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The influence of diluent gas composition and temperature on SiC nanopowder formation by CVD

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Abstract Crystalline cubic silicon carbide (3C-SiC) nanopowders were synthesized using hexamethyldisilane (HMDS) in a resistance heated chemical vapour deposition (CVD) reactor. The effects of different diluent gases on the synthesis of the SiC powder were also studied. The deposited powder was characterized using high-resolution X-ray diffraction (HRXRD) analysis, transmission electron microscopy (TEM), high-resolution TEM (HRTEM) and BET surface area measurements. The crystallite size was estimated to be in the range of nanometer (10–20 nm) from XRD data and the particle size (~10–30 nm) was obtained by TEM, HRTEM and BET. The growth condition was optimized in terms of crystallinity, chemical composition and deposition rate by varying different parameters such as the diluent gas (H_2/Ar ratio) and temperature.

Introduction

Semiconducting nanoparticles exhibit novel electronic, optical, transport, photochemical, electrochemical and mechanical properties markedly different from those of the bulk. This is mainly governed by the finite size inducing charge carrier confinement and quantitisation effects on the band energy structure, and also by the surface and interface effects [1–3]. 3C-SiC is an attractive semiconductor material for high temperature, high frequency and high power electronic applications due to its excellent electronic properties [4]. It has also excellent chemical inertness and mechanical properties. In addition, its high thermal conductivity, low thermal expansion coefficient, excellent resistance to oxidation, have attracted great interest for use as a high temperature structural material [5, 6]. By creating nanopowders of SiC, it is expected that various properties would be modulated due to size confinement effect [7]. As a structural material, the major fields of application of SiC nanopowders are catalysis, porous or dense membranes, nanocomposites and electroceramics. Several methods like chemical vapour deposition (CVD), carbothermal reduction of silica carbon mixture, self-propagating high-temperature synthesis, microwave radiation, sol-gel, plasma etc. have been reported for the preparation of SiC powder [1]. Various source precursors such as $SiCl_4/CH_4$, CH_3SiCl_3/CH_4, SiH_4/C_2H_2, etc. have been used for the synthesis of SiC powder. In the metalorganic CVD technique, for the most part, H_2 has been used as both carrier gas and diluent gas. A carrier gas delivers the source precursor through the bubbler to the reactor and a diluent gas regulates the concentration of the precursor, which is a mixture of source vapour and carrier gas [6].

We have previously reported the formation of 3C-SiC nanoparticles using hexamethyldisilane (HMDS) and H_2 by a modified chemical vapour deposition (CVD) technique in a resistance-heated furnace [8]. In this paper, the effects of different diluent gases on the synthesis of SiC powders have been investigated. The deposition rate of the powdered sample using pure hydrogen as a diluent gas was compared with those of powder prepared using pure argon and a mixture of hydrogen and argon. The method was optimized in terms of crystallinity and deposition rate by

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varying different parameters such as the composition of diluent gas and temperature.

Experimental

3C-SiC nanopowders were synthesized by atmospheric pressure chemical vapour deposition using a resistance-heated furnace (ELECTROHEAT EN345T). The reactor consists of a 1 m long quartz tube in conjunction with two water-cooled flanges at the two ends. A mixture of hydrogen and argon in different proportions was used as the diluent gas. A metalorganic source HMDS (>98%) was used as the single source for both silicon and carbon and H_2 (50 sccm) was used as the carrier gas in all the cases. All gases used were of XL Grade (BOC)—minimum 99.996%. The influence of different parameters such as H_2/Ar flow ratio and temperature on the production of 3C-SiC nanoparticles was studied to optimize the quality and quantity of the deposited particles. The deposition temperature was varied from 1,050 to 1,250 °C.

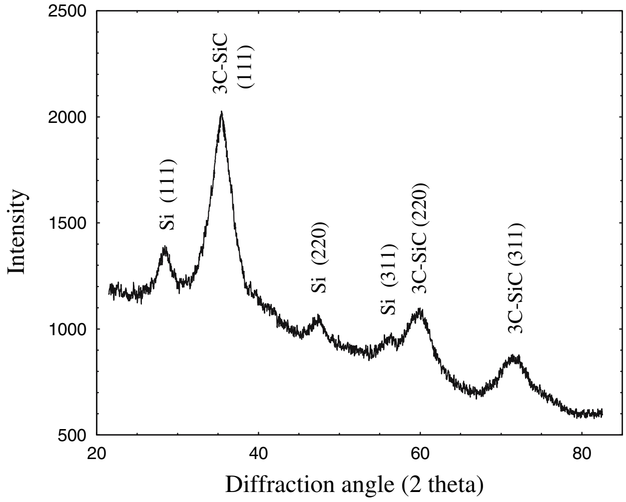


Fig. 1 X-ray diffraction of mixture of Si and 3C-SiC powder deposited at 1,250 °C

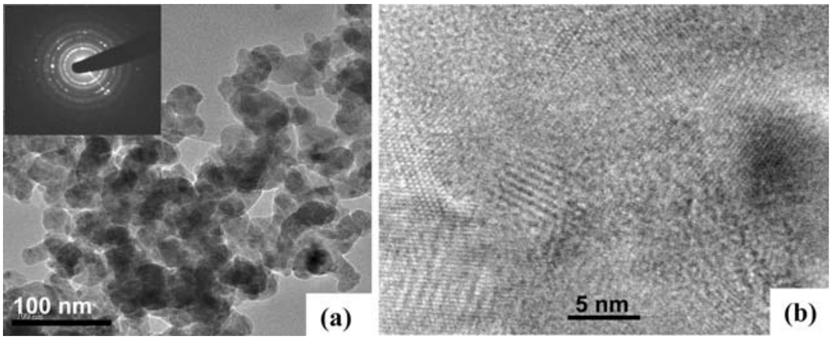
Fine nanosized 3C-SiC powder was deposited on the wall of the reactor. After collecting the 3C-SiC powder, it was characterized by XRD (PANalytical-X'Pert PRO-PW:3040/60 X-ray diffractometer using Cu Kα radiation) and TEM (JEOL 3,010–300 kV electron microscope using carbon-coated copper grids). The crystallinity and crystallite size were determined by XRD and TEM. High-resolution TEM (HRTEM) was also done to study the crystal structure and particle size more precisely. Surface area of the deposited particles was estimated by BET (SMART SORB 92-Surface Area Analyzer).

Results and discussion

The high-resolution X-ray diffraction (XRD) technique using Cu Kα radiation was used to investigate the crystalline phase of the as-deposited SiC powder. Figure 1 corresponds to the diffraction pattern, obtained from the sample synthesized at 1,250 °C using H_2 as the diluent gas. Peaks at 35.42°, 60° and 72° appear due to the diffraction from (111), (220) and (311) planes of the 3C-SiC. In addition, peaks at 28.4°, 47.3° and 56.3° appear due to diffraction from (111), (220) and (311) planes of Si. Existence of several peaks of 3C-SiC and Si indicates that the deposited powder is the mixture of Si and 3C-SiC particles in crystalline phase. The crystallite size of SiC obtained by using the Scherrer equation was ~14 nm.

TEM was carried out on different regions of the mixture of Si and SiC powder sample. A general and low magnification overview TEM image of the nanoparticles is shown in Fig. 2. Clusters with sizes ranging from 20 to 40 nm have been observed. Selected area electron diffraction (SAED) was carried out on the nanoparticle assembly for checking the crystallinity (Fig. 2a inset). The formation of fine and distinct rings in SAED patterns indicates the crystalline nature of the particles. The spots appearing in the SAED pattern appear depending on the number of particles that contribute to the particular grain [9]. Figure 2b is the HRTEM micrograph showing the distribution of nonuniform lattice structure with different

Fig. 2 (**a**) TEM and SAED image of mixture of Si and 3C-SiC particles (**b**) HRTEM image showing lattice fringes of different spacing and orientation



orientations and a wide variation of particle size (5–30 nm). In the HRTEM image, Moiré fringes were observed due to the overlapping of the nanoparticles. Surface area (SA) of the nanoparticles obtained from BET measurement is 97.5×10^3 m^2/kg. The average particle size is ≈20 nm, which is consistent with HRTEM and XRD data:

$$[\text{Average particle size} = 6/(\rho \times \text{SA}); \quad \text{where} \quad \rho \rightarrow \text{density of 3C - SiC} = 3.21 \times 10^3\,\text{kg/m}^3]$$

The influence of diluent gas on the deposition rate of the powder particles was studied by introducing Ar with H_2 in different proportions instead of using pure H_2. The deposition rate at 1,250 °C using H_2 and Ar as the diluent gas with different proportion is shown in Fig. 3. It was observed that the deposition rate increases with increasing Ar content up to a certain proportion (1:1) but after that the deposition rate again decreases with further increase of Ar content in the diluent gas. In case of higher concentration of H_2 (say more than 50%), the H_2 as the diluent gas increased the amount of the loss of the carbon source by the formation of hydrocarbons, which leads to a decrease in the deposition rate [10]. Beyond 1:1 proportion (<50% H_2), the further decrease of H_2 or increase of Ar reduces the decomposition of HMDS to silicon-containing species and carbon-containing species, resulting in lower rate of formation of SiC nanopowder. Therefore decrease of H_2 (i.e. increase of Ar) in the diluent gas eventually decreases deposition rate of SiC powder [6].

Figure 4 shows the X-ray diffraction from the SiC powder deposited at 1,250 °C for various compositions of diluent gas. It was observed that for 100% H_2 (Fig. 4a), both SiC and Si peaks were present. It may be the higher concentration of H_2 favours the formation of silicon along with SiC through the possible pathways [11]:

$$\text{SiC} + 3\text{H} \leftrightarrow \text{CH}_3 + \text{Si}$$

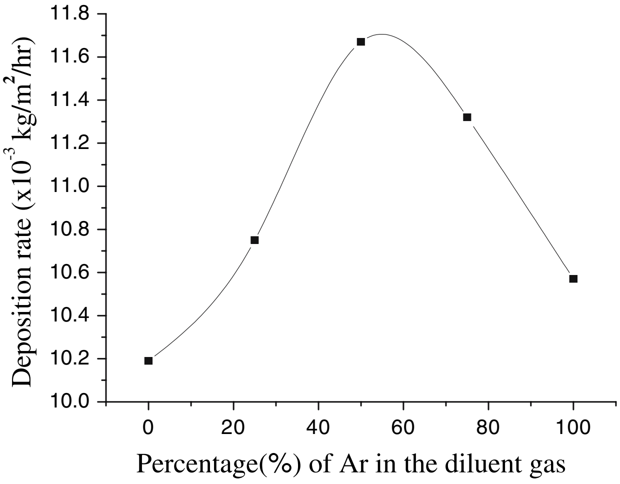


Fig. 3 Dependence of the deposition rate of SiC powder on the Ar content in the carrier gas (remaining part of the diluent gas is H_2)

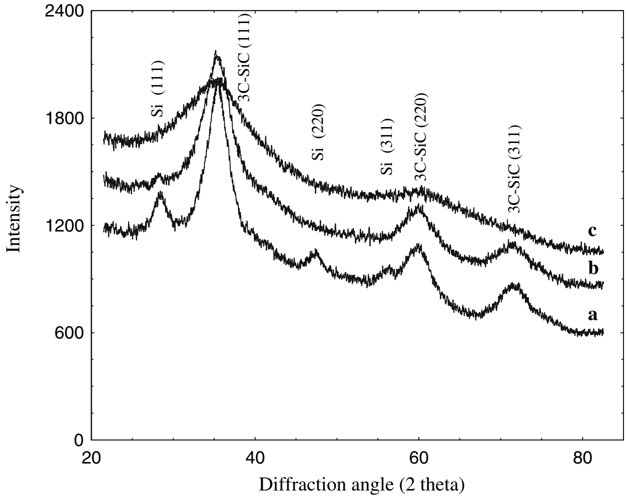


Fig. 4 XRD at 1,250 °C with different composition of diluent gas (**a**) 100% H_2, (**b**) 50% H_2–50% Ar and (**c**) 100% Ar

On the other hand, the powder turned out to be amorphous in nature by using 100% Ar as the diluent gas. The insufficiency of H_2 led to the formation of excess amount of amorphous free carbon that might suppress the formation of crystalline SiC as confirmed by the XRD. However, the mixture of 50% H_2 and 50% Ar (Fig. 4b) as the diluent gas provided the optimum growth of nanopowder in terms of crystallinity and relative composition of the powder. The similar effect of different diluent gas composition was observed at lower temperature (1,050 °C) (Fig. 5). But the

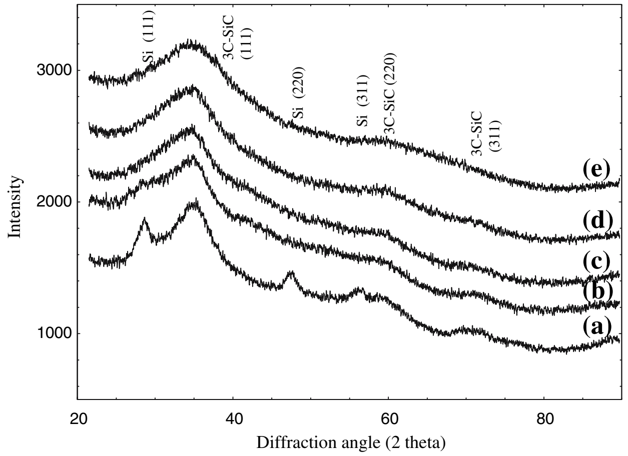


Fig. 5 XRD at 1,050 °C with different composition of diluent gas (**a**) 100% H_2, (**b**) 75% H_2–25% Ar, (**c**) 50% H_2–50% Ar, (**d**) 25% H_2–75% Ar and (**e**) 100% Ar

deposited powder was amorphous in nature due to the low temperature of deposition. The amount of powder deposited on the relatively cold region of the reactor is ~11.67×10^{-3} kg/m^2/h under the optimum growth condition.

The deposition temperature has a direct impact on the formation of SiC nanopowder in terms of its crystallinity. The temperature was varied from 1,050 to 1,250 °C for the diluent gas with optimum proportionality (H_2:Ar = 1:1) and the crystalline phase of the nanopowder was examined using XRD, TEM and SAED measurements. In XRD measurement, at 1,050 °C (Fig. 6a) a broad peak appeared around 35° along with a small hump around 60° showing the amorphous nature of the SiC powder. The number of peaks increase at higher temperature. The presence of more prominent peaks at higher temperature indicate better crystallinity, as shown in Fig. 6. The sharpness of the peaks at 1,250 °C (Fig. 6e), clearly suggests more crystalline phase of 3C-SiC and the crystallite size obtained by using the Scherrer equation was ~10 nm. These results can be explained on the basis of complete decomposition of HMDS into SiC at high temperature. Typically HMDS decomposes via a two-step process to form the solid phase of 3C-SiC [12]:

$$\begin{aligned}&(CH_3)_3 - Si - Si - (CH_3)_3 + H_2\\&\quad \rightarrow (CH_3)_n - Si - H_{4-n}(n = 1-3) + C_nH_m + H_2\\&\quad (\text{low temperature} \sim T < 1,100\ ^\circ\text{C})\end{aligned}$$

$$\begin{aligned}&(CH_3)_n - Si - H_{4-n}(n = 1-3) + H_2\\&\quad \rightarrow \text{SiC (solid)} + C_nH_m + H_2\\&\quad (\text{high temperature} \sim \text{T} > 1,100\ ^\circ\text{C})\end{aligned}$$

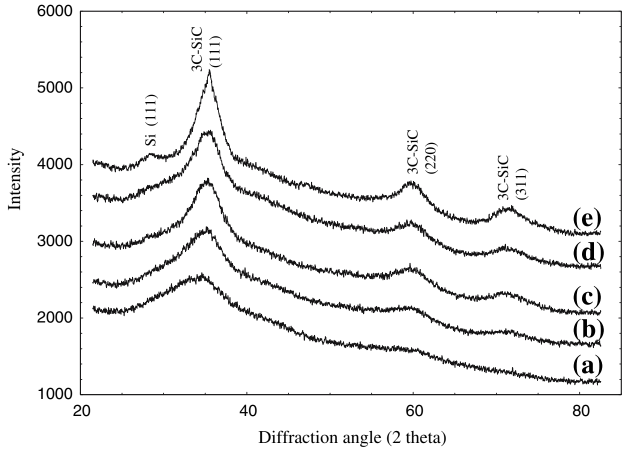


Fig. 6 XRD of powder with 1:1 diluent gas composition at different deposition temperature (**a**) 1,050 °C, (**b**) 1,100 °C, (**c**) 1,150 °C, (**d**) 1,200 °C and (**e**) 1,250 °C

In this case at 1,250 °C (Fig. 6e) an additional peak around 28.7° appeared due to diffraction from (111) planes of Si. This can be attributed to the increase of crystalline phase of Si at high temperature, which was not so prominent to be resolved at the lower temperature. At higher temperature there is a possibility of decomposition of HMDS into hydrocarbons and Si radicals following second-order decomposition schemes as given below [12]:

$$\begin{aligned}&(CH_3)_n - Si - H_{4-n}(n = 1-3) + H_2\\&\quad \rightarrow C_nH_m \text{ or Si (radical) or etc.}\end{aligned}$$

The effect of temperature became evident in the TEM study, as displayed in Fig. 7. The incomplete formation of nanoparticles was observed at 1,050 °C (Fig. 7a). The particles were aggregated in nature. SAED of this sample clearly shows the amorphous nature of the nanopowder. The resolution of nanoparticles was quite good at 1,150 °C but still an amorphous phase is observed in the SAED (Fig. 7b). The crystalline phase appeared at 1,250 °C with well-resolved particle size (diameter) of 20–30 nm (Fig. 7c). Existence of rings in SAED suggests the formation of polycrystalline SiC powder. The analysis shows that the rings are due to the diffraction from (111), (220) and (331) planes of 3C-SiC with lattice constant 0.45 nm, supporting the XRD pattern. Investigation of individual nanoparticles by HRTEM confirms the crystalline character of nanoparticles. Figure 7d is the HRTEM image of the powder deposited at 1,250 °C using H_2 and Ar in a 1:1 ratio showing the lattice structure within the specific region marked by the box. Size of the crystallite particle ~8 nm was observed in the HRTEM image. The calculated interplanar spacing is ~0.2672 nm corresponding to the (111) plane of cubic SiC, which gives the lattice constant ~0.462 nm. Finally, it can be concluded that the optimum condition for deposition of nanocrystalline 3C-SiC powder is 1,250 °C with 1:1 diluent gas (H_2/Ar) ratio.

Conclusion

Crystalline 3C-SiC nanopowder was synthesized using CVD method in a resistance-heated furnace using different diluent gas compositions. The influence of Ar, added to H_2 in various proportions, as the diluent gas, and the deposition temperature were observed to be crucial for the deposition rate and the degree of crystallinity of the SiC nanopowders. Best results were obtained by using a 50% Ar–50% H_2 diluent gas mixture at 1,250 °C. Thus, high purity SiC nanopowders (10–30 nm in size) can be effectively synthesized using a hot wall CVD using HMDS as

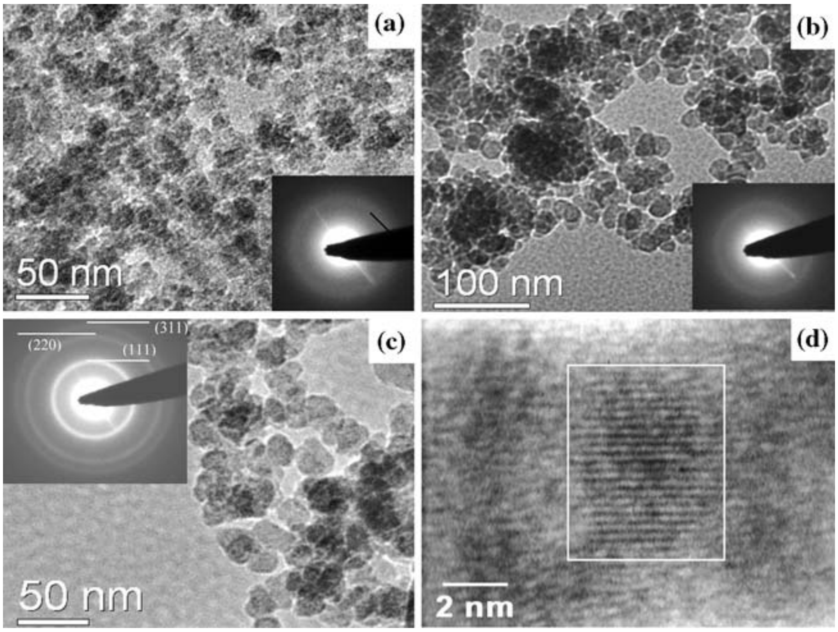


Fig. 7 TEM image and SAED pattern of 3C-SiC nanoparticles deposited at (**a**) 1,050 °C, (**b**) 1,150 °C and (**c**) 1,250 °C with 1:1 diluent gas composition and (**d**) HRTEM micrograph of nanocrystalline SiC particles synthesized at 1,250 °C

the precursor and a mixture of hydrogen and argon as the diluent gas. These powders could potentially be used for nanocomposites, catalytic applications, etc.

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