High-rate deposition of nanostructured SiC films by thermal plasma PVD

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Abstract

With ultrafine SiC powder as starting material, thermal plasma physical vapor deposition has been applied successfully to the deposition of SiC films on Si substrates. The control of processing parameters such as substrate temperature, powder feeding rate and composition of plasma gases, permits the deposition of SiC films on a wide area of around 400 cm\textsuperscript{2} with a variety of microstructures from amorphous to nanostructured and with various morphologies from dense to columnar. For the nanostructured case, the crystallite size was between 3 and 15 nm and the maximum deposition rate calculated based on the actual deposition duty time reached 200 nm/s. The deposition mechanism is discussed briefly.

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1. Introduction

Silicon carbide films and coatings are of great scientific and technological interest because of their outstanding combination of unique physical properties, chemical stability and excellent mechanical properties. A wide range of applications has been reported such as for microelectronic devices, protective coatings against corrosion, X-ray mask, thermonuclear reactor walls protection coating, and so on [1–3]. Moreover, SiC is expected to be used as a thermoelectric material at high temperature [4,5]. To date, SiC films can be deposited by a variety of methods. For example, PVD processes such as sputtering and pulsed laser deposition have been used. However, the deposition rates are lower than 0.1 nm/s [6–8]. Thermal CVD and plasma-enhanced CVD processes have also been used, but the deposition rate is also only around 0.5 nm/s [9] except for one reported by Hirai and coworkers [10], in which a deposition rate of up to 390 nm/s was achieved on the heated graphite substrate at the substrate temperature of 1600 °C using SiCl\textsubscript{4}, C\textsubscript{3}H\textsubscript{8} and H\textsubscript{2} gas mixture.

On the other hand, thermal plasma CVD [11–15] was successfully demonstrated to be a method for depositing SiC films at a high rate which was 2–3 orders of magnitude higher than those achieved by conventional CVD, because a high density of clusters in the boundary layer is available. For example, Murakami and coworkers [12] successfully deposited dense SiC layers at a rate of 138 nm/s on a graphite substrate from SiCl\textsubscript{4} and CH\textsubscript{4}. Bouyer et al. [14] also reported recently that the deposition rate of 330 nm/s was reached from liquid (chlorodisilane and aminodisilane) sources, although the coatings were not dense. However, the necessity to use dangerous or harmful source gases and/or the generation of corrosive by-products is the common disadvantages of CVD processes. Therefore, it is of particular interest to develop a novel method which can overcome the disadvantages of conventional PVD and CVD processes.

In this study, we attempted to deposit SiC films by thermal plasma PVD using SiC powder as the starting material, which could overcome the disadvantages of the CVD process by maintaining a high deposition rate.

2. Experimental procedure

The experimental setup consisted of an rf generator (4 MHz–70 kW), a dc power supply (10 kW), a hybrid plasma torch [11], a deposition chamber, a vacuum system and a powder feeding system. The main parts of the deposition system are similar to those described in Ref. [12]. The gas mixture composed of Ar, H\textsubscript{2} and CH\textsubscript{4} was...
injected tangentially and/or radially through a gap between the anode and the water-cooled Si₃N₄ tube of the hybrid plasma torch. When the plasma gas flow pattern is dominated by the axial component, the plasma flame is focused and extended. In contrast, when the plasma gas flow has a strong swirling component, the plasma flame length is reduced but expanded, and the axial velocity at the substrate is decreased.

The silicon carbide powder to be injected was a high-purity ultrafine 3C–SiC powder supplied by Sumitomo Osaka Cement Co. Ltd, with an average particle size of around 0.1 μm. The ultrafine powder was fed into the Ar arc jet with Ar as carrier gas, and completely evaporated in the Ar–H₂ hybrid plasma. The Si(100) wafer was used as substrate. The substrates were placed on a vertical moving graphite turntable which was set 120 mm off axis from the center of the plasma torch. Prior to deposition, the substrates were preheated 5–10 min by the plasma flame. The substrate temperature was measured by a pyrometer. The typical experimental conditions are listed in Table 1.

Phase identification of the deposited films was mainly accomplished by X-ray diffraction (XRD) and a Fourier transform infrared absorption Spectrometer (FT/IR-700, JASCO). The crystallite size of the films was calculated from the SiC(111) peak in XRD spectra based on the Scherrer equation. The morphology and deposition rate of the obtained films were examined by SEM. The composition was examined by an X-ray photoelectron spectrometer (XPS) with Mg Kα radiation. The cross-sectional atomic structures of the deposited films were observed by a high-resolution transmission electron microscope (HRTEM). Thin foils for cross-sectional HRTEM observations were prepared by a standard technique involving mechanical grinding, mechanical dimpling, and ion milling for perforation using the precision ion polishing system (PIPS™ Model 691, GATAN). Energy dispersive X-ray spectroscopy (EDS) measurement was performed by using a TOPCON EM 002BF electron microscope operating at an accelerating voltage of 200 kV. The diameters of the analyzed spots were around 1 nm.

3. Results

3.1. Film morphology

Fig. 1 shows the cross-sectional SEM photographs of the films deposited under the conditions of rf plasma power of 70 kW and different CH₄/SiC molar ratios. Films deposited without CH₄ showed good dense morphology (Fig. 1(a)). When CH₄ was introduced, a columnar structure developed. The mechanism of the formation of the dense and columnar structures will be discussed briefly in Section 4.

Fig. 2 shows the dependence of the deposition rate on CH₄/SiC molar ratio at an rf plasma power of 70 kW, a powder feeding rate of 20 mg/min and a hydrogen flow rate of 4 slm. Because the substrate was rotating, we defined the deposition rate as that evaluated based on the actual deposition duty time hereafter. It can be seen that as the CH₄/SiC ratio increased, the deposition rate increased first and then decreased. In the case of deposition without CH₄, part of the C source escaped in the form of hydrocarbons such as C₂H₂, which decreased the deposition rate. As the CH₄ concentration increased, the C source was replenished and the deposition rate increased. However, with increasing CH₄ flow rate, the plasma flame shrank since the hydrogen concentration was also increased. This condition led to the formation of powder, causing the decrease of the deposition rate as well as the increase of surface roughness. The maximum deposition rate of around 200 nm/s was achieved at the powder feeding rate of 40 mg/min.

Fig. 3 shows the dependence of the deposition rate on H₂/SiC molar ratio at an rf plasma power of 70 kW, a powder feeding rate of 20 mg/min and a hydrogen flow rate of 4 slm. Because the substrate was rotating, we defined the deposition rate as that evaluated based on the actual deposition duty time hereafter. It can be seen that as the CH₄/SiC ratio increased, the deposition rate increased first and then decreased. In the case of deposition without CH₄, part of the C source escaped in the form of hydrocarbons such as C₂H₂, which decreased the deposition rate. As the CH₄ concentration increased, the C source was replenished and the deposition rate increased. However, with increasing CH₄ flow rate, the plasma flame shrank since the hydrogen concentration was also increased. This condition led to the formation of powder, causing the decrease of the deposition rate as well as the increase of surface roughness. The maximum deposition rate of around 200 nm/s was achieved at the powder feeding rate of 40 mg/min.

Table 1

| Typical processing parameters | DC plasma: current (A) | Gas flow rate (l/min) | RF plasma: power (kW) | Gas flow rate (l/min) | Powder feeding rate (mg/min) | Carrier gas flow rate (l/min) | Substrate rotation speed (rpm) | Chamber pressure (Torr) | Deposition time (min) |
|------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|----------------------------|-------------------------------|-----------------------------|------------------------|---------------------|
|                              | 350–400               | Ar: 10                | 40–70                 | Ar: 30–70             | 10–40                      | 3                             | 18–200                      | 100–500                | 5–30                |
| H₂: 2–10                     | CH₄: 0–5              |                       |                       |                       |                           |                               |                            |                        |                     |

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| H₂: 2–10                     | CH₄: 0–5              |                       |                       |                       |                           |                               |                            |                        |                     |

Fig. 1. Cross-sectional SEM images of films deposited under conditions: rf power, 70 kW; pressure, 250 Torr; L = 65 mm; and CH₄/SiC molar ratios: (a) 0, (b) 16.
the SiC powder evaporated more effectively and thus the deposition rate increased. However, in case of higher H₂ concentration, the hydrogen increased the amount of the loss of C source, together with increasing the boundary layer thickness due to the shrinkage of the plasma flame, leading to the decrease of the deposition rate due to the same reason as mentioned earlier.

3.2. Microstructures

Fig. 4 shows XRD patterns corresponding to two typical experimental conditions, namely (i) the expanded plasma case with the substrate temperature below 600 °C, and (ii) the focused plasma case with the substrate temperature around 750 °C. For the case of condition (i), a broad band at small diffraction angles was detected, which means X-ray amorphous films were formed. In contrast, for the film deposited under condition (ii), the peaks corresponding to β-SiC(111), (220) and (311) planes were clearly presented. Moreover, the (200) and (400) peaks due to the Si substrate were also found because the thicknesses of these two films are only around 2 and 0.5 μm.

FT/IR spectra of the two films are shown in Fig. 5. It can...
be seen that the films deposited under both conditions (i) and (ii) clearly revealed a strong absorption peak around 810 cm$^{-1}$, which is characteristic of the Si–C bond. However, the peak of film (a) broadened compared with that of film (b), which also suggested the amorphous structure of film (a). For focused plasma conditions, all of the prepared films were nanostructured with crystallite sizes between 3 and 15 nm.

Fig. 6 shows the crystallite size and the film composition as a function of H$_2$ flow rate. With increasing hydrogen concentration, the crystallite size is also increased, and the film composition changed from C-rich to Si-rich, which suggests that the increase of hydrogen content favors the escape of the C source. Fig. 7 shows the CH$_4$ flow rate dependence of the total C/Si atomic ratio and the free carbon content measured by XPS. The films deposited without CH$_4$ were Si-rich. As CH$_4$ increased, the film composition changed from Si-rich to C-rich. Further increase of the CH$_4$/
SiC molar ratio had little influence on the C/Si ratio. XPS spectra of C1s were deconvoluted into two peaks at around 283.3 and 285 eV, due to Si–C bonding and free carbon, respectively. The latter peak’s intensity was also affected by the sputtering effect and a single-crystal SiC wafer was used for calibration. It was found that there existed 2–3% free carbon in the films deposited with CH4 injection, while in the films deposited without CH4 injection, almost no free carbon existed.

Fig. 8 shows an HRTEM image of a SiC film deposited under the focused plasma case (ii) with an rf power of 55 kW and a substrate-torch distance of 95 mm. The nanocrystalline film consisted of 3–5 nm grains and was grown on the 3 nm thick amorphous interlayer. A number of grains as encircled in this figure oriented along the (110) zone axis, therefore, both sets of {111} planes are visible. But no orientation relationship was found.

Fig. 9 shows low-magnification and high-magnification TEM images of a sample deposited by focused plasma with an rf power of 55 kW, a substrate-torch distance of 65 mm, and a methane flow rate of 0.5 slm. The nanostructured film showed a columnar structure with the column size between 100 and 220 nm. An amorphous layer was found at the column boundary. The results of EDS spectra taken from the column and the boundary showed that the C/Si ratio in the column boundary was 5 times higher than that inside the column.

4. Discussion

Based on the above results, the deposition process is modeled as follows:

When SiC powder was fed into the plasma flame, it was evaporated completely and decomposed into a vapor mixture of Si and C atoms. H2 and CH4 were also decomposed into H and C atoms. During the quenching process in the boundary layer, Si, C and H atoms recombined into SiC2, SiC, H2, SiH4 and hydrocarbons such as CH3, C2H2. In addition, Si4C3, C and Si clusters were generated depending on the conditions. Fig. 10 shows the schematic diagram of the deposition process. The escape of hydrocarbons in the form of gas led to the loss of the C source, and thus resulted in Si-rich films and a lower deposition rate.

XPS results showed that 2–3% free carbon exists in the films. Because of the low solubility of carbon in SiC, most of the free carbon exists at the grain boundary. There may exist a critical content of free carbon in the grain boundary for the dense structure, namely, when the free carbon content in the grain boundary is higher than the critical content, the grains will be segregated by the carbon and thus dense films cannot be formed.

5. Conclusions

High-rate deposition of nanocrystalline SiC films was demonstrated by applying thermal plasma physical vapor deposition with ultrafine SiC powder as the starting material. Methane and hydrogen contents in the plasma gases had a significant influence on the deposition rate, the morphology and the composition. The films deposited without and with methane showed dense and columnar structures, respectively. For the expanded plasma case at the substrate temperature below 600 °C, amorphous SiC films were deposited, while for focused plasma conditions, all the films were nanostructured β-SiC films with crystallite sizes between 3 and 15 nm. The maximum deposition rate calculated according to the actual deposition duty time reached 200 nm/s.

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