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High-rate chemical vapor deposition of nanocrystalline silicon carbide films by radio frequency thermal plasma

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Abstract

Silicon carbide films were deposited by radio frequency thermal plasma chemical vapor deposition (CVD) at rates up to several hundred micrometers per hour over a 40-mm diameter substrate. The films were primarily β-phase SiC. Film morphology was characterized by columnar growth terminating in hemispherical surfaces. The average crystallite size as determined by X-ray diffraction line broadening ranged from about 5 to 100 nm, and increased with increasing substrate temperature. The film growth rate varied linearly with the input flow rate of $SiCl_4$ precursor, and appeared to be independent of substrate temperature over the range 680–1215 °C.

Keywords: Ceramics; Chemical vapor deposition; Nanomaterials; Silicon carbide; Thermal plasmas; Thin films; Si tetrachlorine precursor

Silicon carbide has a number of properties that make it attractive for electronic and optoelectronic applications and also as a hard coating that has excellent resistance to friction, wear and high-temperature corrosion. A variety of methods are used to deposit SiC films by chemical vapor deposition (CVD). Deposition rates are typically of the order 1 μm h^{-1}. That may be acceptable for growth of epitaxial device-quality material, but higher deposition rates and inexpensive precursors are needed to make silicon carbide more economically viable for hard coating applications.

A few studies have been reported in which thermal plasmas were used to deposit SiC films, and deposition rates up to several hundred micrometers per hour were reported. Several different methods were studied, mostly involving injection of $SiCl_4$ vapor and methane into an argon–hydrogen plasma. These methods included hybrid thermal plasma, which superimposes an RF induction field on a DC arcjet [1]; expansion of a DC arcjet to low pressure [2]; and hypersonic plasma particle deposition (HPPD) [3], which also involves expansion of a DC arcjet. HPPD, however, is not a CVD technique, as it is deliberately designed to nucleate nanoparticles in the rapid expansion, and then to deposit these nanoparticles by hypersonic impaction to create a nanostructured film. Recently, in addition, SiC films were deposited by liquid spray injection of disilanes into an argon–hydrogen RF plasma operating at 20–40 kPa [4].

Here we report experiments in which SiC films were deposited using an RF thermal plasma with vapor-phase reactants. To our knowledge, a pure RF thermal

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plasma with injection of vapor-phase reactants, as distinct from hybrid plasma or liquid spray injection, has not previously been used for CVD of SiC. Films were characterized by scanning electron microscopy (Hitachi S-800 field emission gun SEM), X-ray diffraction (XRD; Bruker AXS (Siemens) D5005 diffractometer) and Rutherford backscattering spectroscopy (RBS). The influence of deposition parameters on film properties and growth rates was examined.

Film deposition experiments were conducted in a custom-designed chamber. An RF induction plasma torch (TEKNA PL-35) operating at 3.3 MHz was mounted in the center of the upper flange of the chamber. Molybdenum substrates were mounted on a water-cooled holder located in the center of the bottom flange. Substrate temperature was controlled using a previously described system [5], and was measured both by a thermocouple (bottom surface) and, in some experiments, by a single-color optical pyrometer that viewed the top surface through a viewport in the chamber. The substrate temperatures reported here are either the temperature measured by the pyrometer, assuming an emissivity of 0.9 for SiC, or, where that was unavailable, the top surface temperature estimated from the thermocouple measurement, corrected to account for heat transfer between the top surface and the thermocouple.

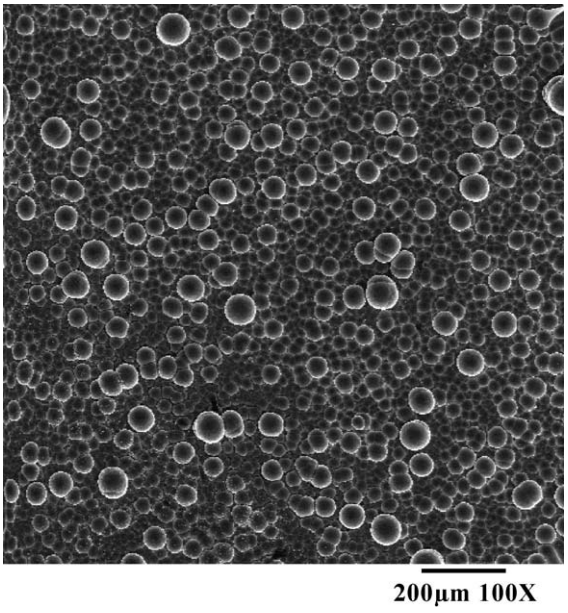

Fig. 1. Low-resolution SEM image of top surface of a SiC film. Deposition conditions: pressure, 250 Torr; substrate temperature, 770 °C, $SiCl_4$ flow rate 100 sccm; C/Si input = 1:1; deposition time = 10 min.

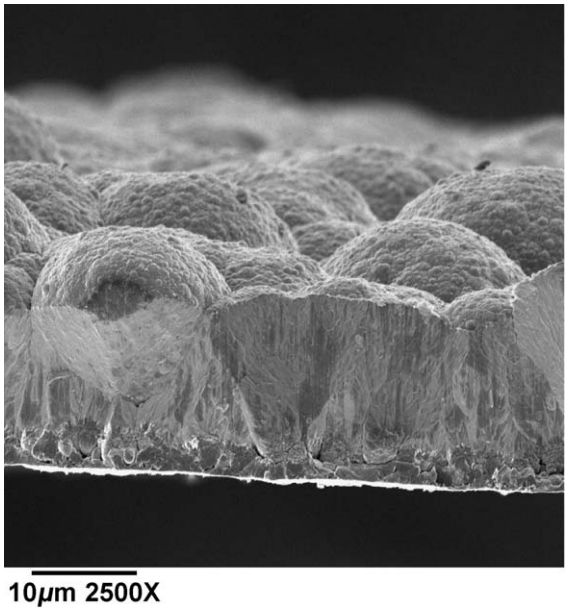

Fig. 2. SEM image of fracture cross-section of a SiC film. Deposition conditions: pressure, 150 Torr; substrate temperature, 730 °C; $SiCl_4$ flow rate = 67 sccm; C/Si input = 2.5:1; deposition time = 6 min.

Fifteen deposition experiments were conducted, for which the chamber pressure was either 20 or 33.3 kPa (150 or 250 Torr), and the RF generator plate power was in the range 10–20 kW. The main plasma gases, argon at 30 slm and hydrogen at 1–2 slm, were introduced into the torch as swirling sheath gases. The reactants, vapor-phase $SiCl_4$ at 6–150 sccm and methane at 1–10 times the $SiCl_4$ flow rate, were introduced together with an additional 12.5 slm of argon through an injection port located at the axial center of the torch. The substrate temperature ranged from 510 to 1275 °C. Deposition times ranged from 5 to 15 min.

All films deposited over the range of substrate temperatures from 680 to 1215 °C consisted primarily of β-phase SiC, exhibited columnar growth that terminated in a hemispherical surface morphology, and were nanocrystalline as determined both by XRD line broadening and by high resolution SEM. The films appeared dark grey in color, except for the thinnest

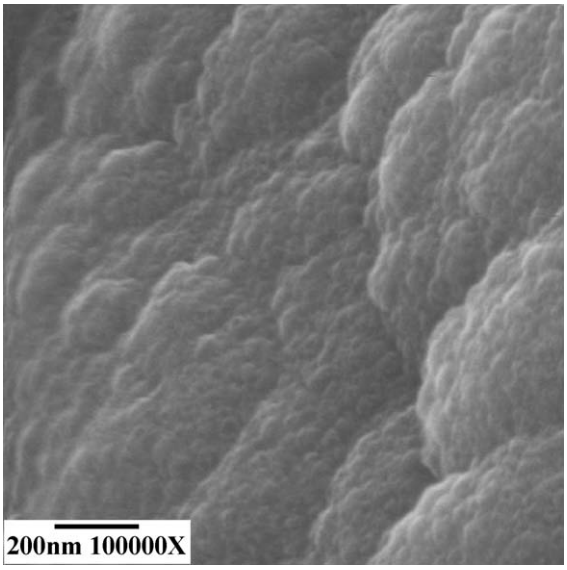

Fig. 3. High-resolution SEM image showing nanoscale grain size, same film as in Fig. 2.

films (~ 4 μm thick), which appeared to be transparent and showed interference fringes. The one experiment conducted at a lower substrate temperature, 510 °C, produced a powdery, greyish-yellow deposit. The two films deposited at the highest substrate temperatures (1260–1275 °C) were black, showed considerable nanoscale porosity under SEM, and their XRD spectra showed a number of peaks tentatively assigned to forms of carbon. RBS spectra were obtained for six films deposited in the range 710–1210 °C. All of these films had some excess carbon, even for input C/Si ratios of 1:1, with x in SiC_x ranging from 1.08 to 1.32. For these films, chlorine incorporation was inversely related to substrate temperature, ranging from 1.85% at 710 °C to undetectable at 1210 °C.

Fig. 1 shows a low-resolution SEM image that illustrates the hemispherical surface morphology. Fig. 2 shows a higher resolution SEM image of an unpolished fracture cross-section of a freestanding piece of a film that delaminated from the substrate. Clearly visible is an initial growth layer, followed by columnar growth terminating in hemispherical structures, which are themselves composed of much finer grains. Fig. 3 is a high-resolution SEM image of this film, showing evident nanoscale grain size. The average crystallite size, as determined by XRD line broadening (see below), is equal to 10.4 nm.

Fig. 4 shows an XRD spectrum measured for a film deposited at a substrate temperature of 1215 °C. The dominant crystalline phase is β-phase SiC, although the presence of some α-phase material is also indicated. The relative heights of the β-SiC peaks are close to the values for random orientation. This was found to be the case for the higher temperature deposits (>900 °C), whereas the XRD spectra for the lower-temperature deposits indicated preferred <111> orientation. Fig. 4 clearly indicates the pres-

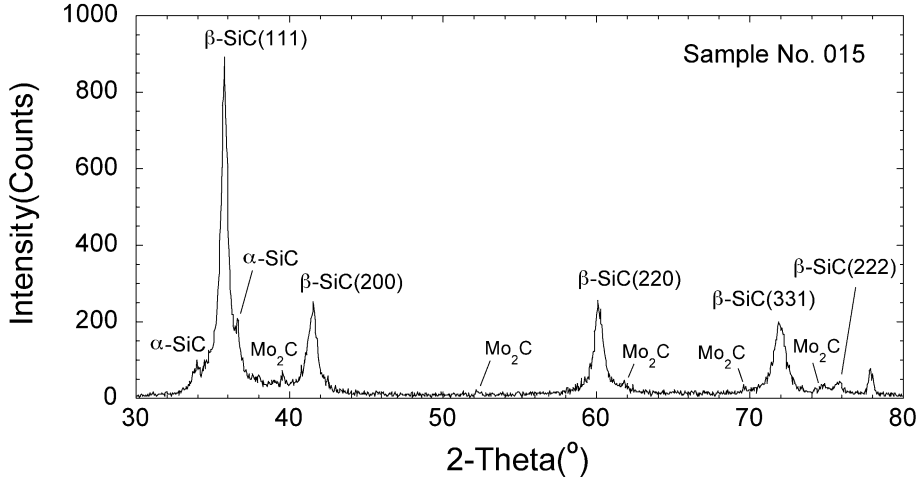

Fig. 4. X-ray diffraction spectrum of a film deposited under the following conditions: pressure, 250 Torr; substrate temperature, 1215 °C; $SiCl_4$ flow rate = 100 sccm; C/Si input = 1:1; deposition time = 10 min.

ence of molybdenum carbide, which was found in the XRD spectra of all films that either were deposited at high substrate temperature (>1200 °C) or were relatively thin (< 5 μm). Molybdenum carbide would be expected to form at the interface between the molybdenum substrate and the SiC film, especially for higher temperatures, where the diffusivity of carbon into the substrate is higher. However, the fact that Mo_2C was identified in the XRD spectrum of a 4-μm-thick film deposited at 680 °C suggests that formation of a Mo_2C interlayer may be a general result, within the window of conditions for which well-adherent SiC films were obtained. The formation of such an interlayer would promote adhesion by chemically binding the film to the substrate.

The roughness of these films makes characterization of film thickness and growth rate somewhat ambiguous. If one measures film thickness with a micrometer, by comparing substrate thickness before and after deposition, then one is essentially measuring to the tops of the hemispheres. By that method, the maximum growth rate measured was 670 μm h^{-1}, for a film deposited at 250 Torr, a substrate temperature of 800 °C, a $SiCl_4$ flow rate of 100 sccm, and an input C/Si ratio of 1:1. This film covered the entire 40-mm diameter exposed area of the substrate. In general, for these films, the roughness height, as estimated from SEM images, is about equal to the underlying film thickness. Thus, a more accurate "average thickness" would be approximately 3/4 the thickness as measured by micrometer. It should also be noted that the film thickness near the edge of the substrate was typically about half its value in the center. Accounting for these factors, we estimate for this film a deposition efficiency (ratio of Si atoms in the deposited film to Si atoms input to the reactor) of about 18%, which is quite high for a CVD process.

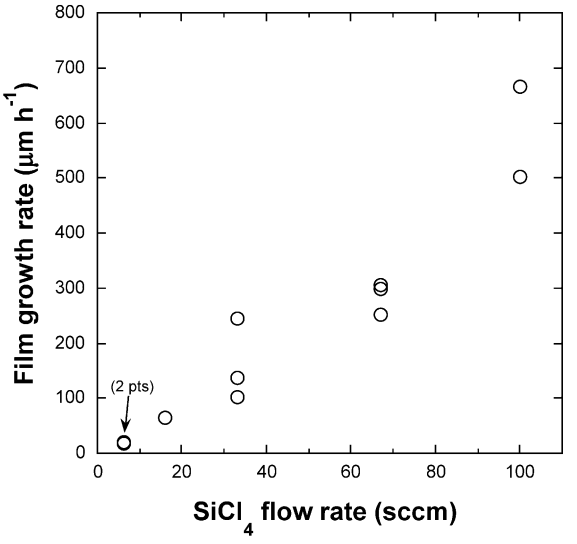

Fig. 5. Film growth rate, as measured by micrometer, versus $SiCl_4$ flow rate. Note that other parameters (pressure, substrate temperature, methane flow rate) varied for these experiments.

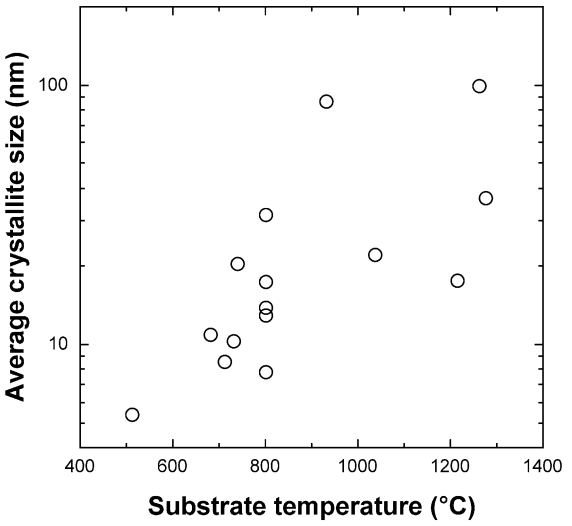

Fig. 6. Average crystallite size versus substrate temperature, regardless of values of other operating parameters.

Fig. 5 plots the film growth rate versus the $SiCl_4$ flow rate for all 12 films deposited in the range 680–1215 °C. The growth rate is seen to scale roughly linearly on the $SiCl_4$ flow rate, regardless of the values of other parameters, including substrate temperature, suggesting that film growth here is gas-phase diffusion-limited, i.e., limited only by the availability of growth precursors reaching the surface.

While substrate temperature did not appear to be correlated with growth rate, it did affect the average crystallite size as determined from the XRD spectra by application of the Scherrer equation to the width of the β-SiC line at $2\theta = 35.6°$. Fig. 6 shows the result for all 15 films. Average crystallite size was found to correlate directly with substrate temperature, and was not correlated with any other parameters, varying from 5.4 nm at 510 °C to over 100 nm at 1260 °C.

This trend is presumably caused by temperature-dependent surface diffusion.

In summary, RF thermal plasma CVD with vapor-phase reactants has been used to deposit nanocrystalline β-SiC films at growth rates up to several hundred micrometers per hour. Further studies are in progress to characterize the mechanical properties of these films using nanoindentation and to study the chemistry of film growth using molecular beam mass spectrometry and kinetic modeling.

Acknowledgements

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