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Li, Xiang; Zhang, Guangqing; Tronstad, Ragnar; and Ostrovski, Oleg, "Synthesis of SiC whiskers by VLS and VS process" (2016). *Faculty of Engineering and Information Sciences - Papers: Part A*. 5234.  

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Disciplines
Engineering | Science and Technology Studies

Publication Details

This journal article is available at Research Online: https://ro.uow.edu.au/eispapers/5234
Synthesis of SiC Whiskers by VLS and VS Process

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Abstract

This study investigates the mechanisms of SiC whisker formation in the carbothermal reduction of quartz to SiC in different gas atmospheres. Reduction of quartz by graphite was studied in Ar, H\textsubscript{2}, and CH\textsubscript{4}-H\textsubscript{2}-Ar gas mixture in a laboratory fixed bed reactor. The reduction products were characterised by XRD, SEM and TEM. Whiskers were not formed in the carbothermal reduction of quartz in argon. Two types of SiC whiskers were observed in the carbothermal reduction of quartz in H\textsubscript{2} and CH\textsubscript{4}-H\textsubscript{2}-Ar gas mixture. In the process of reduction at 1400–1600 °C in H\textsubscript{2} and at 1200–1600 °C in CH\textsubscript{4}-H\textsubscript{2}-Ar gas mixture, whiskers with hexagonal shape with diameter 100–800 nm and length up to tens of microns were formed by the VLS mechanism under catalytic effect of iron. The whiskers with the characteristics of cylindrical shape and high aspect ratio were synthesized in CH\textsubscript{4}-H\textsubscript{2}-Ar gas.

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mixture at 1400–1600 °C by VS mechanism.

**Keywords:** Carbothermal reduction, SiC whiskers, quartz, atmosphere

1. Introduction

Silicon carbide (SiC) has excellent properties, such as high specific strength, specific stiffness, relatively low specific weight, high corrosion and erosion resistance. These qualities make SiC a perfect candidate for high power, high temperature electronic devices as well as abrasion and cutting applications [1, 2]. Silicon carbide has many polymorphs, such as 3C, 2H, 4H, and 6H. The 3C-SiC polytype has the zinc blende structure with a \( \cdots \text{ABCABC}\cdots \) sequence, and the other three polytypes have the hexagonal structure with \( \cdots \text{ABAB}\cdots \) (2H), \( \cdots \text{ABCBABCB}\cdots \) (4H), and \( \cdots \text{ABCACBABCACB}\cdots \) (6H) sequences. 3C-SiC powder is commercially produced by Acheson process which involves carbothermal reduction of SiO\(_2\) at temperatures above 2000 °C [3]. SiC bulk crystals used as semiconductor material are grown on substrates using chemical vapor deposition (CVD) or physical vapor transport (PVT) method [4, 5].

SiC whiskers are nearly single crystals and expected to have very high tensile strengths [6, 7], which makes them excellent candidates for reinforcement and toughening of ceramic and glass matrix composites [8–10]. Several methods and various starting raw materials have been used to grow SiC whiskers. In papers [6, 11–14], SiC whiskers were formed by the
vapour–liquid–solid (VLS) process with transition metals (especially Fe, Co and Ni) as catalysts. This method involves vapour transport of the precursors to a liquid catalyst located at the tip of the whiskers, incorporation of the constituents into the liquid and precipitation of the solid crystal at the liquid–solid interface. The presence of liquid catalyst distinguishes this method from other whiskers growth techniques. SiC whiskers are generally of cubic SiC structure growing in the <1 1 1> direction. Bootsma et al. [6] found that whisker growth by the VLS mechanism, morphology and crystal structure were dependent on temperature, reactant concentration and distribution of catalyst. The whisker diameter was dependent on the dimension of molten catalyst droplets and its wettability of SiC. Milewski et al. [13] revealed that the morphologies of whiskers formed in the VSL process were related to the degree of supersaturation and stoichiometry of the reactive gases. Choi et al. [11] developed a continuous process for synthesis of SiC whiskers. SiO vapour generated by the carbothermal reduction of silica reacted with carbon-carrying vapours (CO and CH₄), producing SiC whiskers on a substrate coated with iron powder.

Growth of SiC whiskers by a vapour phase chemical reaction method with deposition on a substrate (VS process) was reported in papers [15–19]. Carbothermal reduction of silica precursors is the most common VS process for the SiC production. Silica sources included various materials such as rice hulls [20–23], silica [24], silica gel [25], sea sand [26] and geothermal water [27]. The reductants reported in the literature were charcoal [28], carbon black [14] and CH₄ [11]. Other VS processes are based on the pyrolysis and crystallization of preceramic precursors by chemical vapour deposition (CVD) [29, 30].
In the process known as a vapour phase formation and condensation, SiC is heated to high temperature (> 2220 °C) in a closed container to create a high vapour pressure of SiC gas and, upon cooling, the SiC condense out in the form of whiskers [31, 32].

The aim of the present paper was to study the growth of SiC whiskers by the carbothermal reduction of quartz in CH₄-H₂-Ar gas mixture. The paper discusses the effects of gas atmosphere and temperature on the structure and morphologies of SiC whiskers and whiskers’ growth mechanisms.

2. Experimental

Quartz powder (particle size < 70 μm) was obtained by crushing quartz lumps using agate miller. Quartz powder and synthetic graphite (< 45 μm, Sigma-Aldrich Co. Ltd, Germany) were mixed with distilled water (80 wt % of solid mixture) by rolling in a plastic jar with zirconia balls for 8 hours. Water was removed by heating the mixture at 120 °C for 48 hours. Then the mixture was pressed into pellets in a uniaxial hydraulic press by applying 20 KN of load for 2 minutes. The pellets with a mass of approximately 1 g were 8 mm in diameter and about 14 mm in height.

Reduction of quartz by graphite in Ar, H₂, and CH₄-H₂-Ar gas mixture was studied in a laboratory fixed bed reactor heated in an electric vertical tube furnace. A pellet was loaded at the bottom of reactor at room temperature, and then heated to a desired temperature with
control of heating rate. The gases used in the investigation were of 99.999% purity. The total gas flow rate was maintained at 1.0 NL/min at 1 atm. The reduction experiment was stopped after certain duration by raising the reactor above the furnace hot zone and cooling down. After that, the reduced pellet was weighed and subjected to further analysis.

The outlet gas composition was continuously monitored by an infrared CO/CO$_2$/CH$_4$ analyzer (Advanced optima AO2020, ABB, Ladenburg, Germany) connected with a computer. Gas concentrations were recorded every 5 seconds.

The original mixture and reduced samples were analyzed by X-ray diffraction (XRD, MMA, GBC Scientific Equipment, Braeside, Australia). The fine powder of a sample after grinding was scanned at a speed of 0.02° s$^{-1}$ and step size 0.02° with CuK radiation generated at 35 kV and 28.6 mA.

The morphology of the samples was observed by field-emission scanning electron microscopy (FESEM, JCM-6000 and JSM-7001F, JEOL, Tokyo, Japan) operated at 15 KV. The chemical composition of the samples was determined by the energy-dispersive X-ray spectrometer (EDS) equipped on the SEM. The samples for the SEM analysis were coated with gold.

Transmission electron microscope (TEM) images and selected area diffraction patterns (SADE) were recorded on a JEM 2011 electron microscope (JEOL, Tokyo, Japan) operated at
200 KV. For this examination, the sample was dispersed in ethanol using an ultrasonic generator and then deposited on a copper grid.

3. Results and Discussion

3.1 Carbothermal reduction in Ar atmosphere

Synthesis of SiC by carbothermal reduction of quartz in argon was examined by temperature programmed reduction experiment in which the temperature was ramped from 300 °C until 1600 °C at 3 °C/min. Figure 1 presents the XRD patterns of SiO$_2$/C mixture before and after reduction. The patterns reveal that most of quartz was reduced to β-SiC when the temperature increased to 1600 °C. Meanwhile, the unreacted quartz was transformed to cristobalite. The SEM images of sample pellet before and after reduction are shown in Figure 2. The pellet after reduction was cut to two parts for SEM observation on the cross section and surface of the pellet. Unreacted SiO$_2$ particles (cristobalite) were still seen in the cross section (Figure 2(b)) and on the surface of the pellet (Figure 2(c)) after reduction at 1600 °C. The synthesized SiC was in the form of particles.

(Figure 1)

(Figure 2)

The overall reaction of carbothermal production of SiC in Ar can be written as

$$\text{SiO}_2\ (s) + 3\text{C}\ (s) = \text{SiC}\ (s) + 2\text{CO}\ (g) \quad (1)$$
It is generally accepted that SiC is formed through intermediate SiO gas via the following reactions [19]:

\[
C \ (s) + SiO_2 \ (s) = SiO \ (g) + CO \ (g) \quad (2)
\]

\[
SiO_2 \ (s) + CO \ (g) = SiO \ (g) + CO_2 \ (g) \quad (3)
\]

\[
C \ (s) + CO_2 \ (g) = 2CO \ (g) \quad (4)
\]

\[
SiO \ (g) + 2C \ (s) = SiC \ (s) + CO \ (g) \quad (5)
\]

SiO is initially formed at the contact points of carbon and silica according to Reaction (2). Further SiO synthesis proceeds through the gas/solid Reactions (3) and (4). SiC is formed by Reaction (5). Works [11, 33, 34] reported that reaction of the generated SiO vapour with CO vapour produced SiC whiskers by the following reaction:

\[
SiO \ (g) + 3 CO \ (g) = SiC \ (s) + 2 CO_2 \ (g) \quad (6)
\]

In this study, no SiC whisker was observed (Figure 2). Probably, low vapour pressures of SiO and CO in the reduction of quartz in Ar atmosphere were not sufficient for the whiskers formation.

### 3.2 Carbothermal reduction in \( H_2 \) atmosphere

The synthesis of SiC in hydrogen was carried out in temperature programmed reduction experiments. The reduction process was stopped at different temperatures, and the samples were analysed by XRD and SEM to identify the change in phase composition during the carbothermal reduction. Figure 3 presents the XRD patterns of the samples reduced in the
process of heating to 1200–1600 °C. No β-SiC was observed when the temperature was increased to 1200 °C. As the reduction temperature increased to 1300 °C, a weak peak of β-SiC was identified at 2θ = 35.66°. With the increase of temperature, the amount of β-SiC increased significantly. It became the only crystalline phase after reduction at 1600 °C.

(Figure 3)

The microstructures of the cross section and surface of the pellet were quite different. The SEM images of samples reduced at 1400 °C, 1500 °C and 1600 °C are shown in Figure 4, 5 and 6, respectively. A small number of SiC whiskers with diameter from 100 nm to 800 nm were observed on the cross section of the sample after reduction at 1400 °C (Figures 4(a)). Meanwhile, more whiskers were found on the surface of the pellet (Figures 4(b)). The whiskers grew to less than 4 μm, and had a globule at the growing end.

An EDS analysis of a globule in Figure 4(b) showed that it consisted of 9.1 at % of Fe, 3.9 at % of Al, 0.6 at % of Cr with a balance of Si, C, O, and Au. Fe and Cr in the samples originated from contamination of pellet in the process of pressing with stainless steel die. The presence of Al can be attributed to the reduction of alumina tube by H₂ at high temperatures, generating Al₂O vapour which deposited on the sample pellet. Fe and Al were also present as impurities in quartz.

(Figure 4)
Increasing the reduction temperature to 1500 °C promoted the growth of SiC whiskers, as shown in Figure 5. The whiskers on the cross section of the pellet grew to 5–8 μm (Figure 5(a)), and those on the surface of the pellet were much longer (Figure 5(b)). EDS analyses taken from the body of whisker proved that the composition of the whiskers was SiC.

(Figure 5)

After the reduction temperature increased to 1600 °C, the reduction of quartz was close to completion, as proved by the XRD analyses in Figure 3. The growth of SiC ceased when no more SiO vapour was provided. A low magnification SEM image in Figure 6(b) reveals a layer of flurry on the surface of the pellet. The whiskers on the cross section were very thick and straight (Figure 6(a)), while the whiskers on the surface were characterized by the high aspect ratio (Figure 6(c)). Figure 6(d) presents an image of a whisker at a high magnification, which shows it grew in the form of a hexagonal column.

(Figure 6)

**Figure 7(a)** is the TEM image of a typical SiC whisker collected from the surface of the pellet heated to 1600 °C, which also displays the hexagonal structure of the whisker. Figure 7(b) presents a globule at the end of a whisker, exhibiting lower transmission of electrons than SiC whiskers and particles.
As stated previously, the globules on the top ends of the SiC whiskers included metallic iron which was in a molten state at the temperatures of whisker formation. These globules played a catalytic role in the formation process of SiC whiskers, as described below.

In the carbothermal reduction of quartz in hydrogen, $H_2$ reacted with carbon forming $CH_4$ (Reaction (7)), which reacted with $SiO_2$ forming $SiO$ (Reaction (8)).

$$C\ (s) + 2H_2\ (g) = CH_4\ (g)$$  \hspace{1cm} (7)

$$SiO_2\ (s) + CH_4\ (g) = SiO\ (g) + CO\ (g) + 2H_2\ (g)$$ \hspace{1cm} (8)

In the presence of carbon, $H_2$ can also directly reduce silica [35] (Reactions (9) and (10)).

$$SiO_2\ (s) + H_2\ (g) = SiO\ (g) + H_2O\ (g)$$ \hspace{1cm} (9)

$$H_2O\ (g) + C\ (s) = H_2\ (g) + CO\ (g)$$ \hspace{1cm} (10)

The reaction between $CH_4$ and $SiO$ (Reaction (11)) resulted in growth of SiC whiskers under catalytic effect of iron, followed the VLS mechanism.

$$SiO\ (g) + 2\ CH_4\ (g) = SiC\ (s) + CO\ (g) + 4\ H_2\ (g)$$ \hspace{1cm} (11)
Practically, Reaction (11) can occur in multiple steps, involving dissolution of Si and C in the molten Fe globules and the deposition of SiC from the dissolved Si and C:

\[
\begin{align*}
\text{CH}_4 (g) &= [C] + 2 \text{H}_2 (g) \quad (12) \\
\text{SiO} (g) + [C] &= [\text{Si}] + \text{CO} (g) \quad (13) \\
[\text{Si}] + [C] &= \text{SiC} (s) \quad (14)
\end{align*}
\]

3.3 Carbothermal reduction in CH$_4$-H$_2$-Ar gas mixture

The synthesis of SiC by the carbothermal reduction in CH$_4$-H$_2$-Ar gas mixture was examined in temperature programmed experiments using a gas mixture containing 1 vol % of CH$_4$, 70 vol % of H$_2$ and 29 vol % of Ar. The XRD patterns of the samples heated to different temperatures are shown in Figure 8. The phase changes of the sample in reduction in CH$_4$-H$_2$-Ar gas mixture were similar to those observed in reduction in H$_2$. A small amount of \(\beta\)-SiC was identified in a sample reduced at 1200 °C; the peaks of SiC at \(2\theta = 35.66\) in samples reduced in CH$_4$-H$_2$-Ar gas mixture were stronger than the SiC peaks in the XRD spectra of the samples reduced in H$_2$ (Figure 3) at the same temperature. This indicates that introducing 1 vol % of CH$_4$ accelerated the reduction of quartz to SiC. CH$_4$ has a higher reducing capacity compared to that of solid carbon in the carbothermal reduction processes [36]. After reduction at 1600 °C, there was significant amount carbon in the sample, because CH$_4$ was directly involved in the reduction reaction and also cracked to produce solid carbon depositing on the surface of the pellet.
Temperature also had a significant effect on the morphology of SiC whiskers. After reduction at 1200 °C and 1300 °C, only a few SiC whiskers were observed on the surface of pellets, as shown in Figures 9(a) and 9(b). SiC of irregular form (marked by arrows) was also observed, due to the low SiO vapour pressure at the low temperatures [11]. Increasing reduction temperature to 1400 °C and 1500 °C resulted in generation of a large number of SiC whiskers, as shown in Figures 9(c) and 9(d). Most of whiskers grew from the graphite substrate in pellets with a catalyst globule at the tip. A few thin and long whiskers marked with arrows in Figures 9(c) and 9(d), were found to have no catalyst globules at the tips. Their growth directions were also different with whiskers with globules. They laid down on the surface of the pellet, rather than “stand” on the surface.

The SEM images of the cross section of a pellet subjected to temperature programmed reduction in the CH₄-H₂-Ar gas mixture at 1600 °C (Figure 10(a)), show that the layer of SiC fluff was much thicker than that formed in reduction in H₂, ranging from 250 to 500 μm. SiC whiskers with diameter of 300–800 nm and length of 3–10 μm were distributed in the center of the pellet’s cross section, as shown in Figure 10(b). However, the most of SiC was still in the form of irregular particles. Observed from the pellet surface, large amount of long
whiskers without catalytic globules were knit together (Figure 10(c)). These long whiskers grew to more than 100 μm long with uniform diameter of 350–450 nm. Whiskers with globules were also observed under the cover of long whiskers at the surface of pellet, as shown in Figure 10(d).

(Figure 10)

**Figure 11** presents the TEM images and the SAED patterns of two types of SiC whiskers from the sample reduced at 1600 °C. Figure 11(a) represents the images of SiC whiskers with catalyst globules, which show hexagonal column structure, the same as the SiC whiskers synthesized in H₂ (Figure 7(a)). The SAED patterns (Figure 11(b)) of the whisker demonstrated that it was a single-crystal β-SiC, with <111> and <220> as the diffraction crystal surface. While the SiC whiskers without catalyst globules had a smooth cylindrical structure (Figure 11(c)), with <111> as the diffraction crystal surface (Figure 11(d)).

(Figure 11)

The formation mechanism of SiC whiskers with catalyst globules is similar to that formed in reduction in H₂, which occurred at lower temperatures, probable due to higher SiO and CH₄ partial pressures in CH₄-H₂-Ar gas mixture. Based on the fact that Fe-rich globules were presented at the growing tips of SiC whiskers, its formation followed VLS mechanism. Initially, the Fe catalyst was in contact with substrate as the temperature was raised to the
melting points of Fe [37]. The liquid globule absorbed Si and C from SiO and CH$_4$ vapour until it became supersaturated. Nucleation of SiC occurred at the interface with the substrate and continued solution of gas species into the liquid catalyst ball allowed the whiskers to grow as additional SiC precipitated.

The long whiskers shown in Figure 11(c) were formed following a VS mechanism as no catalyst globule was observed at the tips. The formation of long whiskers cannot be explained by gas-gas (SiO-CO) Reaction (6), as no SiC whisker was formed in Ar atmosphere. Therefore, growth of long SiC whiskers via VS mechanism occurred by gas-gas (SiO-CH$_4$) Reaction (11). Higher SiO and CH$_4$ vapour pressures were required for whiskers growth without catalyst via VS mechanism; therefore, long whiskers were formed at higher temperatures (>1400 °C). Non-catalytic formation of long whiskers in the reduction in H$_2$ by VS mechanism was not feasible because significantly lower CH$_4$ pressure, as detected by the infrared gas analyzer (Figure 12).

(Figure 12)

4. Conclusions

SiC whiskers were formed in the carbothermal reduction of quartz in H$_2$ and CH$_4$-H$_2$-Ar gas mixture. In reduction in H$_2$ atmosphere from 1400 to 1600 °C, SiC whiskers with diameter of 100–800 nm were formed following a VSL mechanism under catalytic effect of Fe. Whisker length increased with the increase of temperature. The amount of whiskers was higher on the
surface than inside a pellet. Two different types of SiC whiskers were produced in reduction in a CH$_4$-H$_2$-Ar gas mixture; whiskers in the form of hexagonal columns were produced at 1200–1600 °C by VSL mechanism; whiskers in the form of long cylinders were synthesized at 1400–1600 °C by VS mechanism. The morphology and mechanism of formation of SiC whiskers was affected by the partial pressures of SiO and CH$_4$ which change with reduction atmosphere and temperature.

Acknowledgements

This research was supported under the Australian Research Council Linkage Project funding scheme (Project No. LP100100866) in collaboration with Solar Elkem (Norway). The authors acknowledge use of facilities and the assistance of Mr Mitchell Nancarrow and Dr Gilberto Casillas-Garcia at the UOW Electron Microscopy Centre.

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Figure Captions

Fig. 1 XRD patterns of SiO$_2$-graphite sample before and after reduction in Ar. The sample was reduced at ramping temperature from 300 °C to 1600 °C at 3 °C/min.

Fig. 2 SEM images of a sample: (a) Original pellet, cross section; (b) after reduction in Ar, cross section; (c) after reduction in Ar, pellet surface. The temperature was ramped from 300 °C to 1600 °C at 3 °C/min.

Fig. 3 XRD patterns of samples in the progress of reduction in H$_2$. The temperature was ramped from 300 °C to 1600 °C at 3 °C/min.

Fig. 4 SEM images of a sample after temperature programmed reduction in H$_2$ at 1400 °C: (a) cross section of the pellet; (b) surface of the pellet.

Fig. 5 SEM images of a sample after temperature programmed reduction in H$_2$ at 1500 °C: (a) cross section of the pellet; (b) surface of the pellet.

Fig. 6 SEM images of a sample after temperature programmed reduction in H$_2$ at 1600 °C: (a) and (b) cross section of the pellet; (c) surface of the pellet; (d) a SiC whisker at a high magnification.

Fig. 7 TEM images of (a) SiC whisker body synthesized in H$_2$ at 1600 °C and (b) catalyst globule.

Fig. 8 XRD patterns of samples in the progress of reduction CH$_4$-H$_2$-Ar gas mixture. The temperature was ramped from 300 °C to 1600 °C at 3 °C/min.

Fig. 9 SEM images of the surface of samples reduced in CH$_4$-H$_2$-Ar gas mixture in temperature programmed experiments upon heating to different temperatures: (a)
1200 °C; (b) 1300 °C; (c) 1400 °C; (d) 1500 °C. Arrows in (a) and (b) show SiC of irregular shape; arrows in (c) and (d) point at thin and long SiC whiskers.

Fig. 10 SEM images of a sample after temperature programmed reduction in CH₄-H₂-Ar gas mixture at 1600 °C: (a) and (b) cross section; (c) and (d) surface of the pellet.

Fig. 11 (a) TEM image of SiC whisker synthesized by VLS mechanism; (b) SADE patterns of whisker shown in (a); (c) TEM image of SiC whisker synthesized by VS mechanism; (d) SADE patterns of whisker shown in (c).

Fig. 12 Concentration of CH₄ in the gas phase in the progress of reduction in H₂ and CH₄-H₂-Ar gas mixture.
Fig. 1 XRD patterns of SiO$_2$-graphite sample before and after reduction in Ar. The sample was reduced at ramping temperature from 300 °C to 1600 °C at 3 °C/min.
Fig. 2 SEM images of a sample: (a) Original pellet, cross section; (b) after reduction in Ar, cross section; (c) after reduction in Ar, pellet surface. The temperature was ramped from 300 °C to 1600 °C at 3 °C/min.
Fig. 3 XRD patterns of samples in the progress of reduction in H$_2$. The temperature was ramped from 300 °C to 1600 °C at 3 °C/min.
Fig. 4 SEM images of a sample after temperature programmed reduction in H$_2$ at 1400 °C: (a) cross section of the pellet; (b) surface of the pellet.
Fig. 5 SEM images of a sample after temperature programmed reduction in H₂ at 1500 °C: (a) cross section of the pellet; (b) surface of the pellet.
Fig. 6 SEM images of a sample after temperature programmed reduction in H\textsubscript{2} at 1600 °C: (a) and (b) cross section of the pellet; (c) surface of the pellet; (d) a SiC whisker at a high magnification.
Fig. 7 TEM images of (a) SiC whisker body synthesized in H$_2$ at 1600 °C and (b) catalyst globule.
Fig. 8 XRD patterns of samples in the progress of reduction CH₄-H₂-Ar gas mixture. The temperature was ramped from 300 °C to 1600 °C at 3 °C/min.
Fig. 9 SEM images of the surface of samples reduced in CH$_4$-H$_2$-Ar gas mixture in temperature programmed experiments upon heating to different temperatures: (a) 1200 °C; (b) 1300 °C; (c) 1400 °C; (d) 1500 °C. Arrows in (a) and (b) show SiC of irregular shape; arrows in (c) and (d) point at thin and long SiC whiskers.
Fig. 10 SEM images of a sample after temperature programmed reduction in \(\text{CH}_4\)-\(\text{H}_2\)-Ar gas mixture at 1600 °C: (a) and (b) cross section; (c) and (d) surface of the pellet.
Fig. 11 (a) TEM image of SiC whisker synthesized by VLS mechanism; (b) SADE patterns of whisker shown in (a); (c) TEM image of SiC whisker synthesized by VS mechanism; (d) SADE patterns of whisker shown in (c).
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