Growth of silicon carbide multilayers with varying preferred growth orientation

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ABSTRACT

SiC multilayer coatings were deposited via thermal chemical vapor deposition (CVD) using silicon tetrachloride (SiCl₄) and various hydrocarbons under identical growth conditions, i.e. at 1100 °C and 10 kPa. The coatings consisted of layers whose preferred growth orientation alternated between random and highly (111)-oriented. The randomly oriented layers were prepared with either methane (CH₄) or ethylene (C₂H₄) as carbon precursor, whereas the highly (111)-oriented layers were grown utilizing toluene (C₆H₆) as carbon precursor. In this work, we demonstrated how to fabricate multilayer coatings with different growth orientations by merely switching between hydrocarbons. Moreover, the success in depositing multilayer coatings on both flat and structured graphite substrates has strengthened the assumption proposed in our previous study that the growth of highly (111)-oriented SiC coatings using C₆H₆ was primarily driven by chemical surface reactions.

1. Introduction

Polycrystalline SiC has been an interest of research for decades due to its high hardness, corrosion resistance and phase stability at elevated temperatures. Cubic silicon carbide, also known as 3C-SiC or β-SiC, is often utilized as a hard protective layer because it can be deposited as a coating via chemical vapor deposition (CVD) at moderate temperatures around 1000 °C. The precursors employed in the SiC CVD can be classified into two categories. Multicomponent precursors, e.g. methyltrichlorosilane (MTS) [1–5] and hexamethydisilane (HMDS) [6–9], can function as the source for both Si and C atoms. The other alternative is CVD processes with separate Si- and C-precursors, e.g., silane and silicon tetrachloride are widely used Si-precursors, whereas short-chain hydrocarbons, e.g. methane (CH₄) [11–15], propane (C₃H₈) [14,16–18], ethylene (C₂H₄) [19,20] and acetylene (C₂H₂) [21–23], have been utilized as C-precursors.

As in other anisotropic polycrystalline materials, the physical and chemical properties of SiC coatings are dependent on the growth orientation of the crystals. For instance, (111)-oriented 3C-SiC films have a higher Vickers microhardness than other orientations [24]. On the other hand, since 3C-SiC (110) planes are non-polar [25], with a suitable surface functionalization, (110)-oriented 3C-SiC could be used in biosensors and devices [26]. In the 3C-SiC system, (111) and (110) planes were reported to exhibit the lowest surface energies [27], meaning that under regular circumstances the SiC crystals would grow favorably in both (111) and (110) directions. Several studies have been performed to deposit highly oriented 3C-SiC by tuning the deposition conditions or by utilizing different CVD techniques. Tu et al. have reported the growth of primarily (110)-oriented SiC at T ≥ 1450 °C and Ptot ≤ 10 kPa by thermal CVD [28], whereas both primarily (110)- and (111)-oriented SiC coatings were prepared at various conditions by Zhang et al. via laser CVD [8]. Since the preferred growth orientation depends on the process conditions, a high process stability is required to achieve a constant orientation over the whole substrate and during the whole coating process. To switch between orientations, the growth process would need to be paused and the parameters would need to be changed before the growth continues. In the abovementioned studies, the change of preferred growth orientation was controlled by tuning the deposition temperature and pressure, suggesting that to produce SiC multilayer coatings with different orientations the deposition conditions need to be adjusted constantly.

In our previous work [29], we showed that a highly (111)-oriented
3C-SiC coating can be obtained from a CVD process using silicon tetrachloride (SiCl4) and toluene (C6H5) as precursors. We have demonstrated simulations indicating that the preferred orientation arises from the surface chemistry of C6H5 precursor. In the present work, we put this theory to the test by growing 3C-SiC multilayer coatings with alternating highly (111)- and randomly oriented layers by only switching the C-precursor from C6H5 to CH4 or C2H4 under otherwise constant deposition conditions. This approach also enables a much simpler route to fabricate SiC multilayer coatings of varying orientations without the need of changing process parameters in between growth steps.

2. Experimental details

3C-SiC coatings with layered structures were deposited on isostatic graphite substrates via horizontal thermal CVD process at 10 kPa and 1100 °C using SiCl4 (99.998 %, Sigma-Aldrich Chemie GmbH) and various hydrocarbons. The highly (111)-oriented layers were grown with CH4 (99.9 %, Sigma-Aldrich Chemie GmbH), whereas the other layers were grown with either CH4 (99.9995 %, Linde Gas AB) or C2H4 (99.95 %, Linde Gas AB). Liquid SiCl4 and C2H4 were stored in stainless-steel bubblers and placed in a thermostat-controlled water bath with its temperature being maintained at 23.8 °C. During the measurement, an acceleration voltage of 30 kV was used. The post-analysis of the EBSD data was carried out by an open-source MATLAB package MTEX [31].

3. Results and discussion

3.1. Growth of 3C-SiC single layer coatings using only C2H4, CH4 or C2H4 as C precursor

Fig. 1 depicts the diffractograms of the SiC single layer coatings deposited with SiCl4 and various hydrocarbons. 3C-SiC is the primary phase that was detected in these samples. Under the deposition conditions described in the Experimental details, the resulting SiC using only CH4, C2H4 or C2H6 as C precursor had the coating thicknesses of 31 μm, 99 μm and 99 μm, respectively (corresponding to the growth rates of 62, 198 and 198 μm/h). Since the coating thickness of the sample prepared with CH4 was only 31 μm, graphite peaks from the substrate are also observed. An extra peak appearing at 2θ around 33.6° seen in the coatings deposited with CH4 and C2H4 was reported to arise from the existence of stacking faults in 3C-SiC [32]. Moreover, it can be noticed that by using C2H4 as C precursor, the diffractogram of the resulting SiC only shows one strong sharp peak at 2θ = 35.6° and two rather weak peaks at 2θ = 75.5° and 133.4°, which corresponds to 3C-SiC (111), (222), and (333) planes, respectively. This is an indication of highly (111)-oriented 3C-SiC. The preferred growth orientation towards (111) in this sample is further quantified by calculating the texture coefficient (TC) utilizing Eq. (1). The results are displayed in Table 1. The coating grown with C2H4 alone has a TC(111) of 4.84 with the rest of TC(hkl) being close to 0. On the other hand, even though the TC(111) is the highest in the samples prepared with CH4 or C2H4, the TCs of other planes are relatively close to TC(111), implying a randomly or only slightly oriented SiC growth.

The highly (111)-oriented SiC coating deposited with C2H4 also exhibits distinct features in its surface morphology and cross section, as displayed in Fig. 2. While the samples that are almost randomly oriented (prepared either with CH4 or C2H4) have surfaces consisting of small crystallites and/or irregularly faceted crystals, the SiC crystals on the surface of highly (111)-oriented samples, deposited with C2H4, resembles the top of hexagonal pyramids. It has been reported that the appearance of such 6-fold symmetric pyramids was a result of two twin triangular pyramids growing into each other [33] and was a representative surface feature of (111)-oriented face-centered cubic (FCC) films [34]. The highly (111)-oriented SiC growth seen in the sample prepared with C2H4 can be attributed to the presence of an aromatic hydrocarbon as C precursor. In our previous study [29], we have shown
computationally that in the SiCl\(_4\) + C\(_7\)H\(_8\) process, the primary two carbon-containing active film forming species, C\(_6\)H\(_6\) and CH\(_3\), adsorbed differently on 3C-SiC (111) and (110) planes. CH\(_3\) adsorbed strongly on both planes, whereas C\(_6\)H\(_6\) chemisorbed on the (111) plane, but only physiosorbed on the (110) plane. This preferential adsorption on the (111) plane from both film forming species has led to highly oriented SiC growth towards the \langle 111 \rangle direction.

### 3.2. Growth of 3C-SiC multilayer coatings by switching the C precursor between C\(_7\)H\(_8\) and CH\(_4\) or C\(_2\)H\(_4\)

After characterizing the preferred growth orientation of SiC single layer coatings from C\(_7\)H\(_8\), CH\(_4\) or C\(_2\)H\(_4\), two experiments were performed in which the hydrocarbon was switched multiple times during the deposition. The diffractograms of the resulting multilayer coatings are displayed in Fig. 3. As expected, there exists only 3C-SiC phase in both samples and the peaks from graphite substrates are not detected due to the much thicker SiC multilayer coatings (122 μm and 180 μm in the CH\(_4\)/C\(_7\)H\(_8\) and the C\(_2\)H\(_4\)/C\(_7\)H\(_8\) processes, respectively). Because the topmost layers of both samples were grown with C\(_7\)H\(_8\), the peak intensities of 3C-SiC \langle 111 \rangle are much stronger than others.

The layering effect of switching between different hydrocarbons during deposition is clearly observed in the cross-sectional images of the multilayer samples as shown in Fig. 4. In both cases, the layers 1, 3 and 5 (counting from the substrate) are deposited with either CH\(_4\) or C\(_2\)H\(_4\) and their cross-sectional structures are similar as in the SiC single layer coatings, indicating that they are randomly oriented. The layers 2, 4 and 6 deposited with C\(_7\)H\(_8\) are highly \langle 111 \rangle-oriented, judging from the dense striations perpendicular to the growth direction of SiC grains. One can also observe that in the C\(_7\)H\(_8\)-step the growth of SiC grains remains columnar and \langle 111 \rangle-oriented regardless of the preferred growth orientation or surface morphologies of the previous layers in the CH\(_4\)/C\(_2\)H\(_4\) steps. The growth orientation of each layer was confirmed by EBSD.

Fig. 5(b) presents the EBSD inverse pole figure (IPF) coloring map superimposed with the band contrast (BC) image of the cross section of the 3C-SiC multilayer coating deposited with SiCl\(_4\) and alternating C\(_2\)H\(_4\)/C\(_7\)H\(_8\). The reference axis for the IPF coloring is parallel to the growth direction, which is from bottom to top in the figure. It can be seen that the majority of the grains in the layers 2, 4 and 6 are colored in blue according to the stereographic triangle coloring scheme, indicating that the SiC growth in these layers is highly \langle 111 \rangle-oriented. On the contrary, in the layers 1, 3 and 5, the growth is randomly oriented because the constituent grains are indexed with various colors. The average thickness of the highly \langle 111 \rangle-oriented interlayers in both samples is (30 ± 3) μm, while those of the randomly oriented interlayers deposited with CH\(_4\) and C\(_2\)H\(_4\) are (9 ± 2) μm and (31 ± 1) μm.

### Table 1

Texture coefficients (TC) of the 3C-SiC single layer coatings deposited with various hydrocarbons.

<table>
<thead>
<tr>
<th></th>
<th>TC(111)</th>
<th>TC(220)</th>
<th>TC(311)</th>
<th>TC(200)</th>
<th>TC(331)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_7)H(_8)</td>
<td>4.84</td>
<td>0.03</td>
<td>0.06</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>CH(_4)</td>
<td>1.27</td>
<td>1.52</td>
<td>0.99</td>
<td>0.48</td>
<td>0.8</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>2.16</td>
<td>0.59</td>
<td>1.35</td>
<td>0.19</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Fig. 2. Surface and cross-sectional SEM images of 3C-SiC single layer coatings deposited with SiCl\(_4\) and various hydrocarbons.

Fig. 3. Diffractograms of 3C-SiC multilayer coatings deposited with SiCl\(_4\) and alternating CH\(_4\)/C\(_7\)H\(_8\) or with SiCl\(_4\) and alternating CH\(_4\)/C\(_2\)H\(_4\).
respectively. The nearly 3.5 times difference in the growth rate between using CH\(_4\) and using C\(_2\)H\(_4\) as carbon precursor can be explained by the SiC growth mechanism. It was found before by Danielsson et al. that the main carbon growth species is C\(_2\)H\(_2\) and that C\(_2\)H\(_2\) is more readily formed from C\(_2\)H\(_4\) than from CH\(_4\) [35]. They have shown via computational fluid dynamics that by using C\(_2\)H\(_4\) as carbon precursor the mole fraction of C\(_2\)H\(_2\) increased with decreasing C\(_2\)H\(_4\) along the gas flow direction. In contrast, by using CH\(_4\) as carbon precursor CH\(_4\) was the most abundant species and its mole fraction stayed constant throughout the whole reactor. In a later study conducted by Sukkaw et al., CH\(_4\) was further reported to be inactive towards the growth of SiC [36]. Therefore, the growth rate discrepancy between CH\(_4\)- and C\(_2\)H\(_4\)-grown interlayers could be explained accordingly.

Moreover, one can observe that, upon switching on and off the C\(_2\)H\(_8\), the change of orientation from random to highly (111) seems to occur instantaneously, evidenced by the absence of transition layers shown in Fig. 6, where the interfaces of randomly/highly (111)-oriented and of highly (111)/randomly oriented interlayers are depicted. In a regular scenario, the growth direction of the grains would be slightly directed by the immediately underlying layer in the beginning of growth and it would gradually be taken over by the fast growing directions [37]. Therefore, a transition layer consisting of mixed grains with various orientations is often expected between different layers. However, the absence of such layer in our 3C-SiC multilayer samples indicates that the steering effect of C\(_2\)H\(_2\) is so strong that the growth towards (111) direction is instantly started or halted upon activating or deactivating C\(_2\)H\(_8\).

The robustness of the C\(_2\)H\(_8\) process in growing highly (111)-oriented 3C-SiC was retained even on non-flat substrates. Fig. 7 displays the 3C-SiC multilayer coating deposited on a graphite substrate with step features. It can be observed that the multilayer coating follows the step evenly and the growth of highly (111)-oriented 3C-SiC interlayer perpendicular to the growth surface is not affected by the geometry of the substrate.

4. Conclusion

3C-SiC multilayer coatings with alternating layers of random orientation and strong (111)-orientation were prepared via SiCl\(_4\)-based thermal CVD. Instead of changing process parameters such as temperature and pressure, the different orientations were achieved by only switching between various hydrocarbons. C\(_2\)H\(_8\) was used to deposit highly (111)-oriented layers, whereas the randomly oriented layers were grown with CH\(_4\) or C\(_2\)H\(_4\). Alternating the hydrocarbons gave rise to multilayer coatings with clearly identifiable layers. The growth orientation of each layer, either highly (111)- or randomly oriented, was confirmed by the EBSD IPF coloring map. The multilayer coatings exhibited sharp interfaces between randomly and highly (111)-oriented interlayers, which indicates that the change of orientation must have happened instantaneously during growth. This is unexpected, because in
The rapid change of orientation in this process highlights the very strong impact that toluene has on the grain orientation. This agrees with our previous studies where we have shown via quantum chemical calculation that the highly (111)-oriented SiC growth using C_2H_6 resulted from the preferential adsorptions of active C-containing film forming species on different 3C-SiC planes and was driven primarily by chemical surface reaction. The results also show that there is no substantial directing effect of the growth surface itself.

Well-defined multilayer coatings were also obtained on structured graphite substrates with vertical walls. On these substrates, the step corner was covered evenly with 3C-SiC multilayer coatings and the growth of highly (111)-oriented SiC was not hindered by the substrate geometry. This study not only highlights the potential of precursors which can direct the growth, such as C_2H_6 in CVD, but also opens a simpler way to obtain layered coating of varying orientation.

Competitive growth, grain orientation only develops over time. The rapid change of orientation in this process highlights the very strong impact that toluene has on the grain orientation. This agrees with our previous studies where we have shown via quantum chemical calculation that the highly (111)-oriented SiC growth using C_2H_6 resulted from the preferential adsorptions of active C-containing film forming species on different 3C-SiC planes and was driven primarily by chemical surface reaction. The results also show that there is no substantial directing effect of the growth surface itself.

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