A New Rapid Reduction−Carbonization Route to Nanocrystalline β-SiC

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Nanocrystalline β-SiC was successfully synthesized at 600 °C through a new rapid reduction−carbonization route, in which metallic Na was used as the reductant, and activated carbon and tetrachlorosilane ($SiCl_4$) were used as source materials. X-ray powder diffraction indicates that β-SiC with high crystallinity is obtained. Transmission electron microscopy images show that the as-prepared SiC powders consist of spherical particles with an average diameter of 25 nm. An atomic ratio of Si to C of 1.08:1.00 was determined from X-ray photoelectron spectra. A possible formation mechanism for nanocrystalline β-SiC is proposed.

Introduction

The cubic form of silicon carbide (β-SiC) is a very attractive semiconductor due to its potential for applications such as very high-speed, high-temperature, and high-power devices. β-SiC is suitable for these applications based upon its wide energy band gap, high saturated electron drift velocity, high conductivity, and other factors.[1−3] Recently, SiC ceramic materials made by sintering very fine powder (<100 nm) have received increasing attentions due to the enhancement of mechanical properties, low-temperature densification, and the appearance of superplasticity.[4]

The conventional process for the preparation of SiC powders is the carbothermic reduction of silica,[5] which can be represented by two elementary steps:

$$SiO_2(s) + C(s) \rightarrow SiO(g) + CO\ (g) \qquad (1)$$

$$SiO(g) + 2C(s) \rightarrow SiC(s) + CO\ (g) \qquad (2)$$

The self-propagating high-temperature synthesis (SHS),[6] based on the exothermic reaction between silicon micropowder and active carbon at ignition temperature (1250−1700 °C), has also been developed to prepare β-SiC powders. Polysilane polymer precursors, which were usually prepared by dechlorination of the chlorosilane with sodium, could be pyrolyzed and converted to SiC powder or fiber.[7] In addition, various other methods such as sol−gel,[8] plasma,[9] and microwave radiation[10] technologies were proposed to produce easily sinterable SiC ultrafine powders, which still are unlikely to be commercialized soon.

Recently, there has been increasing interest in a solution route to some fascinating materials. For example, Heath[11] reported the synthesis of crystalline silicon at high temperature and high pressure, based on the reduction of $SiCl_4$ and chloroakylsilanes by sodium metal. Bely and Kauzlarich[12] developed a solution synthesis by reacting the Zintl compound KSi with $SiCl_4$ to produce silicon nanoparticles. Ritter[13] prepared a silicon carbide precursor from the reductive dehalogenation of $SiCl_4$ and CCl_4 with metallic sodium at 130 °C; however, the SiC precursor was amorphous and required heating in the range of 1450−1750° to achieve crystallinity. Herein, we describe a novel chemical synthetic route to nanocrystalline β-SiC at 600 °C by using $SiCl_4$ and C as source materials, and metallic sodium as the reductant. The reaction was carried out in an autoclave and is associated with the following reaction:

$$SiCl_4 + 4Na + C \rightarrow SiC + 4NaCl \qquad (3)$$

The reaction is based on the reduction of $SiCl_4$ by Na and subsequent carbonization of the newly reduced silicon particles.

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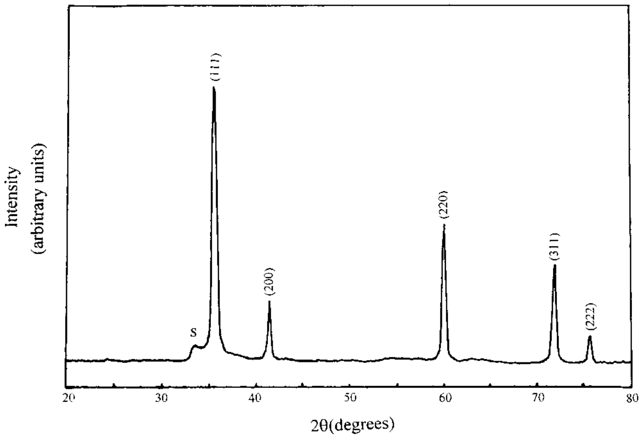

Figure 1. XRD pattern of nanocrystalline β-SiC (s: stacking faults).

Experimental Section

All of the manipulations were carried out in a dry glovebox filled with flowing argon. C (0.36 g), $SiCl_4$ (4 mL), and excess Na (5 g) were put into a titanium alloy autoclave of 50-mL capacity. The autoclave was sealed and maintained at 600 °C for 1.5 h and then cooled to room temperature. The product was collected, and heated again in air at 600 °C for 1 h to remove the unreacted carbon by oxidizing it to CO_2. During the heating, the SiC nanoparticles are no longer stable and undergo a partial oxidation, which strongly increases with decreasing particle size.[14] Therefore, an amorphous SiO_2 layer may form on the surface of the powder's particles. However, this amorphous oxidation coating was leached out by means of dilute HF in our experiment. After the mixture was washed with distilled water to remove NaCl and the other impurities, a gray-white product was obtained with a density of 3.10 g cm^{-3}, which is less than the literature value (3.216 g cm^{-3}). This may be due to a small amount of the residual carbon on the powder surface.

X-ray powder diffraction (XRD) patterns were obtained on a Japan Rigaku D/max A X-ray diffractometer with Cu Kα (λ = 1.5418 Å). Images were taken with a Hitachi H-800 transmission electron microscope (TEM). X-ray photoelectron spectra (XPS) were obtained on a VGESCALABII X-ray photoelectron spectrometer, using nonmonochromatized Mg Kα X-ray as the excitation source.

Results and Discussion

Figure 1 shows the XRD pattern of the sample. All of the strong-intensity peaks could be indexed as β-SiC with a low-intensity peak at $d = 2.675$ Å ($2\theta = 33.60°$) due to stacking faults.[15] The refinement gave the cell constant $a = 4.3558$ Å, which was very close to the reported value in the literature ($a = 4.3589$ Å).[16] No characteristic peaks of impurity phases such as SiO_2 and Si were observed in the XRD pattern. The Scherrer formula gave a mean value for the crystallite size of 22 nm.

The morphology and particle sizes of SiC were determined by TEM. Figure 2 shows a typical image of the sample. It reveals that the particles have a nearly nonagglomerated spherical shape with an average diameter of 25 nm, which is in good agreement with that obtained by the XRD.

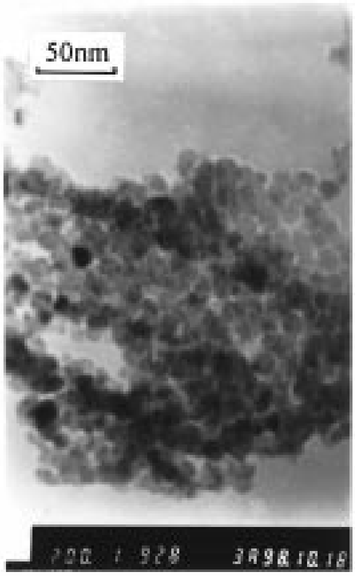

Figure 2. TEM image of the sample.

Further evidence for the formation of SiC can be obtained from the XPS of the sample. Figure 3 shows the spectra of the sample. The spectra displayed two peaks at 100.80 and 283.00 eV corresponding to the Si 2p and C 1s binding energy for SiC,[17] respectively. The quantification of the peak intensities gives an atomic ratio of Si to C of 1.08:1.00. However, the XPS spectra of the sample also displayed another two C 1s peaks at 284.85 and 286.80 eV, which were due to a small amount of residual carbon (284.3 eV of C 1s levels for graphite) adsorbed onto the powder surface. No obvious peaks due to silicon (98.7 eV for Si 2p) or silica (103.5 eV for Si 2p in SiO_2) are observed. A peak assigned to the O 1s (532.10 eV) level in the XPS spectra (the spectrum not shown) indicates adsorbed O_2 on the powder's surface.

The influences of reaction temperature and time on the formation of the nanocrystalline SiC were investigated. A suitable reaction temperature was a key factor for the formation of nanocrystalline SiC. If the temperature was lower than 570 °C, SiC could be obtained, even at elevated pressure; instead, amorphous Si powder formed. If the temperature was higher than 650 °C, the particles grew easily. An optimum reaction temperature for nanocrystalline SiC is about 600 °C. A treatment time at 600 °C in the range of 2−8 h did not significantly affect the crystallinity or the yield (about 60% according to the amount of $SiCl_4$ reacted) of SiC. However, at the time shorter than 1 h, the reaction was very incomplete and the crystallinity was lower. These results demonstrate that the present route diffes from a known SHS reaction mode.[6,18]

According to the recent reports on the solution synthesis of nanocrystalline silicon,[11,12] the reduction of $SiCl_4$ by metal sodium may produce silicon particles. In our route, the fact that the amorphous Si formed at low temperature, rather than SiC, suggests that the formation of SiC could be attributed to the reaction of

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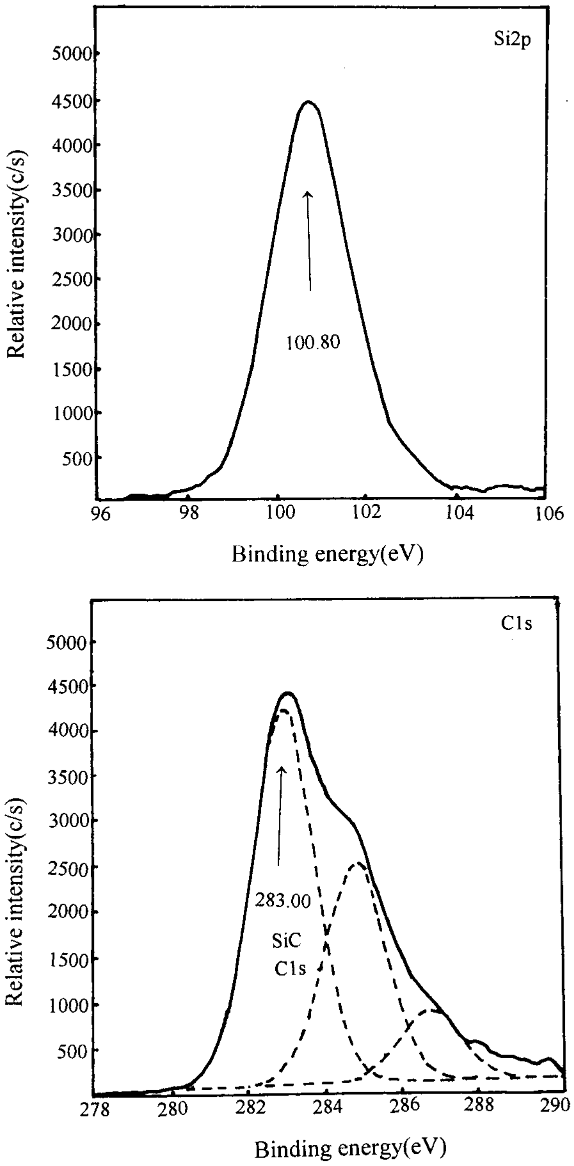

Figure 3. XPS spectra of the sample.

the newly formed Si with the activated carbon, and the solid-state metathesis (SSM)[19] route might be excluded in reaction 3. Therefore, it is reasonable to consider that the synthesis is based on reduction of $SiCl_4$ by Na and subsequent carbonization of the reduced silicon particles. We call it the reduction−carbonization route in reaction 3. The schematic formation process of SiC would then be formulated as follows:

$$SiCl_4(g) + 4Na(g) \rightarrow Si(s) + 4NaCl(l) \quad (4)$$

$$C(s) + Si(s) \rightarrow SiC(s) \quad (5)$$

According to free energy calculations, eq 4 is thermodynamically spontaneous and highly exothermic ($\Delta G_f^0 = -219.1$ kcal mol^{-1}, $\Delta H_f^0 = -236.04$ kcal mol^{-1}).[20] Therefore, the formation of silicon powder is possible, which is somewhat like the synthesis of diamond powder through the reduction of CCl_4 by metallic Na.[21] With increasing furnace temperature, $SiCl_4$ began to vaporize and Na began to melt, so the initiating reduction reaction was carried out in the form of a vapor−liquid surface reaction. Once the reduction reaction is initiated, the heat generated in the process is sufficient to melt the byproduct NaCl and to vaporize the reactant Na (NaCl: mp of 801 °C, Na: bp of 889.9 °C).[20] Thus, the reduction reaction proceeds probably in a vapor-phase of $SiCl_4$ and Na, which allows for a rapid reduction reaction and in turn generates more heat and melts more byproduct. The newly formed Si particles are so active that they can directly react with the activated carbon particles in the NaCl molten flux, which, in turn, could overcome solid-state atomic diffusion barriers to carbonization. Meanwhile, the newly formed SiC is crystallized by the heat remaining in the flux and the salt flux may serve as a medium for the crystallization of the formed SiC.[22] A feature of the present synthetic route is the application of higher pressure in the autoclave, which could play an important role in the formation of SiC. In this reaction system, a higher pressure from the vapor $SiCl_4$ and metallic Na might occur which would promote the crystallization of the SiC. Consequently, a better crystallized SiC could be obtained. To summarize, the formation process of nanocrystalline SiC is via two steps; i.e., the active silicon particles from the rapid reduction form first and then react with the activated carbon in the NaCl molten flux for the carbonization.

Conclusion

A new rapid reduction−carbonization route to nanocrystalline β-SiC was developed by using activated carbon and $SiCl_4$ as the source materials at low temperature (600 °C). This synthesis reaction is based on the reduction of $SiCl_4$ by Na and subsequent carbonization of the reduced silicon particles. The NaCl molten flux and the pressure in the autoclave may play important roles in the formation of the nanocrystalline SiC. In comparison with previous routes, the present route allows for the rapid formation of nanocrystalline SiC with a higher crystallinity and higher yield by using less costly source materials through a simpler process. A similar process could be extended to synthesize other refractory materials, e.g., Si_3N_4. A detailed study of this synthesis method is in progress.

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