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Simple method for SiC nanowires fabrication

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Abstract. In this work, we introduce a simple and convenient approach for growing SiC nanowires (SiCNWs) directly on carbon source from graphite. The commercial SiO powder and the cheap common graphite were used as the source materials. SiCNWs have been synthesized during holding time less than 60-80 min at 1450-1500 °C by using a simple and low-cost method in an industrial furnace with a resistant heater.

Keywords: silicon carbide, nanowires, vapor-solid mechanism, large-scale production.

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1. Introduction

In recent years, a tremendous amount of attention is gained by the synthesis of one-dimensional (1D) nanostructures. There are many different forms of 1D nanostructures: nanorods, nanowires, tubes, ribbons, belts, whiskers, and needles. Their interesting electronic, optical, and magnetic properties, along with a large band gap, have led to a wide range of applications in nanoelectronics, optoelectronics, medical diagnostics, and sensorics. Many research efforts have been devoted to SiC nanowires (SiCNWs) investigation, especially with regard to improvement of their field emission properties. 3C-SiC nanowires high resistance to chemical corrosion shows a potential for their application under a range of harsh environmental conditions including high temperature, high power and high frequency. Due to the combination of outstanding mechanical properties and high thermal and chemical stability, SiC nanorods, nanowires and whiskers have been primarily used as reinforcement materials in composites. In recent several years, a lot of methods of SiCNWs fabrication have been developed, such as carbothermal reduction [1, 2], metal-assisted vapor–liquid–solid (VLS) reaction [3-4], chemical vapor deposition CVD [5-7], metalorganic chemical vapor deposition (MOCVD) [8], sol-gel process [9, 10], arc-discharge process [11], etc. However, most of these methods involve using high-cost starting material, complicated equipment, time-consumption, lower yield of products and metal catalyst introduction, so their applications are limited.

It is necessary to achieve large-scale production of SiCNWs in amount of weight at the gram level by a low-cost method and materials. The method of carbothermal reduction is one of the simplest ways for nanowhiskers formation. In most of other methods, expensive raw materials such as carbon nanotubes (CNTs) or specially treated graphite targets were used [12].

In this work, we introduce a simple and convenient approach to grow SiC nanowires directly on carbon source from the cheap common graphite. The aim of the work reported here is to study the influence of technological factors, such as temperature of the synthesis process and characteristics of carbon target surfaces.

2. Method of experiment

A sketch of the apparatus is given in Fig. 1. The REDMET-30 industrial furnace with resistant heater was used for thermal operations. The crucible was made from vacuum tide graphite with inner diameter 170 mm and length 100 mm. So, as the crucible was reused several times, its inner surfaces were covered with thin dense layer of SiC. The carbon targets were arranged inside the crucible in its top part. The targets were made as cylinder or/and flat graphite plates with different porosities and densities $\rho = 1.65–1.55$ g/cm^3. The coarse-grained powder of high purity SiO with weight 15 to 40 g was placed at the bottom of the crucible.

The temperature-time synthesis regime consisted of several stages:

1. The preliminary stage. Before the reaction start the crucible and inner components were out-gassed at

1000 °C under dynamic vacuum for 2 h in order to desorb impurities from their surfaces. After the temperature ~1200 °C was reached, helium was pumped into the camera (at the pressure P = 200–300 mbar).

2. The holding stage. The moment of SiO melting temperature (1250 °C) reaching was taken as the beginning of synthesis process. Synthesis was carried out under slow dynamic helium pumping out for providing vapor transport to the targets. During this stage, the temperature was slowly increased from 1250 °C to maximum synthesis temperature T_{max} = 1400–1700 °C. The synthesis process duration t_s was determined from the process start to the moment of temperature decrease down to 1250 °C after heating was switched off. The holding time was about t_s = 60–80 min. When heating to the SiO evaporation temperature, reaction of its vapors with carbon of the target surface took place resulting in SiC and gaseous CO formation:

$$SiO(g) + C \rightarrow SiC + CO(g). \quad (1)$$

As far as the temperature inside the reactor was relatively low and carbon vapors pressure could be neglected, the main source of carbon for SiC synthesis was CO vapor:

$$SiO(g) + CO(g) \rightarrow SiC + CO_2. \quad (2)$$

Produced CO_2 vapors could subsequently participate in the reaction

$$CO_2(g) + C(s) \rightarrow CO(g) \quad (3)$$

forming CO again. So, it is seen from the reactions (1) to (3) that CO vapor formation process has behavior of positive feedback [1].

3. The cooling stage. After heating switching off, helium at the pressure P = 250–350 mbar was pumped into the camera for the cooling process acceleration.

3. Results and discussion

Investigations of morphology and composition of deposited materials were carried out using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and Raman spectroscopy (RS). It was found that morphology of obtained SiC deposition on the target surface depends on two factors: the synthesis temperature and properties of graphite target surface.

Our investigations have shown that resulting SiC deposition consists only of microcrystals without any features of nanowires formation when target surface is composed of dense carbon materials with low number of pores and small pore sizes independently of synthesis temperature. This result is obtained for the entire range of synthesis temperatures. SiC nanowires deposition occurs exclusively on the targets composed of porous graphite with low density. Really, it can be seen from Fig. 2 that intensive formation of nanowires on relatively smooth target surface takes place only in the surface region, which is purposely roughened by the scratch (rectangle *b*). The rest of the target surface is mainly characterized by formation of elongated microcrystals (rectangle *c*). Characteristic diameters of nanowires in the roughened region are within the range 90 to 350 nm, while their lengths are 5 to 15 μm. For the (*c*) region, microcrystals with the diameters 300–600 nm and 3–6 μm long are typical. Also, several single wires 8 to 16 μm long and 200 nm in diameter are present in this region.

When graphite targets with medium porosity are used, the mixture of microcrystals and separate nanowires is observed in the deposities (Fig. 3). The nanowire density is about 1×10^6 cm^{-2} ($0.1\,\mu m^{-2}$), while that of microcrystals is 2.4×10^6 cm^{-2} ($0.24\,\mu m^{-2}$).

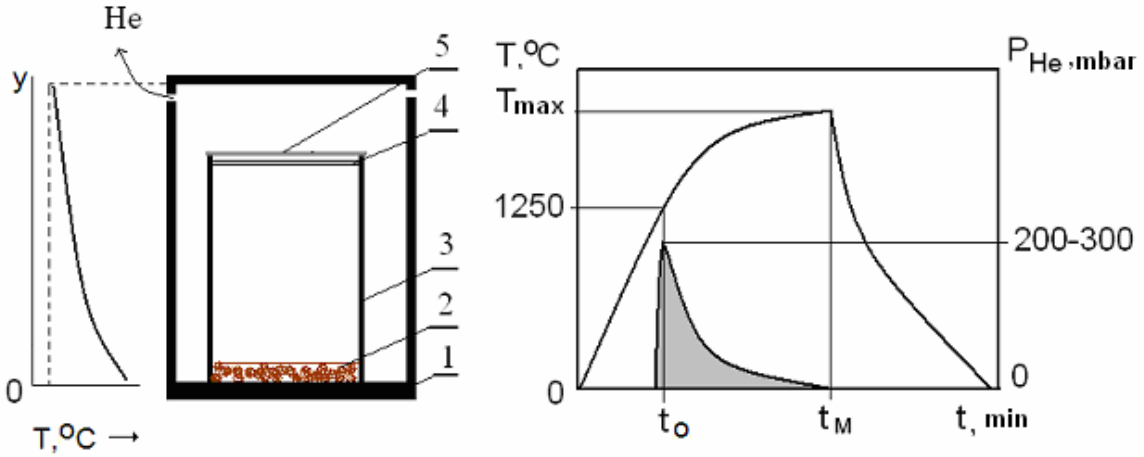

Fig. 1. Temperature distribution inside the reactor, reactor construction and temperature-time regime of synthesis process. *1* - crucible; *2* – SiO powder; *3* – cylinder-shaped graphite target; *4*, *5* – set of flat targets composed of carbon materials.

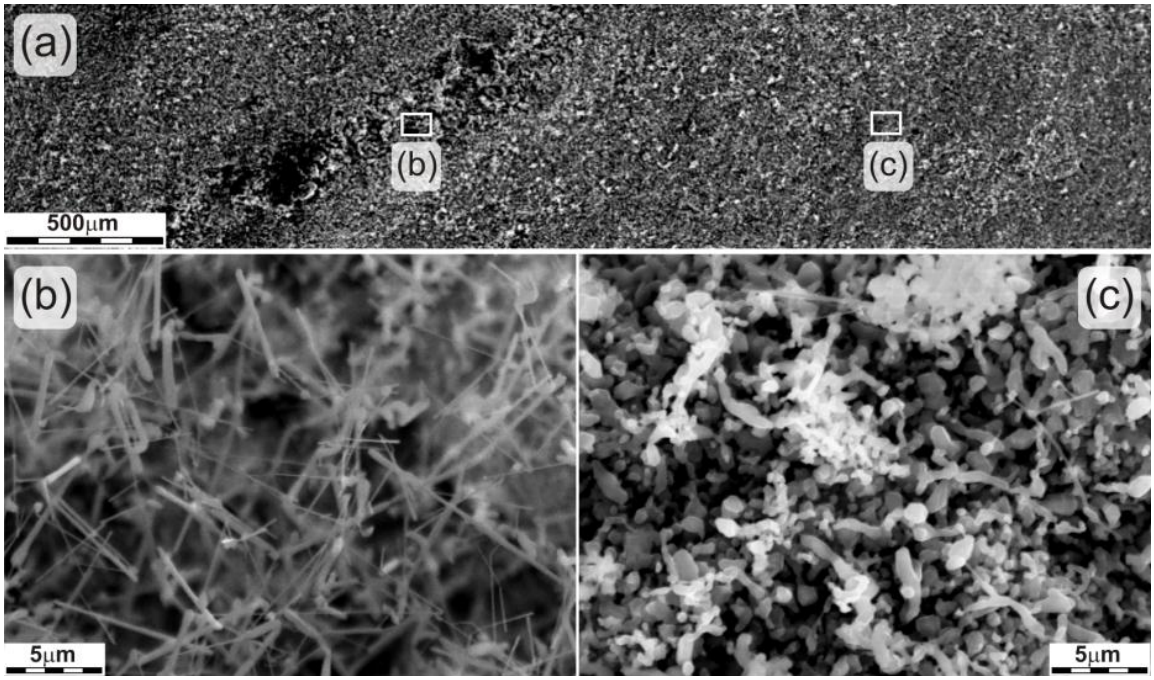

Fig. 2. SEM images of dense graphite target-substrate surface (ρ = 1.65 g/cm^3) (*a*), deposite morphology in a surface region roughened by scratch (*b*) and initial surface (*c*).

Diameters about 30-70 nm and lengths within the range 10-30 μm are characteristic for these nanowires. Microcrystal sizes are close to the previous case (3–7 μm long, 650 nm average size), but their shape is more elongated.

The use of porous graphite targets causes SiC deposition in the form of nanowires. At slightly higher magnification (Fig. 4a, inset), it can be seen that deposite has structure of moss-like knobs with the diameter 40 to 200 μm. More detailed examination reveals that knobs entirely consist of nanowires. The number of nanowires and their diameters are decreasing from the knob center to its periphery. In the region between knobs, the length of separate nanowires can achieve 100 μm. The most probable diameter for these deposition conditions is 100 nm (Fig. 4b, inset).

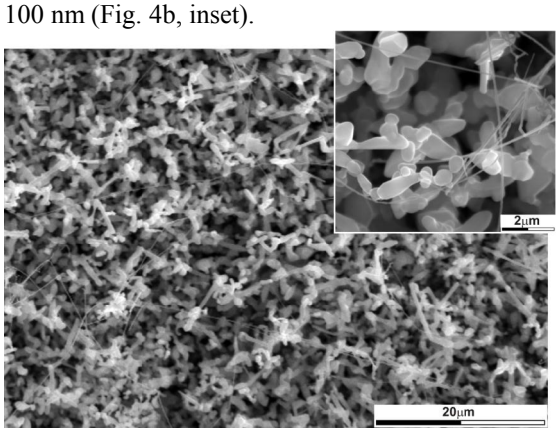

Fig. 3. SEM image of target-substrate surface composed of medium density graphite. Insert shows a zoomed fragment of the surface.

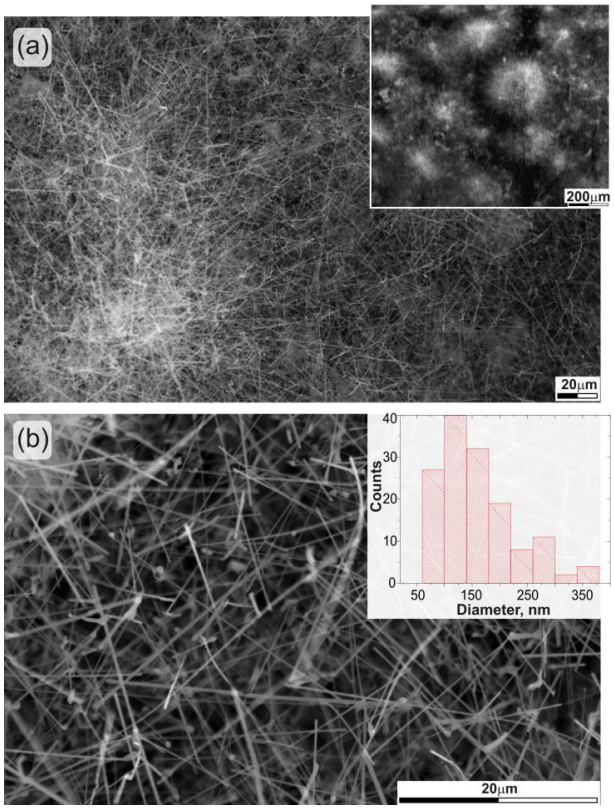

Fig. 4. SEM image of deposite on porous graphite surface with the graphite density ρ = 1.55 g/cm^3 for various magnifications (*a*), (*b*). The histogram of NW diameter distribution is shown in the inset (*b*).

Table 1 presents results of energy-dispersive analysis of the nanowires, which are shown in Fig. 4 (spectra *1–4*). As far as SiC stoichiometric composition corresponds to 70% Si and 30% C, nanowire chemical composition is close to the stoichiometric one with small excess of carbon. EDS data for the target-substrate surface (spectrum *5*) show that it is covered with SiC layer with small excess of silicon.

Table 1. Results of EDS analysis of SiC nanowires and target-substrate of porous graphite (ρ = 1.55 g/cm^3) after the deposition process at the temperature *T* ~1550 °C. All results are shown in weight percents.

Spectrum	C	O	Si	Total
1	39.24	0.97	59.79	100.00
2	34.62	1.06	64.32	100.00
3	43.47	0.89	55.64	100.00
4	34.97	0.34	64.68	100.00
5	26.20	0.00	73.80	100.00

Nanowire deposites are observed at synthesis temperatures $T \leq 1550$ °C. But for $T > 1550$ °C, deposition of SiC microcrystals takes place independently on surface properties. For the sample shown in Fig. 5, the microcrystal height is 4 to 50 μm and their average diameter is 5 μm.

Data obtained by Raman spectroscopy investigation reveal that both nanowires and microcrystals are of cubic 3C-SiC polytype, Fig. 6. Our further investigations suppose to include detailed analysis of the nanowire structure.

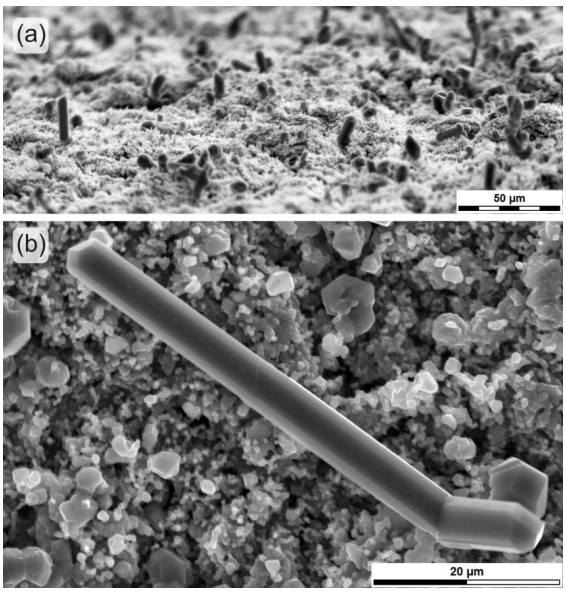

Fig. 5. SEM images of deposite on porous graphite surface (ρ = 1.55 g/cm^3, T_{max} = 1700 °C): side view (*a*) and magnified upper view (*b*).

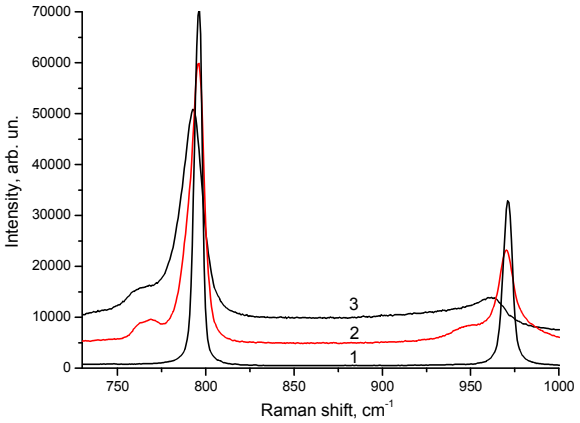

Fig. 6. Raman spectra of: *1* – 3C-SiC monocrystal, *2* – SiCNW on the graphite target shown in Fig. 3b, *3* – SiC microcrystals shown in Fig. 4b.

4. Conclusion

We present a simple, rapid, and low-cost method to synthesize β-SiC nanowires by using an industrial furnace with a resistant heater. Commercial SiO and carbon targets with porous structure from cheap common graphite were used as source materials. The time of heating-up and reaction is less than 3 h. It is shown that deposite morphology depends on technological conditions, namely: temperature and carbon surface properties. Nanowires are deposited on porous surfaces of graphite targets in the narrow temperature range 1400–1550 °C. Temperature increase up to 1700 °C leads to formation of microcrystals. The total weight of the obtained nanowires is determined by graphite substrate surface area and SiO weight. The large size of crucible allows to obtain several grams of SiC nanowires for one synthesis procedure. This method provides a promising approach for industrial fabrication of β-SiC nanowires.

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