Residual stress toughening in ceramic nanocomposite coatings deposited by hypersonic plasma particle deposition

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Abstract: SiC/Si nanocomposite films were deposited on silicon, molybdenum, and alumina substrates using a thermal plasma based hybrid process of chemical vapor deposition and ballistic nanoparticle impaction. The effect of residual stress on fracture toughness of the composite film was studied using rapid thermal annealing and nanoindentation analysis.

Keywords: Nanocomposite, silicon carbide, residual stress, fracture toughness, hypersonic plasma particle deposition

1. Introduction

In the deposition of thin films, especially in the microelectronics field, the presence of residual stresses is typically detrimental to the film’s success. Chung et al. has shown that by rapid thermal annealing (RTA) of a-SiC films on (100) Si single crystals, residual stresses induced during deposition can almost entirely be removed \cite{1}. However, by tuning these stresses appropriately, they can be used to enhance toughness. This is particularly true in ceramic matrix composites, where thermoelastic mismatch stresses are commonly used as a toughening mechanism. In addition to varying the microstructure, residual stress has been used as a design tool in silicate glass to improve the toughness through ion distribution \cite{2}. In the current study, SiC based nanocomposites deposited on a variety of substrates are used to understand the competing influences on residual stress induced toughening.

2. Methods

Films were deposited using hypersonic plasma particle deposition (HPPD), which is a thermal plasma based hybrid process of chemical vapor deposition and ballistic nanoparticle impaction. Details of this process are discussed in previous publications \cite{3}. As reported earlier, the growth of the film varies from a mainly particle impacted region in the center of the deposition to a vapor growth dominated outer region \cite{4, 5}. The plasma was operated at 30 slm Ar, 3-4 slm H\textsubscript{2}, and 8-10 kW. Precursors were injected for 10 min at 40 sccm for SiCl\textsubscript{4} and 240 sccm for CH\textsubscript{4}. Temperature was monitored with a thermocouple on the back side of the substrate and ranged from 450-550°C. Assuming 1-D heat transfer through the substrate, the film deposition temperature is most likely 80°C warmer than the measured value. Films were deposited on three substrates: molybdenum, (100) silicon, and alumina (single crystal). The Mo substrates were mechanically polished, using a 20 nm colloidal silica solution for the final polish. The Si and Al\textsubscript{2}O\textsubscript{3} substrates were cleaned with acetone followed by isopropanol. Except in the case of results labeled as-deposited, films were rapidly thermally annealed (Modular Process Rapid Thermal Annealer) following the deposition process. The system was purged with 8 slm Ar for 2 minutes, followed by heating at a rate of 50°C/s and a 20 sec hold at temperatures from 900-1200°C. Samples were cooled to < 200°C before removing from the Ar environment.

Structural and compositional characterization of the films were performed using x-ray diffraction (Bruker-AXS Microdiffractometer) and scanning electron microscopy (FEG-SEM JEOL-6700). Focus ion beam milling (FEI Quanta 200 3D) was used for cross sectional analysis. Mechanical response was measured using dynamic nanoindentation (Agilent NanoIndenter XP), with a target strain rate of 0.050 s\textsuperscript{-1}. Films were indented using a cube corner diamond indenter with a tip radius of curvature of approximately 120 nm. From displacement depths of 50-100 nm, elastic modulus and hardness were calculated using the Oliver-Pharr method \cite{6}. Fracture toughness was determined using a standard Vickers crack measurement technique developed by Anstis et al. \cite{7}. This method was extended to thin film analysis with cube corner indentation by Pharr \cite{8} and is given as

\begin{equation}
K_c = \alpha \left( \frac{E}{H} \right)^{1/2} \left( \frac{P}{c^{3/2}} \right)
\end{equation}

where \( \alpha \) is an empirical factor accounting for the tip geometry, \( E \) is the elastic modulus, \( H \) is the hardness, \( P \) is the maximum applied load, and \( c \) is the average crack length measured from the center of the indentation impression. For a cube corner indenter, Pharr found \( \alpha = 0.040 \). Surface roughness and indentation impressions were measured with contact mode atomic force microscopy (Digital Instruments Nanoscope III Multimode) with a radius of curvature of approximately 40 nm.

Residual stresses were estimated by the mismatches in the coefficients of thermal expansion between the film and the substrate, given as

\begin{equation}
\sigma_{\text{th}} = E_f \left( \alpha_s - \alpha_f \right) (T_s - T_f)
\end{equation}
where \( E \) is the elastic modulus, \( \alpha \) is the coefficient of thermal expansion, \( T \) is the temperature, and subscripts denote the film (\( f \)), substrate (\( s \)), and ambient conditions (\( a \)). While a wafer curvature measurement would give a better estimate of the residual stress in the film, gradients in the film structure limit the sample size to below the curvature measurement requirements.

3. Results

3.1 Structure

Film thicknesses were between 300-400 nm (cross sectional SEM) and found to be nominally independent of substrate. This is a much slower growth rate (30 nm/min) than reported in previously grown SiC films using HPPD (0.5-2 \( \mu \)m/min) \[4, 5\]. The decrease can be explained by the radial dependence of the growth mechanism. At a radial position of 19 mm, the current position is more than twice as far from the center of the deposition spray as the higher rate depositions. At this position, there is equal exposure to the vapor rich boundary layer, but less of a contribution to the film structure from particle impaction due to the gas dynamics. An advantage of this slower deposition rate is a much smoother film (RMS roughness <10 nm as deposited).

Table 1 summarizes the elastic modulus (\( E \)) and hardness (\( H \)) measurements for each of the substrates. As discussed earlier, these measurements were taken with a cube corner diamond indenter from displacements of 50-100 nm. This range was selected to minimize distortions from indentation size effect at the low end and substrate effects at larger indentation depths. It is also important to note that while a cube corner indenter gives results comparable to a Berkovich geometry indenter, slight deviations in both hardness and modulus have been observed in certain combinations of displacement ranges and material systems \[9\]. To initiate cracking, films were indented to depths of 200 and 400 nm. Fracture toughness (\( K_{\text{IC}} \)) results for each of the film-substrate combinations at RTA temperatures from 900-1200° are summarized in Figure 2.

![Fig. 1 XRD pattern for Si/SiC on Mo substrate. Peaks for Si (1), 3C-SiC (2), and Mo (3) are labeled.](image1.png)

![Fig. 2 Fracture toughness for the SiC/Si films on each substrate as a function of RTA temperature. Diamonds represent films on Si, circles for Mo, and triangles for Al\(_2\)O\(_3\). Solid shapes are to 400 nm while open shapes are to 200 nm displacement.](image2.png)

4. Discussion

The evaluation of fracture behavior in thin film systems presents a number of challenges with respect to crack initiation and confinement. In order to initiate cracking, there is a minimum stress that must be reached. However, even with a sharp indenter geometry such as a cube corner, the threshold stress for cracking may be at large enough displacements that the substrate begins to influence the measured response. In addition, the crack dimensions...
must be sufficiently large to be accessible experimentally (SEM, AFM, etc.). Considering these limitations, an understanding of the substrate’s influence on the measured properties is essential. Table 2 summarizes the thermal expansion coefficient ($\alpha$), elastic modulus, hardness, and fracture toughness reported in the literature for the materials of interest.

<table>
<thead>
<tr>
<th>property</th>
<th>SiC</th>
<th>(100) Si</th>
<th>Mo</th>
<th>Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$ ($^\circ$C$^{-1}$)</td>
<td>4.3-4.8</td>
<td>2.5</td>
<td>4.9</td>
<td>7.2-8.8</td>
</tr>
<tr>
<td>E (GPa)</td>
<td>395</td>
<td>160</td>
<td>320</td>
<td>380-406</td>
</tr>
<tr>
<td>H (GPa)</td>
<td>24-32</td>
<td>9</td>
<td>2.3</td>
<td>18-24</td>
</tr>
<tr>
<td>$K_Ic$ (MPa·m$^{1/2}$)</td>
<td>3.3</td>
<td>0.7</td>
<td>8-22</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 2. Summary of relevant material properties

†Ref. [10-12]

In the case of measured hardness, there is little variation in the result across the three substrates. The plastic zone can be approximated as

$$c = \left( \frac{3P}{2\pi\sigma_{ys}} \right)^{1/2}$$

(3)

where $c$ is the plastic zone radius, $P$ is the applied load, and $\sigma_{ys}$ is the yield strength. Using the yield strength as one third of the hardness and the applied loads from 100 nm displacements, the plastic zone is 260 ± 11 nm. Thus, for 50-100 nm displacements in the 300-400 nm film, there is no overlap of the plastic zone into the substrate. However, the elastic interaction zone is much larger, as evidenced by the measured modulus results tracking much more closely with the substrate modulus.

The fracture toughness results are not as straightforward. As shown in Figure 2, the measured toughness for Si/SiC films deposited on Si decreases with increasing annealing temperature. This trend is most likely due to the thermal expansion mismatch between the primarily SiC film and the Si substrate. From Eqn 2, the as-deposited SiC/Si on Si would be in tension. As the annealing temperature increases, the magnitude of the tensile residual stress increases and helps drive the indentation induced cracking. Thus, the measured toughness decreases with increasing RTA due to increased residual tensile stress.

Figure 3 shows representative images of indentations into bare Si and a Si/SiC film deposited on Si. Comparing the bare Si impressions (a, c) with the Si/SiC film (b, d), there is a distinct difference between the crack paths. The cracks in the Si/SiC films follow a much more jagged path than the bare Si, presumably due to the fine grain structure and intergranular fracture. However, the impression sizes and crack lengths are roughly the same at both indentation depths, suggesting (from Eqn 1) no improvement in toughness for the Si/SiC film. In Figure 4, a 400 nm indent into Si/SiC on Si was cross sectioned normal to one of the crack paths by focused ion beam milling. The top surface and cross sectional profile show the effects of ion beam damage, giving it a much smoother appearance. Following the crack path down the film cross section, the crack clearly passes from the film (lighter layer) to the substrate (darker layer). Thus, the measured toughness is a response of the film-substrate system as a whole.

For the Si/SiC films deposited on Mo, the toughness again follows a downward trend with increasing annealing temperature. However, in this case, the film should be relatively neutral as deposited due to a close match of the thermal expansion coefficients. Figure 5 shows representative indentation impressions for an as-deposited film and films annealed at 900, 1000, and 1100°C. In addition to an increase in the crack length, there is also a substantial increase in the grain size, with the most pronounced example at 1100°C (Fig. 5d). While the RTA should minimize grain growth compared to conventional annealing, it is unclear why only the films on Mo showed this type of abnormal grain growth.

Of additional interest with the Si/SiC films deposited
on Mo is the ring cracking observed in Fig. 5b. This feature was consistently observed at combinations of high loads (and depths) and low annealing temperatures. One explanation of this phenomenon could be the formation of a molybdenum carbide or silicide at the substrate-film interface due to carbon diffusion from the SiC to the Mo. Diffusion of silicon and carbon in Mo has been shown to be greatly enhanced at temperatures approaching 1200°C, with Mo acting as a gettering agent for carbon at SiC-Mo interfaces [13, 14]. Since Mo2C is much harder (H ~ 15 GPa) than Mo [14], the film is evenly supported under the indenter load. However, at high loads and/or low annealing temperatures, the round indenter tip (finite sharpness) can push the hard film into the soft substrate without causing crack formation. Once the indenter reaches a depth where the cube corner geometry comes in contact with the film, cracks are initiated outward from the point where the sharp faces contact the film. This leaves a circular trench from where the Mo was deformed. This explanation also agrees with the downward trend in toughness with annealing temperature, as the Mo2C is more brittle than Mo and will increase crack growth from the film. Thus, it is the substrate hardness and carbide interlayer which dominates how the SiC/Si on Mo responds.

In the case of the SiC/Si on the Al2O3 substrates, there is a sharp increase in toughness at an annealing temperature of 900°C following by a decrease at 1200°C. The increase can be attributed to the thermal mismatch, as the film will be in compression after deposition. At 1200°C, one possible explanation for the decrease in toughness is from creep. Assuming the film is under the residual compression prior to the observed decrease in toughness, creep mechanism maps assembled by Ashby and coworkers show that the both the SiC/Si film and Al2O3 substrate are in the power law creep regime [15, 16]. This would lead to enhanced vacancy diffusion and dislocation climb. A second explanation for the toughness decrease is unstable growth of cracks due to the thermal shock during RTA treatment. This type of abrupt drop in fracture strength has been observed in Al2O3 rods subjected to high thermal stresses [17, 18]. With either explanation, it is unclear why there is not a corresponding drop in the measured hardness.

4. Conclusion
SiC/Si nanocomposites were deposited on Si, Mo, and Al2O3 substrates. Measured hardness was relatively invariant to deposition surface while the modulus was strongly affected by the substrate. Using rapid thermal annealing, the residual stress in the film was varied and the changes in the fracture toughness were measured. By studying three substrate-film combinations, additional effects from elastic, plastic, and fracture properties of the substrate were much more apparent. Films deposited on Si showed low fracture toughness due to a tensile residual stress while those deposited on Mo become more brittle with increasing annealing temperature due to the formation of carbides. For the films on Al2O3, the initial benefits of a compressive residual stress are overshadowed by creep or thermal shock at a high annealing temperature. By understanding the competing influences on the fracture toughness of thin films, residual stresses can be used as an effective tool in materials design.

5. Acknowledgements
This work was partially supported by the National Science Foundation (CTS-0506748) and the Air Force Office of Scientific Research (AOARD-08-4134). Parts of this work were carried out in the Institute of Technology Characterization Facility, University of Minnesota, a member of the NSF-funded Materials Research Facilities Network (www.mrfn.org).

References