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Band offsets of epitaxial cubic boron nitride deposited on polycrystalline diamond via plasma-enhanced chemical vapor deposition

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Cubic boron nitride (c-BN) has been deposited on nitrogen-doped polycrystalline diamond films via plasma-enhanced chemical vapor deposition employing fluorine chemistry. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were utilized to characterize the c-BN/diamond interface. TEM observations indicated local epitaxy of c-BN on diamond, while h-BN was also observed at the interface. XPS measurements indicated that c-BN growth continued after nucleation. The band offsets between c-BN and diamond were deduced from XPS measurements. The c-BN valence band maximum (VBM) was 0.8 ± 0.1 eV above the diamond VBM, which corresponded to the c-BN conduction band minimum (CBM) of 1.7 ± 0.1 eV above the diamond CBM. Comparison with offsets predicted by theoretical calculations suggests that a C-N interface was obtained. *Published by AIP Publishing.* https://doi.org/10.1063/1.5009089

Cubic boron nitride (c-BN) is similar to diamond, with sp^3 hybridized bonds, a lattice constant of 3.615 Å,[1] giving a 1.36% lattice mismatch with diamond,[2] a large thermal conductivity of 13 W/cm K,[3] and a large bandgap reported to range from 6.1 to 6.4 eV.[4] As with diamond,[5,6] *p*-type doping and *n*-type doping of c-BN have been reported using Be and Si impurities, respectively.[7,8] The large bandgap yields a breakdown field reported to be 8 MV/cm,[9] which would enable c-BN based devices to block larger voltages compared to devices with GaN ($E_g = 3.4$ eV[10]) or 4H-SiC ($E_g = 3.3$ eV[10]). The large thermal conductivity of c-BN would allow for more effective cooling solutions to be engineered compared to GaN ($k = 1.3$ W/cm K) and 4H-SiC ($k = 4.5$ W/cm K).[10]

The high thermal conductivity and compatibility with GaN may attract interest for combining c-BN with GaN-based devices. The large bandgap and high thermal conductivity of c-BN make it an attractive candidate for applications with power electronic devices. While large single crystals of c-BN are not routinely available, there have been recent reports of relatively large diamond substrates (10 mm × 10 mm),[11] and epitaxy between c-BN and diamond has been reported.[12] Epitaxy would enable c-BN/diamond heterostructures which may be suitable for electronic or optoelectronic applications, but these will depend on the band alignment at the c-BN/diamond interface.

Epitaxial growth of c-BN has been reported on single crystal diamond via physical vapor deposition (PVD)[12,13] and on polycrystalline diamond via plasma-enhanced chemical vapor deposition (PECVD) employing fluorine chemistry.[14] In the study that reported epitaxy via PECVD,[14] local epitaxy of c-BN was observed by transmission electron microscopy (TEM), while sp^2 BN was reported to have formed at several areas of the interface. The fraction of sp^2 BN content and the band offsets were not reported.

Several theoretical studies have investigated the band offsets of (110) and (100) c-BN/diamond interfaces.[15,16] For the (110) interface, the diamond valence-band maximum (VBM) was reported to be positioned above the c-BN VBM by ≥1 eV. For (100) orientation, interfaces with C-B or C-N bonding were reported to result in different band offsets.[17] Analysis indicated that the C-N interface would result in the c-BN VBM being positioned ∼0.1 eV above the diamond VBM, and the C-B interface would result in the diamond VBM being ∼2.0 eV above the c-BN VBM.

An alternative interface alignment model was proposed by Tejedor and Flores.[18] The charge neutrality level (CNL) model postulates that the CNL is the point of alignment facilitated by charge transfer at the interface. The CNL is the energy of a state in the gap of a material that has equal contributions from donor-like and acceptor-like states. The reported CNL of c-BN is ∼3.9 eV above the VBM,[19,20] and the CNL of diamond is 1.4 eV above the VBM.[21] Thus, the CNL model would predict the diamond VBM to be positioned 2.5 eV above the c-BN CBM, with the diamond CBM at 1.6 eV above the c-BN VBM. The goal of the present study is to deduce the band offsets using *in situ* x-ray photoelectron spectroscopy (XPS) measurements and infer possible bonding configurations through comparison with theoretical studies and the CNL model.

In this study, c-BN films were deposited via PECVD employing F chemistry on N-doped polycrystalline diamond.[22] *In situ* XPS was utilized to characterize the c-BN films and determine the band offsets at the c-BN/diamond interface. Cross-sectional TEM was used *ex situ* to confirm epitaxy and to establish the epitaxial relationship between the deposited c-BN and the diamond substrate.

Cubic BN films were deposited on ∼1-μm-thick N-doped polycrystalline diamond films. A bias of −60 V was applied to the substrate during deposition, which was performed with a microwave power of 1.4 kW for 10 min, 30 min, and

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105 min for different samples. *In situ* XPS measurements were performed after each deposition. The binding energies of the core level peaks and the VBM were measured for the plasma-cleaned diamond substrates and the c-BN films, and the band offsets were deduced. XPS was also used to identify the presence of sp^2 bonded BN. The fraction of h-BN and c-BN was estimated using the measured π-plasmon: B *1s* intensity ratio, as described in the supplementary material. The c-BN fractions of films deposited for 10, 30, and 105 min were estimated be $39\% \pm 13\%$, $89\% \pm 2\%$, and $\sim 100\% \pm 2\%$, respectively.

Samples suitable for the TEM study were prepared using an FEI Nova 200 dual-beam focused-ion-beam system, and observations were performed using an FEI Titan 80–300 aberration-corrected TEM operated at 300 keV. A cross-sectional image of a BN film deposited for 30 min is shown in Fig. 1(a). The (111) planes of the polycrystalline diamond layer are clearly evident. The image also shows BN sp^2 basal planes, indicating the presence of h-BN, and (111) planes of c-BN are visible at the interface with diamond, parallel to the (111) diamond planes. Fourier analysis of selected diamond and c-BN regions, shown in Fig. 1(b), indicates that both regions had the same crystal structure, confirming the epitaxy of c-BN on the diamond substrate. The BN film thickness was measured to be $\sim$13 nm, giving a growth rate of $\sim$4.3 Å/min.

Based on the cross-sectional TEM observations and Fourier analysis, local epitaxial growth of (100) c-BN on (100) diamond was evident. The intensity of the π-plasmon in the B *1s* spectra decreased as the deposition continued, suggesting that growth of c-BN dominated h-BN growth. The h-BN content was estimated from the π-plasmon: the B 1s intensity ratio was calibrated using an h-BN surface and a c-BN surface. The BN film was determined from TEM to be $\sim$4.3 nm thick after 10 min of deposition. The fraction of h-BN present in the film after 10 min was estimated to be $68\% \pm 13\%$, corresponding to an h-BN layer thickness of $\sim$2.6 nm. This is consistent with the TEM measurements, which indicated a non-uniform h-BN layer of thickness $\sim$2–3 nm at the interface. The presence of h-BN at the interface was consistent with a previous report of c-BN growth on polycrystalline diamond.[14]

The method of Waldrop, Grant, and Kraut[23] was used to deduce the valence-band offsets (VBOs). This approach requires determination of the difference between the core level and VBM ($E_{CL} - E_{VBM}$) for each material and the relative core level positions of each material at the interface. The difference between the C 1s core level binding energy and the diamond VBM position was determined from the XPS spectra of plasma-cleaned diamond, shown in Fig. 2(a). The C 1s core level was positioned at 285.7 ± 0.1 eV, while the VBM was positioned at 2.4 ± 0.1 eV below the Fermi level, and $E_{CL} - E_{VBM} = 283.3 \pm 0.1$ eV. The XPS scans of the 105 min deposited c-BN, shown in Fig. 2(c), were used to determine $E_{CL} - E_{VBM}$ for the N *1s* and the B *1s* core levels. For c-BN deposited for 105 min, the N *1s* and B *1s* core levels were positioned at 398.8 ± 0.1 eV and 191.0 ± 0.1 eV, respectively. From the XPS scan, the c-BN VBM was positioned 2.0 ± 0.1 eV below the Fermi level. A UPS scan performed after deposition for 105 min is shown in the supplementary material. The VBM (determined from linear fitting) was positioned at 1.9 ± 0.05 eV below the Fermi level. The UPS and XPS measurements indicate the difference between the N *1s* and B *1s*, and the VBM ($E_{CL} - E_{VBM}$) is 396.8 ± 0.1 eV or 189.0 ± 0.1 eV, respectively.

The VBO at the interface was deduced by subtracting $E_{CL} - E_{VBM}$ of each material from the measured positions of the C 1s, N 1s, and B 1s core levels from the XPS spectra of a c-BN film deposited for 30 min [Fig. 2(b)]. For the c-BN/diamond structure, the C *1s*, N *1s*, and B *1s* core levels were positioned at 285.8 ± 0.1 eV, 398.5 ± 0.1 eV, and 190.7 ± 0.1 eV,

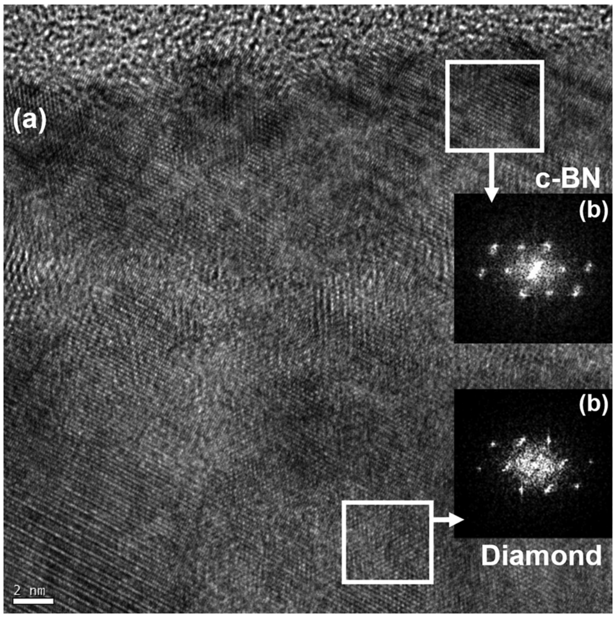

FIG. 1. (a) Cross-sectional TEM image of c-BN deposited for 30 min on polycrystalline diamond. (b) Fourier analyses of the diamond and c-BN regions are shown separately and confirm the epitaxy of c-BN on diamond.

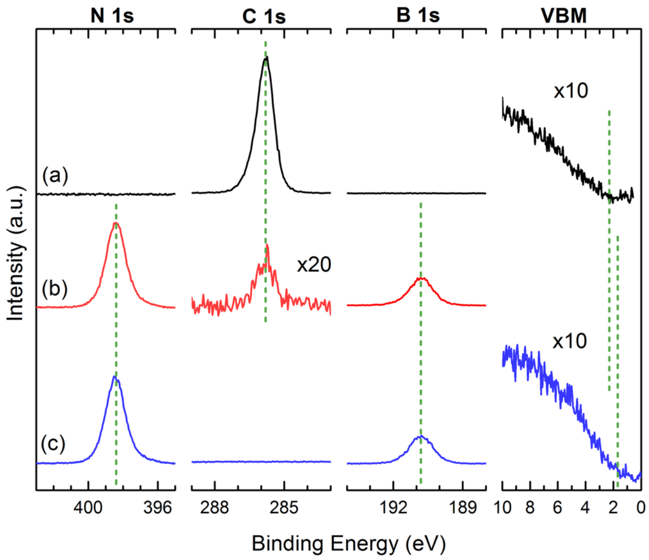

FIG. 2. The N 1s, C1s, B 1s, and valence-band maximum (VBM) XPS spectra of: (a) H_2 plasma-cleaned diamond; (b) c-BN after 30 min of deposition; and (c) c-BN after 1 h 45 min of deposition. Some spectra are scaled as indicated. The core level peaks and VBM in (a) and (c) are shifted to align with the positions of the core levels with (b). The dashed lines mark the core level alignment and the positions of the respective VBM.

respectively. The diamond VBM was deduced to be 2.5 ± 0.1 eV below the Fermi level. Using both the N and B 1s core level positions, the c-BN VBM was deduced to be 1.7 ± 0.1 eV below the Fermi level. The band offset schematic, shown in Fig. 3, shows the c-BN VBM positioned 0.8 ± 0.1 eV above the diamond VBM and the c-BN CBM at 1.7 ± 0.1 eV above the diamond CBM. The bandgap of c-BN was assumed to be 6.4 eV.

For a different film also deposited for 30 min, the C *1s*, N *1s*, and B *1s* core levels were 285.4 ± 0.1 eV, 398.0 ± 0.1 eV, and 190.3 ± 0.1 eV, respectively. Using the B *1s* core level to determine the VBO indicated the c-BN VBM to be positioned 0.8 ± 0.1 eV above the diamond VBM. Thus, the c-BN CBM was also positioned at 1.7 ± 0.1 eV above the diamond CBM. Alternatively, the VBO determined using the N *1s* core level indicated that the c-BN VBM was positioned 0.9 ± 0.1 eV above the diamond VBM, with the c-BN CBM at 1.8 ± 0.1 eV above the diamond CBM. The similarity of these two measurements with different samples and likely different amounts of h-BN suggests that the diamond/c-BN epitaxial interface is largely responsible for determining the band offset.

The band offsets determined by XPS were compared with the reported theoretical band offsets. The c-BN VBM was deduced to be 0.8 eV above the diamond VBM. In contrast, theoretical calculations for the (110) interface indicated the c-BN VBM to be positioned at least 1 eV below the diamond VBM.[15,16] The calculated band offsets of a C-B (100) interface also reported the c-BN VBM positioned ∼2 eV below the diamond VBM.[17] However, for the C-N (100) interface, the calculation indicated that the c-BN VBM was positioned 0.1 eV below the diamond VBM and the c-BN CBM was 0.8 eV above the diamond CBM.[17]

The CNL model, based on the CNL values for c-BN and diamond,[19,20] predicts the VBM of diamond 2.5 eV above the VBM of c-BN. However, the CNL model does not agree with the modelled (100) C-N interface nor the band offsets deduced from XPS. This disagreement suggests that the CNL model does not consider the interface composition/polarity, especially since the model predicts one VBO where different VBOs are expected for the different bonding. The inability to reconcile the interface polarity does not inherently exclude the possibility of charge transfer at the interface.

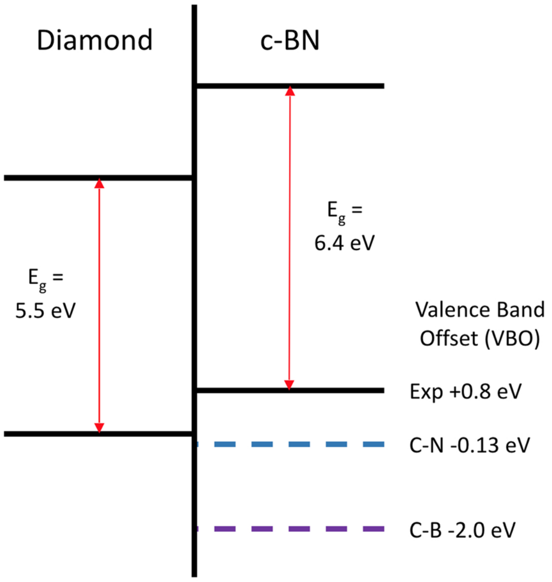

FIG. 3. Experimental band offsets between diamond and c-BN (Exp: solid black) deduced from XPS measurements of c-BN (30 min. deposition) on diamond. The colored dashed lines indicate the theoretical VBO for a C-N or C-B bonded (001) interface (Ref. 17).

While the experimental band alignment differs substantially from the theoretical results, the comparison could suggest that C-N bonding may occur for the ECR plasma-deposited c-BN on n-type diamond. The formation of a C-N interface differs from the results obtained in a TEM study by Chen *et al.*[24] where a C-B (111) interface was deduced for heterostructures prepared by high-pressure, high-temperature synthesis. This difference may be dependent on the growth method. A theoretical study modeling MBE growth of c-BN on diamond indicated that an initial B layer on diamond would be stable, whereas a N layer on the diamond surface tended to result in desorption of N ad-dimers.[25] For ECR plasma CVD of c-BN, it was proposed that N surface sites are terminated by H during deposition.[26] The H-termination could stabilize the deposited N layer against desorption, which could enable a stable C-N interface for growth of c-BN. Because of the theoretical and experimental uncertainties, high resolution microscopy of c-BN on single crystal diamond substrates should be performed to confirm the interface structure.

In summary, epitaxial growth of c-BN was achieved on polycrystalline diamond. XPS and TEM results indicated that h-BN regions formed at the interface, but c-BN growth dominated after growth of several nanometers. The band offsets were determined from XPS and indicated that the CBM and VBM of c-BN were positioned above the CBM and VBM of diamond, respectively. Comparison with theoretical models suggested the formation of a c-BN-diamond interface with C-N bonding. Further study of the band offsets focusing on epitaxial c-BN on (100) and (111) single crystal diamond would provide insight into c-BN/diamond heterojunctions for electronic applications.

See supplementary material for details on the c-BN film growth, the XPS measurements of the c-BN fraction, and the c-BN UPS scan with fitting for the valence band maximum.

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