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Cleaning of pyrolytic hexagonal boron nitride surfaces

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Hexagonal boron nitride (h-BN) has recently garnered significant interest as a substrate and dielectric for two-dimensional materials and devices based on graphene or transition metal dichalcogenides such as molybdenum disulfide (MoS_2). As substrate surface impurities and defects can negatively impact the structure and properties of two-dimensional materials, h-BN surface preparation and cleaning are a critical consideration. In this regard, we have utilized X-ray photoelectron spectroscopy to investigate the influence of several *ex situ* wet chemical and *in situ* thermal desorption cleaning procedures on pyrolytic h-BN surfaces. Of the various wet chemistries investigated, a 10:1 buffered HF solution was found to produce surfaces with the lowest amount of oxygen and carbon contamination. Ultraviolet/ozone oxidation was found to be the most effective *ex situ* treatment for reducing carbon contamination. Annealing at 1050 °C in vacuum or 10^{-5} Torr NH₃ was found to further reduce oxygen and carbon contamination to the XPS detection limits. Copyright © 2015 John Wiley & Sons, Ltd.

Keywords: boron nitride; surface cleaning; XPS; 2D materials; h-BN

Introduction

Boron nitride (BN) is a synthesized III-V compound material that exhibits a variety of different sp²-bonded and sp³-bonded phases and microstructures.^[1-4] Because of a unique combination of extreme properties such as a high melting point,^[5] high elastic modulus,^[6–8] high thermal conductivity,^[9,10] low thermal expansion coefficient,^[11] low dielectric constant,^[12,13] wide bandgap,^[14] n-type and p-type dopability,^[15,16] negative electron affinity (NEA),^[17] and high neutron capture cross section,^[18] BN is of interest for numerous thermal,^[19] mechanical,^[20] optical,^[5,21] electrical,^[5,22,23] and nuclear^[24] applications as either a ceramic, a semiconductor, or a substrate. Recently, sp²-bonded hexagonal BN (h-BN)^[25-27] and its two-dimensional (2D) analog boronitrene^[28] have garnered significant interest as a potential substrate, [29-31] epitaxial gate dielectric,^[32–34] or tunnel barrier^[35,36] in graphene channel field effect transistor^[37,38] or spintronic devices^[39] due to the excellent lattice matching between these two materials (<2% mismatch).^[40] The excellent atomic planarity of h-BN has also made it of interest as a substrate for other 2D materials including transition metal dichalcogenides (TMDs) such as molybdenum and tungsten disulfide (MoS₂ and WS₂).^[41,42]

As the properties of 2D materials have been shown to be sensitive to the substrate,^[43–46] surface defects,^[47–50] and impurities,^[50–53] graphene, TMD, and h-BN surface cleaning and preparation procedures are critically needed.^[54–59] However, relatively few investigations of h-BN surface cleaning have been reported, and most of these have focused on pure thermal annealing/desorption procedures.^[60–64] Surface cleaning is also critically important to electron-emitting devices based on the NEA exhibited by various BN surfaces.^[17,65] Studies by various authors have shown that the presence of a NEA for a BN surface can be sensitive to both *ex situ* and *in situ* thermal processing.^[64,65]

In this regard, we have utilized X-ray photoelectron spectroscopy to investigate the influence of a variety of *ex situ* wet chemical and *in situ* thermal desorption cleaning procedures on the surface contaminants present on pyrolytic BN (PBN) substrates.^[66–68] PBN is commonly produced by high-temperature, low-pressure chemical vapor deposition.^[69,70] Depending on the exact process conditions, PBN typically consists of highly oriented microcrystal-line h-BN with some amorphous sp² BN also potentially present.^[64–70] PBN is commonly utilized as a nonporous, high-temperature ceramic crucible, or electrical insulator.^[19] Thus, the described surface cleaning study has implications to the use of h-BN both as a substrate for 2D semiconductor applications and other electronic and structural ceramic applications.

Experimental

The 1-in diameter PBN substrates utilized in this study were supplied by General Electric (Fairfield, CT, USA) and utilized as received. Complementary metal-oxide semiconductor grade acids and bases and high resistivity (~18.4 M Ω) de-ionized (DI) water were used in all *ex situ* wet chemical cleaning processes. The wet chemical cleans investigated included various mixtures of acids and bases commonly utilized in surface cleaning and etching of III–V nitride compounds such as 38% HCl, 49% HF, 56% NH₄OH, 30% H₂O₂, 85% H₃PO₄, and 50% NaOH (concentrations are in weight percent).^[71,72]

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Unless otherwise noted, the PBN substrates were rinsed in DI water and blown dry with N₂ after all wet chemical processes. Ultraviolet (UV)/ozone cleaning was additionally performed on some samples using a high-intensity Hg lamp positioned ~1 cm from the BN substrate. To increase the concentration of ozone (O₃) generated, the UV/ozone box was purged with 1-l/s O₂ during the UV exposure.^[73] After wet chemical or UV/ozone cleaning, the samples were subsequently mounted on a molybdenum sample holder and loaded into a vacuum load lock for transfer into the XPS system through an ultrahigh vacuum (UHV) linear transfer system.

In situ thermal desorption cleaning was performed using a custom-built gas source molecular beam epitaxy (GSMBE) system specifically designed for SiC surface cleaning^[74,75] and heteroepitaxial growth of III–V nitrides (AIN, GaN, and SCN).^[76–78] Briefly, the GSMBE system was mounted to the same UHV linear transfer line and was equipped with NH₃ (99.9995%) that was further purified via an inline metalorganic resin purifier connected directly to a leak valve mounted on the GSMBE chamber. A base pressure of 10^{-10} Torr was achieved in the GSMBE system via a 400-l/s turbo pump and a 500-l/s ion pump. Substrate temperatures of 1100 °C were achieved via a hot tungsten filament heater.^[79,80]

The XPS system and measurements have been previously described.^[76,81] Briefly, all XPS spectra were collected using Al Ka radiation (hv = 1484.6 eV) in a 2 × 10⁻¹⁰ Torr UHV system equipped with a 100-mm radius hemispherical electron energy analyzer (VACGEN CLAMII, Castleham Industrial Estate, St Leonards-on-Sea, East Sussex, United Kingdom). Calibration of the binding energy scale for all scans was achieved by periodically taking scans of the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks from standards and correcting for any discrepancies with the known values (83.98 and 932.67 eV, respectively).^[82] A combined Gaussian-Lorentzian curve shape with a linear background was found to best represent the XPS data. Sample charging (which was significant) was accounted for by aligning the B 1 s core level to 189.7 eV based on prior measurements by Preobrajenski^[83] of monolayer h-BN on Rh surfaces where sample charging was likely minimal. The XPS spectra were charge corrected using the B 1s core level as opposed to the common practice of aligning the C 1s core level to 284.8 eV in order to observe relative changes in the chemical state of residual carbon contamination post ex situ and in situ cleaning.

The relative concentration of B, N, O, C, and other contaminants for the PBN surfaces exposed to various *ex situ* and *in situ* cleans was estimated using a homogeneous model. Specifically, the integrated intensity of each peak was corrected for sensitivity differences using published calibration factors, and the concentration for each element was estimated as the peak intensity divided by the sum of peak intensities for all elements.^[81] However, as O, C, and other surface contaminants are not homogeneously distributed within the BN substrate, the presented surface concentrations should be taken only as an evaluation of relative changes in chemical composition with the various surface cleaning procedures.

Results and discussion

Figures 1–4 display representative XPS spectra of the B 1 s, N 1 s, O 1 s, and C 1 s core levels, respectively, acquired from the surfaces of the as-received PBN and after wet chemical and UV/ozone cleaning. As shown in Fig. 1, the various wet chemical treatments investigated (1:1 NH₄OH:H₂O₂, 1:1 HCI:DI, and 1:10 HF:DI) had relatively little impact on the intensity or shape of the B 1 s core level with all spectra being well fitted using a single mixed Gaussian–



Figure 1. XPS spectra of B 1 s core level from pyrolytic boron nitride (a) as-received and after (b) $1:1 \text{ NH}_4\text{OH}:H_2O_{2r}$ (c) 1:1 HCI: de-ionized H_2O , (d) 1:10 HF: de-ionized H_2O , and (e) ultraviolet/ozone surface treatments.



Figure 2. XPS spectra of N 1 s core level from pyrolytic boron nitride (a) as-received and after (b) $1:1 \text{ NH}_4\text{OH}:H_2O_{2r}$ (c) 1:1 HCI: de-ionized H_2O , (d) 1:10 HF: de-ionized H_2O , and (e) ultraviolet/ozone surface treatments.



Figure 3. XPS spectra of O 1 s core level from pyrolytic boron nitride (a) as-received and after (b) $1:1 \text{ NH}_4\text{OH}:H_2\text{O}_2$, (c) 1:1 HCI: de-ionized $H_2\text{O}$, (d) 1:10 HF: de-ionized $H_2\text{O}$, and (e) ultraviolet/ozone surface treatments.



Figure 4. XPS spectra of C 1 s core level from pyrolytic boron nitride (a) as-received and after (b) $1:1 \text{ NH}_4\text{OH}:H_2O_2$, (c) 1:1 HCI: de-ionized H_2O , (d) 1:10 HF: de-ionized H_2O , and (e) ultraviolet/ozone surface treatments.

Lorentzian line shape with a full width half maximum (FWHM) of ~1.6 eV. However, fitting of the B 1 s core level for the UV/ozone-treated PBN surface required the addition of a small higher binding energy peak at ~191.6 eV that is attributed to the formation of some surface boron oxide species.^[84,85] The N 1 s core level (Fig. 2) similarly showed relatively little variation in intensity with the various surface treatments and was also reasonably well fitted using a single peak with an FWHM of ~1.6 eV. Some variation in the position of the N 1 s core level (by up to 0.1–0.2 eV) was observed and attributed to variation in the significant charge buildup during the XPS measurements.

More significant changes due to the *ex situ* surface treatments were observed in the XPS spectra for the O 1 s and C 1 s core levels. For the as-received PBN surface, relatively low levels of O contamination were observed (Fig. 3a). The intensity of the oxygen contamination was reduced with increasing efficiency, respectively, by the 1:1 HCI:DI, 1:1 NH₄OH:H₂O₂, and 1:10 HF:DI treatments (Fig. 4b–d). However, the oxygen contamination was significantly increased by the UV/ozone treatment (Fig. 3d). For the latter, the O 1 s core level was located at 532 eV with an FWHM of 2.2 eV. This is consistent with the binding energy for O–B bonding and the second B 1 s core level observed at 191.6 eV for the same surface that was previously attributed to B–O species.^[85,86]

In contrast, significant carbon contamination was observed for the as-received PBN surface. As shown in Fig. 4, the position of the C 1 s was located at 284.0-284.2 eV (FWHM = 1.8-1.9 eV) for all surfaces. This is consistent with general ambient hydrocarbon contamination.^[71] As for oxygen contamination, the carbon contamination was reduced with increasing efficiency, respectively, by the 1:1 HCI:DI, 1:1 NH₄OH:H₂O₂, and 1:10 HF:DI treatments (Fig. 3b-d). While the 1:10 HF:DI treatment produced the lowest carbon contamination of the three, in some cases, a higher binding energy peak at 286 eV was observed that could be attributed to the presence of some C-O surface species.^[71,75] In contrast, the UV/ozone treatment dramatically reduced the carbon contamination to almost below the detection limit of XPS. The latter result is consistent with prior surface cleaning investigations of III-N surfaces where the UV/ozone treatment was observed to reduce surface carbon contamination via oxidation mechanisms but also grew a group III surface oxide.[71,72]

In addition to oxygen and carbon, additional surface contamination species were observed. Specifically, some fluorine contamination



Figure 5. XPS spectrum of F 1 s core level from pyrolytic boron nitride after 1 :10 HF : de-ionized H_2O treatment.

was observed for 1:10 HF:DI-treated surfaces (Fig. 5), and some phosphorous contamination was observed for PBN surfaces etched in concentrated H₃PO₄ (not shown). It is important to also note that other possible contamination species such as CI and Na from HCI: DI-treated and NaOH-treated surfaces were not detected within the sensitivity limits of XPS. For the observed F contamination after 1:10 HF: DI treatment, a broad (FWHM = 2.6 eV) F1 s core level peak was detected at 685.6 eV. This is consistent with prior investigations of AIN surface cleaning where some residual fluorine species were observed after treatment in a 1:10 $\rm HF:DI$ solution. $^{[71,72]}$ In that study, the F 1 s was deconvoluted into two components at 686.8 and 688.5 eV that were attributed to surface AI-F and N-F bonding. Based on these prior observations and the reported F1 s binding energy of ~686 eV for B–F bonding,^[82] the observed F 1 s peak in this study is attributed primarily to fluorine bonded to boron and some nitrogen. As the position of the N 1 s core level for N-F bonding is at higher binding energies relative to that for B-N bonding,^[82] this may also partially explain a slight shifting of the N 1 s for the 1:10 HF: DI-treated PBN surface to higher binding energies by 0.1–0.2 eV.

To judge the ability of the various wet chemical treatments to reduce surface oxides on BN surfaces, additional experiments were performed where the PBN surface was intentionally given a UV/ozone treatment followed by one of the wet chemical surface treatments. In this case, similar results to those for the as-received PBN surfaces were obtained. Table 1 provides estimates for the relative concentration of B, N, O, and C for the various PBN surfaces

Table 1. Summary of XPS composition for pyrolytic boron nitride surfaces exposed to various <i>ex situ</i> and <i>in situ</i> surface treatments					
Treatment	% B	% N	% O	% C	Other
As-received	42.8	45.8	2.7	8.8	
$1:1 \text{ NH}_4 \text{OH}: \text{H}_2 \text{O}_2$	44.9	46.8	2.2	6.1	
1:1 HCI:DI	44.8	46.4	2.5	6.3	
1:10 HF:DI	43.8	48.9	2.1	4.5	0.7% F
UV/ozone	44.4	48.7	4.9	2.0	
H ₃ PO ₄	41.5	46.9	4.5	7.0	
NaOH	38.8	35.3	11.7	13.8	<0.5% P
1050 °C UHV	47.1	51.9	≤1%	0	
1050 °C NH ₃	47.5	51.5	≤1%	0	
DI, de-ionized H_2O ; UHV, ultrahigh vacuum; UV, ultraviolet.					



investigated. As can be seen, the 1:10 HF: DI-treated PBN surfaces exhibited the lowest amount of carbon and oxygen contamination but also exhibited some fluorine contamination that presumably displaced/prevented the adsorption of additional O and C contaminants. The H_3PO_4 -treated and NaOH-treated surfaces (not shown in Figs 1–4) exhibited the highest amount of contamination, indicating that while these chemistries may be useful for etching BN, they were not particularly effective wet chemical cleans.

To gauge the effectiveness of *in situ* thermal desorption cleaning, the aforementioned wet chemically processed PBN surfaces were subjected to various vacuum anneals in the previously mentioned GSMBE. Figures 6–9 display representative spectra for the B 1 s, N 1 s, O 1 s, and C 1 s core levels, respectively, from a PBN surface cleaned in H₃PO₄ at 85 °C. As illustrated in Figs 6 and 7, relatively little changes were observed for the B 1 s and N 1 s cove levels after annealing in 10^{-10} Torr vacuum or 10^{-5} Torr NH₃ at 1050 °C for 30 min. However, both annealing treatments were observed to reduce the intensity of the oxygen and carbon contamination to the XPS detection limits (Figs 8 and 9). These thermal treatments were similarly observed to completely desorb the F and P contamination from HF and H₃PO₄ surface treatments.



Figure 6. XPS spectra of B 1 s core level from pyrolytic boron nitride after (a) H_3PO_4 etching, (b) annealing in ultrahigh vacuum at 1050 °C, and (c) annealing in 10^{-5} Torr NH₃ at 1050 °C.



Figure 7. XPS spectra of N 1 s core level from pyrolytic boron nitride after (a) H_3PO_4 etching, (b) annealing in ultrahigh vacuum at 1050 °C, and (c) annealing in 10^{-5} Torr NH₃ at 1050 °C.



Figure 8. XPS spectra of O 1 s core level from pyrolytic boron nitride after (a) H_3PO_4 etching, (b) annealing in ultrahigh vacuum at 1050 °C, and (c) annealing in 10^{-5} Torr NH₃ at 1050 °C.



Figure 9. XPS spectra of C 1 s core level from pyrolytic boron nitride after (a) H_3PO_4 etching, (b) annealing in ultrahigh vacuum at 1050 °C, and (c) annealing in 10^{-5} Torr NH₃ at 1050 °C.

The aforementioned thermal desorption cleaning results are consistent with prior reports by Chambers et al. of vacuumannealed PBN crucibles^[62] and Shrestha et al. of vacuum-annealed BN powders.^[62,63] Using an *in situ* guadrapole mass spectrometer, Chambers et al. observed the desorption of H₂O, CO, N₂, and various hydrocarbons for PBN crucibles heated in UHV at 670 °C.^[62] After baking in UHV at 1600 °C for 1 h, the H₂O and hydrocarbon guadrapole mass spectrometer signals were significantly reduced, and in situ AES similarly showed a reduction in surface carbon from 12% to 1%. Using argon vapor pressure isotherms, Shrestha et al. similarly investigated the desorption of impurities from BN powders at temperatures between 500 and 900 °C. In their case, they determined that vacuum annealing at 900 °C was not always sufficient to eliminate all surface impurities from their BN powders but that washing with methanol prior to annealing at 900 °C produced high-guality substrates. These results are reasonably consistent with our results where carbon, oxygen, and other surface contaminants were observed to be reduced below the detection limits of XPS after annealing PBN surfaces at 1050 °C.

The aforementioned results merit some discussion with respect to h-BN surface cleaning for specific applications. For 2D device applications employing graphene, h-BN, or TMDs, a particular challenge is the removal of organic contaminants introduced by the transfer of exfoliated crystals and subsequent lithographic processing steps.^[54,58,59] As discussed by Garcia *et al.*,^[60] removal of such organic residues is typically attempted via using some combination of solvent cleaning in acetone and isopropyl alcohol followed by annealing at 350–500 °C in an Ar/H₂ or Ar/O₂ ambient. While the nonsurface-sensitive Raman studies of Garcia *et al.*^[60] have shown that these procedures may be successful in removing gross organic surface contamination from h-BN surfaces, the results of this study and those by Chambers *et al.*^[61] and Shrestha *et al.*^[62] suggest that higher temperature annealing (\geq 900 °C) may be needed to fully desorb all surface contaminants and completely minimize their impact on 2D transport properties.

Surface condition is also critically important to BN NEA electronemitting devices.^[17,65] Studies by Powers et al.^[65] and Loh et al.^[17,64] have shown that the NEA exhibited by various BN surfaces is air stable and retained even after intentional surface oxidation using an O₂ plasma. However, vacuum annealing at 950–1100 °C has been observed to induce a change from a NEA to a positive electron affinity. This is roughly the temperature at which surface oxide, organic, and other contaminants have been observed to be nearly completely desorbed in this study and others. The rough correspondence suggests the possibility that the presence of one or more of these contaminants is responsible for the observed NEA. This is partly supported by additional experiments performed by Loh *et al.* that have shown that reannealing BN surfaces in H_2 at 950-1100 °C can restore the NEA state and suggests that surface or subsurface hydrogen may help promote the NEA.^[17,64] Accordingly, BN thermal desorption cleaning procedures that incorporate some source of hydrogen may be useful for preserving the NEA state while obtaining atomically clean surfaces. In this regard, annealing BN surfaces in NH₃, as demonstrated here, may be a particularly useful thermal desorption cleaning procedure. While the oxygen and carbon contamination levels were similar for UHV versus NH₃ annealing, the presence of hydrogen from NH₃ may help maintain a NEA while obtaining an atomically clean surface.

Conclusions

In conclusion, we have investigated the effectiveness of various *ex situ* and *in situ* cleaning procedures for reducing PBN surface contamination. Of the *ex situ* cleans investigated, UV/ozone oxidation was found to produce surfaces with the lowest carbon content but also the highest surface oxidation. Wet chemical treatments consisting of $1:1 \text{ NH}_4\text{OH}:H_2\text{O}_2$ and 1:1 HF:DI were found to produce BN surfaces with both reduced oxygen and carbon contamination. O, C, F, and P contaminants left over by *ex situ* treatments were reduced to the XPS detection limits by *in situ* thermal desorption at 1050 °C in either UHV or 10^{-5} Torr NH₃.

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