Effect of deposition atmosphere on the phase composition and microstructure of silicon carbide films prepared by laser chemical vapour deposition

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Abstract: β -SiC films were prepared by laser chemical vapour deposition using a Nd:YAG laser in a H_2 or Ar atmosphere. The effects of the deposition atmosphere on the film phase composition and microstructure were investigated. In a H_2 atmosphere, (111)-oriented β -SiC films consisting of submicron-sized grains were grown at 1273–1473 K, while carbon was codeposited with the β -SiC films grown at 1573–1673 K. In an Ar atmosphere, amorphous Si–C–O films were grown at 1073–1373 K, while (111)-oriented β -SiC films that did not contain free carbon were grown at 1473–1723 K. The deposition rates of the (111)-oriented β -SiC films were 1500–2000 $\mu m h^{-1}$.

Keywords: β -SiC; laser chemical vapour deposition; high-speed deposition; thick film

1. Introduction

Silicon carbide (SiC) shows promise as a protective material because of its excellent thermal shock and oxidation resistances [1,2]. SiC coatings can be prepared by various techniques. For instance, chemical vapour deposition (CVD) is suitable for preparing high-purity, high-density, and conformal films at high deposition rates. Even though halide-based CVD is used extensively for the production of SiC films at relatively high deposition rates [3–5], this technique requires high deposition temperatures (greater than 1700 K) and generates hazardous chlorides as by-products.

Films of various oxides [6,7], carbides [8], and nitrides [9] have been prepared at high deposition rates (100–1000 $\mu\text{m h}^{-1}$) by laser CVD. β -SiC films have been grown on graphite substrates at a deposition rate of 2200 $\mu\text{m h}^{-1}$ [8]. The high-speed epitaxial growth of (111)- and (110)-oriented β -SiC films has been achieved on (111) and (110) Si substrates, respectively [10].

Hexamethyldisilane (HMDS, $\text{C}_6\text{H}_{18}\text{Si}_2$) has been used widely as a SiC precursor during CVD because its vapour pressure at room temperature is moderately high and because it does not form hazardous and corrosive by-products. However, its carbon content is three times that of silicon and results in free carbon being present in the synthesised SiC films. Free carbon degrades the chemical, mechanical, and electrical properties of SiC but can be removed by adding either H_2 gas or an oxidant (*i.e.*, O_2 and H_2O), which form hydrocarbons (*e.g.*, CH_4) or carbonates (*e.g.*, CO_2) in gaseous form, respectively. For instance, the addition of O_2 gas, which

is a powerful oxidant of free carbon and may oxidise β -SiC to SiO_2 , is easy and safe. On the other hand, in the case of laser CVD, the source gases are activated by laser irradiation. Therefore, trace amounts of O_2 in the common Ar gas (O_2 content less than 2 ppm) can eliminate the free carbon from the synthesised β -SiC films.

In the present study, SiC films were prepared by laser CVD in a H_2 or Ar atmosphere, and the effects of the deposition atmosphere on the film phase composition and microstructure were investigated.

2. Experimental

The laser CVD apparatus used has been described in detail elsewhere [11]. HMDS (LS-7120; Shin-Etsu Chemical, Japan) was evaporated at 293 K and its vapour was transported to the deposition chamber using H_2 or Ar as the carrier gas. The O_2 impurity level in the Ar gas was less than 2 ppm. The carrier gas was introduced into the chamber separately through a double-tube nozzle. The total pressure in the chamber was maintained at 800 Pa. The entire graphite substrate (10 mm in diameter and 1 mm in thickness) was irradiated with a continuous-wave Nd:YAG laser ($\lambda = 1064$ nm). The deposition temperature (T_{dep}) was measured using a pyrometer. T_{dep} was increased from 1073 to 1723 K by increasing the laser power from 60 to 245 W. The deposition rate was calculated using the film thickness and deposition time (0.6 ks).

The film phase compositions were determined through X-ray diffraction (XRD) analyses, which were performed using Cu K α radiation (Rigaku, Ultima-IV; 40 kV and 40 mA). The cross-sectional microstructures of the synthesised films were observed with a scanning electron microscopy (SEM) system (Hitachi, S-3100H) and a transmission electron microscopy (TEM) system (Topcon, EM-002B). The binding energies of the C, Si, and O atoms were measured with X-ray photoelectron spectroscopy (XPS), which was performed using Al K α radiation (Shimadzu-Kratos AXIS-ULTRA DLD). The spectra were fitted with a Gaussian function with baseline correction. The C–C peak at 284.8 eV was used as the charge reference.

3. Results and discussion

3.1 SiC films prepared in a H₂ atmosphere

Figure 1 shows the XRD patterns of SiC films prepared at various T_{dep} in a H₂ atmosphere. Only peaks related to the graphite substrate were observed at 1173 K, implying that the corresponding film was amorphous (Fig. 1(a)). In the case of the film grown at 1273 K, a broad peak was observed at $2\theta = 36^\circ$; this was indexed as belonging to 111 β -SiC (ICSD #24217) (Fig. 1(b)). A (111)-oriented β -SiC film was obtained at 1473 K (Fig. 1(c)). At 1673 K, carbon was codeposited with the synthesised (111)-oriented β -SiC film (Fig. 1(d)). The (0001) peak at $2\theta = 26^\circ$ could be deconvoluted into two peaks, which were attributable to the deposited carbon ($2\theta = 25.5^\circ$) and the graphite substrate ($2\theta = 26.4^\circ$).

Figure 2 shows the Si 2*p* XPS spectra of SiC films prepared at various T_{dep} in a H_2 atmosphere. In the case of the film grown at 1173 K, the Si 2*p* peak could be deconvoluted into peaks related to Si–C₄, Si–C₃–O, Si–C₂–O₂, and Si–C–O₃ (Fig. 2(a)). The Si 2*p* binding energies in SiC (Si–C₄) and SiO₂ (Si–O₄) are 100–101 and 103–104 eV, respectively. The Si 2*p* peak observed at approximately 101 eV was associated with Si–C₄ (101.0 eV), Si–C₃–O (101.8 eV), Si–C₂–O₂ (102.4 eV), Si–C–O₃ (102.9 eV), and Si–O₄ (103.6 eV) [12–15]. The C atoms in the Si–C₄ tetrahedron were partially substituted by an O atom. Therefore, the amorphous nature of the film prepared at 1173 K may explain the formation of the Si–C–O film. The presence of residual oxygen in the precursor furnace and the deposition chamber may account for the formation of Si–C–O. At 1473 K, the Si 2*p* peak became slightly sharper and almost fitted the spectrum of Si–C₄ at 101.0 eV (Fig. 2(b)).

Figure 3 shows cross-sectional SEM and TEM images of the SiC films prepared at 1473 and 1673 K in a H_2 atmosphere. At 1473 K, the deposited SiC film consisted of fine grains (Fig. 3(a)). Further, the nanosized β -SiC particles formed a three-dimensional network (Fig. 3(b)). We estimated their grain size to be 98 nm using the Debye–Scherrer equation; this value was in agreement with the TEM observations. The selected-area electron diffraction (SAED) pattern showed a Debye–Scherrer ring, which was indexed as belonging to β -SiC (inset, Fig. 3(b)).

The β -SiC film prepared at 1673 K displayed a lamellar structure in the cross-sectional

SEM and TEM images (Figs. 3(c) and 3(d)). The arc-like patterns and diffraction spots observed in its SAED pattern were attributable to carbon and β -SiC, respectively (inset, Fig. 3(d)). Consequently, the lamellar structure corresponded to (0001)-oriented carbon, whereas the vertical grains (darker part) were associated with (111)-oriented β -SiC.

3.2 SiC films prepared in an Ar atmosphere

Figure 4 shows the XRD patterns of SiC films prepared at various T_{dep} in an Ar atmosphere. At 1173 K, only peaks related to the graphite substrate were observed, indicating that the corresponding film was amorphous (Fig. 4(a)). At 1273 K, a halo pattern was observed at $2\theta = 36^\circ$ (Fig. 4(b)). The XRD patterns of the films formed at 1473 (Fig. 4(c)) and 1673 K (Fig. 4(d)) suggested that the films had a (111) orientation. The (111) orientation became more pronounced at 1673 K; however, no free carbon was detected in the β -SiC films prepared at temperatures of 1473–1673 K.

Figure 5 shows the Si 2p XPS spectra of SiC films prepared at various T_{dep} in an Ar atmosphere. In the case of the film synthesised at 1073 K, the Si 2p peak could be deconvoluted into those corresponding to Si-C₄, Si-C₃-O, Si-C₂-O₂, Si-C-O₃, and Si-O₄ (Fig. 5(a)). When T_{dep} was increased from 1073 to 1473 K, the Si 2p peak observed was almost similar to that for Si-C₄ (Fig. 5(c)).

Figure 6 shows cross-sectional SEM and TEM images of the SiC films prepared at

1273 and 1723 K in an Ar atmosphere. The Si–C–O film prepared at 1273 K had an amorphous structure (Fig. 6(a)); no grains were observed in the TEM images (Fig. 6(b)). The SAED pattern of the film showed a Debye ring that could be indexed as belonging to β -SiC (inset, Fig. 6(b)). On the other hand, the β -SiC film prepared at 1723 K consisted of columnar grains with conical tops (Figs. 6(c) and 6(d)). Its SAED pattern confirmed that the columnar grains grew in the (111) direction (inset, Fig. 6(d)).

3.3 Comparison of phases and microstructures of films synthesised in H_2 and Ar atmospheres

Figure 7 displays the phases and microstructures of the films synthesised in H_2 and Ar atmospheres. In the H_2 atmosphere, when T_{dep} was increased from 1073 to 1523 K, the Si–C–O phase transformed into β -SiC, with a mixture of β -SiC and carbon resulting eventually. The Si–C–O films formed at 1173–1473 K were amorphous, whereas the β -SiC films consisted of nanosized grains assembled into a three-dimensional network. The β -SiC/carbon mixture exhibited a lamellar structure at 1673 K. Therefore, it can be assumed that, in the H_2 atmosphere, the small amount of O present contaminated the β -SiC film at a low T_{dep} (~ 1273 K). Further, the free-carbon content increased with an increase in T_{dep} .

In the Ar atmosphere, amorphous Si–C–O films were formed for temperatures of 1073–1373 K, whereas (111)-oriented β -SiC films were formed at temperatures greater than

1423 K. When T_{dep} was increased from 1423 to 1723 K, the (111) orientation of the β -SiC films became more pronounced, and their microstructure changed from cauliflower-like to columnar. No carbon was identified in the β -SiC films. Highly crystalline (111)-oriented β -SiC films were grown at 1423 K using the Nd:YAG laser. This T_{dep} value is lower than that for similar films obtained by conventional thermal CVD and laser CVD using a CO_2 laser [8]. The CO_2 laser has a longer wavelength (10.6 μm), which falls in the infrared region, and might not interact with the gas phase. In contrast, the Nd:YAG laser has a medium wavelength (1064 nm) and can interact with the precursor gases. As a result, intermediate species can form [16]. Presumably, this is why the Nd:YAG laser produced β -SiC films at a lower T_{dep} value than that for the CO_2 laser.

Figure 8 shows the relation between the reciprocal of T_{dep} and the deposition rate (R_{dep}) of SiC films formed by conventional CVD and laser CVD. Table 1 lists the experimental conditions. In this study, in the H_2 atmosphere, when T_{dep} was increased from 1173 to 1473 K, R_{dep} increased from 10 to 1400 $\mu\text{m h}^{-1}$ before decreasing to 200 $\mu\text{m h}^{-1}$ at temperatures greater than 1473 K. In the Ar atmosphere, R_{dep} increased from 10 to 2000 $\mu\text{m h}^{-1}$ when T_{dep} was increased from 1073 to 1473 K before decreasing to 600 $\mu\text{m h}^{-1}$ at temperatures greater than 1473 K. R_{dep} increased exponentially with an increase in T_{dep} at temperatures below 1500 K in both the H_2 and the Ar atmosphere, leading to activation energies (E_a) of 150 and 238 kJ mol^{-1} , respectively. In the case of CVD, activation energies (E_a) greater than 100 kJ mol^{-1} generally

correspond to reaction-limited processes on the substrate surface, whereas low E_a values (*i.e.*, those on the order of several tens of kJ mol^{-1}) are indicative of diffusion-limited processes in the gas phase [17]. Therefore, it can be concluded that, in this study, the β -SiC films were deposited through a reaction-limited process at temperatures below 1500 K. The decrease in R_{dep} at temperatures greater than 1500 K may result from premature gas-phase reactions, such as those related to powder formation.

Halide CVD using SiCl_4 and hydrocarbon precursors produces β -SiC films at high R_{dep} but requires high T_{dep} values (1700–1900 K) to achieve highly crystalline films [4,5]. Plasma-enhanced, low-pressure, and atmospheric-pressure CVD processes can produce β -SiC films at temperatures lower than 1300 K at R_{dep} of 0.01–10 $\mu\text{m h}^{-1}$ [18–24], values that are 100 times lower than those observed in the present study. Metalorganic compounds, such as tetramethylsilane (TMS: $\text{Si}(\text{CH}_3)_4$) [25], monomethylsilane (MMS: CH_3SiH_3) [22], 1,3-disilacyclobutane (DSB: $\text{SiH}_3\text{CH}_2\text{--SiH}_2\text{CH}_3$) [24], and hexamethyldisilane (HMDS: $\text{Si}(\text{CH}_3)_3\text{--Si}(\text{CH}_3)_3$) [8,10,15,20,23], are typically used as precursors during metalorganic CVD. In addition, H_2 gas is used at high flow rates to generate β -SiC films that do not contain any free carbon; however, this significantly degrades the deposition rate. In this study, β -SiC films without free carbon could be deposited in an Ar atmosphere between 1473 and 1673 K at significantly high deposition rates (1500–2000 $\mu\text{m h}^{-1}$).

Conclusions

β -SiC films were deposited by laser CVD using a Nd:YAG laser. In a H_2 atmosphere, the amorphous Si-C-O phase transformed into β -SiC, eventually resulting in a mixture of β -SiC and carbon, as the deposition temperature was increased. The β -SiC films comprised fine submicron-sized grains, which formed a three-dimensional network. The β -SiC phase with small amounts of free carbon had a lamellar structure. In an Ar atmosphere, the amorphous Si-C-O phase produced β -SiC with an increase in T_{dep} . β -SiC films without free carbon were obtained at temperatures of 1473–1673 K at R_{dep} values of 1500–2000 $\mu\text{m h}^{-1}$. These films exhibited a (111)-oriented columnar structure.

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Figure captions

- Figure 1** XRD patterns of the SiC films prepared in a H_2 atmosphere at T_{dep} of (a) 1173 K, (b) 1273 K, (c) 1473 K, and (d) 1673 K.
- Figure 2** Si 2*p* XPS spectra of the SiC films prepared in a H_2 atmosphere at T_{dep} of (a) 1173 K and (b) 1473 K.
- Figure 3** (a, c) Cross-sectional SEM and (b, d) TEM images of the SiC films prepared in a H_2 atmosphere at T_{dep} of (a, b) 1473 K and (c, d) 1673 K. Insets show the corresponding SAED patterns.
- Figure 4** XRD patterns of the SiC films prepared in an Ar atmosphere at T_{dep} of (a) 1173 K, (b) 1273 K, (c) 1473 K, and (d) 1673 K.
- Figure 5** Si 2*p* XPS spectra of the SiC films prepared in an Ar atmosphere at T_{dep} of (a) 1073 K, (b) 1273 K, and (c) 1473 K.
- Figure 6** (a, c) Cross-sectional SEM and (b, d) TEM images of the SiC films prepared in an Ar atmosphere at T_{dep} of (a, b) 1273 K and (c, d) 1723 K. Insets show

the corresponding SAED patterns.

Figure 7 Phases and microstructures of the SiC films prepared in (a) H₂ and (b) Ar atmospheres.

Figure 8 Relationship between the reciprocal of T_{dep} and R_{dep} for SiC films grown using conventional CVD and laser CVD.

Fig.01

Fig.02

Fig.03

Fig.04

Fig.05

Fig.06

Fig.07

(a) H_2 atmosphere

(b) Ar atmosphere

Fig.08

Table 1 Preparations of SiC film by CVD in literature and in the present study.

CVD type [†]	Precursor [‡]	Reactant	Max. R_{dep} ($\mu\text{m h}^{-1}$)	Ref.
Halide CVD				
LP, CW	SiCl ₄	H ₂ + C ₃ H ₈	1400	[4]
AP, CW	SiCl ₄	H ₂ + C ₃ H ₈	1400	[4]
LP, CW	SiCl ₄	H ₂ + CH ₄	1125	[5]
PE, CW	SiCl ₄	H ₂ + CH ₄	8	[18]
MOCVD				
LP, HW	HMDS	H ₂	3	[19]
LP, HW	TMS	H ₂	0.08	[25]
LP, HW	DSB	-	4	[24]
LP, CW	MMS	H ₂	0.5	[22]
AP, CW	HMDS	H ₂	4.5	[20]
AP, CW	HMDS	H ₂	0.6	[23]
Laser CVD				
LP, CW	TEOS	C ₂ H ₂	370	[15]
LP, CW	HMDS	-	2200	[8]
LP, CW	HMDS	-	3600	[10]
LP, CW	HMDS	-	2000	Present study
LP, CW	HMDS	H ₂	1400	

[†] LP: low-pressure CVD; AP: atmospheric-pressure CVD; CW: cold-wall type chamber; HW: hot-wall type chamber

[‡] TMS (tetramethylsilane: Si(CH₃)₄); TMS (tetramethylsilane: Si(CH₃)₄); MMS (monomethylsilane: CH₃SiH₃); DSB (1,3-disilacyclobutane: SiH₃CH₂-SiH₂CH₃); HMDS (hexamethyldisilane: Si(CH₃)₃-Si(CH₃)₃); TEOS (tetraethyl orthosilicate: Si(C₂H₅O)₄)