

Nanowires of Silicon Carbide and 3D SiC/C Nanocomposites With Inverse Opal Structure

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Abstract – Synthesis, morphology, structural and optical characteristics of SiC NWs and SiC/C nanocomposites with an inverse opal lattice have been investigated. The samples were prepared by carbothermal reduction of silica (SiC NWs) and by thermo-chemical treatment of opal matrices (SiC/C) filled with carbon compounds which was followed by silicon dioxide dissolution. It was shown that the nucleation of SiC NWs occurs at the surface of carbon fibers felt. It was observed three preferred growth direction of the NWs: [111], [110] and [112]. HRTEM studies revealed the mechanism of the wires growth direction change. SiC/C- HRTEM revealed in the structure of the composites, except for silicon carbide, graphite and amorphous carbon, spherical carbon particles containing concentric graphite shells (onion-like particles).

I. INTRODUCTION

Studies on the synthesis of nanostructures with new functional properties expand the area of their potential use and, therefore, highly desirable. We have studied synthesis, morphology, structural and optical characteristics of SiC nanowires and SiC/C nanocomposites with an inverse opal lattice.

II. EXPERIMENTAL

Carbothermal reduction of silica is most useful method for the synthesis of SiC NWs. In this work we used both silica and colloidal carbon in carbothermal reduction method as a Si and C sources, respectively.

SiC/C composites in silicon dioxide were obtained using an opal matrix which was a three-dimensional close-packed system of monodisperse sphere-shaped (globules) silicon dioxide particles (240 - 280 nm in diameter). The samples were prepared by thermo-chemical treatment of opal matrices filled with carbon compounds which was followed by silicon dioxide dissolution [1]. The samples were studied by electron microscopy, x-ray diffraction, photoluminescence, IR and Raman scattering spectroscopy. The samples implantation has been carried out by He⁺ ions with energy 40 keV and doses of 10¹³-10¹⁵ ions/cm².

III. SiC NANOWIRES

Fig. 1(a) shows FESEM images of the synthesized product general view on the carbonic felt surface. From the image, the product consists of the wires with a

diameter of 20-200 nm and a length of tens to hundreds of micrometers. Figures 1(c-g) further reveals, that the nanowires have different types of the morphology. From the TEM images (d-g), all the wires have a well-pronounced striped structure, which indicates the presence of twins and stacking faults (SFs) in the wires. Mainly, the three types of the wires morphologies were assigned: «smooth» (fig.1e,f), «bamboo-like» (fig.1d, c) and “Y-types” (fig.1 g) wires. In turn, «smooth» wires have SFs, which placed either perpendicular (fig.1e) or at an angle to the growth axis of the SiC wires (fig.1f). In general case, the “smooth” wires

growth in a hexagonal-prism shape as shown in fig. 1(b).

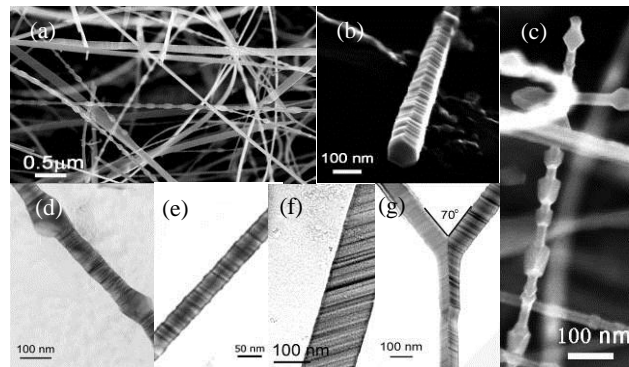


Fig. 1. (a)- FESEM image of the NWs general view; (b,c) – FESEM images of the single hexagonal prism-shaped wire and bamboo-like wire, respectively; (d-g) – TEM bright-field images of the NWs types.

Electron microscopy studies have shown that “smooth” wires could have different growth axes depending on the wire’s diameter. The NWs with diameter size < 100 nm (“thin” wires) have high-density of SFs. The growth axis of the wire coincide with normal to the close-packed planes and so with [111] crystallographic direction of 3C – structure. The NWs with diameter size >100 nm (“thick” wires) can have either the [110] or the [112] growth axis.

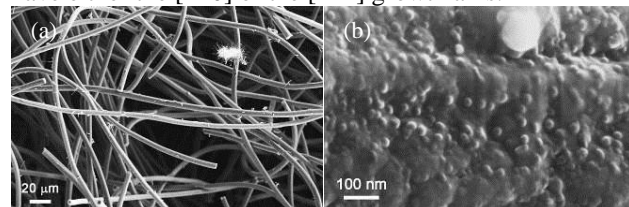


Fig. 2. (a) - FESEM image of the carbon felt before synthesis; (b) – magnified view of the carbon fiber surface.

The carbon substrate consists of carbon fibers with a diameter of 5 – 8 μm (fig.2 a). Figure 2b shows a magnified FESEM image of the fiber surface before the SiC wires synthesis. From the image, the fiber surface is covered by a randomly distributed ball-shaped “hillocks”

with a size of 20 – 50 nm (however the hillocks with a size of 300 nm are observed at scanning of the fiber surface). The EDX analysis reveals a low concentration (~0.08 atomic %) of Si of the initial carbon fiber. The silicon is uniformly distributed over the fiber surface and Si content varies within the range 0.05 – 0.1 at. %. Taking

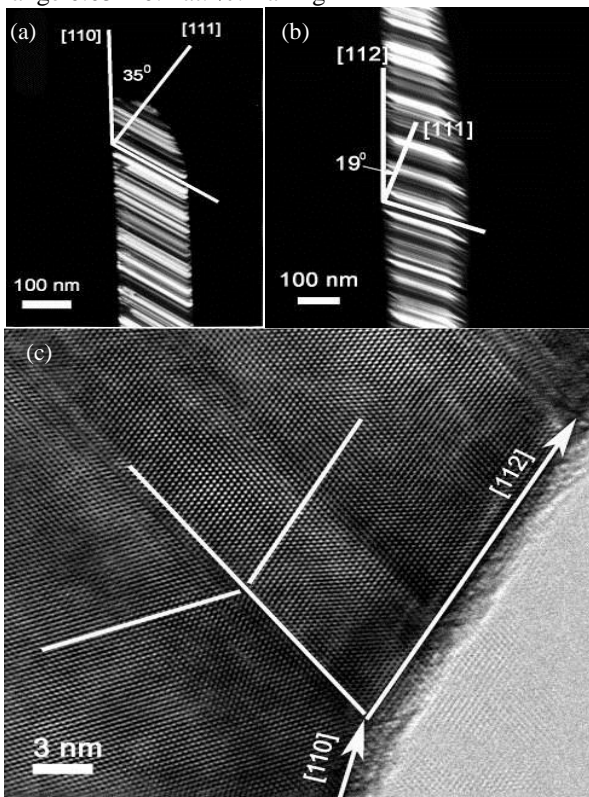


Fig.3. (a) –dark field TEM image of [110] orientation of the wire;

(b)–dark field TEM image of [112] orientation of the wire;

(c)–HREM image of the twin part showing change the growth direction depending on the direction of the lateral boundaries of twin domains.

into account un-uniform distribution of the SiC crystallites over carbon fibers we assume that some hillocks” can be places of silicon agglomerations and the templates for further SiC NWs nucleation.

Figure 3 (a, b) shows TEM dark-field images of the “thick smooth” wires. From figure 3a, the boundaries of SFs ({111} close-packed planes in cubic structures) are inclined at the angle of 55° (125°) with respect to the wire growth axis and so the boundaries normal makes the angle 35° with the growth axis. This angle is close to the crystallographic angle between the [111] and the [110] directions of a cubic structure. Hence, the growth axis of the wire is the [110]. In the case of the wire (fig. 3b), the boundaries normal of the close-packed planes is inclined at the angle 19° with respect to the wire growth axis, which corresponds to the angle between the [111] and the [112] directions of a cubic structure. Therefore, the wire growth axis is [112].

Figure 3c shows HRTEM image of the region of the wire with [112] growth direction. From image, there is defect-free section with the twin 3C-structure in the wire. The bottom domain has the side boundary with the [110] direction, while

the upper domain has the side boundary with the [112] direction (white lines show the traces of the {111} planes). Though the average growth axis of the wire is [112], because of such type domains are predominant in the wire.

Thus, the certain type of 3C-structure twin domains in the “thick smooth” wires generates the crystallographic orientations of the SiC close-packed planes and the wire’s growth direction, respectively.

The SiC NWs with core (SiC) – shell (SiO₂) structure were reported in many works. The physical properties of such wires very differ from the “bare” ones. In this report, the core-shell wires were produced via annealing of the initial “bare” SiC wires at the temperature of 850^oC for 4 h in air.

IV. SiC/C NANOCOMPOSITES WITH INVERSE OPAL STRUCTURE

The electron microscopy data revealed a highly porous periodic structure which was a three-dimensional replica of the voids of the initial opal lattice (Fig. 4, 5).

High temperature treatment (1770 – 1870K) causes sintering of the composite with 15% shrinkage calculated by the change of the diameter of the silicon dioxide sphere. Etching-out of silicon dioxide results in formation of highly porous structure (figure 4), whose density is

estimated as 0.03 g/cm³ (~1.3% of graphite density). The specific surface measured by the BET method was 275 -430 m²/g in dependence of silica globule size. All the inside cuts demonstrate a three-dimensional replica of the voids of the initial opal lattice (figure 4, 5). The pictures show distinct void semispheres with oval-shaped holes pointing to the sites of the silicon dioxide sphere contact in the initial opal structure. Three holes in each semisphere can be seen in figure 4 and in figure 5 there are four holes which corresponds to the structure of the opal (111) and (100) faces. Beside such windows smaller random holes (defects) occur in the sphere shells (figure 2). The shell thickness estimated by SEM pictures varies from 4 nm до 10 nm.

The hexagonal silicon carbide was found to be non-uniformly distributed throughout the volume, its greater part located in the surface layer up to 50 micron deep. Correlation of the data of element and diffraction analysis yields the following data on the phase composition of the sample after etching in HF solution: The SiC content in the sub-surface layer is ~55% wt., inside the sample 1% wt., the carbon content on the sample surface was ~32% wt., in the bulk ~90% wt. ; the silicon dioxide content on the sample surface and in the bulk varies about 10% wt. There is a natural explanation of the large amount of silicon carbide in the surface layer compared to that in the bulk. The reaction of carbothermal reduction of SiO₂ with SiC formation requires removal of gaseous carbon oxide which is realized in subsurface layers and hindered in the sample bulk on closure of nanopores in the course of sintering.

As to the SiO₂ phase state, it is worth mentioning the absence of narrow diffraction peaks is indicative of the amorphous state of silicon dioxide in our samples.

The data of x-ray diffraction, IR and Raman scattering spectroscopy enabled us to assume that the composite had hexagonal diamond fragments. The assumption of the presence of the diamond phase in the composite based on the x-ray data was confirmed by RS and IR spectroscopy. The RS spectrum of the sample under study consists of two 1318 cm^{-1} (halfwidth 75 cm^{-1}) and 1258 cm^{-1} (halfwidth 40 cm^{-1})

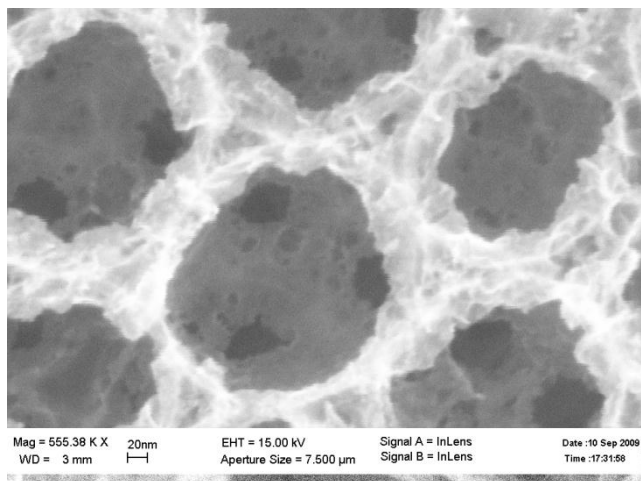


Fig. 4 (111) side cut of SiC/C inverse opal upon etching in HF solution

lines. The intensity of the second line is by an order of magnitude less than that of the first. The IR transmission spectrum of the composite shows a 2000 cm^{-1} band which is in the region of intrinsic absorption of the diamond crystal lattice. No such absorption line is observed in the spectra of

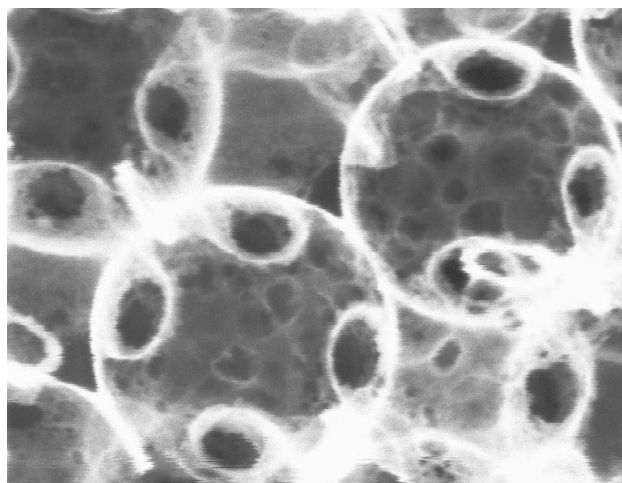


Fig. 5. (100) side cut of SiC/C inverse opal upon etching in HF solution.

different graphite types. The weak intensity and large halfwidth indicate that the phase is strongly disordered and the crystalline sizes do not exceed several nanometers.

Implanted samples show weak photoluminescence in the blue - green region of about $3.1 - 2.5\text{ eV}$ ($400 - 500\text{ nm}$). Annealing after implantation at temperature of 800° C in an inert atmosphere leads to the emergence of local dots in the sample, glowing orange-red (ORD). PL spectra of two typical points are given in Fig. 6 (curves 1 and 2). Curve 3 (Fig. 6) measured with the sample area, where there were no glowing orange-red. Its intensity in the blue spectral region is almost two orders of magnitude below the intensity of

ORD (Fig. 6, curves 1 and 2). It should be noted that the orange-red dots (ORD), were detected in only one of the 4 samples of the series.

Band with maximum of about 2.16 eV (574 nm) (Fig. 6, curve 2), 0.40 eV FWHM, similar to the band, as observed in [1]. Radiation of ORD (curve 1) represents a broader band with a maximum of about 2.12 eV (585 nm), which admits the expansion (see inset in Fig. 6) into two bands with maxima at about 2.17 eV (571 nm) and 2.0 eV (620 nm), which are characteristic for two types of N - V centers in diamond: the neutral $(\text{NV})^0$ center (575 nm) and negatively charged $(\text{NV})^-$ center (638 nm) [2,3].

Peaks shift and the large width of the lines indicate the small size of the radiation centers, comparable with 5-nm nanodiamonds [4]. While studies temporal instability of the PL centers have been found. About a few months of ORD disappeared in the samples. It should be noted that the comparison samples used in the irradiation with helium ions, did not show an orange-red luminescence.

In order to identify structural fragments of the diamond samples were investigated by transmission electron microscopy, high resolution (HRTEM). At the structure of the composites, except for silicon carbide, graphite and amorphous carbon, spherical carbon particles containing concentric graphite shells (onion-like particles) were found.

In [5] have shown that when such particles are heated to 700° C and irradiated with electrons so their nuclei can transform into a diamond. The distance between carbon planes in onions decreases as we move from the outer to inner shells in the range of $0.34\text{ nm} - 0.22\text{ nm}$. This decrease in the interplanar distance is the result of compression of the

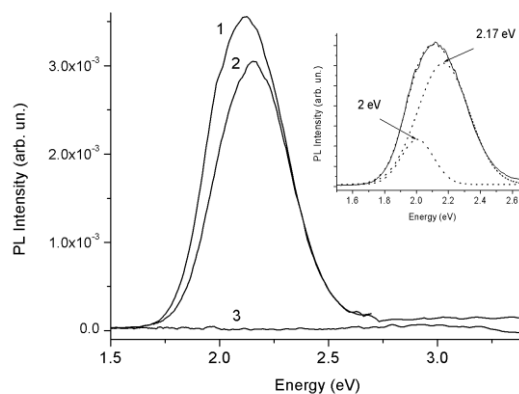


Fig. 6. PL spectra of two typical orange-red dots (curves 1 and 2) and site without ORD.

irradiated particles, which leads to the formation of diamond particles in the nucleus. In [5] the pressure inside the particle was estimated, which can exceed the equilibrium pressure of the transition of graphite - diamond. The formation of diamond nuclei was observed for many onions -like particles, with the number of shells of more than 15. The size of crystalline diamond in the nucleus varies from 2 nm to 50 nm . At room temperature, however, the lattice of the irradiated onions -like particles broken because of the many defects such as boundaries, which reduce the stability of onions [5].

Fig. 7 shows a composite image of SiC / C, containing onion-like particles. Interplanar distance in the nucleus corresponds to the graphite phase of carbon. On one of

twenty different parts of the sample giant onion-like particle with diameter of 100 nm was observed. Fig. 8 shows images of the upper half of the particle. Apparently, a giant onion-like particle formed at the site of the octahedral voids in the opal lattice, completely filled with carbon, since the size of the octahedral cavities is $0.42D_{\text{SiO}_2}$, where D_{SiO_2} is ball diameter.

We used in this study silica spheres about 260 nm in size. Dimensions of oktaporous in this matrix corresponds to the inscribed sphere of diameter about 100 nm. As seen from the images (Fig. 8), the continuity of the graphite layers disrupted in many places. There are areas of disorientation

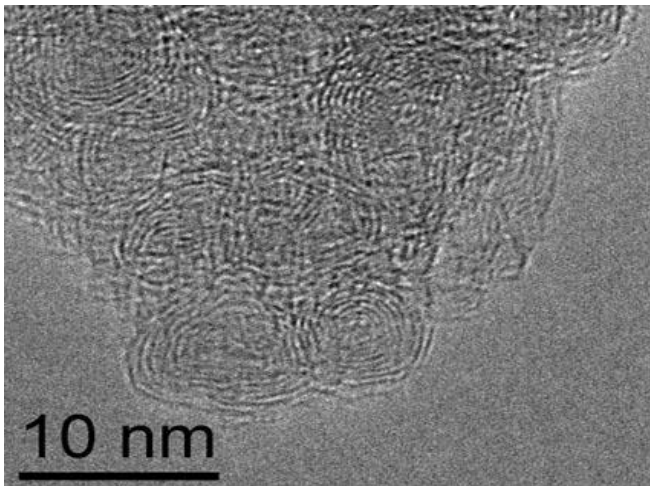


Fig. 7 Spherical carbon particles, consisting of concentric graphite shells (onion-like particles), HRTEM.

and disordering the graphite layers at the atomic level, which is consistent with observations in [5].

Analyzing results of measurements of set of parts of a composite, it is possible to note, that the typical size of

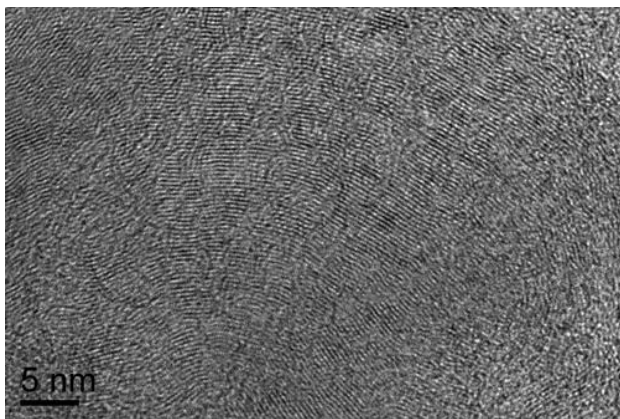


Fig. 8. SEM image of giant onion-like particle with diameter of 100 nm (upper half of the particle)

onion-like particles makes about 10 nanometers. The kernel in such particle has the size about 2 nanometers according to data [5].

Such small size of particles logically explains their temporary instability. It is possible to assume, that the kernel is formed in the form of a diamond phase as a result of high-temperature processing a composite opal - carbon. In due course the thermodynamic instable phase of diamond is transformed to graphite at room temperature. Implantation of a composite by ions of helium initiates N - V centers formation in a diamond phase that ORD luminescence confirms. After transformation of diamond in graphite ORDs also disappear.

In the investigated samples we could not to detect fragments of a diamond phase, including and in kernels of onion-like-particles. It is no wonder if to consider the lowest concentration ORDs in samples (1 ORD per cm^2), high localness of HRTEM method and thermodynamic instability small (2-3 nanometers) diamond clusters.

V. CONCLUSION

The SiC NWs were synthesized via carbothermal reduction method using both the colloidal graphite and the colloidal SiO_2 as carbon and silicon sources, respectively. It was detected the SiC NWs of the two types: "smooth" and "bamboo-like" wires. The "smooth" wires with the diameter < 100 nm have the [111] growth direction, while the wire with diameter > 100 nm can have either the [110] or the [112] growth direction. SiC/C-HRTEM revealed in the structure of the composites, except for silicon carbide, graphite and amorphous carbon, spherical carbon particles containing concentric graphite shells (onion-like particles). It was established that the onion-like particles formed during the manufacture of SiC / C nanocomposite at high temperature treatment. It is shown that after implantation followed by heat treatment samples exhibit of the luminescence characteristic for the N - V centers in diamond. It is suggested that the diamond crystallites formed in the center of the onion-like particles during high temperature treatment of the composite.

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