Superconformal silicon carbide coatings via precursor pulsed chemical vapor deposition

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In this work, silicon carbide coatings (SiC) were successfully grown by pulsed chemical vapor deposition (CVD). The precursors silicon tetrachloride (SiCl₄) and ethylene (C₂H₄) were not supplied in a continuous flow, but were pulsed alternately into the growth chamber with H₂ as a carrier and a purge gas. A typical pulsed CVD cycle was SiCl₄ pulse – H₂ purge – C₂H₄ pulse – H₂ purge. This led to the growth of superconformal SiC coatings, which could not be obtained under similar process conditions using a constant flow CVD process. We propose a two-step mechanism for the SiC growth via pulsed CVD. During the SiCl₄ pulse, a layer of Si is deposited. In the following C₂H₄ pulse, this Si layer is carburized, and SiC is formed. The high chlorine surface coverage after the SiCl₄ pulse is believed to enable the superconformal growth via a growth inhibition mechanism.
I. INTRODUCTION

Cubic silicon carbide, also named 3C- or β-SiC, is known for its high temperature stability, corrosion resistance and superior mechanical and thermal properties. The state-of-the-art technique for fabricating 3C-SiC coatings is chemical vapor deposition (CVD). The precursors employed in the SiC CVD process can be classified into two categories. Multicomponent precursors, such as methyltrichlorosilane (MTS, CH₃SiCl₃)¹⁻³ and hexamethyldisilane (HMDS, Si₂(CH₃)₆)⁴⁻⁶, contain both C- and Si-atoms. Single-component precursors, on the other hand, contain only C or Si and, thus, two single-component reactants are required for deposition of SiC. The commonly utilized Si precursors are silane (SiH₄) and silicon tetrachloride (SiCl₄), whereas short-chain hydrocarbons, e.g. methane (CH₄)⁷⁻⁹, propane (C₃H₈)¹⁰⁻¹² and ethylene (C₂H₄)¹³,¹⁴, are often used as C precursors. Both types of precursors have been used successfully in the preparation of 3C-SiC coatings and epitaxial films via CVD¹⁵.

The utilization of multiple single-component precursors allows for alternate precursor pulsing, creating an additional degree of freedom in process design. If the pulses from different precursors are fully separated, no gas phase interaction between them would occur, and the growth process would be only dictated by surface reactions, which can change the character of the deposition process. Such pulsed CVD processes have shown benefits for some deposition processes. One example is the deposition of GaN nanowires without metal catalyst on a SiNx-masked Si substrate using trimethyl gallium (Ga(CH₃)₃) and ammonia (NH₃) as precursors¹⁶. In the conventional CVD mode, where both precursors are flowing into the chamber simultaneously, a continuous GaN film was obtained, while the alternate pulses of precursors resulted in uniform arrays of GaN nanowires. The extreme end of the pulsed CVD spectrum enables conformal film growth when the pulsing
of gases renders a self-limiting surface chemistry, i.e., the chemisorption stops when no more surface sites are available. This type of pulsed CVD is normally called atomic layer deposition (ALD)\(^{17}\). Several attempts to grow crystalline SiC by ALD at \(T > 800 \, ^\circ\text{C}\) have been reported\(^{18-22}\), but, strictly speaking, they are not ALD process because the surface chemistry is not self-limiting at such high temperature and the resulting high growth rate also indicates that a CVD growth is involved\(^{23}\). The self-limiting surface chemistry of ALD also makes it impossible to achieve a superconformal growth\(^{24}\) necessary for applications where recessed features should be filled. The conformality of a coating or film is assessed by the step coverage (SC), which is defined as the ratio of the growth rate at the lower sidewall (close to the bottom) to that at the upper sidewall (close to the top) of a trench or a via. A SC < 1 indicates a subconformal growth, whereas SC = 1 and SC > 1 imply a conformal and a superconformal growth, respectively.

In this work, we explore the possibility of growing 3C-SiC coatings via a precursor pulsed CVD process using SiCl\(_4\) and C\(_2\)H\(_4\) as precursors. A two-step mechanism was proposed for the SiC growth via precursor pulsing. Furthermore, with the precursor pulsed CVD, it is possible to deposit superconformal SiC coatings with a SC between 3.5 and 9 at \(T = 1200 \, ^\circ\text{C}\).

II. EXPERIMENTAL

3C-SiC coatings were deposited at \(p_{\text{total}} = 1 \, \text{kPa}, \, T = 1000 – 1200 \, ^\circ\text{C}\) via pulsed CVD using SiCl\(_4\) (99.998\%, Sigma-Aldrich Chemie GmbH) and C\(_2\)H\(_4\) (99.95\%, Linde Gas AB) as precursors. In this precursor pulsed CVD process, the substrate was exposed to SiCl\(_4\) (100 sccm) and C\(_2\)H\(_4\) (50 sccm) in alternating pulses with a H\(_2\)-purge after each precursor
exposure. Purified H\textsubscript{2} with a constant flow rate of 3200 sccm was used both as a carrier gas for the precursors and as a purge gas. During the precursor pulse, H\textsubscript{2} functioned as a carrier gas and entered the reactor together with the precursor. During the purge step, H\textsubscript{2} was responsible for flushing out residual precursors and reaction byproducts. It should be noted that H\textsubscript{2} also takes part in the chemical reactions in the SiC CVD process\textsuperscript{25}. The liquid SiCl\textsubscript{4} was stored at 24 °C in a stainless-steel bubbler placed in a thermostat-controlled water bath, rendering a SiCl\textsubscript{4} vapor pressure of 30.7 kPa. The flow of SiCl\textsubscript{4} vapor from the bubbler was controlled by regulating the flow of H\textsubscript{2} through the bubbler and the headspace pressure in the bubbler.

A pulsed-CVD cycle consisted of \(x\) seconds (s) SiCl\textsubscript{4}, \(z\) s purge, \(y\) s C\textsubscript{2}H\textsubscript{4} and another \(z\) s purge. These steps will be simplified as Si-pulse – purge – C-pulse – purge in the rest of this work. Two continuous CVD reference depositions with a SiCl\textsubscript{4} flow of 100 sccm and C\textsubscript{2}H\textsubscript{4} flow of 50 sccm was also performed at \(p_{\text{total}} = 1\) kPa, \(T = 1000\) °C and 1200 °C. During the deposition, the graphite susceptor holding the substrate was heated inductively, and its temperature was monitored by an optical pyrometer. The total deposition time, i.e. the sum of all precursor and purge pulses, was kept constant at 30 minutes for all samples. In this work, the growth rate is represented by growth per cycle (GPC) because the total time that the substrate is exposed to the precursors within 30 minutes differs depending on the duration of precursor pulse and purge. Structured graphite substrates (25 mm x 50 mm x 3 mm) with trenches having a depth of 1000 μm and various widths from 250 μm to 1000 μm were used in the conformal studies, whereas flat graphite substrates (25 mm x 60 mm x 1.5 mm) were used in the GPC studies. The error bars for
SC in the conformal studies were calculated by the propagation of uncertainty using the following equation\textsuperscript{26}:

$$\sigma_{\text{SC}}^2 = \left( \frac{\delta \text{SC}}{\delta \text{GPC}_{\text{lower}}} \right)^2 \sigma_{\text{GPC}_{\text{lower}}}^2 + \left( \frac{\delta \text{SC}}{\delta \text{GPC}_{\text{upper}}} \right)^2 \sigma_{\text{GPC}_{\text{upper}}}^2$$  

(1)

where $\sigma$ is the standard deviation, $\text{GPC}_{\text{lower}}$ and $\text{GPC}_{\text{upper}}$ denotes the growth per cycle at the lower and the upper sidewalls of a trench, respectively.

The chemical phase of the deposited coatings was investigated by an x-ray diffractometer operating at a voltage of 45 kV and a current of 40 mA. The x-ray with a characteristic wavelength of 1.54 Å generated from a Cu target was used to probe the samples at $\theta/2\theta$ geometry with $2\theta$ scanning from $20^\circ$ to $140^\circ$. A nickel filter was placed in front of the detector during the measurement to remove the undesired Cu-κβ radiation. The resulting diffractograms were compared with the Powder Diffraction File (PDF) cards for identifying the chemical phases in the coatings. Scanning electron microscope (SEM) was utilized to investigate the surface morphology and cross sections of the samples.

III. RESULTS AND DISCUSSION

A. Deposition mechanism

A series of SiC coatings were deposited on flat graphite substrates at 1000 °C via pulsed CVD using different pulsing schemes to study the pulsed process. A first group of samples were prepared with a fixed Si-pulse of 3 s and a varying C-pulse of 0 to 5 s. A second group of samples were grown with a fixed C-pulse of 3 s and a varying Si-pulse of 0 to 5 s. The H\textsubscript{2} purge was 1 s for all samples. The total deposition time for all samples were 30 minutes and their x-ray diffractograms are displayed in Figure 1. Peaks from the
graphite substrates and 3C-SiC are present in both groups of samples, indicating that it is possible to grow 3C-SiC without having the two precursors in the chamber at the same time. The sample prepared using only a C-pulse of 3 s (and 0 s Si), does not show any sign of 3C-SiC phase, whereas on the sample deposited with a Si-pulse of 3 s (and 0 s C), the XRD shows a coating consisting mostly of Si with a slight incorporation of 3C-SiC, which may result from the reaction of Si species with the surface of graphite substrates in the beginning of the deposition.

From these observations, we propose a two-step mechanism for the growth of 3C-SiC deposited via pulsed CVD. In the first step, i.e., during the Si-pulse, a layer of Si is deposited on the graphite surface. In the second step, i.e., during the C-pulse, the Si layer is carburized. Here, the carbon species react with the Si to form 3C-SiC. From Figure 1 (a), the strong Si (111) peak at 2θ = 28.4°, seen for 3 s Si + 0 s C, disappears when a C-pulse is added, supporting the assumption that the C-pulse is a carburization step. In Figure 1 (b), a weak Si (111) peak appears for 5 s Si + 3 s C, suggesting that with such a pulsed-CVD cycle there are not enough carbon species to carburize the previously grown Si layers.

In the proposed mechanism, we assume that the Si-pulse will be the primary step that contributes to the overall growth per cycle (GPC). This assumption is supported by the significant increase in GPC with elongated Si-pulse at a fixed C-pulse as shown in Figure 2, where the GPC is plotted against the durations of both C-pulse (with a fixed Si-pulse of 3 s) and Si-pulse (with a fixed C-pulse of 3 s). One can notice that with a fixed C-pulse of 3 s the GPC increases with increasing duration of the Si-pulse. In contrast, a fixed Si-pulse of 3 s results in a Si layer with a GPC of 7 nm/cycle without the C-pulse (C-pulse of 0 s). A longer C-pulse only results in a slight increase in GPC.
FIG. 1. X-ray diffractograms of samples deposited at 1000 °C with either a fixed Si-pulse of 3s (a) or a fixed C-pulse of 3 s (b). Note: the SiC (220) and graphite (103) peaks overlap at $2\theta \approx 60^\circ$. 
FIG. 2. Growth rate per cycle (nm/cycle) of the samples deposited at 1000 °C with either a fixed Si-pulse of 3 s (denoted with squares) or a fixed C-pulse of C (denoted with circles).

B. Surface chemical mechanism

The surface chemistry of the pulsed process was probed by using graphite substrates with trenches to study the influence of precursor pulsing on the coating step coverage (SC). The initial pulsed-CVD cycle was chosen as 3 s Si-pulse – 1 s purge – 3 s C-pulse – 1 s purge, which was one of the combinations that did not result in co-deposition of elemental Si (Figure 1). In contrast to a subconformal SiC coating deposited at 1200 °C by continuous CVD reported in our previous studies, a superconformal SiC growth with a SC of nearly 9 was achieved at 1200 °C in a trench with an aspect ratio (AR) of 4 via pulsed CVD. The thickness difference between the top and the bottom corner of a trench in the 3C-SiC coatings deposited by pulsed and continuous CVD can be seen in Figure 3.
The coating prepared by pulsed CVD is thicker at the bottom corner than at the top, while the one prepared by continuous CVD exhibits the opposite result. To understand the surface chemical mechanisms leading to such a drastic improvement in coating conformality by pulsed CVD, the GPC and the SC in 1-mm deep trenches with widths ranging from 250 μm to 1000 μm were investigated for H₂ purge durations of 1 s and 5 s. Figure 4(a) and 4(b) display the variations of GPC and SCs, respectively, for increasing trench width. It can be observed that a longer purge generally results in higher GPCs of both upper and lower sidewalls of the trench, whereas a shorter purge results in higher SCs.

A possible explanation for these results is a gas trapping effect, where the precursors are trapped in the lower part of the trenches, rendering a local continuous CVD leading to a higher SC. The GPC with 1 s purge in the lower part of trenches (black solid line in Figure 4(a)) seems to be independent of the trench width, while the GPC with 5 s purge in the lower part of the trench decreases with decreasing trench width (red solid line in Figure 4(a)). Since a gas trapping effect should be more pronounced in a narrower trench, resulting in a higher GPC in the lower part of the trenches with smaller widths, these results speak against a gas trapping effect. The average GPC at the lower part of the trenches is higher with 5 s purge compared with 1 s purge, which further contradicts the gas trapping effect as a longer gas purge would aid in removing the residual precursor molecules from the trenches.
**FIG. 3.** Cross sectional SEM micrographs of 3C-SiC coatings deposited by pulsed CVD (a), (b) and (c), and by continuous CVD (d), (e) and (f), in a 1 mm deep and 250 μm wide trench. (a) and (e) are upper sidewall/top corners, while (b) and (f) are lower sidewall/bottom corner of the trench. (c) and (d) are the overview of the trenches and share the same scale bar.
Figure 4. The GPCs at 1200 °C of upper (approximately 75 µm from the opening) and lower (about 5 µm from the bottom) sidewalls of the 1 mm deep trenches with different widths and with a purge duration of either 1 s or 5 s (a). Step coverage of SiC coatings at 1200 °C in the trenches with different widths. The grey and red curves denote the coating deposited by pulsed CVD with a purge length of either 1 s or 5 s, while the blue curve denotes the coating prepared by continuous CVD (b).

Instead, we consider a surface chemical inhibition effect to explain the improved conformality. In a seminal work, Kumar et al. reported an enhanced conformality of TiB₂ thin films deposited by continuous CVD using Ti(BH₄)₃(dme) as the precursor and dme as the inhibitor, where dme= 1,2-dimethoxyethane. Later, Yanguas-Gil et al. have proposed several possible mechanisms explaining how the addition of an inhibitor would improve the film conformality. In our SiCl₄ + C₂H₄ process, Cl atoms on the surface are regarded as growth inhibitors. It has been shown by Schulberg et al. that HCl molecules would
inhibit the growth of 3C-SiC by the site-blocking mechanism\textsuperscript{30}, and HCl is also one of the products from the hydrogenation of SiCl\textsubscript{4}\textsuperscript{25}. Formation of HCl is also expected from the surface chemical reactions as the main Si-containing growth species, i.e. SiCl\textsuperscript{31}, brings Cl to the film surface. This means that at the upper part of the trench there is an inflow of HCl from gas phase reactions between SiCl\textsubscript{4} and H\textsubscript{2} during the Si-pulse as well as the HCl produced from the surface chemical reactions between the SiCl species and the surface moieties terminated by H, e.g. CH\textsubscript{x}, at the lower part of trench, which diffuses upwards. These effects increase the partial pressure of HCl closer to the trench opening, resulting in a higher inhibition effect and a lower GPC in the upper part of the trenches, as seen in Figure 4. In a continuous CVD process, both Si- and C-precursor molecules arrive at the surface at a similar rate, leading to a mix of surface species. In our pulsed CVD process, only Si- or C-precursors arrive at the surface during a precursor pulse. During the Si pulse, it is expected that the whole surface is covered with SiCl\textsubscript{x} species, rendering a stronger inhibition effect compared to a continuous CVD process, where there is a more even mixture of SiCl\textsubscript{x} and CH\textsubscript{x} surface species. This would explain the extremely high SC values of up to 9.

Comparing the GPC between the trenches with different purge durations, it can be noticed that the GPC of the trenches deposited with 5 s purge is higher than that with 1 s purge. We speculate that a longer H\textsubscript{2} purge step after Si-pulse would remove more Cl terminations on the surface, replacing them with H terminations. The higher bond enthalpy of the Si–Cl bond (400 kJ/mol) than that of the Si–H bond (323 kJ/mol)\textsuperscript{32} means a non-favored replacement from thermodynamics, suggesting that longer purge time should be able to increase the replacement. The GPC at the lower part of the trenches increases with
increasing trench width, which can be explained by a larger gas volume being replaced in a wider trench during the purge, leading to higher degree of surface termination replacement in a wider trench. This effect is more noticeable in the trenches deposited with 5 s purge, presumably because more growth inhibitors are removed from the surface with longer purge, as is described above. The growth mechanism proposed for the 3C-SiC coatings deposited by pulsed CVD is summarized in Figure 5.

FIG. 5. Summary of growth mechanism proposed for the 3C-SiC coatings deposited by pulsed CVD

IV. SUMMARY AND CONCLUSIONS

In this work, we have demonstrated the capability to grow 3C-SiC coatings on graphite via pulsed CVD. SiCl₄ and C₂H₄ were pulsed alternately into the growth chamber with each precursor pulse being separated by a H₂-purge. We suggest a mechanism based on deposition of Si from the SiCl₄ pulse followed by carburization to form SiC during the C₂H₄ pulse. Superconformal SiC growth was achieved by the pulsed CVD process in trenches with ARs ranging from 1 to 4 at 1200 °C. Continuous CVD at the same
temperature rendered subconformal SiC. We ascribed this superconformal growth behavior to enhanced Cl termination in the opening of the trench as a result of the pulsed precursor supply.

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AUTHOR DECLARATIONS

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES