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Synthesis and Characterization of SiC Nanowires through a Reduction−Carburization Route

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Cubic silicon carbide (3C−SiC) nanowires were synthesized through a reduction−carburization route by using silicon powders and tetrachloride (CCl_4) as Si and C sources, and metallic Na as the reductant at 700 °C. The as-prepared SiC nanowires were characterized and studied by X-ray powder diffraction, transmission electron microscopy, X-ray photoelectron spectra, Raman backscattering, and photoluminescence spectra at room temperature. The SiC nanowires produced from the present route typically have diameters of 15−20 nm and lengths of 5−10 μm. The influencing factors of the formation of the SiC nanowires were discussed and a possible growth mechanism for the SiC nanowires was proposed.

Introduction

One-dimensional (1D) structures with nanometer diameters, such as nanowires and nanotubes are attracting increasing interest due to their remarkable optical, electrical, and mechanical properties and their potential applications ranging from probe microscopy tips to interconnections in nanoelectrical devices.[1,2] Therefore, current attention has focused on the development of new methods for the preparation of nanoscale one-dimensional structures.

Silicon carbide belongs to IV−IV semiconductors and there exist more than 130 polytypes due to the different orders of stacking of the SiC layers.[3] They have wide energy band gaps from 2.3 eV for 3C−SiC to 3.3 eV for 2H−SiC at room temperature, and have good physical stability, high thermal conductivity, and high breakdown electric field.[4] These excellent physical properties make SiC a promising semiconductor material for device applications at high temperature, high power, and high frequency.[5] There are many reports on the synthesis of silicon carbide whiskers. The conventional methods fall into the following three standard categories: (1) thermal decomposition of organic silicon compounds,[6,7] (2) reaction between $SiCl_4$ and CCl_4 in the presence of hydrogen,[8] and (3) carbonthermal reduction of SiO_2.[9−11] The diameters of SiC whiskers prepared by these traditional methods were typically >1000 nm, although diameters as small as 100 nm have been observed. Recently, Dai et al.[12] adopted an approach to prepare silicon carbide nanorods with diameters between 2 and 20 nm, in which the carbon tubes were converted into silicon carbide nanorods by reacting with Si and I_2 at 1200 °C. Our research group has successfully synthesized diamond powder on the reduction of CCl_4 by Na at 700 °C.[13] In the present study, SiC nanowires were synthesized at 700 °C by the reduction−carburization method, in which CCl_4 and silicon powder were used as source materials and metallic Na as the reductant. The reaction was carried out in an autoclave and can be expressed as follows:

$$Si + CCl_4 + 4Na \rightarrow SiC + 4NaCl \qquad (1)$$

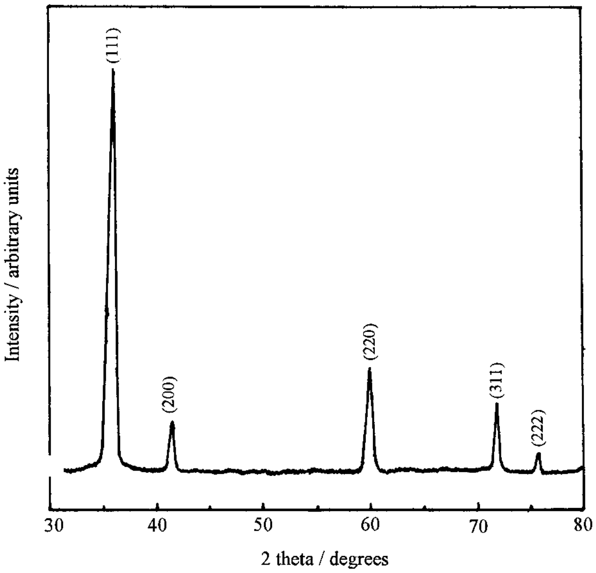

Figure 1. X-ray powder diffraction pattern of the sample prepared by a reduction-carburization route.

Experimental Section

In a typical experimental procedure, appropriate amounts of CCl_4 (5.0 mL), Si powders (1.44 g), and Na (4.74 g) were put into a titanium alloy autoclave of 50 mL capacity. The autoclave was sealed and maintained at 700 °C for 10−48 h and then cooled to room temperature. At the beginning of the reaction, there was a high pressure in the autoclave. As the CCl_4 was reduced by Na, the pressure deceased. The product was collected and treated by dilute $HF+HNO_3$ to eliminate the unreacted silicon. The free carbon in the product was removed by heating in air at 600 °C for 3 h. However, the product also suffered partial oxidation during the heating, and amorphous SiO_2 may have formed on the product surface. So, the product was treated with dilute HF again to eliminate amorphous SiO_2 coating. After washing with distilled water to remove NaCl and other impurities, a gray−white product was obtained.

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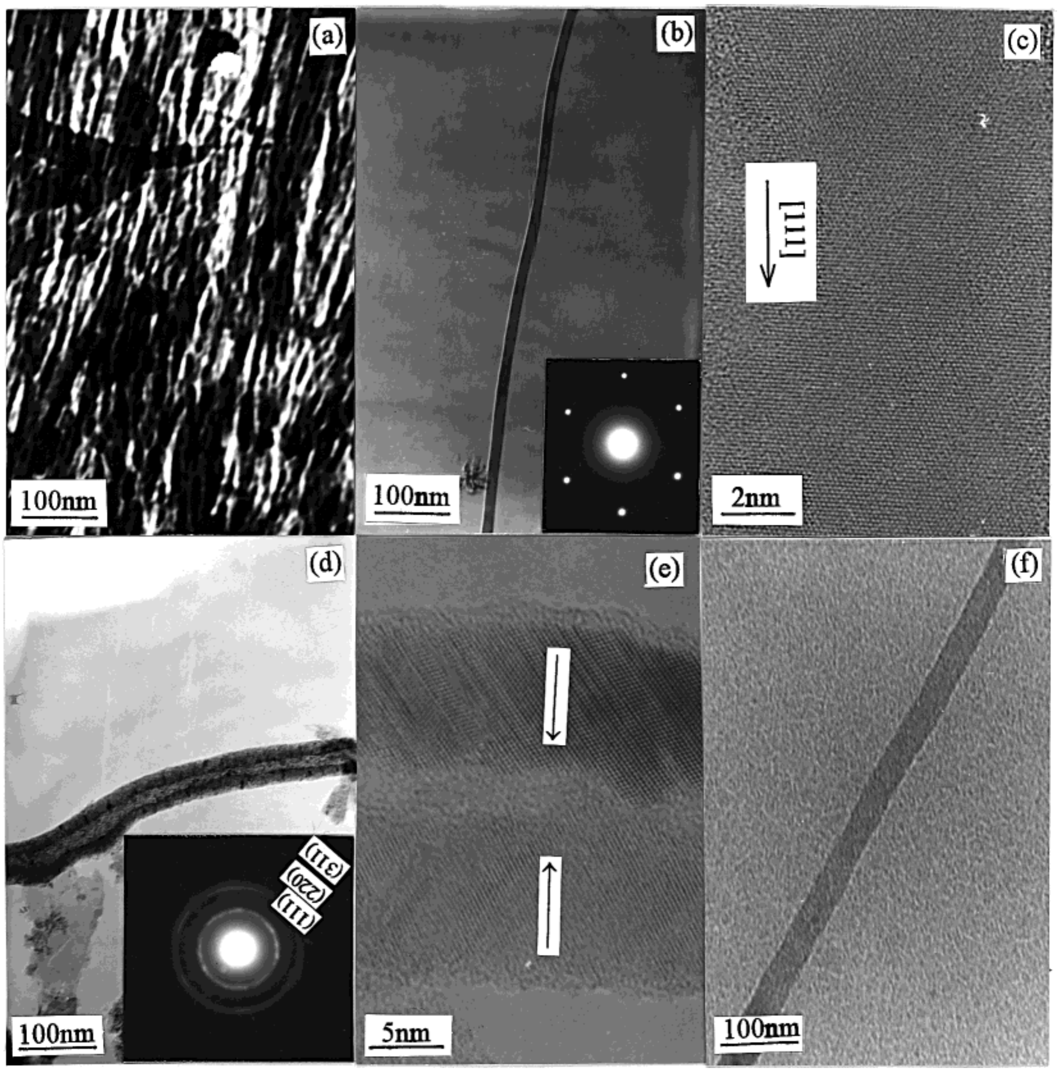

Figure 2. (a) TEM image of SiC nanowires . (b) TEM images of a straight single SiC nanowire and its ED pattern. (c) HRTEM image of the nanowire SiC shown in (b). (d) TEM image of a hollow-structure SiC nanowire and its ED pattern. (e) HRTEM image of the hollow structure SiC nanowire.The arrows showing the hollow nature. (f) TEM image of a carbon nanorod obtained from the reduction of CCl_4 by Na at 700 °C.

The X-ray powder diffraction (XRD) pattern was recorded on a Japan MAC SCIENCE MXP18AHF X-ray diffractometer with graphite monochromatized Cu Kα (λ = 1.54056 Å) radiation. Transmission electron microscopy (TEM) images and selected-area electron diffraction (ED) patterns were taken with an Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. High-resolution electron microscopy (HREM) images of the SiC nanowires were taken on a JEOL-2010 transmission electron microscope. X-ray photoelectron spectra (XPS) were carried out on a VGES-CALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg Kα X-ray as the excitation source. The Raman spectra were produced at room temperature with a Spex 1403 Raman spectrometer using an Ar-ion laser exciation with a wavelength of 514.5 nm and with a backscattering configuration. Photoluminescence (PL) spectra of the SiC nanowires were measured in an Hitachi 850 fluorescence spectrophotometer with a Xe lamp at room temperature.

Results and Discussion

Figure 1 shows the XRD pattern of the sample. All of the strong intensity peaks could be indexed to the zinc blende structure 3C−SiC. The refinement gave the cell constant, a = 4.3565 Å, which was consistent with the reported value in the literature (a = 4.3589 Å).[14] No other crystalline impurities, such as Si and SiO_2, were detected in the XRD pattern.

Figure 2 shows the TEM images and ED patterns of the samples. It can be seen that the sample consists mainly of nanowires. The SiC nanowires produced from present route typically have diameters of 15−20 nm and lengths of 5−10 μm (Figure 2a, 2b). The inset ED patterns (Figure 2b) are consistent with the high crystallinity. The HRTEM image (Figure 2c) demonstrates that the transparent section of this smooth nanowire is well-defined 3C−SiC single crystal and possess a very low density of planar defects. Further studies suggest that the nanowires have grown in a ⟨111⟩ direction. It is of considerable interest that a small fraction of hollow structures is clearly revealed by the TEM images (as shown in Figure 2d, 2e). The ratio of the structures to nanowires was about 5%. The structure generally has a diameter of 40−45 nm, a length of 1 μm, and a wall thickness of 15−25 nm. The ED pattern (Figure 2d) shows the polycrystalline rings [(111), (220), and (311)] of the 3C−SiC, which confirms the XRD result. However, the HRTEM image (Figure 2e) indicates that this hollow morphology contains heavy stacking faults on the basal planes in contrast to the well-defined 3C−SiC single crystals nanowires. These defect planes are basically rotational microtwins on the (111) basal planes.[15,16] The fact that carbon nanorods

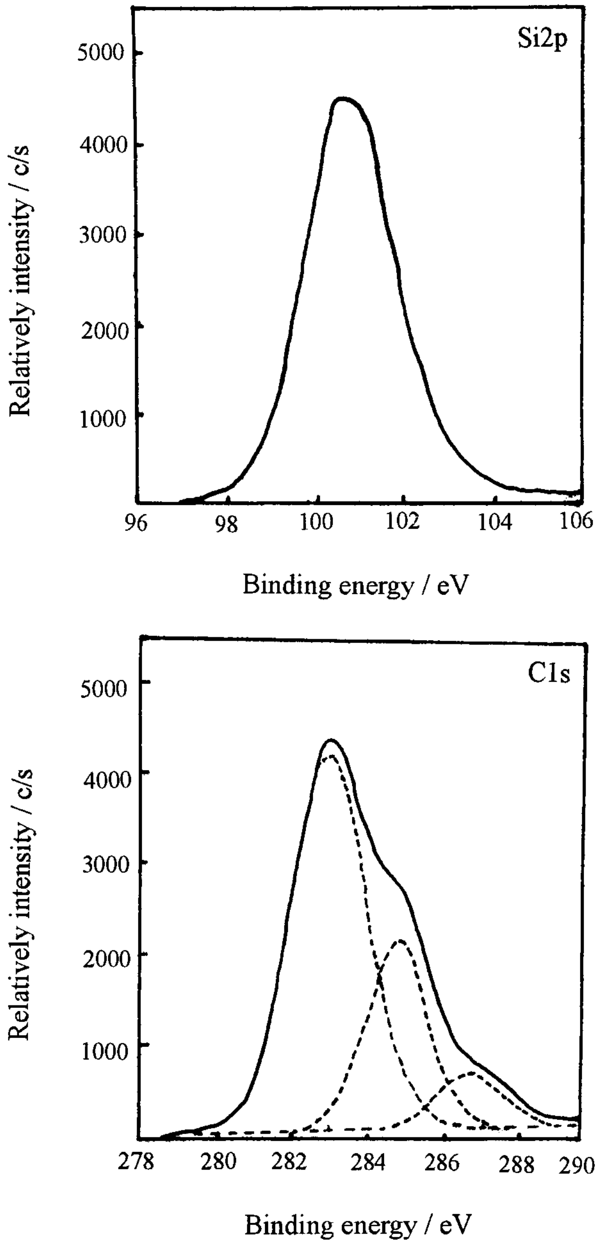

Figure 3. XPS spectra of SiC nanowires.

(Figure 2f) formed in the reduction of CCl_4 by Na at 700 °C suggests that the formation of the hollow structures may be based on the use of carbon nanorods as templates. Several SiC nanowires were coated on the carbon nanorods first and then the carbon in the core was oxidized into CO_2 by heating at 600 °C in air, and thus the polycrystalline hollow structure formed.

Figure 3 shows the XPS spectra of the sample. The two strong peaks at 100.20, and 282.40 eV correspond to Si2p and C1s binding energy, respectively, for SiC.[17] Quantification of the peak intensities gives an atomic ratio of Si to C of 1.11:1.00. However, the spectrum also displayed the other two C1s peaks at 284.45 and 286.10 eV, which can be attributed to a small amount of residual carbon (284.3 eV of C1s levels for graphite) and the adsorbed CO_2 onto the sample surface. No obvious peaks due to silicon (98.7 eV for Si2p) or silica (103.5 eV for Si 2p in SiO_2) are observed.

Figure 4 shows the Raman spectra for the SiC nanowires with a backscattering configuration. Two broadened bands at around 776 and 954 cm^{-1} were recorded, which correspond to the TO and LO phonon at the Γ point of cubic SiC. We note that the Raman spectral features are strikingly different from others reported in the literature.[5,18−20] Not only is the TO (Γ) phonon line much stronger than LO (Γ) phonon line but also the two lines are both shifted by 19−20 cm^{-1} toward lower energy. The reason for this exception may originate from the small grain sizes of the SiC and from the growth faults of the nanowires.

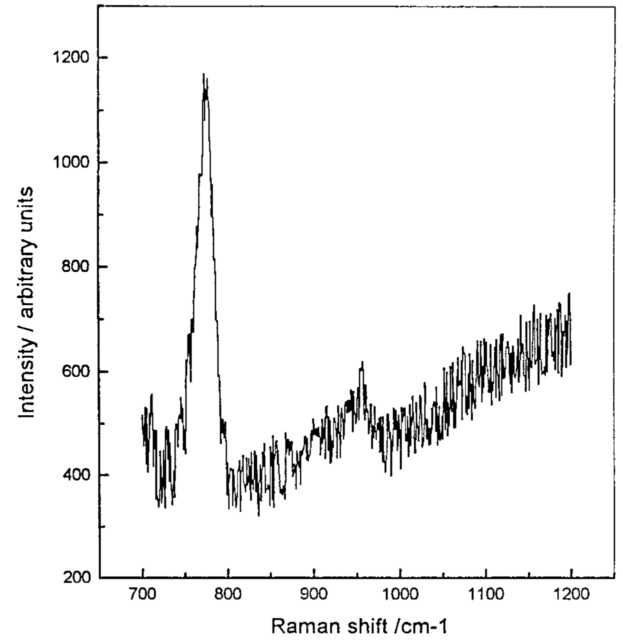

Figure 4. Room-temperature Raman spectra from the SiC nanowires .

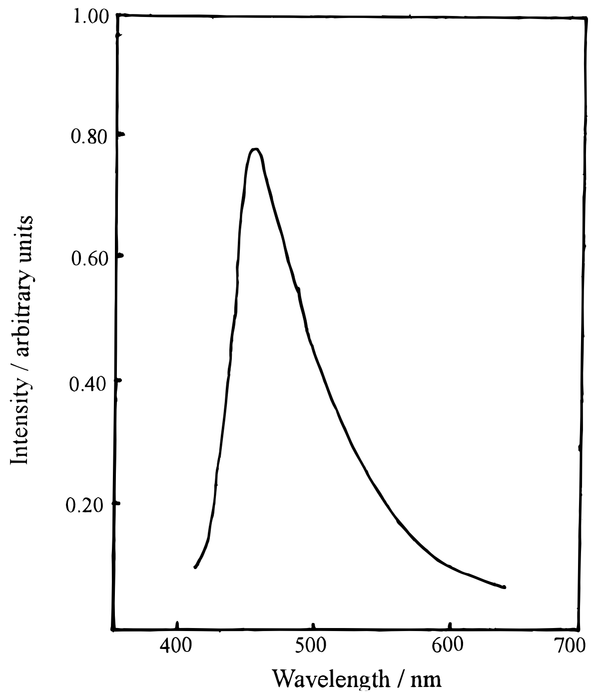

Figure 5. Photoluminescence spectra for the SiC nanowires at room temperature.

Figure 5 shows the PL spectra from the SiC nanowires at room temperature. The excitation wavelength was 385 nm and the filter wavelength was 430 nm. It is clear that a strong peak centered at 448 nm is observed. No sharp PL lines, which are attributable to impurity-bound excitons and their phonon replicas, or simple defects introduced by electron irradiation[21−23] are clearly seen in this spectrum. Furthermore, compared with the blue−green luminescence from the films 3C−SiC,[24] a blue−

violet luminescence in the SiC nanowires is indicative of a blue shift. The reason for the results is yet unknown, and a deeper study on this work is clearly needed.

The influences of reaction temperature and time on the formation of the SiC nanowires were investigated. It was found that a suitable reaction temperature was a key factor for the formation of SiC nanowires . If the temperature was lower than 630 °C, the SiC nanowires could not be obtained, even at elevated pressure; instead, amorphous C formed. If the temperature was higher than 800 °C, the diameters of the SiC nanowires increased easily. An optimum reaction temperature for the SiC nanowires is about 700 °C. The reaction time must be sufficient to ensure the carburization of Si powders. For a higher yield of the SiC nanowires (about 38% according to the amount of Si used), a treatment time longer than 10 h at 700 °C was needed. These results demonstrate that the present route differs from the known SHS reaction mode.[25,26]

There are two well-accepted whisker growth mechanisms: the screw dislocation mechanism[27] and the vapor−liquid−solid (VLS) mechanism.[28] The TEM images of the SiC nanowires showed no evidence of axial screw dislocations, suggesting that the SiC nanowires were not grown by the screw dislocation mechanism. The liquid globules, inherent to the VLS mechanism, were found on the tip of the nanowires (not shown). This fact suggests that the VLS mechanism was dominant in the SiC nanowire synthesis. According to free energy calculations, the reduction of CCl_4 by Na is thermodynamically spontaneous and highly exothermic ($\Delta G_f 0 = -\ 355.7$ kcalmol^{-1}, $\Delta H_f 0 = -360.7$ kcalmol^{-1}).[29] In our experiment, substituting Si powders with bulk Si platelet and keeping the other reaction conditions constant, it was found that the Si platelet could melt (Si mp of 1400 °C).[29] This fact, together with the free energy calculations, suggests that the large amount of heat generated in this process can result in a high-temperature molten NaCl−Si flux. The surface of the molten NaCl−Si flux may has a large accommodation coefficient and is therefore a preferred site for deposition of atoms from the vapor phase reactant CCl_4 (CCl_4 bp of 76 °C),[29] which can benefit the VLS nucleation for the SiC. Meanwhile, the molten NaCl−Si flux may also play a role in facilitating the growth of the SiC nanowires . Since crystal growth involves the exchange of atoms at the growth front planes, the high-temperature molten NaCl−Si flux could keep the impinging atoms from being dislodged by thermal diffusions and thermal vibrations, and thus enhance the nanowire growth. A feature of this synthesis route is an initially high pressure in the autoclave, coming from the vaporization of CCl_4, which may facilitate the VLS nucleation of the SiC nanowires .

Conclusions

In summary, the 3C−SiC nanowires were successfully synthesized through a reduction−carburization route. The SiC nanowires produced from the present route typically have diameters of 15−20 nm and lengths of 5−10 μm. The SiC nanowires with very small diameters are expected to have special electrical, optical, and mechanical properties, and may be constituents of novel nanoscale materials and device structures. This process has inherent advantages, including the availability of low cost raw materials and the simplicity of the production procedures. This versatile method may be used to synthesize other carbide nanowires.

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