Thermal plasma synthesis of nanostructured silicon carbide films

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Abstract

Two methods for the synthesis of nanostructured silicon carbide films are discussed and compared, thermal plasma chemical vapour deposition (TPCVD) and hypersonic plasma particle deposition (HPPD). Both methods produce \( \beta \)-SiC films with high growth rates on the order of 10 \( \mu \)m min\(^{-1}\). In TPCVD the generation of nanoscale grain sizes is caused by the fact that the film growth rate is much higher than the rate of surface diffusion. In HPPD a nanostructured film is grown by direct nanoparticle impact. In general, the films grown by TPCVD are denser and harder than in HPPD. X-ray diffraction spectra show that \( \beta \)-SiC is essentially the only crystalline phase in the TPCVD films, whereas in HPPD a silicon crystalline phase is also present, even for films that are overall carbon-rich. Evidence is presented to support the hypothesis that HPPD films actually grow by a combination of nanoparticle impact and CVD. If this parallel process can be controlled, it could potentially lead to the design and high-rate synthesis of new nanostructured materials.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The uniqueness of thermal plasmas as chemical reactors derives from the fact that their high temperature makes it possible to completely dissociate molecules to their elemental constituents. As the elemental gas is transported to colder regions, which typically occurs across steep temperature gradients, recombination chemistry occurs, in the gas phase and/or on surfaces. Depending on the chemical composition, geometry and conditions, one can then form a condensed phase by either of two routes: formation of nanoparticles by gas-phase nucleation or growth of a film on a macroscopic surface by chemical vapour deposition.

We here discuss and contrast two different approaches to synthesizing nanostructured silicon carbide films, both utilizing an argon–hydrogen thermal plasma into which vapour-phase \( \text{SiCl}_4 \) and methane are injected. In the first approach, termed thermal plasma chemical vapour deposition (TPCVD), the hot plasma impinges in stagnation flow on a water-cooled substrate, and a silicon carbide film grows by chemical vapour deposition. In the second approach, termed hypersonic plasma particle deposition (HPPD), the hot plasma is quenched by expansion through a ceramic nozzle, driving the homogeneous nucleation of nanoparticles. These nanoparticles are accelerated in a hypersonic expansion and impact a substrate at high velocity to form a nanoparticle film.

As these two approaches are fundamentally different from each other, it is of interest to compare the films produced by each method, which is the purpose of this paper.

2. Description of the two approaches for SiC film deposition

The basic elements of TPCVD are illustrated in figure 1. The boundary layer that separates the hot plasma, at a freestream temperature greater than 4000 K, from the cooled substrate, at a temperature on the order of 1000 K, is only about 1 or 2 mm thick, depending on the flow velocity [1]. Thus the chemical composition across the boundary layer deviates strongly from equilibrium, but the pressure is high enough that significant homogeneous chemistry can occur. The gas composition arriving at the substrate is neither frozen at its fully dissociated freestream condition nor in equilibrium at the substrate temperature. High fluxes of radical species react at the surface to grow a film by CVD. Grain sizes in the resulting film can lie in the nanoscale regime if film growth rates are
high relative to rates of surface diffusion. As film growth rates by TPCVD are typically much higher than in virtually all other vapour deposition processes, and as surface diffusivity is exponentially temperature-dependent, TPCVD is more likely than other methods to produce nanostructured films, especially at relatively low substrate temperatures.

TPCVD has been used extensively for growth of diamond films, with the plasma generated either by a dc arc or by RF induction. In addition several investigators have reported using TPCVD to deposit SiC films. Methods have included hybrid thermal plasma (superimposition of a RF induction field on a dc arcjet) [2] and dc arcjet expanded to low pressure [3].

Recently we reported using TPCVD to grow films consisting primarily of β-SiC, with average grain sizes of around 10 nm [4, 5]. For substrate temperatures above 870 °C these films were found to be superhard (defined as hardness greater than 40 GPa), with hardness values measured by nanoindentation exceeding 50 GPa for substrate temperatures above 1200 °C. In addition these films exhibited excellent fracture toughness and very low coefficient of friction. The plasma in these experiments was generated using an RF induction plasma torch (a modified Tekna PL-35) operating at 3.3 MHz, with an RF generator plate power of 15–21 kW. SiCl₄ vapour and methane were injected into an argon–hydrogen plasma, with typical flow rates of 30–35 slm argon, 2–6 slm hydrogen, 40 sccm SiCl₄, and methane flow rates ranging up to 15 times the SiCl₄ flow rate. Substrate temperatures have typically been in the range 750–900 °C. While the highest hardness measured for SiC nanoparticle films deposited by HPPD, 37.3 GPa [15], is well above the ~28 GPa value for commercial SiC wafers, that result was anomalous, with more typical values lying around 22 GPa [16].

3. Comparison of results

Film growth rates for both methods are high. Linear growth rates have ranged from 4 to 15 μm min⁻¹ in TPCVD and from 2 to 60 μm min⁻¹ in HPPD. Typical deposition times equal ~10 min. It should be noted that the film growth rate in TPCVD is orders of magnitude higher than film growth rates in conventional CVD or other vapour deposition methods, which are typically on the order of 1 μm h⁻¹ or lower.

While the linear growth rates of the two systems are similar, in TPCVD experiments the film completely covered the substrate, whose diameter equaled either 19 or 38 mm, while in HPPD the deposit was limited to the central portion of the substrate and measured about 8 mm in diameter. This difference is clearly due to the different types of deposition. In TPCVD the stagnation flow establishes a uniform boundary layer over the entire substrate, except for possible nonuniformities near the edges, and chemical species react and diffuse to the substrate across this boundary layer, producing a uniform coating. In HPPD film growth occurs primarily by nanoparticle impact and is confined by the fact

![Figure 1](https://example.com/f1.png)  
**Figure 1.** Thermal plasma chemical vapour deposition.

![Figure 2](https://example.com/f2.png)  
**Figure 2.** Hypersonic plasma particle deposition.
that the nanoparticles follow linear trajectories from the nozzle exit to the substrate. The nozzle exit diameter in the HPPD system equals 5 mm, and the substrate is usually located 20 mm downstream of the nozzle exit. The nanoparticle trajectories lie within a conical envelope that produces a deposit somewhat larger than the nozzle exit area. As the deposition rates are quite high, presumably a uniform coating over a much larger area could be obtained by acentrically rotating the substrate in the plane normal to the flow, although so far such a system has not been implemented.

From the above observations one can estimate the deposition efficiency for each process. For a rough estimate, let us define the deposition efficiency as the fraction of silicon atoms introduced into the plasma that are converted to solid silicon (in any form) in the film. For the range of typical experimental flow rates and growth rates, and assuming fully dense films, the calculated deposition efficiency equals 1–2% for HPPD and 3–6% for TPCVD (based on the 19 mm diameter substrate).

Figure 3 shows low-resolution scanning electron microscopy (SEM) images of the top surface of films deposited by TPCVD (a) and HPPD (b). The morphologies are notably different. The TPCVD film is characterized by a ball-like surface morphology, which SEM imaging of film cross-sections reveals to be the result of columnar growth terminating in hemispherical tops [4]. The HPPD film, while it does reveal numerous round features, has a more heterogeneous structure, with some areas having a more granular appearance and others that are smoother.

Figure 4 shows high-resolution SEM images of films deposited for the same conditions as the corresponding images in figure 3, again for a TPCVD film (a) and an HPPD film (b). Both images clearly show nanoscale grain sizes. The grains in the HPPD film appear to be more discrete than in the TPCVD film, consistent with film formation by nanoparticle impact rather than vapour deposition. In addition nanoscale porosity is evident in the HPPD film but not in the TPCVD film.

X-ray diffraction (XRD) measurements of films deposited by TPCVD show them to be composed primarily of $\beta$-SiC. Figure 5 shows XRD spectra of TPCVD films deposited at substrate temperatures ranging from 710 to 1215 °C. The spectra for all these films are dominated by the $\beta$-SiC (1 1 1) peak at $2\theta = 35.6^\circ$. As substrate temperature increases this peak as well as other peaks associated with $\beta$-SiC become more pronounced, and the peak at 35.6° develops shoulders ascribed to $\alpha$-SiC. No other crystalline phases are observed.

XRD spectra of TPCVD films were analysed by Fourier analysis, and the Warren–Averbach method [17] was used to
determine average crystallite sizes. In addition, the crystalline fraction in the films was estimated using the software JADE (Materials Data, Inc.). Figure 6 shows these results. For substrate temperatures below \( \sim 1150 \, ^\circ\text{C} \) the average crystallite size lay in the range \( \sim 4 \sim 9 \, \text{nm} \). Higher temperatures caused the average grain size to increase to about 20 nm. At the same time, increases in substrate temperature caused the fractional crystallinity in the films to increase, from about 40\% at 750 \, ^\circ\text{C} to 80\sim 85\% for substrate temperatures above 1100 \, ^\circ\text{C}.

Analysis of the TPCVD films by Rutherford backscattering spectrometry, using a commercial SiC wafer as a reference, indicated that they were all within a few percent of stoichiometric SiC. The ratio of CH\(_4\)-to-SiCl\(_4\) in the reactant gases for TPCVD lay in the range 1.0\sim 1.2. In marked contrast, in HPPD much higher ratios of CH\(_4\)-to-SiCl\(_4\) were required to produce films whose elemental composition corresponded to stoichiometric SiC. Figure 7 shows elemental depth profiles obtained with Auger electron spectroscopy for two HPPD films. In these figures, 1 min of sputter time corresponds to approximately 2 nm in depth from the top surface of the film. In figure 7(a) the input CH\(_4\)-to-SiCl\(_4\) ratio equalled 7, yet the film is seen to contain substantial excess silicon, with a Si : C ratio of approximately 58 : 42. (Oxygen is seen to be confined to the top \( \sim 100 \, \text{nm} \) of the film.) In figure 7(b), with the CH\(_4\)-to-SiCl\(_4\) ratio increased to 15, the film is now seen to contain excess carbon, though by only a few percent.

Furthermore, XRD measurements of the films deposited by HPPD show the presence of a free silicon crystalline phase, even when the overall film composition is carbon-rich. This is another difference between films obtained by the two methods, as XRD measurements show that the TPCVD films do not contain free crystalline silicon. Figure 8 shows XRD spectra corresponding to the two HPPD films whose elemental depth profiles are shown in figure 7. In figure 8(a), where the overall film composition is significantly Si-rich, the XRD spectrum shows strong peaks associated with crystalline Si, as well as peaks due to \( \beta \)-SiC. In figure 8(b), where the overall composition is slightly carbon-rich, the XRD spectrum still shows crystalline Si peaks, although they are smaller than in the silicon-rich case. At the same time, the broad underlying hump in figure 8(b) indicates that the film contains a significant fraction of amorphous material. Comparing figures 7(b) and 8(b), it can be concluded that this amorphous material is carbon-rich.
S L Girshick and J Hafiz

Intensity (a.u.)

20 30 40 50 60

2-θ

Si

β−SiC

Si

β−SiC

Si

Si

β−SiC

20 30 40 50 60

2-θ

Figure 8. XRD spectra of two films deposited by HPPD, for the same conditions as the corresponding elemental depth profiles in figure 7.

To summarize, both TPCVD and HPPD have been used to deposit nanostructured SiC films, primarily the cubic (β) phase, at comparably high deposition rates on the order of 10 μm min⁻¹, which is orders of magnitude higher than in other SiC film deposition methods. Both methods produce films with grain sizes on the order of 10 nm. The TPCVD films consist of stoichiometric SiC. They are dense and superhard [5], in fact much harder than conventional SiC, especially for temperatures around 1200 °C, where the average grain size equals 10–20 nm and the crystalline fraction equals 80–85%. The HPPD films exhibit nanosized grains that are more discrete and have greater porosity. They show the presence of a free silicon crystalline phase, even under conditions where the overall film composition is carbon-rich. Considering these factors it is not surprising that their hardness, which averages around 22 GPa, is lower than for the TPCVD films. In fact it is noteworthy that the HPPD films are as hard as they are, given their porosity and the presence of free silicon, which is much softer than SiC, as well as the fact that the deposition temperatures have been below those for which the best TPCVD results were obtained. While the substrate temperatures in HPPD have been limited by the lower heat flux to the substrate than in TPCVD, experiments in which HPPD-deposited SiC films were post-treated with both hot isostatic pressing and pressureless sintering showed substantial grain growth for temperatures above ~1000 °C [18]. However, this does not necessarily imply that grain growth would occur if the deposition temperature itself were above 1000 °C, and work aimed at depositing at higher substrate temperatures is in progress.

4. Discussion

As the HPPD films grow primarily by nanoparticle impact, it is of interest to ask whether the grain size as well as the chemical and phase composition of the films are identical to the size and composition of the impacting particles.

Figure 9 shows a transmission electron microscopy (TEM) image of nanoparticles that were deposited by HPPD for the same conditions (a CH₄-to-SiCl₄ ratio of 7) as for the results shown in figures 3(b), 4(b), 7(a) and 8(a). To obtain samples for TEM analysis, part of the film was scraped into alcohol solution, which was then repeatably sonicated. Drops from the solution were then deposited onto lacy carbon TEM grids. The nanoparticles are seen to be mostly discrete and rather monodisperse, with a diameter around 5 nm. The inset at the top right corner of the figure shows a high-resolution TEM (HRTEM) image of a single particle. One observes lattice fringes whose spacing, 0.253 nm, corresponds to the 0.252 nm value for the (1 1 1) plane of β-SiC. Analysis of a number of particles by HRTEM found that the large majority were composed of β-SiC. No evidence of an α-SiC phase was observed, and only a small fraction of the nanoparticles were silicon.

The sizes of the nanoparticles seen in figure 9 can be compared to size distribution measurements obtained during film deposition with an in situ sampling probe interfaced to a scanning mobility particle sizer (SMPS) [19]. The probe samples particles in flight at the same location as the substrate for film deposition, and thus measures, in effect, the size distribution of the impacting nanoparticles.
Thermal plasma synthesis of nanostructured silicon carbide films

Figure 10. (a) Size distribution of particles sampled in flight and measured by SMPS; (b) size distribution determined by image analysis of TEM images of sonicated particles scraped from film. Conditions for both graphs were the same as in figure 9. Note that the lower detection limit of the SMPS system equalled 4 nm.

Figure 10 shows the results of this comparison, for the same conditions as in figure 9. Figure 10(a) shows the size distribution of particles sampled in flight and measured by the SMPS. Note that a lower cutoff of 4 nm in particle diameter has been applied, as that was the effective lower detection limit of the instrument. Figure 10(b) shows the corresponding size distribution based on image analysis of multiple TEM images, for which the effective lower detection limit was set to 3 nm.

As can be seen by inspection, the two size distributions both peak in the 4–5 nm range, and are otherwise quite similar. This strongly suggests that the nanoparticles seen in figure 9 are indeed the particles that impact the surface, and that the impaction process does not significantly alter the particle size for these deposition conditions.

The above observations—from measurements of the HPPD nanoparticles and films by TEM, SMPS, XRD and Auger spectroscopy—can be summarized as follows. For the case where the CH₄-to-SiCl₄ ratio equalled 7, the impacting nanoparticles are primarily composed of β-SiC, yet the overall film composition is significantly silicon-rich, and the XRD spectrum shows strong peaks of crystalline Si. For the case where the CH₄-to-SiCl₄ ratio equalled 15, the overall film composition is slightly carbon-rich, but peaks of crystalline Si are still evident in the XRD spectrum, together with an amorphous carbon (or at least carbon-rich) phase.

These results therefore lead to the conclusion that the free silicon phase in the HPPD films is deposited not by nanoparticle impact, but by CVD, which occurs in parallel with nanoparticle impact. This requires that the following hold: (1) the nanoparticles that form by gas-phase nucleation in the nozzle expansion are composed overwhelmingly of β-SiC; (2) not all of the silicon vapour condenses into particles, leaving some available for vapour deposition at the surface of the growing film; and (3) the conditions of vapour deposition at the surface are not conducive to the formation of crystalline SiC—instead Si deposits as free crystalline Si, and carbon (if sufficient carbon is present) deposits in an amorphous phase, both by vapour deposition not nanoparticle impact.

It is likely that not all the silicon vapour in the nozzle condenses into nanoparticles. Vapour condensation would not be expected to occur past the point where the vapour supersaturation was relieved. Thus a rough lower bound of the Si vapour that does not condense into nanoparticles by the nozzle exit is given by the equilibrium vapour pressure of Si at the nozzle exit temperature. If the SiCl₄ completely decomposes, and if, for example, 90% of the Si vapour condenses into particles, then, based on the input flow rates in the system, the mole fraction of Si vapour at the surface of the growing film would equal \( \sim 10^{-4} \), a significant mole fraction for a radical species that can be assumed to stick on the relatively cold substrate with high probability. It should also be noted that the total gas pressure increases downstream of the bow shock, so that the actual partial pressure of Si vapour at the film surface could be high enough to produce CVD growth rates that are comparable to those produced by HPPD.

To provide further support for the conclusion that nanoparticle impact and CVD film growth may occur simultaneously, it is interesting to note that, in separate experiments using the HPPD system, nanoparticle-coated silicon nanowires were grown [20], such as shown in figure 11. The nanowire cores are single-crystal silicon, believed to grow by CVD on titanium catalyst particles deposited in the first step of the process (the particle at the tip of the nanowire is composed of TiSi₂), while the nanoparticles decorating the surface of the nanowire are believed to arrive by nanoparticle impact, as supported by separate SMPS measurements. Following the deposition of a
plasma process.

production of nanostructured materials by a high-rate thermal

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finely tuned control of the relative contributions of nanoparticle

rate deposition, and possibly the production of material

the design principles for superhard nanocrystalline materials

as illustrated in figure12. This could potentially follow

unambiguously that it occurs. If this hypothesis is correct,

then it is interesting to speculate as to whether this parallel

process can be controlled so as to yield films that consist of

$\sim 5$ nm crystalline nanoparticlres of a hard substance such as SiC (as seen in figure 9), with the interfacial regions between

the particles completely filled by softer or amorphous material,

as illustrated in figure 12. This could potentially follow

the design principles for superhard nanocrystalline materials

enuciated by Veprek [21], while offering a means for high-

rate deposition, and possibly the production of material

combinations not accessible by CVD. Clearly, obtaining such a

fianly tuned control of the relative contributions of nanoparticle

impact and CVD would require an advanced fundamental

understanding of both particle nucleation and chemistry in the

hypersonic plasma.

5. Conclusions

Two methods of synthesis of nanocrystalline silicon carbide

films are compared, TPCVD and HPPD. Both methods have

proven capable of quite high deposition rates, on the order of

10 $\mu$m min$^{-1}$ or higher, but the films produced by TPCVD are
denser and harder than those produced by HPPD. Evidence

is presented that the HPPD films are in fact produced by a

combination of nanoparticle impact and CVD. If this parallel

process can be controlled it may open new vistas for the production of nanostructured materials by a high-rate thermal plasma process.

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