

# Three-dimensional crystalline SiC nanowire flowers

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## Abstract

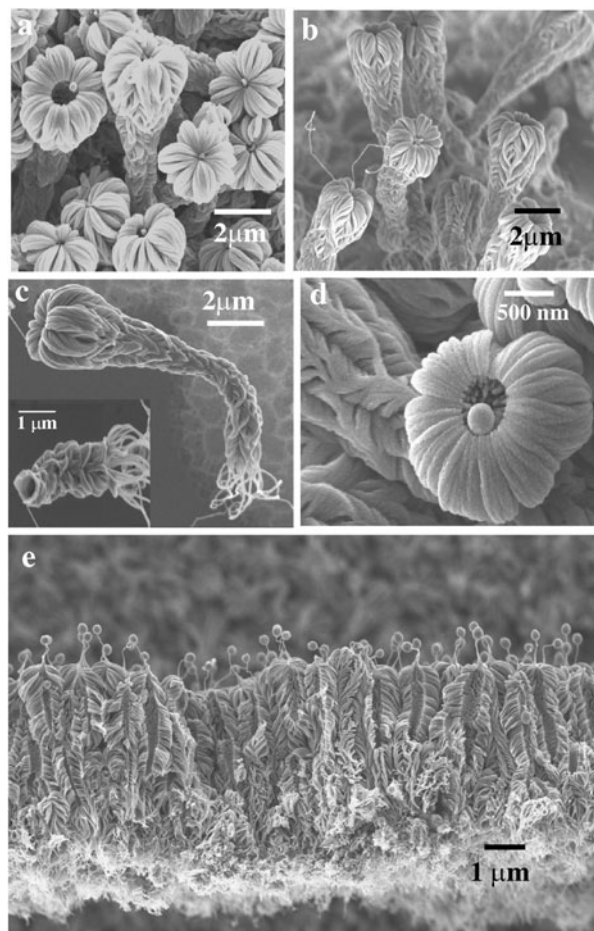
Several techniques have already been developed for synthesizing silicon carbide (SiC) material in the form of nanospheres and nanowires/rods. Here, we report the synthesis of a distinctly different kind of SiC nanostructure in the form of three-dimensional crystalline nanowire-based flower-like structures. Interest in such structures centres around the combination of a simple growth process based on SiC nanowire formation, with a resultant structure having potentially complex mechanical and optical properties, the latter a consequence of the wide band gap of bulk SiC. The synthesis of these SiC nanowire flowers is via a vapour–liquid–solid (VLS) process, on which a detailed study of both the chemical and structural composition has been carried out.

## 1. Introduction

Silicon carbide (SiC) is a well-known wide band gap semiconductor with high breakdown electric field, high thermal conductivity, chemical inertness and strong mechanical properties. Given these unique electronic and physical properties, it is well suited for the fabrication of electronic devices operating at high temperature, high power and high frequency [1]. There is significant interest in the synthesis of SiC nanostructures [2–5] (nanospheres, nanowires and nanorods) as novel functional materials for nanoscale engineering. SiC nanostructures have been shown to exhibit more superior properties (greater elasticity and strength) than bulk SiC [6]. In addition, the electron field-emission properties of SiC nanowires have a threshold field comparable to that of a carbon nanotube-based material with stable emission [7]. SiC has also attracted much interest due to its potential application in blue–green light-emitting diodes and UV photodetectors, since intense visible photoluminescence has been observed in SiC nanostructures [8, 9]. Here we describe the synthesis and characterization of a novel three-dimensional SiC-based material that essentially consists of complex interwoven SiC nanowires that evolve to form micron-scale flower-like structures.

## 2. Experimental details

In this study, a conventional chemical vapour deposition method was used for the synthesis of the SiC nanowire flowers. An alumina work tube was mounted inside a horizontal tube furnace within which an alumina boat loaded with a silicon substrate and gallium nitride powder was centrally placed. The gallium nitride powder was placed upstream from the silicon wafer. The alumina tube was initially evacuated to  $\sim 2 \times 10^{-6}$  Torr by a rotary and turbo pump. Argon gas was then admitted at 300 sccm at a pressure of  $\sim 5$  Torr, while a temperature of 1100 °C was ramped to at a rate of 25 °C min<sup>-1</sup>. When the desired temperature was attained, the argon flow was switched off and a steady flow of 300–400 sccm methane gas at a pressure of 5–7 Torr was maintained for 15 min, during which time growth took place. The chamber was then cooled down to room temperature in argon ambient. The surfaces of the resultant silicon substrates were observed to be black or dark greyish in colour. The morphology, structure, and chemical composition were characterized by scanning electron microscopy SEM (field-emission LEO 1530 VP), x-ray diffractometry (Philips x-ray diffractometer equipped with a graphite monochromator Cu K $\alpha$  radiation



**Figure 1.** (a) SEM images of, and (b) an overview of, nanowire flowers grown on the silicon substrate; (c) a detached flower showing its base made up of bundles of nanowires (inset: cross-sectional view of a broken SiC nanowire flower); (d) a typical flower with a catalyst particle attached to the tip; (e) a cross-sectional view which displays the highly aligned and closely packed nanowires.

( $\lambda = 1.541 \text{ \AA}$ )), Raman spectroscopy (Ramanscope 1000, excitation wavelength 514 nm from an argon ion laser) and high resolution transmission electron microscopy (FEI Tecnai F20-G2 FEGTEM).

### 3. Results and discussion

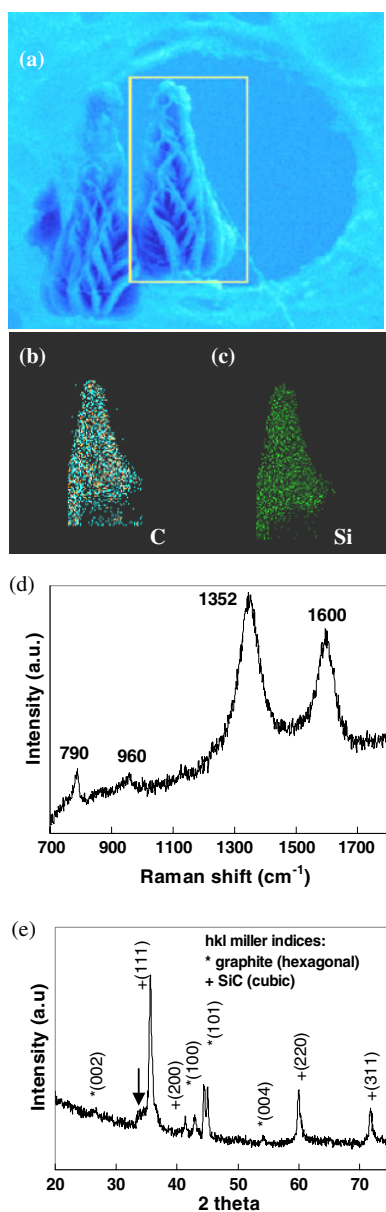
After growth, scanning electron microscopy reveals flower-like structures of diameter 1–2  $\mu\text{m}$  and length 3–5  $\mu\text{m}$  growing normal to, and completely covering, the silicon wafer (figures 1(a) and (b)). A typical flower (figures 1(c) and (d)) is composed of an intertwined/weaved stem, a bulbous head consisting of a tight bundle of nanowires of diameter  $\sim 100\text{--}200 \text{ nm}$ , and a single catalyst particle attached at the top end of the nanowire flowers. In addition, the cross-section of the broken base (figure 1(c) inset) reveals a hollow stem of  $\sim 400\text{--}800 \text{ nm}$  in diameter. A cross-sectional view through the layer (figure 1(e)) reveals that the hollow axis of the flowers is predominantly normal to the silicon substrate with a high density of packing.

The growth of these SiC nanowire flowers is via the VLS process where a catalyst particle, initially on the silicon

surface, acts as a nucleation site where vapour radicals coalesce to form SiC nanowires that grow radially from the catalyst surface. At the end of the growth process a catalyst particle is evident at the tip of each flower (figure 1(e)). A similar process is reported by Pan *et al* [10] for the synthesis of SiO<sub>2</sub> nanowire flowers. We propose two stages of VLS growth. In the first stage, thermal decomposition of gallium nitride occurs, producing gallium vapour which condenses into liquid gallium droplets on the silicon surface [10]. Next, hydrogen from decomposed methane gas ( $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ ) etches the silicon substrate to generate silyl radicals in the vapour phase [10]. There are then two possible processes by which the growth progresses. The silyl radicals may react with the decomposed methane gas to yield SiC that nucleates on to the catalyst particles [11], or carbon and silicon radicals may diffuse into the gallium droplets and, at supersaturation, initiate nanowire growth at the droplet surface [10]. As the radial growth of SiC nanowires continues, the newly formed nanowires begin to detach the catalyst particle from the surface, pushing the particle upward and essentially leaving behind a tubular cavity. We will return to this point later.

To confirm that the flowers were composed of SiC, we carried out a detailed study of both the chemical and structural composition. The chemical composition of the flowers was derived from elemental mapping and quantitative analysis using energy dispersive x-ray spectroscopy (EDX). Elemental mapping of an isolated flower was performed in order to address composition variation along the length of the flower (figures 2(a)–(c)). The maps show both carbon and silicon to be uniformly distributed along the length of the flower. There is no abrupt interface or transition of chemical composition observed, indicating that a ready supply of silicon and carbon vapour was available throughout the growth process. Detailed spectra and elemental mappings revealed that there was no variation in the SiC ratio within individual parts of a flower and between different flowers. The chemical composition of carbon and silicon was found to be approximately 1:1 by atomic ratio. EDX analyses on the catalyst particles seem to indicate predominantly silicon and carbon with no or occasional traces of gallium detected within the catalyst particles in those particles present at the end of the growth process. The absence or trace levels of gallium in the catalyst particles can be explained by the complete or partial sublimation of gallium, which has a low melting point. This may also explain why the flower structure seems to evolve from the hollow stem to the expanded head and the observation that all flowers are the same length—indicating that the growth process may be limited by catalyst exhaustion.

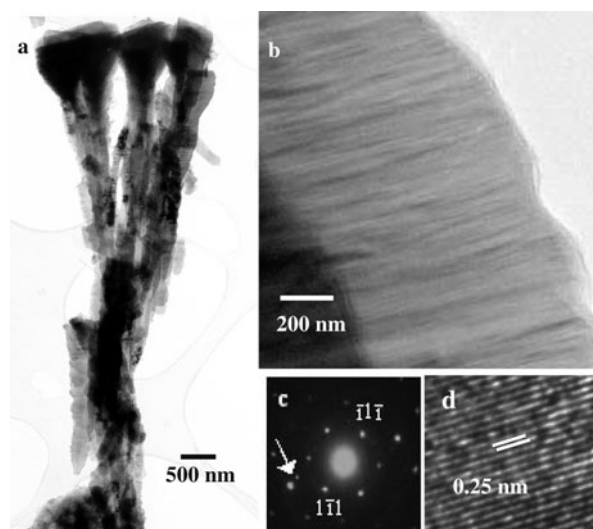
Raman spectra of the SiC flowers (figure 2(d)) were obtained at room temperature with an excitation wavelength of 514 nm (Ar<sup>+</sup> ion laser). Two peaks (around 790 and 960  $\text{cm}^{-1}$ ) are observed. These correspond to the transverse optical (TO) mode and longitudinal optical (LO) mode phonons of cubic SiC, and confirm the presence of crystalline  $\beta$ -SiC nanostructures [11]. The asymmetric broadening of the peak at 790  $\text{cm}^{-1}$  indicates stacking faults of SiC nanocrystallites [9]. Bulk  $\beta$ -SiC has a TO mode at 796  $\text{cm}^{-1}$  and LO mode at 972  $\text{cm}^{-1}$ , and it is believed that the red frequency shift may be due to defects or confinement effects on the Raman scattering of optical phonons [12]. Characteristic



**Figure 2.** (a) SEM image of the region (within the drawn box) where an EDX spectrum of a SiC flower dispersed on a Cu grid was taken; (b), (c) elemental mapping of the carbon and silicon content; (d) Raman scattering spectrum showing peaks at 790, 960, 1352 and 1600  $\text{cm}^{-1}$  corresponding to TO, LO mode phonons of cubic SiC and  $E_{2g}$ ,  $A_{1g}$  graphite modes; (e) XRD spectrum, showing diffraction peaks associated with SiC and graphite, of a film of SiC nanowire flowers grown on a silicon substrate.

graphite peaks are also observed between 1200 and 1800  $\text{cm}^{-1}$ . A  $E_{2g}$  graphite mode is present at 1600  $\text{cm}^{-1}$  which normally appears at 1582  $\text{cm}^{-1}$  for a perfect graphite crystal. The  $A_{1g}$  mode peak at 1352  $\text{cm}^{-1}$  is similar to the disordered-induced relaxation of the  $k$ -conservation rule and/or finite crystal size effect observed in pyrolytic graphite [13].

The crystallographic structure of the flowers was carried out by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD spectrum in figure 2(e) demonstrates the crystalline nature of the material, with diffraction peaks consistent with a mixture of primarily  $\beta$ -



**Figure 3.** (a) TEM images of a general overview of the flowers; (b) a closer view at the side of the flowers showing streaks of stacking fault structures; (c) the corresponding SAED pattern indexed to SiC with the extra streaks (indicated with an arrow) attributed to stacking faults or twinning; (d) high magnification image showing lattice fringes equal to the spacing of the  $\{111\}$  planes of  $\beta$ -SiC.

SiC [14] with some residual graphite. Further evidence of the SiC is provided by the presence of the shoulder indicated by an arrow at  $d = 2.675 \text{ \AA}$ . This has previously been shown to be associated with stacking faults, a common feature of SiC material [14].

The low resolution TEM micrograph of figure 3(a) shows the general morphology of the SiC flowers dispersed on a holey carbon grid, and, at higher magnification, striations with lamellar contrast are observed to be made up of high-density planar defects (figure 3(b)). These stacking faults are an inherent characteristic of SiC material [2, 5]. A selected area electron diffraction (SAED) pattern (figure 3(c)) was recorded along the  $[110]$  zone axis, revealing the single crystal structure. The extra streaks are characteristics of twinning or stacking faults [2, 5]. The spacing of the crystallographic planes calculated from the diffraction pattern or measured from the high-resolution image (figure 3(d)) is 0.25 nm, corresponding to the  $(111)$  lattice planes of the crystalline zinc blende  $\beta$ -SiC [2]. This indicates that the SiC nanowire flowers have grown in the  $\langle 111 \rangle$  direction with respect to the SiC crystallographic structure. High resolution TEM (not shown here) indicate the presence of residual carbon on the outer surface of the flower stem, corroborating the XRD and Raman observations.

We now return to the precise role of the catalyst particle in the growth process, where there is scope for further work so as to elucidate the detailed mechanism. In the absence of the gallium nitride in the growth process no flowers are observed, only individual nanowires. It is likely therefore that either the gallium allows for growth through a solution mechanism where Si and C dissolve in the gallium, as previously reported [10, 15], in addition to, or in competition with, a purely vapour phase mediated coalescence, or that the gallium droplets themselves act as more efficient nucleation sites for vapour-mediated growth. The fact that the stems of the flowers are hollow indicates that growth does not take place equally over the

catalyst surface, but rather at the periphery. With a fuller understanding of these processes a greater control over the growth process, resultant morphology and potential material systems will evolve.

#### 4. Conclusions

We have demonstrated the synthesis of SiC nanostructures in the shape of crystalline nanowire flowers. The synthesis can be controlled over a large area at optimal experimental conditions consistent with a VLS growth mechanism. Detailed characterization of the as-prepared SiC nanowire flowers has been carried out. We also observed that the grown nanowire flowers have a high surface–volume ratio and a basic structure of fused bundles of SiC nanowires, a length scale where dimensional or confinement effects have been previously observed. This combination of high surface area and complex structuring at the nanoscale can be expected to produce physical and chemical properties different from the bulk SiC material. The synthesis approach presented here may also be extended to the fabrication of other composite nanostructures via modification of gas-phase reactants.

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