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ARTICLE *in* CRYSTAL GROWTH & DESIGN · JANUARY 2007

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CRYSTAL GROWTH & DESIGN
2007
VOL. 7, NO. 1
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Self-Assembled Hierarchical Single-Crystalline β-SiC Nanoarchitectures

Guozhen Shen,* Yoshio Bando, and Dmitri Golberg

Nanoscale Materials Center, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received April 16, 2006; Revised Manuscript Received October 24, 2006

ABSTRACT: Hierarchical single-crystalline β-SiC nanoarchitectures have been successfully synthesized using a catalyst-assisted thermochemical process. Their morphology and structure were investigated by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. Studies found that the central nanowires have diameters of ∼10−20 nm and the branched nanoplatelets have thicknesses of 5−10 nm. Field emission measurements showed that the hierarchical β-SiC nanoarchitectures have a turn-on field of ∼12 V/μm.

Introduction

Full control of architectures, sizes, morphologies, and patterns within inorganic crystals is a dominant theme in materials science since these parameters are the key elements that determine electrical and optical properties.[1−3] Hierarchical self-assembly of nanoscale building blocks, such as nanoclusters, nanowires, nanobelts, nanoplatelets, nanotubes, etc. is an important process for the fabrication of functional electronic and photonic nanodevices.[4,5] Many techniques have recently been developed to shape nanoscale materials into hierarchical nanoarchitectures, such as ZnO nanocombs,[6] nanowindmills,[7] and nanocantilever arrays,[8] hierarchical single-crystalline AlN nanoarchitectures,[9] dendritic micropines of α-Fe_2O_3,[10] ZnO microtrepangs, nanowheels,[11] self-assembled hierarchical Si−SiO_2 heterostructures,[12] ZnS−SiO_2 nanowire heterostructures,[13] and hierarchical ZnO nanostructures with 6-, 4-, and 2-fold symmetries,[14] and so forth.

As an important carbide semiconductor material with a wide band gap of 2.30 eV at 300 K, SiC is a potential candidate for the fabrication of electronic devices. It has superb hardness and high thermal conductivity even at a high temperature.[15] In addition, SiC wires exhibit good field-emitting properties.[16] Until now, a variety of functional SiC nanostructures have been successfully fabricated, including nanowires, nanotubes, nanoboxes, hollow nanospheres, and nanocables. An existing promise that these nanostructures may dramatically improve prime functional properties of many bulk materials has indeed stimulated great research enthusiasm.[17−27] In this paper, we report on the first time synthesis of hierarchical SiC nanoarchitectures through the epitaxial growth of SiC nanoplatelets on SiC nanowires under a simple chemical vapor deposition process.

Experimental Section

The hierarchical SiC nanoarchitectures were synthesized in a vertical-induction furnace consisting of a fused quartz tube and an induction-heated cylinder made of high purity graphite coated with a C fiber thermo-insulating layer. The furnace had inlet C pipes on its top and outlet on its base, respectively. A graphite crucible containing SiO (1.0 g), Ga_2O_3 (0.05 g), and graphite powder (0.15 g) was placed at the center cylinder zone. After evacuation of the quartz tube to ∼0.2 Torr, pure Ar flows were set within the carbon cylinder at constant rates of 150 sccm (from the top) and 200 sccm (from the base), respectively. The furnace was rapidly heated and kept at 1350 °C for 1 h.

After the reaction was terminated and the furnace was cooled to room temperature, the collected products were characterized using X-ray powder diffraction (XRD, RINT 2200) with Cu Kα radiation, scanning electron microscopy (SEM, JSM-6700F), and transmission electron microscopy (HRTEM, JEM-3000F). Field emission measurements on the synthesized hierarchical SiC nanoarchitectures were performed in a vacuum chamber at a pressure of ∼1.1×10^{-5} Torr. A rod-like aluminum probe with a cross-section of 1 mm^2 was used as the anode and a nanomaterial film was used as the cathode. A direct-current 200−1100 V was applied to the sample.

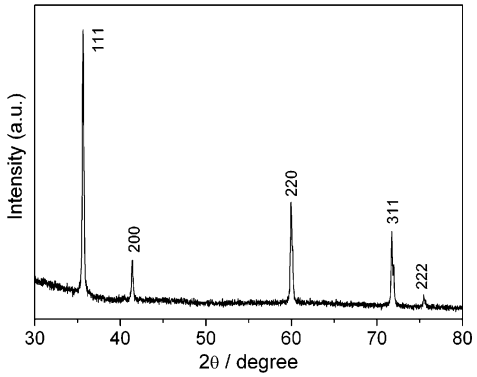

Figure 1. Typical XRD pattern of a SiC product after reaction over 1 h.

Results and Discussion

After the synthesis, light-greenish powders were found in a graphite crucible. Figure 1 shows a typical powder X-ray diffraction (XRD) pattern of the obtained product. All peaks in this pattern can be readily indexed as the cubic β-SiC structure with a lattice constant of $a = 4.361$ Å (JCPDS, No. 29-1129). No impurity phases, such as SiO, Si, and Ga_2O_3, were detected in the XRD pattern.

Scanning electron microscopy (SEM) examination was further conducted to investigate the morphology characteristics of the as-synthesized SiC product. The low magnification SEM images shown in Figure 2a,b display the formation of numerous strings made of platelet structures. As indicated by SEM images, most of the nanostructures are straight; however, some highly bent structures were also observed during SEM observations. The strings are 50−70 nm in diameter and several tens of micrometers in length. Closer examination (Figure 2c,d) of the strings

* Corresponding author. E-mail: shen.guozhen@nims.go.jp; gzshen@ustc.edu.

10.1021/cg060224e CCC: $37.00
Published on Web 12/07/2006

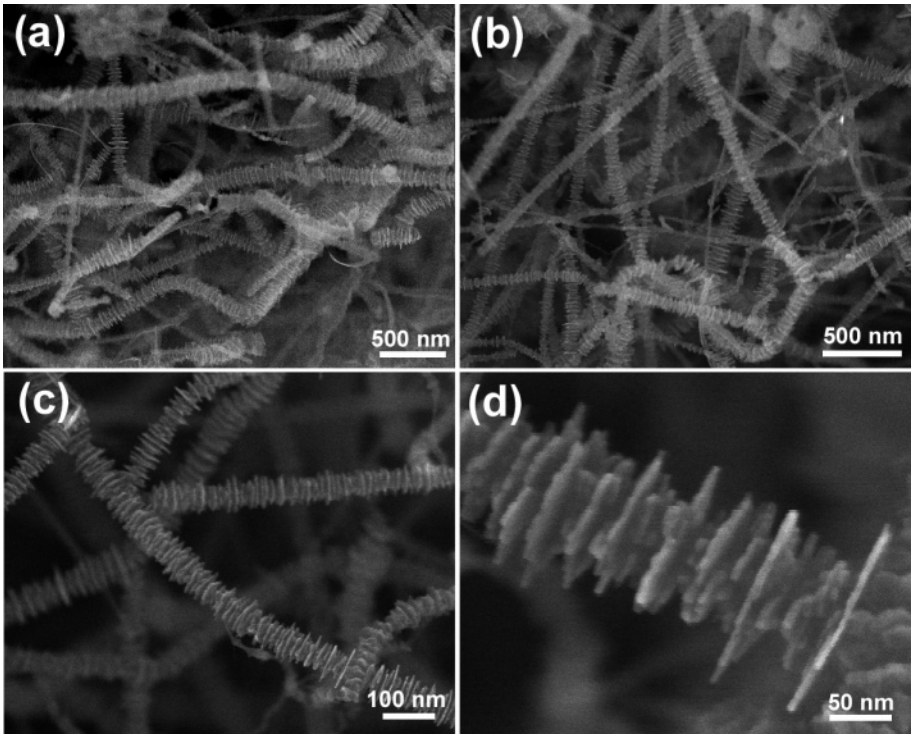

Figure 2. SEM images with different magnifications of a SiC product. Those clearly indicate the hierarchical morphology in which every hierarchical nanoarchitecture is self-assembled revealing numerous thin nanoplatelets parallel to each other and perpendicular to the core stem.

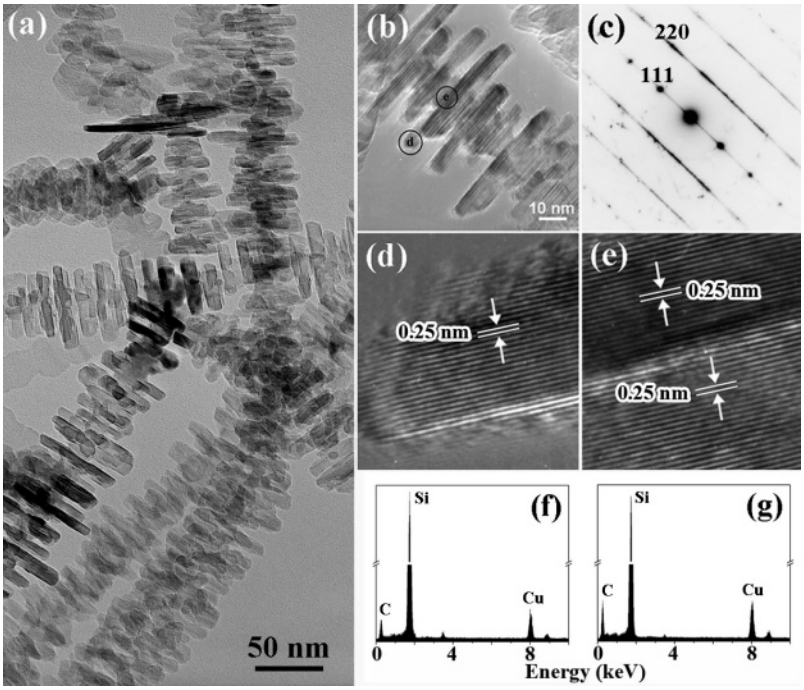

Figure 3. (a) TEM image of the hierarchical SiC nanoarchitectures. (b) TEM image of a single hierarchical SiC nanoarchitecture. (c) Corresponding SAED pattern. (d) and (e) HRTEM images recorded from the parts marked in panel b, respectively. (f) and (g) EDS patterns recorded from a single SiC nanoplatelet and the core stem.

indicates that the platelets possess a well-preserved orientation relationship. All platelets grow out of the stems and are parallel to each other. The thickness of the platelets is ~5−10 nm. Each platelet has a size ranging from 10 to 150 nm. The lack of evenness in the size of the individual platelets may due to the high reaction temperature and rapid growth time. Similar phenomena were observed for the thermal evaporation of hierarchical AlN nanoarchitectures at high temperature.[9]

The morphological details of the hierarchical SiC nanoarchitectures are highlighted in transmission electron microscopy (TEM) images (Figure 3). The low magnification image in Figure 3a shows that all platelets grow perpendicular to the central core nanowires. There is perfect ordering and alignment between the platelets, which suggests a possible crystallographic orientation relationship among them.

Figure 3b shows the higher magnification TEM image of a single hierarchical SiC nanostructure. It clearly displays the perpendicular growth of small SiC platelets with respect to the

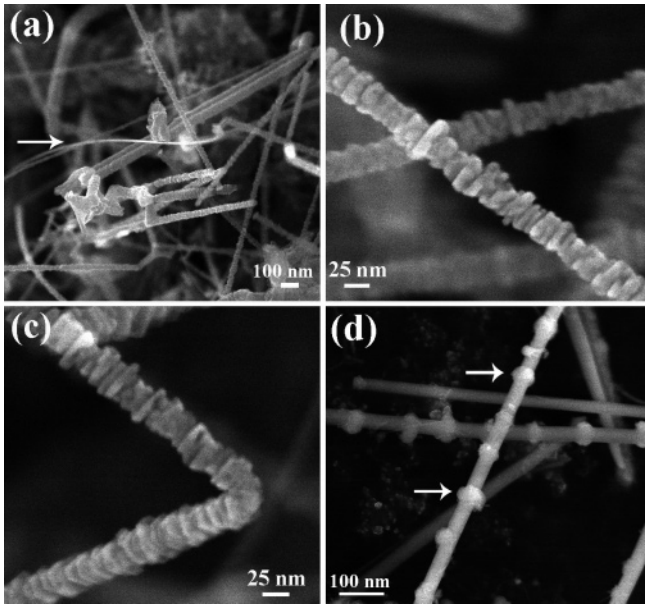

Figure 4. SEM images of the products obtained after a reaction over 30 min.

longitudinal axial of the nanostructure. The small SiC platelets have diameters of ~5 nm. The corresponding selected area diffraction (SAED) pattern recorded along the [110] zone axis shows bright spots, as well as streaks, indicating that some defects exist within the nanostructures. It is well-known that if such streaks are perpendicular to a given stacking fault, the existence of (111) stacking faults may be verified through the alignment of an electron beam along the [110] direction of β-SiC.[28] High-resolution TEM (HRTEM) lattice images of a single SiC platelet and the core stem of a hierarchical SiC nanostructure (recorded from the encircled domains in Figure 3b) are depicted in Figure 3, panels e and f, respectively. The observed *d* spacings are 0.25 nm for both the SiC platelet and the core stem, thus corresponding well to the {111} planes of β-SiC. It indicates that the core stem of the nanostructure grows along the <111> direction. The local chemical compositions of the platelet and the core stem were analyzed by energy-dispersive X-ray spectroscopy (EDS) using a nanoprobe. The results are presented in Figure 3f,g. Both spectra reveal the Si and C peaks as well as the peaks of Cu originating from the TEM grid. Therefore, the results further confirm that both the platelet and the core stem are solely composed of SiC.

To investigate the possible formation process of the hierarchical SiC nanoarchitectures, the products obtained under the reaction over 30 min were checked. Figure 4 shows the corresponding SEM images. In these images, very small platelet-attached hierarchical SiC nanoarchitectures with diameters of ~20−30 nm are seen. Some smooth nanowires with diameters of ~10 nm were also detected, as indicated with an arrow in Figure 4a.

For the formation of hierarchical nanostructures, usually two kinds of growth mechanisms are proposed. One is the formation of inner 1D core structures and then the epitaxial growth of secondary branches.[29] The other is the self-assembly of nano-building blocks, such as platelets, into hierarchical structures.[9] During our experiments, it was found that SiC nanowires decorated with small nanoplatelets can be obtained by carefully control of experimental parameters (shown in Figure 4d). By combining all the above-mentioned experimental results, it is reasonable to suggest that the formation of hierarchical SiC nanoarchitectures is a two-step epitaxial process (Figure 5)

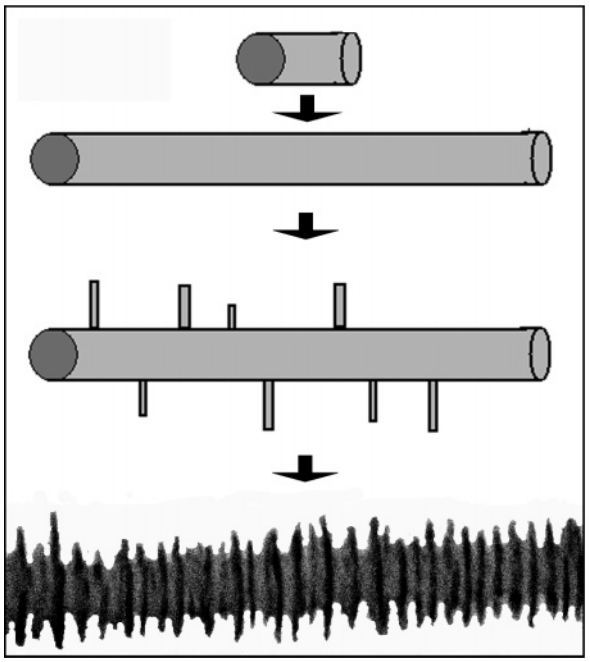

Figure 5. Schematic illustration of a possible hierarchical SiC nanoarchitecture growth process.

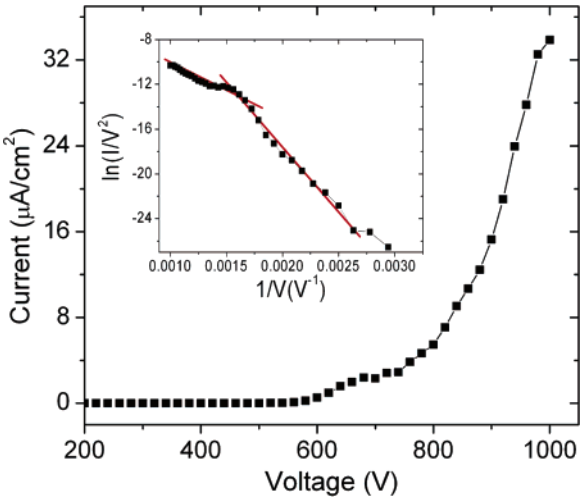

Figure 6. Field-emission $J-V$ curves recorded from hierarchical SiC nanoarchitectures. The inset is the corresponding Fowler-Nordheim (FN) plot in which two distinct linear regimes are highlighted with the red lines.

instead of the self-assembly of fused preformed platelets. First, the core stem SiC nanowires were formed and then the epitaxial growth of SiC platelets took place. In the present experiments, Ga_2O_3 plays an important role for the synthesis of hierarchical SiC nanoarchitectures. It is assumed here that the growth is dominated by the vapor−liquid−solid mechanism, albeit we did not find the particles attached to the tips. Importantly, without the usage of Ga_2O_3, no hierarchical SiC nanoarchitectures could be obtained. At a high reaction temperature, Ga is formed due to the decomposition of Ga_2O_3, and the newly formed Ga clusters/droplets are transported and deposited on the inner wall of the graphite crucible. These droplets are favorable sites for the growth of one-dimensional (1-D) SiC nanowires (Figure 5a,b). The growth of SiC nanowires is a very fast process followed by the nucleation and epitaxial growth of small SiC platelets perpendicular to the growth direction of the mother

SiC nanowires (Figure 5c). As a result, hierarchical SiC nanoarchitectures are formed (Figure 5d).

In recent years, 1-D nanostructures have attracted great attention with respect to the fabrication of field emission displays (FED). This relies on their high efficiency, and reduction of the production cost and device size compared to conventional thermionic emitters.[9,18] Field emission properties of many kinds of 1-D nanostructures have been already investigated by our group.[30−34] Recent field emission measurements of the SiC nanowires has suggested that the SiC nanowires are potential candidates for the cold cathode FED due to a unique combination of electrical, chemical, and mechanical properties. Interestingly enough, the reported turn-on fields (E_{to}) of 1-D SiC nanostructures vary in a wide range of 1−27 V/μm.[35,36] In the present work, we also measured the field emission properties of the formed nanoarchitectures, as shown in Figure 6. Field emission measurements were performed in a vacuum chamber at a pressure of $\sim 1.1 \times 10^{-5}$ Torr. Figure 6 displays an emission current density, J, measured versus an applied field at an anode-sample separation of 50 μm. Here, we define the turn-on field (E_{to}) and the threshold field (E_{thr}) as the electronic fields required to produce a current density of 10 and 10 mA cm^{-2}, respectively. It is found that a turn-on field is 12 V/μm, which is a little lower than the smooth SiC nanowires.[36] Such emitted current density is enough for application in flat panel display.

The Fowler-Nordheim law relates the emitted current and the local field E at the emitter surface,

$$J = (E^2\beta^2/\Phi)\exp(-B\Phi^{3/2}/E\beta)$$

where J is the emission-current density, E is the local applied field (where $E = Vd^{-1}$, and d is the anode-sample distance), Φ is the work function of the material, β is the enhancement factor, and B is a constant. The characteristic Fowler-Nordheim plot is shown in the inset to Figure 6. Two linear behaviors were observed within the measurement range. According to the previous reports, the two linear behaviors may be due to the current saturation. The latter phenomenon is attributed to possible adsorbents on the nanostructure appearing under a higher electric field or caused by the space charge effect.[36]

Conclusion

In conclusion, hierarchical β-SiC nanoarchitectures were self-assembled via a simple chemical vapor deposition process. The hierarchical β-SiC nanoarchitectures are composed of core stems growing along the <111> direction and platelets grown perpendicular to them. Field emission measurements on this novel nanomaterial reveal a turn-on field of 12 V/μm. This kind of new hierarchical nanoarchitectures may find applications in flat-panel displays or nanodevices.

Acknowledgment. We thank Y. Uemura for advice during material synthesis, K. Kurashima for technical assistance in TEM work, and Y. Gao for valuable discussions.

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CG060224E