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Laser chemical vapor deposition of SiC films with CO_2 laser

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ABSTRACT

SiC films were prepared by laser chemical vapor deposition using a CO_2 laser (maximum laser power: 245 W) with HMDS (hexamethyldisilane) precursor and the effects of deposition conditions on the phase, microstructure and deposition rate were investigated. At pre-heating temperature of 323 K and laser power (P_L) above 119 W (deposition temperature (T_{dep}) above 1410 K), (1 1 1)-oriented 3C SiC (β-SiC) films were obtained. With increasing T_{dep}, the microstructure of these SiC films changed from glass-like ($T_{dep} < 1460$ K) to cauliflower-like ($T_{dep} = 1460$–1560 K) to granular ($T_{dep} > 1560$ K). Conical facets formed on the surface of granular SiC films at around $T_{dep} = 1650$ K. The deposition rate (R_{dep}) of SiC films showed a maximum at $T_{pre} = 473$ K and $P_L = 119$ W ($T_{dep} = 1490$ K) and reached 2200 μm h^{-1}.

1. Introduction

Silicon carbide (SiC) has excellent wear, oxidation resistance and high-temperature strength, and thus SiC-coated carbon composites and SiC fiber-reinforced aluminum alloys are widely used as high-temperature structural materials with high thermal shock resistance and high specific strength [1,2]. Moreover, superior functionalities of SiC such as high electron mobility, impurity controllability of p/n types and high breakdown voltage, make SiC attractive for use as wide bandgap semiconductors and power devices [3,4].

Chemical vapor deposition (CVD) has been commonly used for SiC coatings. Conventional thermal CVD often uses silicon halides, mainly $SiCl_4$ and methyltrichlorosilane (CH_3SiCl_3), as precursors with H_2 gas [5,6], and we have reported achievement of high-speed deposition (2000 μm h^{-1}) of SiC film by using $SiCl_4$ and C_3H_8 gases [7]. Since H_2 gas and intermediate Si–C–H–Cl compounds are highly explosive, safety during experimentation is an important issue. Moreover, by-products of Cl-containing species, mainly HCl, are corrosive, and therefore the inside of the CVD chamber and exhaust gas line should be carefully designed to prevent corrosion. Low pressure CVD (LPCVD) [8–13] and plasma-enhanced CVD (PECVD) [14] using metalorganic compounds containing Si are possibly available to avoid explosion and corrosion; however, the deposition rate of SiC films, less than several 10 μm h^{-1}, is too low to obtain a thick coating. Laser-assisted CVD has been conducted to prepare SiC films, but the deposition rate as with those of LPCVD and PECVD, is still too low. Furthermore, the deposition is limited to a small area, less than a few mm^2 hardly applicable to practical usage for oxidation and wear-resistant engineering coatings [15].

We have previously reported high-speed, low-temperature deposition of thick Y_2O_3, TiO_2 and Al_2O_3 films with several hundred micrometers in thickness onto substrate with a relatively large area (12.5 mm × 12.5 mm) by laser CVD (LCVD) using a continuous wave of a high-power Nd:YAG laser (260 W) [16–18], and succeeded in coating a practical complex-shaped gas turbine blade by moving and rotating the substrate [19,20]. Unlike the conventional LCVD process [21], with a high-power laser, plasma can be produced by ionizing precursor gases, which enhances the chemical reactions in the gas phase, and also accelerates the surface mobility of absorbed species on the substrate surface.

In the conventional CVD process using metalorganic compounds as precursors, O_2 or H_2 gases are added to eliminate excess hydrocarbon species. However, it is almost impossible to obtain non-oxide compounds in an O_2 containing atmosphere, and H_2 gas would inevitably result at the potential risk of explosion. In the present study, SiC films were prepared in a wide area (15 mm in diameter) at a high deposition rate by laser CVD with a CO_2 laser using an organic precursor in the absence of H_2 and O_2 gases. Moreover, the effects of laser power and pre-heating temperature on the phase, microstructure and deposition rate were investigated.

2. Experimental procedure

Fig. 1 depicts a schematic of the LCVD apparatus, and Table 1 lists the deposition conditions. HMDS (hexamethyldisilane; $Si(CH_3)_3$–$Si(CH_3)_3$) liquid was used as a precursor. It was slightly heated to a vaporization temperature (T_{vap}) of 298 K and carried into the CVD chamber with Ar gas. The gas flow rate of Ar gas was 1.7×10^{-6} m^3 s^{-1} (100 sccm) and the total pressure (P_{tot}) was fixed at 400 Pa. A graphite disc (Sankyo Carbon Co., Ltd., IGS-743, 15 mmϕ × 1 mm) was used as

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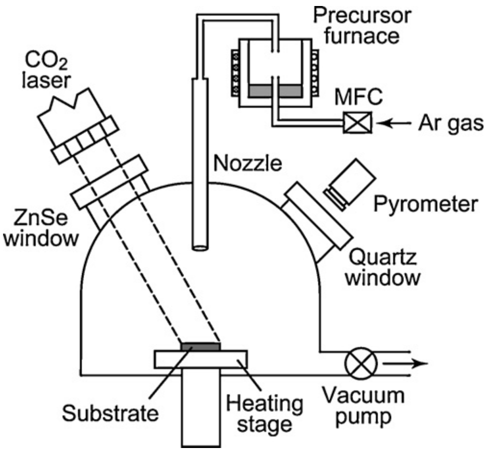

Fig. 1. Schematic of laser CVD apparatus.

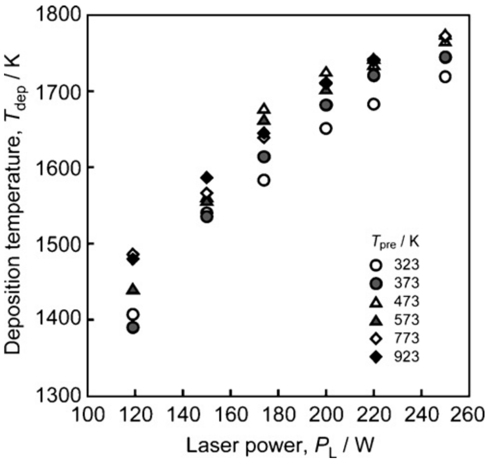

Fig. 2. Effects of P_L and T_{pre} on the T_{dep} at P_{tot} = 400 Pa.

Table 1
Deposition conditions.

Precursor	Hexamethyldisilane (HMDS)
HMDS vaporization temperature (T_{vap})	298 K
Substrate	Graphite plate
Pre-heating temperature (T_{pre})	323–923 K
Ar gas flow rate	1.7×10^{-6} m^3 s^{-1}
Total pressure (P_{tot})	400 Pa
Distance between nozzle and substrate	30 mm
Laser output power (P_L)	0–245 W

the substrate and was pre-heated on a hot stage at T_{pre} = 323–923 K. The distance between the nozzle and the substrate was fixed at 30 mm. A CO_2 laser beam in a continuous wave mode (wavelength: 10.6 μm; Synrad Inc. firestar f200) was collimated by lenses to irradiate the whole substrate (15 mm in diameter) and introduced into the CVD chamber through a ZnSe window. The laser power (P_L) was increased up to 245 W. The T_{pre} and deposition temperature (T_{dep}) was measured with a two-color pyrometer (CHINO corp. IR-AH).

The crystal phase was determined by X-ray diffraction (θ–2θ XRD; Rigaku RAD-2C). The surface and cross-sectional morphologies were observed by a scanning electron microscope (SEM; Hitachi S-3100H). The deposition rate (R_{dep}) was calculated from the thickness and the deposition time.

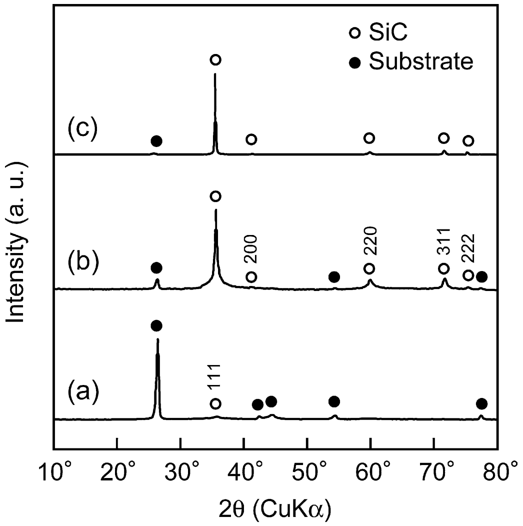

Fig. 3. XRD patterns of the SiC films prepared at T_{pre} = 323 K and P_L = 119 W (T_{dep} = 1410 K) (a), 150 W (1540 K) (b) and 245 W (1720 K) (c).

3. Results and discussion

The T_{dep} is one of the most dominant parameters in the CVD process, and is usually determined by input power or radiation heat to the substrate. On the other hand, the T_{dep} was determined by a combination of T_{pre} and P_L in the present LCVD as shown in Fig. 2. The T_{dep} increased with increasing P_L. The higher the T_{pre}, the higher the T_{dep}, but the increase in T_{dep} tended to be smaller at higher T_{pre}.

Fig. 3 shows the XRD patterns of SiC films prepared at T_{pre} = 323 K and various P_L. No films were deposited at P_L < 119 W (T_{dep} < 1410 K). (1 1 1)-Oriented 3C SiC (β-SiC) films were prepared at P_L > 119 W (T_{dep} > 1410 K) (Fig. 3(a)). Although more than 100 polymorphs have been reported for SiC, cubic 3C phase has been most commonly formed from a vapor phase [22]. By using a 6H SiC single-crystal substrate, 6H SiC epitaxial film can also be prepared [23]. With increasing P_L to 245 W (T_{dep} = 1720 K), the XRD intensity of the (1 1 1) peak increased while the FWHM (full width at half maximum) decreased (Fig. 3(b) and (c)).

Fig. 4 shows the surface and cross-sectional SEM images of the SiC films prepared at T_{pre} = 323 K and various P_L. At P_L = 119 W (T_{dep} = 1410 K), the SiC films had a flat, smooth surface and a dense, glass-like cross section (Fig. 4(a) and (b)). Cauliflower-like grains were observed at P_L = 150 W (T_{dep} = 1540 K) (Fig. 4(c) and (d)), whereas conical facets were formed on the surface of granular

Table 2
Literature data for the CVD SiC films using HMDS precursor. Asterisk indicates epitaxial growth.

CVD	Substrate	T_{dep}/K	Phase	R_{dep}/μm h^{-1}	Ref.
APCVD	Si (0 0 1), Si (1 1 1)	1173–1573	3C*		[26]
MOCVD	Si (0 0 1), Si (1 1 1)	1473–1523	3C*		[27]
APCVD	Si (0 0 1)	1623	3C*	4.3	[28]
LPCVD	Si (1 1 1)	1123–1323	3C	0.05–3	[13]
APCVD	SiO_2/Si	1473	3C	0.6	[29]
LCVD (ArF)	Quartz glass	300–673	3C	0.7–2.9	[30]
PECVD	Polymer	293	3C	3–13	[31]
LCVD (CO_2)	Graphite	1400–1720	3C	300–2200	Present study

APCVD: atmospheric pressure CVD.

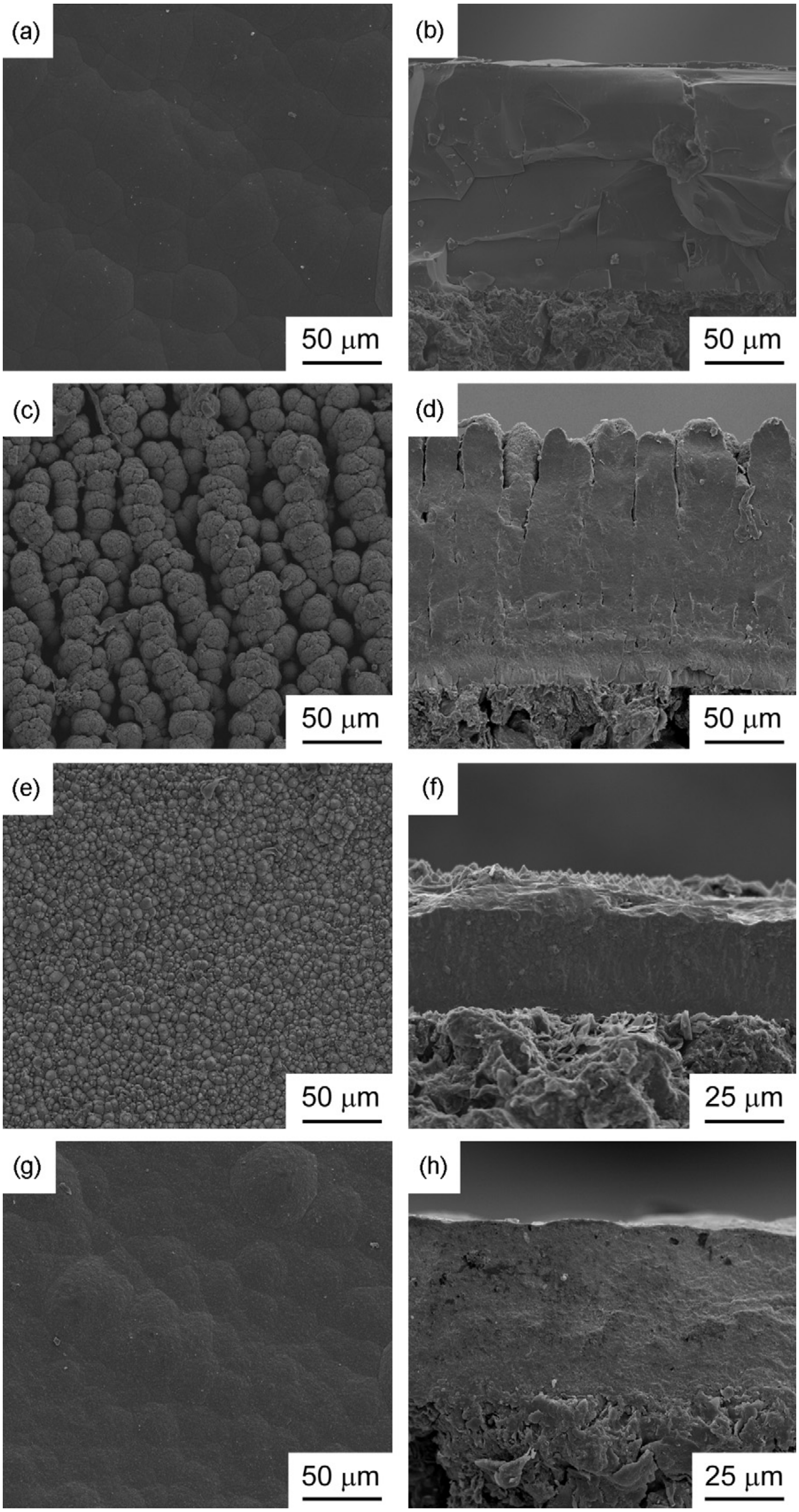

Fig. 4. Surface and cross-sectional SEM images of SiC films prepared at $T_{\mathrm{pre}} = 323$ K and $P_{\mathrm{L}} = 119$ W ($T_{\mathrm{dep}} = 1410$ K) (a and b), 150 W (1540 K) (c and d), 174 W (1570 K) (e and f) and 220 W (1660 K) (g and h).

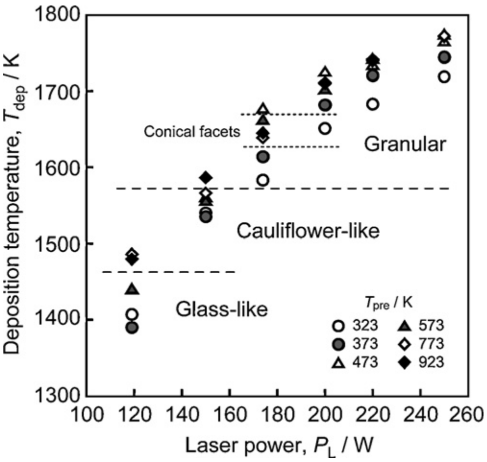

Fig. 5. Effects of P_L and T_{dep} on the morphology of the SiC films prepared at various T_{pre}.

film at $P_L = 174$ W ($T_{dep} = 1570$ K) (Fig. 4(e) and (f)). At $P_L = 220$ W ($T_{dep} = 1660$ K), the SiC film was dense and consisted of uniform fine granular grains (Fig. 4(g) and (h)). Fig. 5 depicts the effects of P_L and T_{dep} on the morphology of SiC films prepared at various T_{pre}. Glass-like SiC films were prepared at $T_{dep} < 1460$ K and a cauliflower-like structure was observed between $T_{dep} = 1460$ and 1570 K. At $T_{dep} > 1570$ K, granular SiC films were prepared and conical facets formed at around $T_{dep} = 1650$ K. With increasing P_L and T_{dep}, the morphology changed from glass-like to cauliflower-like to granular.

Fig. 6 shows the effects of P_L on the R_{dep} of the SiC films prepared at various T_{pre}. At $T_{pre} < 373$ K (open and filled circles), the R_{dep} showed maxima at $P_L = 150$ W, while at $T_{pre} > 473$ K (open and filled triangles and diamonds), the R_{dep} showed maxima at $P_L = 119$ W and reached 2200 μm h^{-1}. The P_L for the maximum R_{dep} decreased with increasing T_{pre}. The R_{dep} was almost constant, ranging between 300 and 500 μm h^{-1} at $P_L > 174$ W. Fig. 7 summarizes the effects of T_{dep} on the R_{dep} and morphology of SiC films prepared at various T_{pre} and P_L. At T_{dep} between 1350 and 1500 K, the R_{dep} increased with increasing T_{dep} and the SiC films had a glass-like structure. At around $T_{dep} = 1500$ K, the R_{dep} showed a maximum value of 2200 μm h^{-1} and a cauliflower-like structure was observed. Such microstructure has often been observed in CVD film prepared at a high R_{dep}. The R_{dep} declined with increasing T_{dep} and the morphology changed to a granular structure at $T_{dep} > 1500$ K. The R_{dep} was almost constant at $T_{dep} > 1660$ K. This decline in R_{dep} suggested that the premature reaction in the gas phase might occur at a high temperature, causing the decrease in the precursor concentration around the substrate.

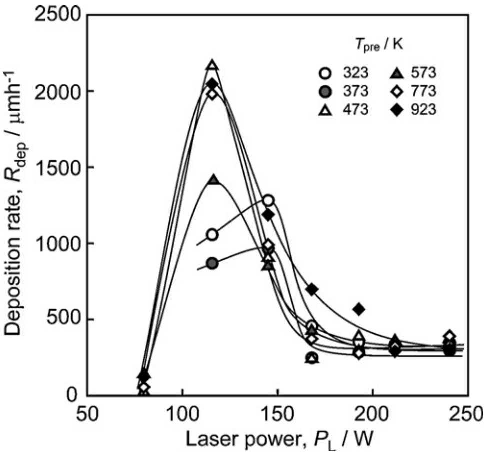

Fig. 6. Effects of P_L on R_{dep} of the SiC films prepared at various T_{pre}.

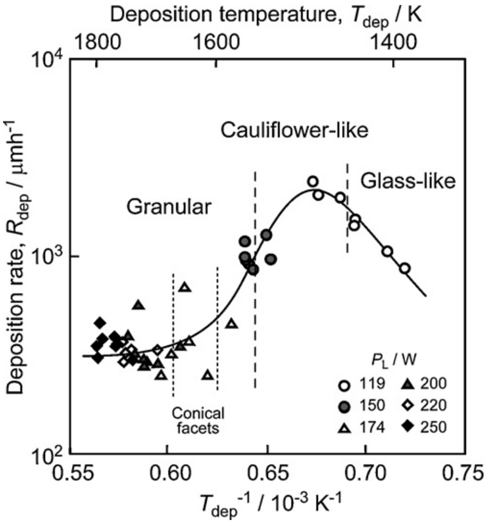

Fig. 7. Effects of T_{dep} and R_{dep} on the morphology of SiC films prepared at various P_L.

Many studies on the preparation of SiC films by CVD have been reported, particularly by using silicon halide ($SiCl_4$ and SiF_4) and hydrocarbon (C_3H_8 and CH_4) gases as precursors. The preparation of SiC by CVD using various precursors in a wide-range of conditions has been reviewed in detail by Schlichting [24,25]. Table 2, therefore, summarizes the literature data on SiC films prepared by CVD using HMDS as a precursor. By using a Si single-crystal substrate and relatively high T_{dep} (1500 K), the epitaxial growth of 3C SiC films has been reported [26–28]. For the preparation of polycrystalline SiC films, (1 1 1)-oriented 3C SiC films has been prepared [13,29–31]. Low-temperature depositions of SiC films from room temperature to 673 K by CVD using an ArF laser and radio-frequency plasma have been reported; however, the SiC films contained unreacted precursor compounds and the R_{dep} was a few to 13 μm h^{-1} [30,31]. A short wavelength excimer laser, such as pulsed ArF laser (wavelength: 193 nm), is expected to directly break bonds in a precursor molecule. This nonthermal process is suitable for a low-temperature deposition, but in fact eliminating the existence of hydrocarbon compounds and powder-like by-products in the films requires an intense laser beam with high photon density, or a decrease in partial pressure of precursor [30]. In contrast, infrared CO_2 laser is effective to excite vibrational modes in a precursor molecule. Under the CO_2 laser irradiation, highly excited intermediate species promotes chemical reactions around the SiC film surface, leading to a significant high deposition rates ($R_{dep} = 300$–2200 μm h^{-1}) in the present LCVD process.

4. Conclusions

SiC films were prepared by LCVD using a CO_2 laser with HMDS precursor and the effects of T_{pre} and T_{dep} on the phase, morphology and R_{dep} were investigated. With increasing T_{dep}, the microstructure of SiC films changed from glass-like ($T_{dep} < 1460$ K) to cauliflower-like ($T_{dep} = 1460$–1560 K) to granular ($T_{dep} > 1560$ K). Conical facets formed on the surface of granular SiC films at around $T_{dep} = 1650$ K. The R_{dep} showed a maximum at $T_{pre} = 473$ K and $P_L = 119$ W ($T_{dep} = 1490$ K) and reached 2200 μm h^{-1}.

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