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Photo-induced site-specific nitridation of plasma-deposited B_{10}C_{2}H_{x} films: A new pathway toward post-deposition doping of semiconducting boron carbides

Swayambhu Behera a, Justin Wilks b, Peter A. Dowben c, M. Sky Driver d, A.N. Caruso d, Jeffry A. Kelber b,⁎

a Department of Physics and Center for Electronic Materials Processing and Integration, University of North Texas, Denton, TX, 76203, United States
b Department of Chemistry and Center for Electronic Materials Processing and Integration, University of North Texas, Denton, TX, 76203, United States
c Department of Physics and Astronomy, Nebraska Center for Nanostructures and Materials, University of Nebraska-Lincoln, Lincoln, NE 68588, United States
d Department of Physics, University of Missouri-Kansas City, Kansas City, MO 64110, United States

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We show that dopant impurities can be introduced in a controlled, site-specific manner into pre-deposited semiconducting boron carbide films. B–N bond formation has been characterized by X-ray photoelectron spectroscopy for semiconducting B_{10}C_{2}H_{x} films exposed to vacuum ultraviolet photons in the presence of NH_{3}. Core level photoemission data indicate that B—NH_{2} bonds are formed at B sites bonded to other boron atoms (B–B), and not at boron atoms adjacent to carbon atoms (B–C) or at carbon atom sites. Nitridation obeys diffusion-limited kinetics. These results indicate that dopant species can be introduced in a controlled, site-specific manner into pre-deposited boron carbide films, as opposed to currently required dopant incorporation during the deposition process.

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Semiconducting boron carbide films (B_{10}C_{2}H_{x}) – amorphous molecular solids – are of broad and increasing interest in many applications, including neutron detection [1–4], novel semiconductor devices [5–14], biomedical applications [15] and spintronic or magnetoresistance-based devices [12,14,16,17]. These applications are typically controlled or enhanced by the introduction of impurities, either as part of the B_{10}C_{2} icosahedral “cage” [11–14,17], through the use of different carborane isomers [1,4,5], or as linking units between cages, as with phosphorous [18]. Until now, such doping has required carborane precursor modification [1,4,5,13,18], or addition of dopant precursors (e.g. metalloccenes) to the gas feed during vapor deposition [11,12,14,17]. These methods do not allow for selective-area doping, as is possible with the delta doping of silicon with boron [19]. We demonstrate here that exposure of pre-deposited semiconducting B_{10}C_{2}H_{x} films to vacuum ultraviolet (VUV) light in the presence of NH_{3} (10⁻⁴ Torr) results in formation of B–N bonds specifically at B atoms bound to other boron atoms (B–B sites), and not at boron atoms adjacent to carbon atoms (B–C) or at carbon sites. No nitrogen adsorption occurs with NH_{3} exposure alone, in the absence of VUV irradiation. Thus, nitridation is selective to areas exposed to VUV, and results only in B–N bond formation at specific B sites. Further, the nitrogen incorporation obeys diffusion-limited kinetics, thus allowing control over the depth of nitrogen incorporation, as well as, in principle, the area of incorporation through the use of masks to define areas exposed to radiation. This allows the formation of in-plane, spatially well-defined doped regions of controlled depth for device fabrication.

Experiments were carried out in a combined introduction-processing and UHV analysis system described previously [20]. Briefly, core level photoelectron spectra were acquired with a 100 mm mean radius hemispherical sector electron energy analyzer operated in constant pass energy mode (50 eV), and with an unmonochromated MgKα X-ray source. The analyzer energy scale was calibrated by setting the main C 1s peak (due to adventitious carbon) at 285 eV. Gaussian–Lorentzian lineshapes were used to simulate spectra for comparison with experiment. B_{10}C_{2}H_{x} films ~1 μ thick were formed by plasma-enhanced chemical vapor deposition on oxidized Si substrates using orthorcarborane precursors, and characterized by ellipsometry and FTIR, by a procedure described previously [21]. Samples 1 cm × 1 cm were scribed from the substrate and mounted on a Ta sample holder. Sample temperature was monitored by a type K thermocouple spotwelded to the sample holder. The sample was at room temperature during all UHV exposures, and no significant temperature excursions were observed during these experiments. Prior to exposure to vacuum ultraviolet radiation in the presence of NH_{3} (VUV/NH_{3}), the films were subjected to Ar⁺ bombardment (1000 eV), which removed some adventitious carbon. The sample preparation chamber was equipped with a sealed Xe...
discharge lamp (Resonance Ltd.) emitting a flux of 8.4 eV photons estimated at $10^{15}$ cm$^{-2}$ sec$^{-1}$. Nitridation of the film was observed only in the presence of both NH$_3$ and VUV irradiation. No nitridation was observed in the absence of VUV irradiation.

The evolutions of B (1 s), C (1 s) and N (1 s) spectra as a function of VUV/NH$_3$ exposure are shown in Fig. 1. (Some O (1 s) intensity was observed, but did not change significantly during the course of these experiments, and is not shown here.) The B (1 s) spectrum before exposure (Fig. 1a-i) is well fit by two components centered at 187.8 eV and 189.4 eV, in good agreement with reported results [15,22–24] and attributed, respectively, to B–B and B–C bonding environments. A high binding energy (>191 eV) tail is attributable to B–O environments [22]. The C (1 s) spectrum (Fig. 1b-i) is similarly decomposed into components at 286.7 eV, 285 eV and 282.7 eV attributable to C–O, C–C (adventitious) and C–B (carbidic) bonding environments, respectively [15]. The boron/carbidic carbon (B/C$_{282.7}$) atomic ratio is 4.27 — determined from B/C$_{282.7}$ relative intensities normalized to atomic sensitivity factors appropriate to this analyzer [20]. This value is close to the value expected from the B$_{10}$C$_2$H$_x$ stoichiometry. The ratio of B–B to B–C intensities, however, is 2.9, reflecting a ratio of 2.9 B–B bonds for every C–B bond. A small, broad N (1 s) feature is observed prior to VUV/NH$_3$ exposure, and even without a sample (Fig. 1c-i), due to contamination of the sample holder, and is not significant.

There is nitrogen adsorption upon exposure of the semiconducting boron carbide to NH$_3$ in the presence of VUV radiation. The B (1 s) spectrum exhibits a decrease in B (1 s) intensity near the low binding energy (B–B) portion of the spectrum, and the growth of a new feature near 192 eV (Fig. 1a;ii–iv), identified as being due to B–N bonding environments [15]. The growth of the N (1 s) feature near 398.3 eV (Fig. 1c;ii–iv) is similarly identified as due to N bound to B [15]. This observed N (1 s) binding energy is substantially lower than that of cubic boron nitride — 399.1 eV, (when referenced to an adventitious C (1 s) value of 285 eV [25], and indicates that the N atom in these experiments is in a dissimilar environment to c-BN, and consistent with nitrogen incorporation at an extra-polyhedral site, e.g., as a B–NH$_2$ species. During VUV/NH$_3$ exposure, however, no change is observed in either width or intensity of the B–C component of the B (1 s) spectrum (Fig. 1a). This indicates an absence of N–B bond formation at B–C sites. The C (1 s) spectrum (Fig. 1b) exhibits a decrease in the high binding energy portion of the spectrum — opposite to what would be expected for C–N bond formation. There is no significant change in the carbidic portion of the C (1 s) spectrum, and the feature attributable to adventitious carbon (near 285 eV) exhibits a gradual but monotonic increase in intensity with VUV/NH$_3$ exposure. The data (Fig. 1b) therefore indicate that VUV/NH$_3$ exposure results in a decrease in oxidized carbon and increase in adventitious carbon components — possibly due to generation of hydrogen and reaction with background contaminants. There is, however, no significant N bond formation at C sites. In summary, the XPS data in Fig. 1 indicate that during VUV/NH$_3$ exposure, N bond formation occurs specifically at B–B sites.

The increase in nitrogen content of the B$_{10}$C$_2$H$_x$ film during the VUV exposure, as measured by N (1 s) intensity, obeys diffusion kinetics (Fig. 2). The increases in C (1 s)$_{285}$ (adventitious carbon), B (1 s)$_{191.6}$ (B–N) and N (1 s)$_{398}$ component intensities with time are linear with the square root of exposure time. The increase in adventitious carbon is very gradual, and may indicate a reaction due to low levels of contaminants in the turbomolecularly-pumped chamber. (We have noticed a similar effect in similar conditions with a SiO$_2$ substrate and no NH$_3$). The increase in N content shown in Fig. 2 indicates the diffusion of NH$_3$ or other N-containing species into the B$_{10}$C$_2$H$_x$ film, interacting with free radical sites (e.g. dangling cage bonds from photo-induced dissociation of hydrogen) created by photo-irradiation. The

Fig. 1. Evolution of (a) B (1 s), (b) C (1 s) and (c) N (1 s) XPS spectra for a B$_4$C film as a function of exposure to a flux of 8.4 eV photons in the presence of 10$^{-4}$ Torr NH$_3$ at room temperature; (i) no exposure, (ii) 30 min, (iii) 60 min, (iv) 180 min.
Fraction of photons adsorbed by reaction with NH$_3$ is only ~10$^{-5}$ from an orthocarborane parent ion (B$_{10}$C$_2$H$_{10}$) consistent with recent gas phase experimental and theoretical data did not play a detectable role in these experiments.

Nitridation. Thus, direct surface reaction of excited gas phase species directed parallel to and several inches from the plane of the sample (i.e., no direct irradiation of the surface), yielded no observable nitridation. Thus, direct surface reaction of excited gas phase species did not play a detectable role in these experiments.

The site-specific nature of the nitridation process (Fig. 1) is consistent with recent gas phase experimental and theoretical data indicating that the energetically preferred photo dissociation pathway from an orthocarborane parent ion (B$_{10}$C$_2$H$_{10}$) is the concerted loss of two hydrogen atoms at sites opposite the carbon atoms, with evolution of H$_2$. This analysis is reported elsewhere [28]. A likely mechanism is the reaction of NH$_3$ with such reactive sites ($\text{B}^\text{π}$) to yield $-$NH$_2$ groups bonded to the boron carbide cages:

$$\text{B}^\text{π} + \text{NH}_3 \rightarrow \text{B} - \text{NH}_2 + \frac{1}{2}\text{H}_2$$

resulting in B–N bond formation at boron sites opposite carbon atoms in the icosahedra. The introduction of nitrogen (probably $-$NH$_2$) species at B–B sites withdraws significant valence electron density at the B site, as indicated by the large B (1 s) binding energy shift to higher binding energies. We estimate that the charge transfer is about 1/10 of electron per boron site, from the calculated Mulliken charge densities, consistent with the core level charge energy shifts observed. A previous study, involving the use of modified precursors with bridging PH$_2$ groups between carbon atoms of adjacent icosahedra [18] resulted in a 3.5% P content, two orders-of-magnitude decrease in conductivity and significant increase in band gap. One can therefore anticipate that doping with pnictide groups using this procedure may have similarly significant effects, and that the use of certain electron-donating species may also be practical. While the diffusion kinetics of the existing process may place certain limitations on the size of the dopant species, the following of diffusion kinetics should permit accurate predictions of the depth and concentration of dopant groups as a function of time and irradiation conditions.

The incorporation of extra-polyhedral nitrogen occurs only with VUV illumination. Thus, a promising route to the practical, site-specific introduction of dopant impurities into pre-deposited B$_{10}$C$_2$H$_x$ films would be photo-irradiation in the presence of low pressures of gas phase species (e.g., NH$_3$). This method is dependent primarily on the interaction of the photons with the solid film, rather than on gas phase photon-dopant interactions, and thus spatial localization of the dopant is possible across the face of semiconducting boron carbides, much in the same way p-type doping of silicon can be spatially localized with the delta doping of silicon with boron. [19] The data in Figs. 1 and 2 therefore suggest a route towards the practical, site-specific doping of pre-patterned regions of deposited films, using hard masks and dopant depth/concentration profiles predictable on the basis of diffusion kinetics. Although XPS is obviously limited in the ability to monitor diffusion depth, there would be, in principle, no limit to the doping depth achievable, and the rate of nitrogen diffusion would presumably increase at higher temperatures.

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