single-crystal 6H-SiC nanowires obtained at a pressure of 0.4 MPa had the diameter of 15–18 nm and length of 200–600 nm. Thus, the experimental results showed that SiC nanoparticles are formed according to the nucleation mechanism, whereas SiC nanowires are formed according to the nucleation mechanism and SiC nanowires form by the known vapor–solid mechanism, in which the growth of nanowires proceeds through the vapor condensation on particles located on the surface of the unevaporated electrode.

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