

A simple route to nanocrystalline silicon carbide

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Abstract

Nanocrystalline silicon carbide has been prepared via reacting magnesium silicide (Mg_2Si) with carbon tetrachloride (CCl_4) in an autoclave at 450–600°C. X-ray diffraction patterns of the products can be indexed as the cubic cell of SiC with the lattice constant, $a = 4.352 \text{ \AA}$, in good agreement with $a = 4.349 \text{ \AA}$ (JCPDS card No. 75-0254). The transmission electron microscopy images show that the sample mainly consists of nanoparticles with an average size from 30 to 80 nm co-existing with a small fraction of nanorods and nanowires. Typically the nanorods range from 20 to 40 nm in diameter and the nanowires have diameters of 20 nm and lengths up to 10 μm . The Raman spectrum shows a characteristic sharp peak at 790 cm^{-1} . X-ray photoelectron spectra (XPS) gives an atomic ratio of Si to C as 1.08:1.00 from the quantification of the peak intensities. Photoluminescence spectrum reveals that the SiC sample emits ultraviolet light of 328 nm. A possible mechanism and the influence of temperature on the formation of crystalline SiC are proposed.

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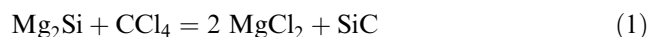
Keywords: Silicon carbide; X-ray diffraction; Transmission electron micrographs

1. Introduction

Silicon carbide has shown great promise in terms of availability of reproducible high-quality single crystal wafers and inherent electronic properties [1]. Silicon carbide has some outstanding characteristics such as good mechanical properties, chemical inertness, and thermal stability. These features have attracted great interest in its structure and its potential application as oxidation protection coatings for carbon/carbon composites exposed to oxygen and abrasive environments, especially at elevated temperatures [2,3]. Conventionally, the process for the preparation of SiC powders is the carbothermal reduction of the silica carbon mixture approaching temperatures between 1550°C and 1800°C [4], polycarbosilane precursor method affected by pre-pyrolysis heat treatment [5], self-propagating high temperature synthesis (SHS) [6], microwave radiation [7], sol-gel [8], plasma [9] and so on. Recently, new convenient methods have also been used to prepare SiC

crystals such as the 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 [10,11], solvothermal synthesis through reacting SiC₄ (or Si powders), C₆Cl₆ and sodium at 700°C [12].

In this paper, we report a new route to crystalline silicon carbide by reacting magnesium silicide (Mg_2Si) with carbon tetrachloride (CCl_4) in an autoclave. The reaction can be described as follows:



2. Experimental procedures

2.1. Preparation of nanocrystalline SiC

The reaction was carried out in a stainless-steel autoclave with a glass liner of about 50 ml capacity. Typically, about 45.6 mmol of magnesium silicide (Mg_2Si , analytical grade) and 51.8 mmol of carbon tetrachloride (CCl_4 , analytical grade) were put into the autoclave. The autoclave was sealed and maintained at 450°C for 12 h. When the heating was over, the autoclave was cooled to room temperature naturally. The contents were collected and then washed with

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diluted nitric acid and hydrofluoric acid, hydrochloric acid, distilled water; absolute ethanol to remove the MgCl_2 , silicon and other impurities. Gray products were obtained by drying under vacuum at 60°C for 6 h.

2.2. Characterization

The X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku D/max rA X-ray diffractometer with $\text{CuK}\alpha$ radiation [wavelength $\lambda = 1.54178 \text{ \AA}$]. The scan rate of $0.06^\circ/\text{s}$ was applied to record the patterns in the 2θ range of $30\text{--}80^\circ$. Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were taken with a Hitachi H-800 transmission electron microscope. The Raman spectra were produced at room temperature with a LABRAM-HR Confocal Laser MicroRaman spectrometer. Photoluminescence (PL) spectrum of the sample was measured in a Hitachi 850 fluorescence spectrophotometer with a Xe lamp at room temperature.

3. Results and discussion

The XRD pattern of the sample prepared through reacting Mg_2Si with CCl_4 in an autoclave at 450°C is shown in Fig. 1. All the five peaks at d -spacings of 2.509, 2.175, 1.539, 1.314, 1.257 \AA were indexed as cubic SiC [(111), (200), (220), (311), (222)]. The rms error of fit was 1.969×10^{-4} , with the lattice constants $a = 4.352 \text{ \AA}$, in good agreement with $a = 4.349 \text{ \AA}$ (JCPDS card No. 75-0254). There is no evidence that α -, β -SiC and silicon are formed in the products.

Fig. 2 shows the TEM images and SAED pattern of the sample. The TEM images in Fig. 2 show the particle sizes and the shapes of the samples. Fig. 2(a) shows that

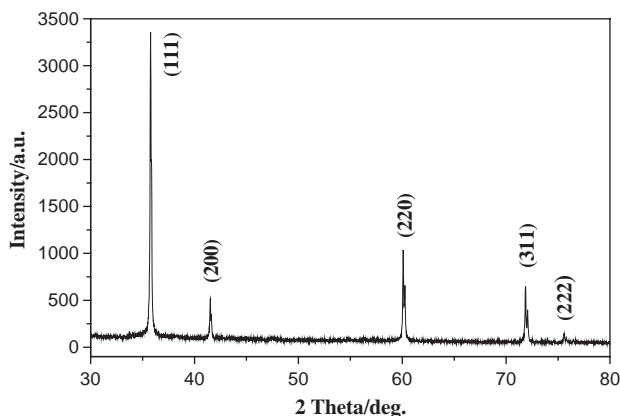


Fig. 1. X-ray powder diffraction pattern of the sample prepared by reacting magnesium silicide with carbon tetrachloride at 450°C for 12 h.

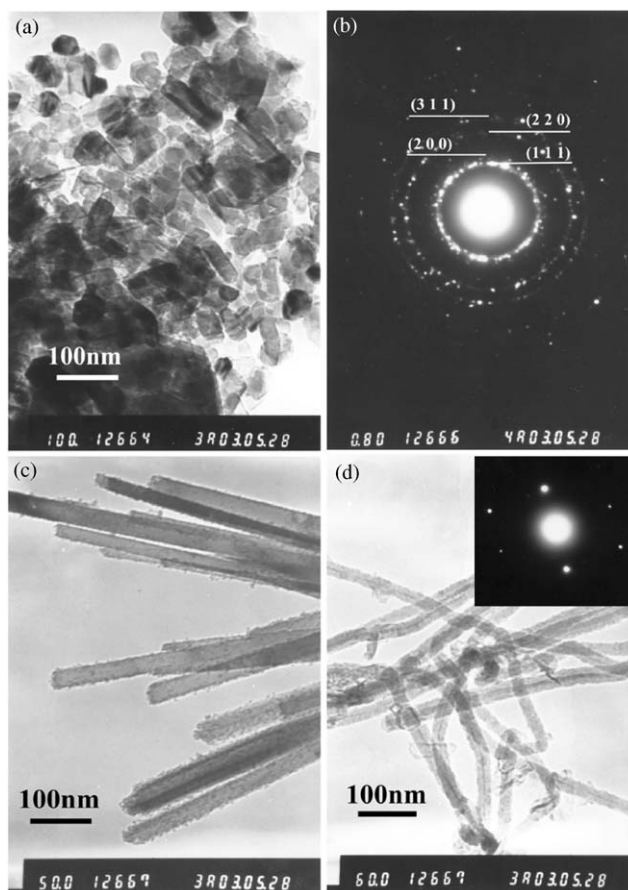


Fig. 2. (a) TEM images of SiC nanoparticles. (b) SAED pattern of SiC nanoparticles. (c) TEM images of SiC nanorods. (d) TEM and SAED images of SiC nanowires.

crystalline SiC nanoparticles have an average size between 30 and 80 nm. Besides the nanoparticles, some nanorods and nanowires are also observed. The yield of SiC nanoparticles to the total product is about 75%. From Fig. 2(c), it can be seen that the average diameter of SiC nanorods ranges from 20 to 40 nm. The TEM and SAED images in Fig. 2(d) show the nanowires of the samples. The SiC nanowires typically have diameters of 20 nm and lengths upto $10 \mu\text{m}$. The corresponding SAED pattern is shown in Fig. 2(b). The three strong polycrystalline rings in accordance with cubic SiC [(111), (220) and (311)] confirm the XRD result.

X-ray photoelectron spectra (XPS) are measured to derive the composition of the samples. Fig. 3 shows the two strong peaks at 100.97 and 282.98 eV corresponding to Si $2p$ and C $1s$ binding energy for Si [13] C, respectively. Quantification of the peak intensities gives an atomic ratio of Si to C as 1.08:1.00. However, the spectrum also displayed the other two C $1s$ peaks at 284.58 and 285.56 eV, which can be attributed to a small amount of residual carbon (284.6 eV of C $1s$ levels for graphite) and the adsorbed CO_2 onto the sample

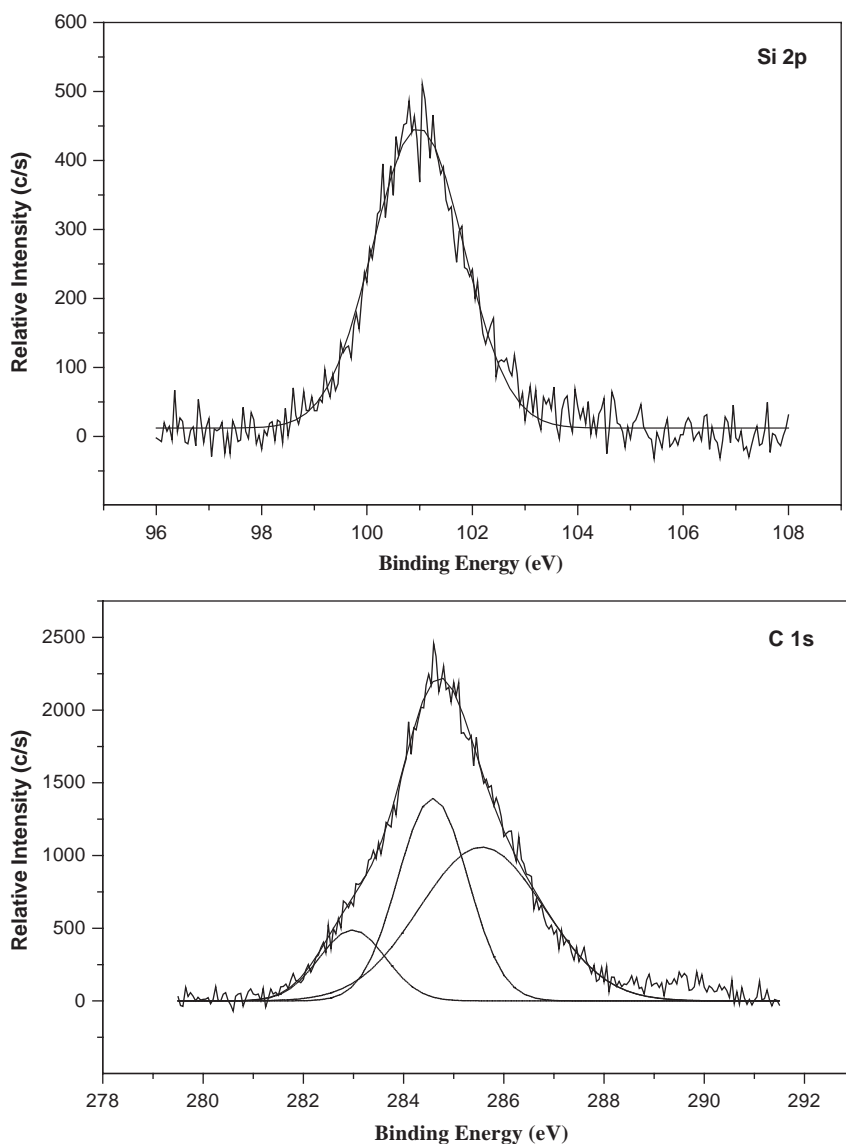


Fig. 3. XPS spectra of the as-prepared SiC product.

surface. No obvious peaks due to silicon (99.6 eV for Si2p) or silica (103.5 eV for Si2p in SiO₂) are observed.

The as-obtained SiC sample was also characterized by Raman spectroscopy and its result is shown in Fig. 4. The Raman spectrum shows the presence of a sharp peak at 790 cm⁻¹, which confirms that the sample is well-crystalline cubic SiC [10].

Fig. 5 shows the PL spectrum from the as-prepared SiC product at room temperature. The excitation wavelength was 230 nm and the filter wavelength was 310 nm. It is clear that a strong peak centered at 328 nm (corresponding to 3.88 eV) is observed. No other sharp PL lines attributing to impurity-bound excitons and their phonon replicas, or the simple defects introduced by electron irradiation [14–16] are clearly seen in this spectrum. Furthermore, compared with the blue-green

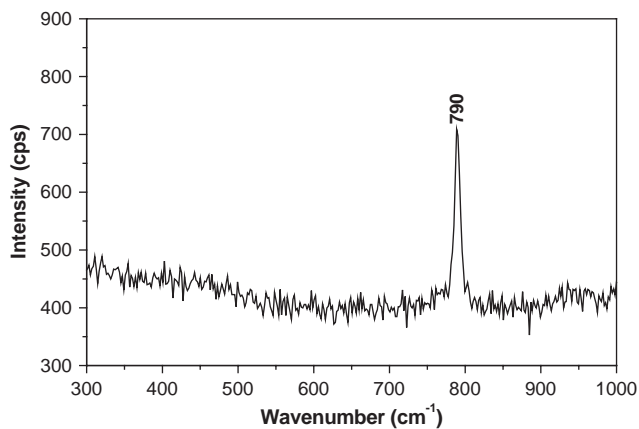


Fig. 4. Room-temperature Raman spectrum from the nanocrystalline SiC.

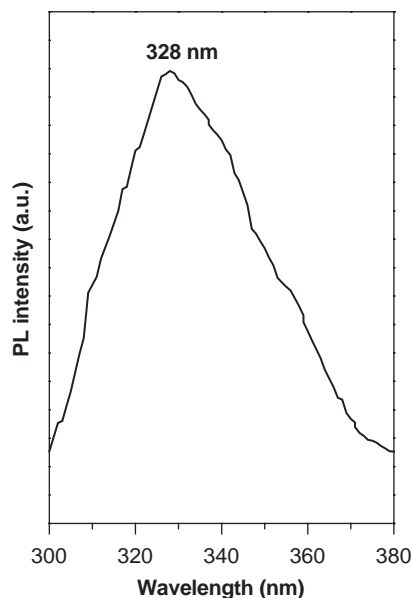


Fig. 5. Photoluminescence spectra of the as-prepared SiC product.

luminescence from the films 3C-SiC [17], a blue-violet luminescence in the as-prepared SiC product is indicative of a blue shift, which is able to drastically modify the electronic structure of nanocrystalline SiC where quantum confinement effects occur [18].

According to free energy calculations, our synthetic route is thermodynamically, spontaneously and highly exothermic ($\Delta G = -1064.4$ kJ/mol, $\Delta H = -1148.6$ kJ/mol). The vaporization of CCl_4 (b.p. = 76.8°C) during the reaction process can bring about high pressure in the autoclave that facilitates the nucleation of SiC nanostructures and makes the crystalline SiC form at relatively low temperatures. Based on the ideal gas law, the highest pressure in the autoclave can be about 6 MPa, which is also beneficial to the formation of crystalline SiC.

The influence of the reaction temperature was investigated. It was found that the product could be obtained if the temperature ranged from 450°C to 600°C . The result of the preparation by the same system at 550°C and 600°C (figures are not shown) is very similar to the XRD pattern of Fig. 1. After comparison, we conclude that it is the proper way to obtain nanocrystalline SiC at 450°C for 12 h.

4. Conclusions

In conclusion, 30–80 nm crystalline nanoparticles of SiC with the cubic cell has been successfully

prepared via reacting magnesium silicide with carbon tetrachloride in an autoclave. A small fraction of nanorods and nanowires having diameters of 20 nm and lengths up to $10\ \mu\text{m}$ co-exist. Neat crystalline cubic SiC is also proved by the Raman spectrum with the presence of a sharp peak at $790\ \text{cm}^{-1}$. Under PL excitation at 230 nm, SiC emits ultraviolet light at 328 nm (corresponding to 3.88 eV). The band gap (3.88 eV) indicates that the product is a wide gap semiconductor.

Acknowledgments

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