Scanning tunneling microscopy investigations of silicon carbide nanowires


Department of Solid State Physics, Division of Physics and Technology of Nanometer Structures, University of Łódź, Pomorska 149/153, 90-236 Łódź, Poland

Department of Chemistry, Warsaw University, Pasteura 1, 02-093 Warsaw, Poland

Military University of Technology, Kaliskiego 2, 00-908 Warsaw, Poland

School of Computing, Engineering and Information Sciences, Northumbria University at Newcastle, Ellison Building, Newcastle-upon-Tyne, NE1 8ST, UK

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Abstract

Scanning tunneling microscopy (STM) images have been obtained from the surfaces of silicon carbide nanowires produced in the thermolysis-induced carbonization of halocarbons (combustion synthesis). The morphology of the nanowires shows trench-like features perpendicular to the fibres’ axis, which is assigned to the existence of microfacets on their sidewalls. For the first time high-resolution STM images of the SiC nanowires are presented. The results are in agreement with the previous reports suggesting the presence of microfacets on the SiC whiskers’ surface.

Keywords: Silicon carbide; Nanowires; Nanofibres; Scanning tunneling microscopy

1. Introduction

Silicon carbide nanowires have been extensively studied during the past several years. Theoretical and experimental investigations of SiC nanofibres are motivated mainly by their unique physical properties, e.g. mechanical strength [1–3], electronic properties [4,5], luminescence and optical behaviour [5,6] and field emission properties [7,8]. As a result SiC nanowires are considered as candidates for the fabrication of modern electron emitters, nanoelectronic devices and for improvement of composites. SiC nanowires have been synthesized so far in many various ways such as carbon nanotubes-confined reaction [9], arc discharge process [10], chemical vapour deposition [11], laser ablation [12], carbothermal reduction of SiO₂ xergels [13] and many others. However, SiC nanowires can be also prepared by thermolysis-induced carbonization of halocarbons (combustion synthesis)

which is efficient single step chemical reaction performed in a closed reactor without external heating the reactants [14].

The crystallography of silicon carbide shows the existence of many polytypes. The 3C cubic zincblende structure (also known as the β-SiC) has been confirmed as a dominant polytype for SiC nanowires and also for the ones obtained in combustion synthesis [15]. The nanofibres’ axis lies usually in the [1 1 1] direction but the objects with [1 0 0] orientation have been also observed [7]. As has been shown by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) SiC nanowires exhibit many structural defects-like bends, junctions and twists [16–18]. The crystallographic structure of the SiC nanofibres and their internal defects are the subjects of many investigations. However, the knowledge about their surface morphology and electronic structure is still lacking and needs further theoretical and experimental studies. Many elongated nanostructures like carbon nanotubes [19] and boron-nitride nanotubes [20] have been imaged so far by using scanning tunneling microscopy (STM). High-resolution STM topographies have revealed their surface structure in atomic scale and some defects of their morphology. Successful STM measurements performed on carbon and boron-
nitride nanotubes suggest that the STM technique can be also applied to the investigations of the SiC nanowires.

The goal of our studies was to explore the surface morphology of the SiC nanowires produced in the thermolysis-induced carbonization of halocarbons by the STM technique. Our STM topographic images exhibited trench-like structures approximately perpendicular to the axis of nanowires. Moreover, the high-resolution STM images suggested that the surface roughness can be attributed to the microfaceted structures. In our opinion we are dealing with the \{1 0 0\} microfacets on the SiC nanowires that have been previously proposed to explain the morphology of larger SiC whiskers [21].

2. Experimental

The STM/STS/CITS experiments were performed with a commercial VT-STM/AFM system in UHV condition (Omicron GmbH, Germany) and SEM measurements were carried out with Quanta 200 (FEI). The tips used were prepared by mechanical cutting 90%Pt–10%Ir alloy wires (Goodfellow). All the topographic images were recorded for positive sample voltages (tunneling into the empty electronic states of the sample). Silicon carbide nanowires were produced by the thermolysis-induced carbonization of halocarbons (combustion synthesis) [14]. The initial reactant composition comprised of polytetrafluoroethylene (PTFE, 57.8 wt.%) and calcium disilicide (CaSi₂, 42.2 wt.%) that gave the highest SiC yield. The obtained product was purified by calcination in air (900 K, 1 h) and a subsequent washing with KOH (30 wt.%), H₂SO₄ (96 wt.%) and HCl (36 wt.%). Washing the material with distilled water and drying followed each stage of purification. A piece of the purified product was diluted in 1,2-dichloroethane using the ultrasonic treatment (about 15 min). Then, we put a droplet of the mixture on the highly orientated pyrolytic graphite (HOPG) or Au (1 1 1) substrate and left the sample to dry up.

3. Results and discussion

The STM investigation of elongated objects like nanotubes or nanowires is a demanding task. Positioning of the STM tip in a tangle of fibres usually causes the tip-crash. Additionally, the tip can be damaged when the diameter of the scanned object is too high (usually higher than 100 nm). The geometry of nanowires and their arrangement on the substrate are also of great importance. For this reasons we performed the preliminary tests using SEM to estimate the concentration and the arrangement of the SiC nanowires on prepared samples. Low-magnification SEM image of the SiC nanofibres deposited on the Au (1 1 1) substrate is presented in Fig. 1a. The concentration of objects was locally high (region denoted as #1 in Fig. 1a) and large conglomerates were usually observed. This level of concentration is unacceptable for the STM measurements. However, we also observed regions with low concentration of the SiC nanowires (denoted as #2 in Fig. 1a). Furthermore, some objects protruding from the edges of conglomerates (see Fig. 1b) with well-exposed sections were also detected. It should be noticed that most of fibres lied in plane of the substrate. Additionally, the SEM results showed that the fibres’ diameter ranged from ~10 nm to ~100 nm and that most of nanowires were almost perfectly straight. These facts argued us that STM scans can be performed because of the reasonable height and well-defined geometry of nanowires.

Typical STM topographies of the SiC nanowires deposited on Au (1 1 1) and HOPG substrates are presented in Fig. 2a and b, respectively. Usually we observed objects with relative height between 5 nm and 150 nm. The relative height of the first object (Fig. 2a) ranged from about 7 nm to 20 nm depending on position. The nanofibre probably protruded from the conglomerate and we scanned only its clearly exposed part to prevent the tip damage. The presented section of the object was stable
which we attributed to two reasons: it was stabilized by the conglomerate at one end (right-down corner of Fig. 2a) and by the trench in the Au (1 1 1) substrate at another end (left side of Fig. 2a). We could not examine this object outside the presented area because the measurement was unstable and the fibre tended to move in plane of the sample. The second object (Fig. 2b) was probably a bundle of SiC nanofibres lying on the HOPG substrate. The splitting of the object is clearly visible on their left side and this fact excludes the possibility of multiple-tip effect. We suppose that this bundle was composed of individual nanofibres or smaller bundles. Its relative height was about 100 nm. In the case of both fibres the measured size in the plane of the substrate was a few times greater than their height that can be explained basing on the STM tip convolution effect [22].

The detailed topography of the SiC nanowires was strongly affected by their curvature so it was reasonable to use the filtering procedure to enhance existing surfaces steps and edges. In our case we used the standard deviation filter. The applying of this procedure clearly exhibited trench-like features existing on the nanowires’ sidewalls that are presented in Fig. 3. We detected relatively flat regions extending from a few nanometers up to several dozen of nanometers along the fibre. These regions were separated by the steps that had winding structure and they were approximately perpendicular to fibres’
axis (which is supposed to be [1 1 1]). They were observed in the case of bundles and also for isolated nanowires. It should be admitted that in our case some irregularities and distortions were also detected on the surface of nanowires which sometimes made difficult proper height measurements. However, the cross-section profile presented in Fig. 4 performed along the fibre’s axis revealed steps of 0.5 nm and 0.25 nm in height (denoted as #1 and #2, respectively). It was taken from the unfiltered topographic image (section #d, Fig. 3). The theoretical step-heights for the (1 0 0) oriented crystallographic planes for β-SiC structure equal 0.436 nm (the unit cell dimension) and 0.218 nm (1/2 of the unit cell dimension). In this context it seems to be reasonable to suppose that locally we may deal with the {1 0 0} microfacets on the SiC nanowires’ surface.

Microfaceted structures existing on the surface of the SiC fibres were reported previously [21]. The {1 1 0}, {1 0 0} and {1 1 1 ¯} facets were proposed to explain the morphology of triangular and hexagonal SiC whiskers (including the whiskers with internal microtwin crystals). In our case the existence of the {1 0 0} microfacets seems to be confirmed by high-resolution STM images. These images revealed the characteristic arrangement of the corrugation maxima on the nanowires’ surface (Fig. 5a). The observed rows are spaced by ~0.32 nm that is believed to be the distance between neighbouring rows of atoms on the (1 0 0) surface. However, it should be admitted that the measurement for negative sample voltage was not performed and the question about the real position of atoms cannot be answered. Additionally, there is no visible corrugation along observed rows which probably can be attributed to the influence of the tip or specific surface reconstruction. The model showing the arrangement of atoms on the (1 0 0) microfacet and the projection of the unit cell on the (1 0 0) surface are presented in Fig. 5b. The carbon-terminated surface is shown but the (1 0 0) surface can be also silicon-terminated (for more information about carbon- and silicon-terminated reconstructions on β-SiC (1 0 0) surface see [23]). It should be noticed that the distance between the neighbouring carbon atoms equals \( a = \sqrt{2}/2a_0 = 0.308 \) nm (where \( a_0 = 0.436 \) nm is the β-SiC lattice constant). Basing on our STM data it is difficult to determine which type of atoms was imaged by the tip. However, performed X-ray photoelectron spectroscopy (XPS) deep profile measurements (unpublished data) showed that the subsurface region of nanowires is probably carbon enriched. This fact suggests that observed microfacets may be carbon-terminated. Furthermore, the XPS data revealed the presence of nitrogen atoms in the sample which in turn can explain relatively good conductivity of the nanowires (n-type semiconducting character). Recently, we have also examined the electronic structure of these SiC nanowires by scanning tunneling spectroscopy (STS) [24]. These studies shown substantial band-gap decrease which suggest semiconducting or metallic character of the nanowires.

High-resolution STM images were obtained for areas ranging from 5 nm × 5 nm up to 10 nm × 10 nm and scan velocities between 50 nm/s and 80 nm/s. These parameters were established basing on successful high-resolution measurements on HOPG and Au (1 1 1) substrates. They were sufficient to prevent the influence of the thermal drift on the topographies and to exclude the STM instabilities. The STM images recorded on the SiC nanowires revealed only ~0.32 nm spaced rows and we did not detect any structures with different spacing distance. According to this fact we believe that we probably dealt mainly with {1 0 0} microfacets but it should be admitted that we obtained high-resolution STM images only in few experiments. Bearing in mind that the {1 0 0} facets have higher surface energy than for example {1 1 1} facets (according to [21]) it is to be supposed that other microfaceted structures can exist on the SiC nanowires’ sidewalls but they have not been imaged. On the other hand the combustion synthesis is an extremely rapid reaction and in this context one can expect that non-equilibrium structures are prone to form (see [25] and references therein). This fact can explain predominant existence of the {1 0 0} microfacets. However, more experimental and theoretical work needs to be done to

![Fig. 5.](image-url)
resolve the surface geometry of the SiC nanowires and to incorporate the influence of the combustion synthesis mechanism on their morphology.

4. Summary

Silicon carbide nanowires obtained in the thermolysis-induced carbonization of halocarbon were investigated by scanning tunneling microscopy. High-resolution STM topographies have shown the trench-like features on the surface of nanowires perpendicular to the nanowires’ axis. The observed step heights and high-resolution images obtained on the SiC nanowires’ sidewalls were attributed to the existence of the \{1 0 0\} facets that are believed to be carbon-terminated. Our studies also show that STM is a powerful technique for investigation of the surface of SiC nanostructures and can be applied to reveal their local morphology in atomic scale.

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References