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DEVCOM ARMY RESEARCH LABORATORY

Plasma-Enhanced Chemical Vapor Deposition on Diamond Powders to Enable Next-Generation Hard Armor

by Thomas Parker

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14. ABSTRACT

Coating of diamond powders with silicon dioxide (SiO_2) was explored using plasma-enhanced chemical vapor deposition (PECVD). These coatings were investigated as a possible oxygen barrier to aid in the consolidation of diamond ceramic composites. A PECVD system was modified to accommodate a fluidized bed to agitate powders during the deposition. A hexamethyldisiloxane vapor precursor source was constructed and installed on the system. The chemistry was tuned via input gas ratios and the resultant film chemistry was measured via X-ray photoelectron spectroscopy (XPS). Deposition rates and through thickness chemistry were investigated with focused ion beam cross-sectioning and XPS sputter depth profiling. The SiO_2 deposition rates were found to be 10 nm per minute and through-thickness chemistry was found to be uniform.

15. SUBJECT TERMS
diamond, plasma-enhanced chemical vapor deposition, PECVD, silicon dioxide, SiO_2, silica, oxygen barrier, armor

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1. Introduction

The use of diamond grit has found widespread application in industrial cutting and grinding applications. As such, high-quality diamond grit is a readily available material in large-scale quantities from a wide range of suppliers. In hard ballistic armor applications, it is commonly believed that the harder the armor, the better the performance (e.g., protection afforded). Diamond is an extremely hard material as well as having a relatively low density. The combination of hardness and low density makes diamond-based armor materials a good candidate for both hard vehicle armor and, in particular, hard body armor. In the body armor application, the use of low-density materials is of particular importance in order to reduce the weight burden on Soldiers.

In cutting and grinding applications, diamond grit is formed into a composite with a matrix material. Typically, materials such as titanium carbide are used as the binder material for low-temperature sintering. However, typical industrial sintering matrices such as titanium carbide are not considered low density. As the Army needs low-density hard materials, new matrix materials and processing must be developed to form lightweight and hard composites.

While some might suggest just sintering the diamond grit into a large piece of diamond armor, this is not possible, as diamond is a metastable form of carbon (C) and cannot formed at pressures and temperature ranges in bulk sizes in industrial processes. As such, alternative sintering matrices must be explored.

A traditional hard armor material such as silicon carbide (SiC) is an ideal candidate as it is hard and has a low density. However, an issue arises when trying to sinter materials such as SiC: the temperatures required quickly cause diamond to transform into a soft carbon allotrope, graphite.

In this work, we describe the development of a process to coat diamond particles in a plasma-enhanced chemical vapor deposition (PECVD) process with silicon dioxide (SiO_2). The concept being that SiO_2 could provide two benefits when trying to sinter diamond with matrices such as SiC. First, the graphitization process in diamond is known to be a multistep process when the diamond surface is oxidized first, after which graphitization then occurs. SiO_2 is well known to act as a barrier to oxygen (O), so this should, in principle, help slow/minimize the graphitization process. Second, SiO_2 softens before large-scale graphitization in diamond occurs, thus this softening/plasticity can help with the diamond/matrix conformity, resulting in a reduction of deleterious defects such as porosity.

2. Methods, Assumptions, and Procedures

A PECVD system was modified to coat SiO_2 on powders. Vacuum deposition techniques are, for the most part, line of sight. The low pressures in a vacuum deposition chamber result in molecules undergoing very few collisions. As they undergo few collisions, the molecules will not fill the voids and pathways found in a pile of powder. As such, the molecules will only make contact with the surfaces that are in line of sight.

Thus, a way to exposure buried surfaces in a powder bed is needed. To accomplish this, a low-frequency vibrator (typically in the range of 20–40 Hz) was installed next to the vacuum chamber. A high-vacuum mechanical feedthrough was used to couple the motion of the vibrator to a sample stage within the vacuum chamber. In this way, during the deposition process, the powder bed was agitated to expose buried surfaces and permit coating of the entire powder bed. Figure 1 shows a photo of the deposition in progress. The plasma electrode is at the top of the image and the fluidized bed is at the bottom. The schematic on the right depicts the deposition system. The deposited film chemistry is controlled via the input gases. A 13.56-MHz generator was run at 100 W of power during the deposition process.

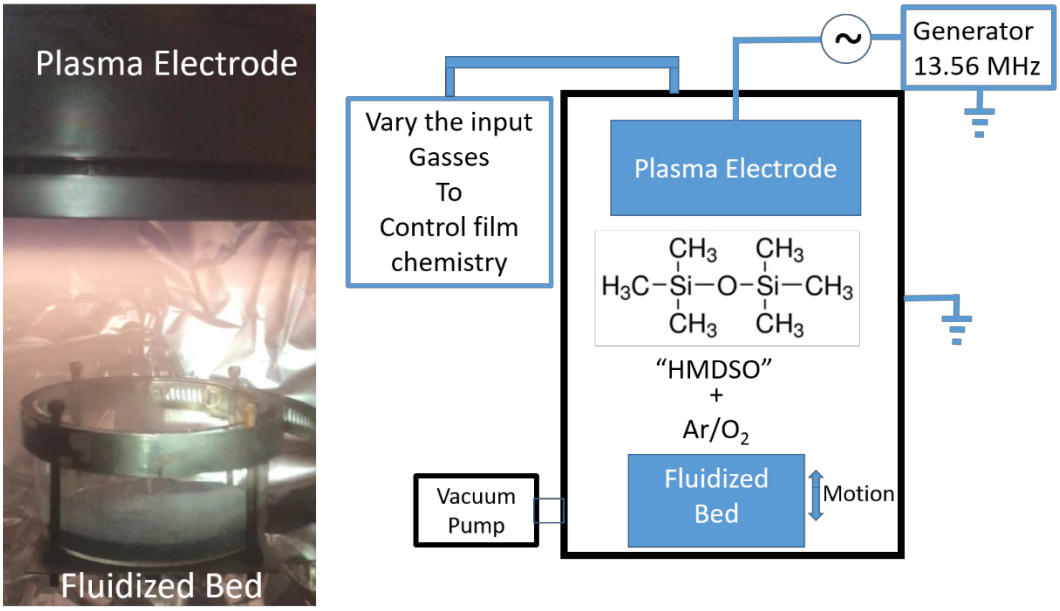

Fig. 1 (Left) PECVD system with the fluidized bed during a deposition. (Right) A schematic of the deposition process.

A vapor precursor assembly was built and installed on the chamber. It consisted of an ultra-high vacuum (UHV) glass vial to hold the liquid precursor. This glass vial was coupled to an UHV needle valve, which was used to control the flow of the vapor into the chamber. A hexamethyldisiloxane (HMDSO) source was chosen as

the SiO_2 precursor as it has a significant vapor pressure at room temperature, removing the need for precursor heating. HMDSO also is not pyrophoric, acutely toxic, or hygroscopic, and is chemically stable and inexpensive.

3. Results and Discussion

In Fig. 2, the image on the left is a scanning electron microscopy (SEM) image of a coated diamond particle with a horizontal width of 414 μm. The image on the right shows a zoomed-in SEM image of the diamond particle's surface; the horizontal width of the image is 5.18 μm. The image of the diamond particle shows the single-crystal nature of the particles. A standard Wulff construction for a face-centered cubic lattice would indicate that the 6-sided facets in the image are the faces of the (111) planes and the 4-sided facets are faces of the (100) planes. This indicates that each particle is in fact an individual crystallite or a single crystal. The close-up SEM image of the coated diamond particle's surface shows some roughness and nodule formation. These structures are expected for a PECVD film as it will grow with a columnar structure, where the topmost surface of the columns can be seen in the SEM and present as nodules.

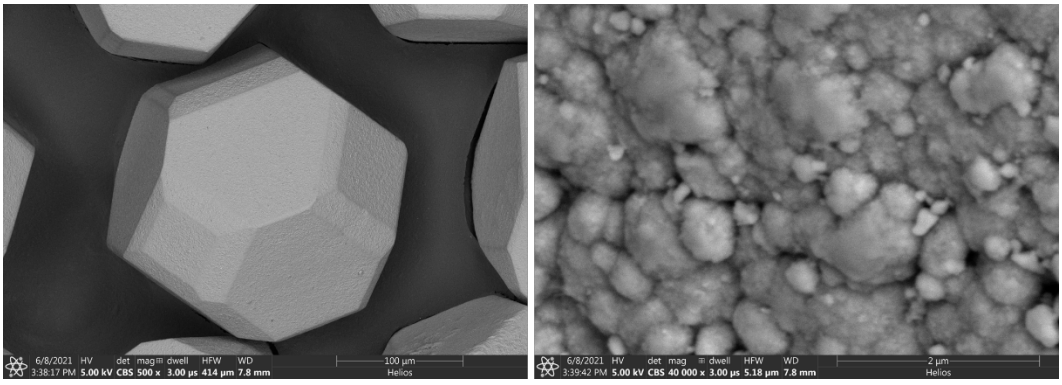

Fig. 2 (Left) SEM image of a SiO_2-coated diamond particle. (Right) Zoomed-in SEM of a SiO_2-coated diamond particle's surface.

Figure 3 shows a high-resolution X-ray photoelectron spectroscopy (XPS) scan of the C 1s peak of uncoated diamond. The C 1s peak is deconvolved into three separate peaks. The peak located at 284.5 eV corresponds to the C-C and C-H bonding. The main peak with the slightly higher binding energy at blue center at approximately 285 eV is attributed to the C-O bonding state. The final peak centered at approximately 287 eV corresponds to the C=O bonding state.

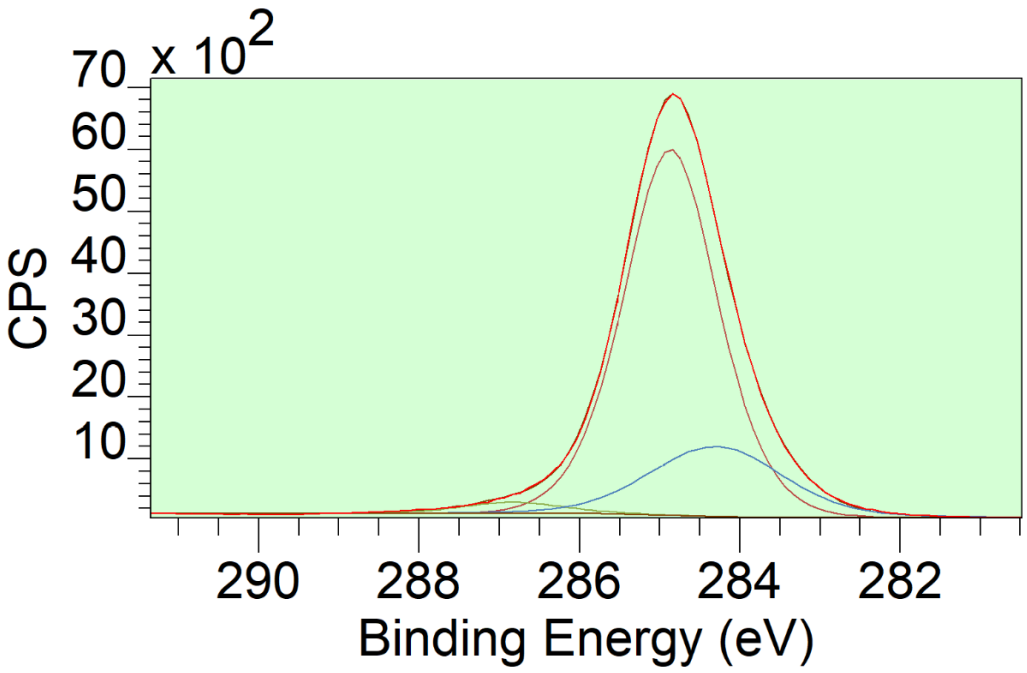

Fig. 3 High-resolution XPS of as-received diamond C 1s

In Fig. 4, the high-resolution XPS of the C 1s peak of SiO_2-coated diamond is shown. The C 1s peak is deconvoluted into three peaks again. The peak centered at approximately 284.8 eV is attributed to the C-C and C-H bonding states. The peak located at approximately 286.2 eV is attributed to the C-O bonding state and the final peak at approximately 287.75 is attributed to the C=O bonding state.

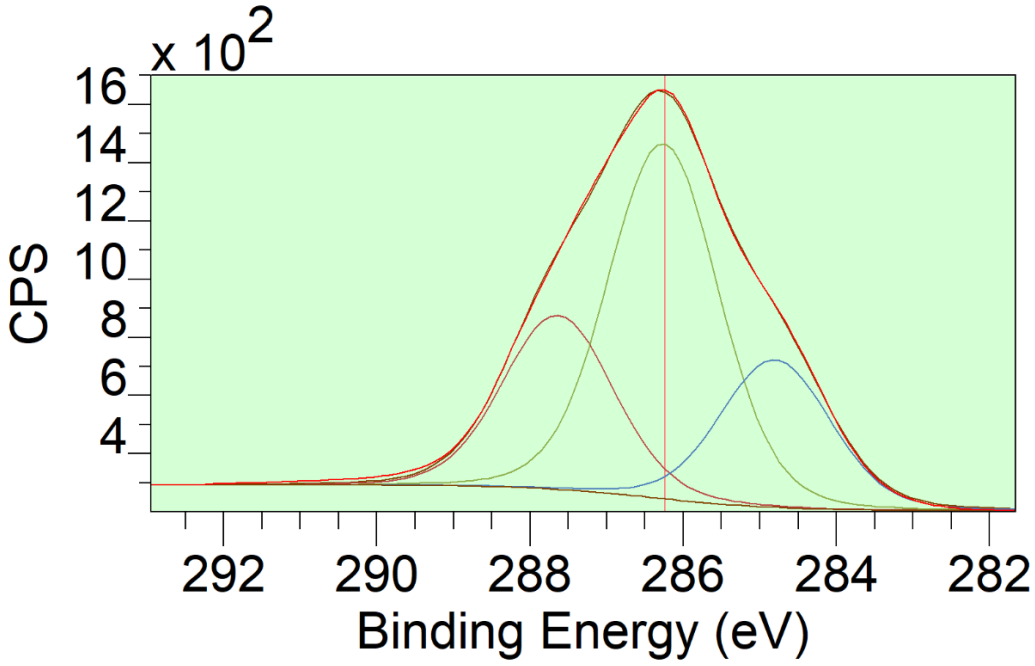

Fig. 4 High-resolution XPS of the C 1s peak of SiO_2-coated diamond

In Fig. 5, the first derivative of the C KLL Auger peak is shown for the as-received diamond. The D parameter, or the spacing between the minimum located at 1213eV and the maximum located at 1232 eV, is 19 eV. From literature,[1] a D parameter of 19 eV indicates the C found near the surface of the diamond is primarily in the sp2 hybridization or graphitic in nature.

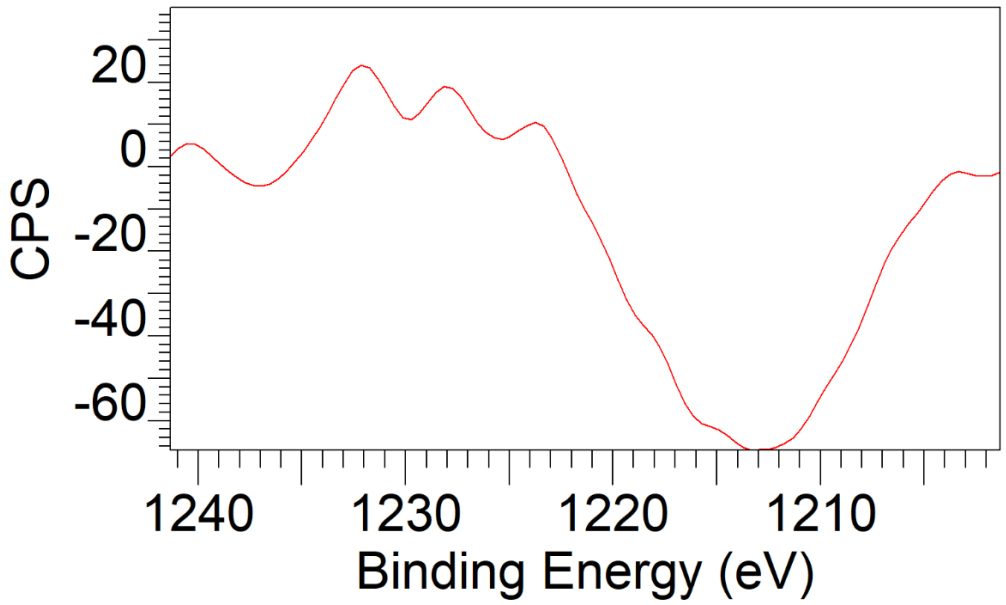

Fig. 5 First derivative of the high-resolution XPS of the as-received diamond C KLL Auger peak, separation (D parameter) between minimum (1213 eV) and maximum (1232 eV), is 19 eV.

In Fig. 6, the first derivative of the high-resolution XPS C KLL Auger peak for SiO2-coated diamond is shown. The minimum is found at 1215.5 eV and the maximum at 1235 eV, yielding a D parameter of 19.5 eV. Again, as with the uncoated diamond, the D parameter indicates the C at the surface is primarily bonded in the sp2 hybridization or graphitic.

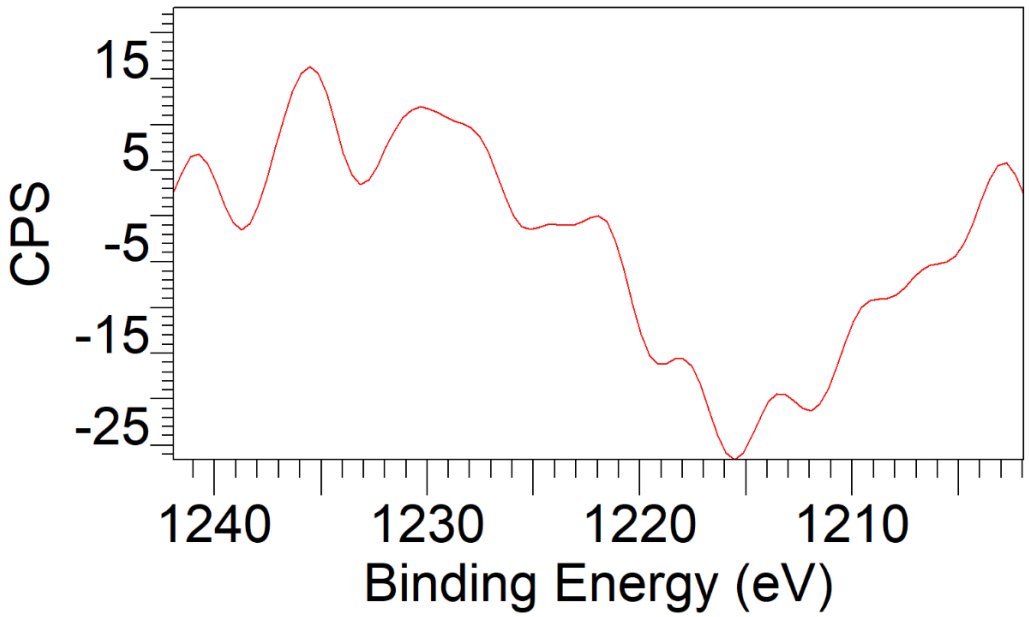

Fig. 6 First derivative of the high-resolution XPS of the coated diamond C KLL Auger peak, separation (D parameter) between the minimum (1215.5 eV) and the maximum (1235 eV), is 19.5 eV

In Fig. 7, the higher-resolution XPS of the Si 2p for a PECVD-coated diamond sample is shown. The peak is deconvoluted with fits showing the Si 2p 1/2 spin and Si 2p 3/2 spin. The area of the 3/2 spin state is fixed at two times that of the 1/2 spin state. The full width at half maximum of the peaks is given a fixed relationship of equality; the fitting yields a value of 2.09 eV. The offset between the spin state peaks was also fixed at a value of 0.69 eV. The Si 2p 1/2 position was 104.45 eV and the Si 2p 3/2 was 103.76 eV, and the overall peak position was 103.94 eV. This indicates that the Si in the film is in a +2 bonding state corresponding to the chemical state of SiO_2.

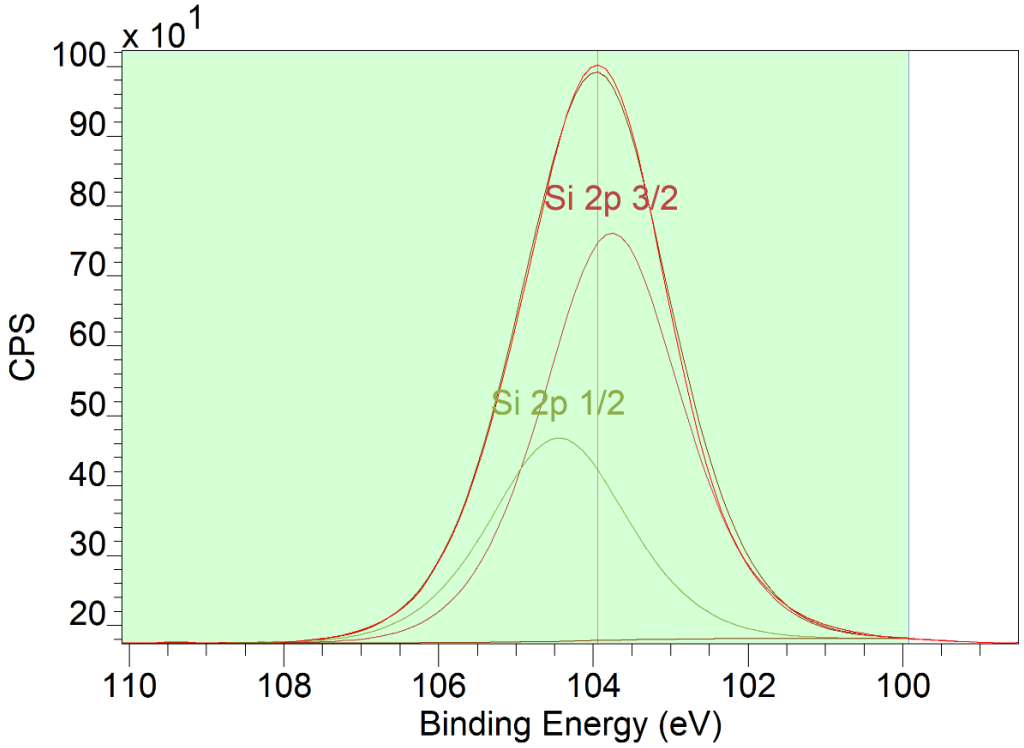

Fig. 7 High-resolution XPS of the Si 2p peaks of the coated diamond

In Fig. 8, the high-resolution XPS of the O 1s peak for the as-received diamond is shown. The peak is fitted with a single peak, which is centered at 531.5 eV. Binding energies in this range are attributed to O-C bonds, in agreement with the C 1s data in Fig. 3.

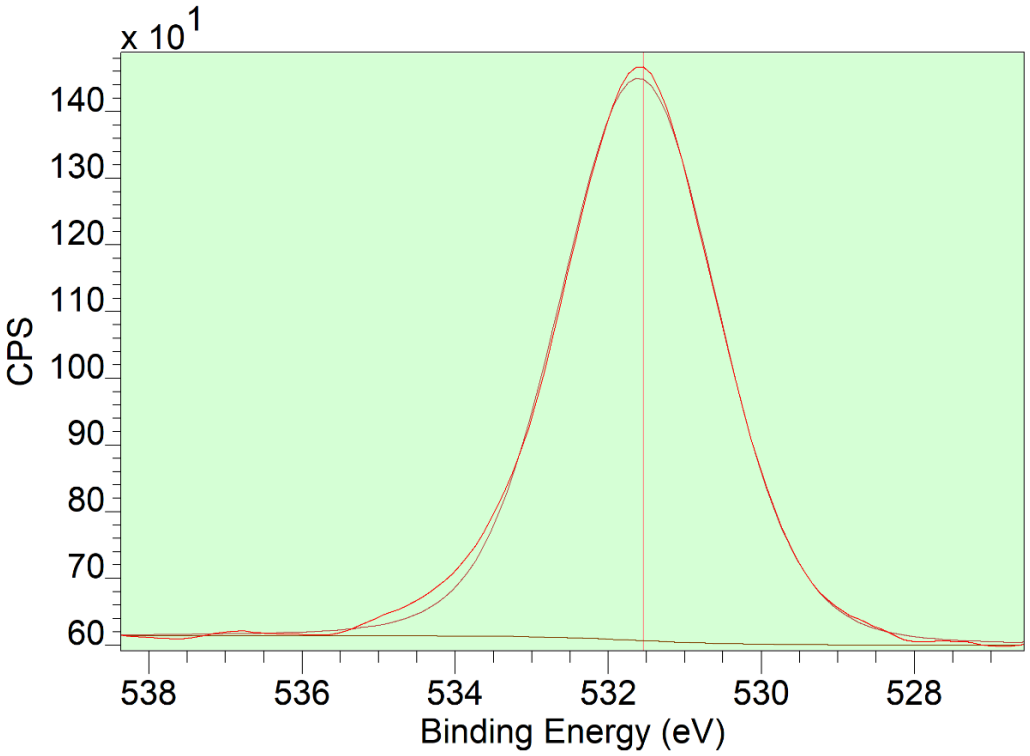

Fig. 8 High-resolution XPS of the O 1s peak of the as-received diamond

In Fig. 9, the high-resolution XPS of the O 1s peak in coated diamond is shown. The y-axis is in count per second (CPS). The peak fit yields a binding energy position of 533.1 eV. This is very close to the expected binding energy for O in SiO_2 of 532.9 eV and is in agreement with the data from the high-resolutions XPS for the Si 2p peak in Fig. 7.

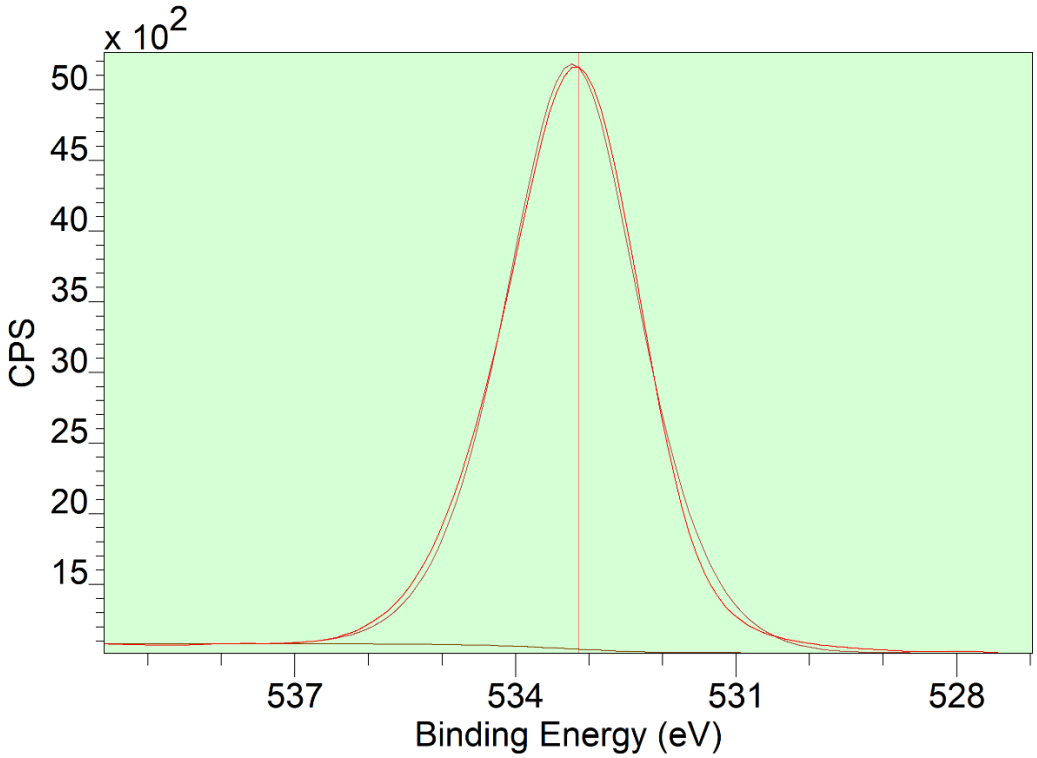

Fig. 9 High-resolution XPS of the O 1s peak of the coated diamond

In Fig. 10, using the high-resolution XPS scans of the C 1s, Si 2p, and O 1s, the composition of the SiO_2 film was determined. The Si was found to be 38.86 at%, the O was 63.59 at%, and the C was 1.56 at%. From the ratios of the input O_2 and HMDSO, the O-to-C ratio was 96:1. From Fig. 10, the total deposition thickness of 160 nm over 10 min yields a deposition rate of 16 nm per minute.

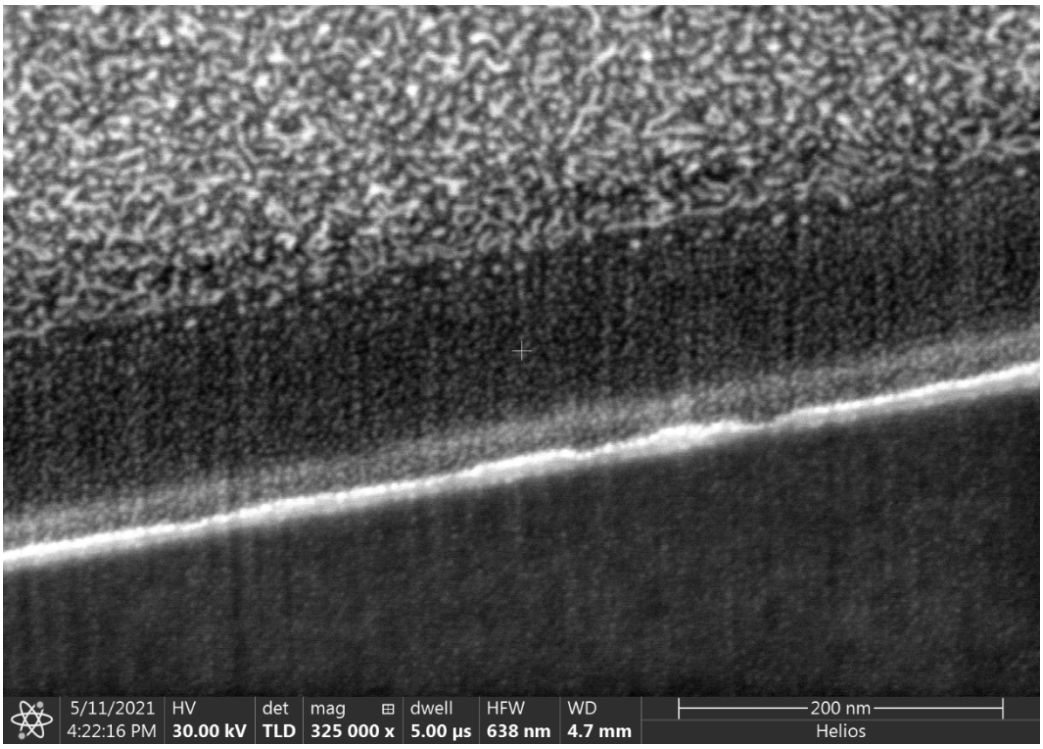

Fig. 10 Focus ion beam–prepared cross section cut out from a coated diamond particle. Platinum layer at the top and diamond at the bottom, with the middle layer being the PECVD coating and a thickness of approximately 160 nm.

Film chemistries other than pure SiO_2 were explored by varying the O-to-C ratio during the deposition on a Si wafer. In Fig. 11 an XPS sputter depth profile of one of these chemistries is shown for a film with a 6:1 O-to-C ratio. The stoichiometry of this film was found to be $SiO_{1.69}C_{0.68}$. This composition was determined from high-resolution XPS of the C 1s, O 1s, and Si 2p peaks (not shown). The atomic composition was determined to be C 20.70, O 49.92, and Si 29.38 at%.

During the sputtering, in Fig. 11, an argon ion beam is used to incrementally sputter away, or remove, the film. The ion beam was set with an accelerating voltage of 4 kV and an ion current of 5 mA. The film was sputtered for 1 min after which XPS spectra of the Si 2p were taken (Fig. 11). Each sputtering step removed approximately 14 nm of the film. The peak on the left, located at approximately 102 eV, corresponds to the deposited SiC film. The peak position of approximately 102 eV indicates the Si is in an organic bonding state with C; this is expected given the significant C concentration found in the 6:1 ratio films. Through the thickness of the film, the peak remains very stable in position and amplitude, indicating that film is uniform through the thickness in both composition and bonding state. Once the film is sputtering completely away, the Si 2p peak shows a large shift in binding

energy. The shift to the right with a binding energy of 99.2 eV indicates the Si is in a metallic state, as is expected for the Si wafer.

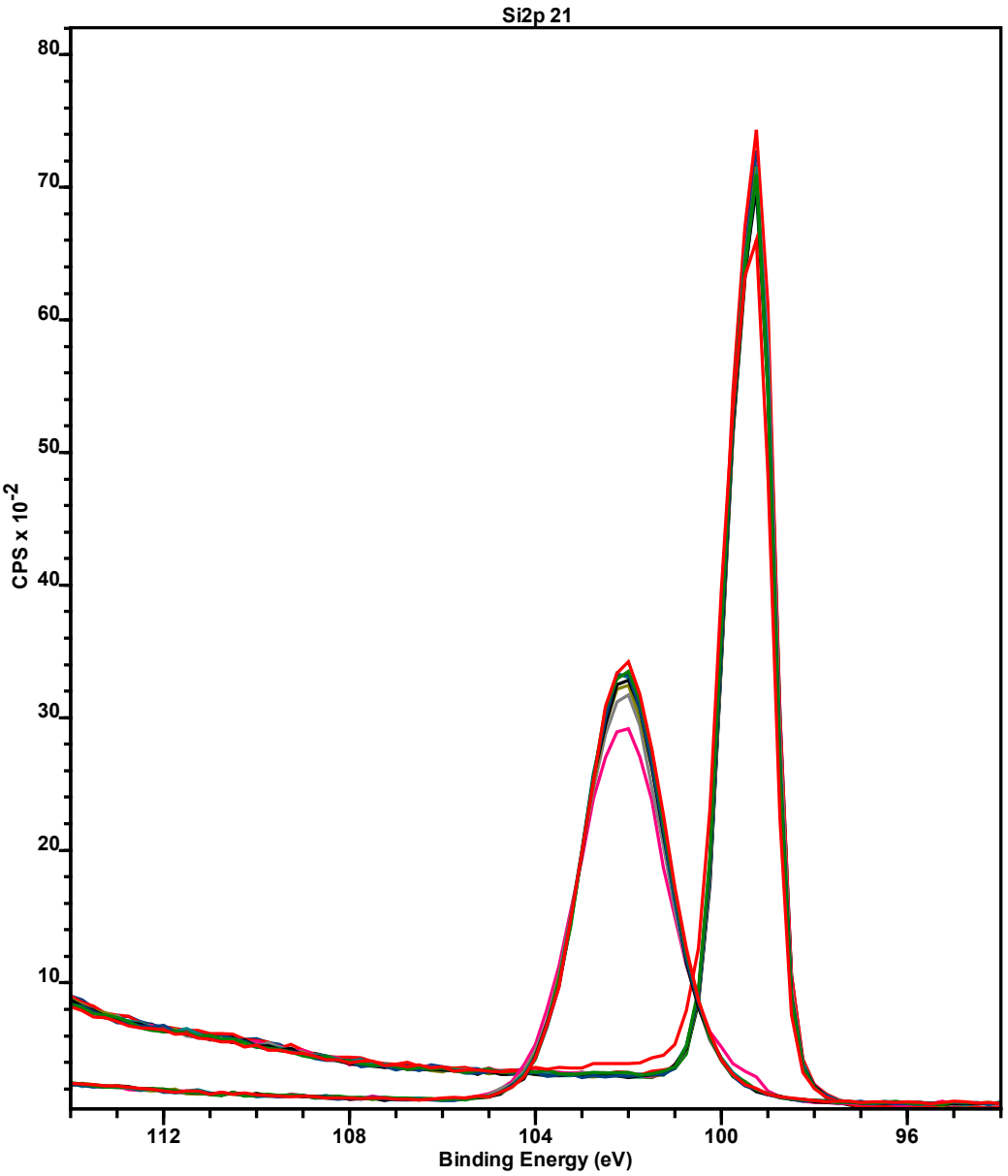

Fig. 11 An XPS depth profile of a PECVD $SiO_{1.69}C_{0.68}$ film on an Si wafer

4. Conclusion

A method to coat diamond powders with a conformal SiO_2 coating was developed. A box-style vacuum chamber, pumped by a 1000-L/min turbo pump and backed by a multi-stage lobe pumping, was utilized for the depositions. This system underwent several modifications to accomplish the depositions. A downward-facing, 8-inch-diameter electrode was installed. A fluidized bed system was

installed on a vacuum chamber to permit mixing and hence uniform coating of the diamond powders. Finally, a liquid-vapor precursor source was built, installed, and tested on the system using HMDSO as a source material. Control of the film composition and chemistry was demonstrated using XPS and correlated with the ratios of O to C in the input gases. A ratio of 96:1 (O:C) produced very pure SiO_2 films, whereas a ratio of 6:1 produced $SiO_{1.69}C_{0.68}$.

This method may be utilized to enable next-generation hard armor composites.

5. Reference

1. Mezzi A, Kaciulis S. Surface investigation of carbon films: from diamond to graphite. Surf Interface Anal. 2010;42:1082–1084. https://doi.org/10.1002/sia.3348.

List of Symbols, Abbreviations, and Acronyms

C	carbon
CPS	count per second
H	hydrogen
HMDSO	hexamethyldisiloxane
O	oxygen
PECVD	plasma-enhanced chemical vapor deposition
SEM	scanning electron microscopy
Si	silicon
SiC	silicon carbide
SiO_2	silicon dioxide
UHV	ultra-high vacuum
XPS	X-ray photoelectron spectroscopy

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