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Valence band offset and Schottky barrier at amorphous boron and boron carbide interfaces with silicon and copper

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ABSTRACT

In order to understand the fundamental charge transport in a-B:H and a-BX:H (X = C, N, P) compound heterostructure devices, X-ray photoelectron spectroscopy has been utilized to determine the valence band offset and Schottky barrier present at amorphous boron compound interfaces formed with (1 0 0) Si and polished poly-crystalline Cu substrates. For interfaces formed by plasma enhanced chemical vapor deposition of a-B_{4-5}C:H on (1 0 0) Si, relatively small valence band offsets of 0.2 ± 0.2 eV were determined. For a-B:H/Cu interfaces, a more significant Schottky barrier of 0.8 ± 0.16 eV was measured. These results are in contrast to those observed for a-BN:H and BP where more significant band discontinuities (>1–2 eV) were observed for interfaces with Si and Cu.

1. Introduction

Due to extreme thermal-mechanical properties [1–3], low atomic number (Z), high neutron capture cross section [4], negative electron affinity [5], and low dielectric constant (k) [7], boron and boron compound materials are of interest for numerous applications including neutron detectors [4,7], diffusion barriers [8], protective optical coatings [9], field emission devices [5,10], and low-k interlayer dielectrics [6]. In many of these applications, charge transport across the interface between the boron compound and another material is an important factor in the success of the device. As one example, B and BX compound (X = C, N, P, As) neutron detectors rely on electrons and holes created by nuclear collisions within the active BX layer to be swept across a pn heterojunction interface with Si [4,11–16]. A determining factor for the charge transport across this interface is the valence and conduction band alignment between the boron compound and Si [17]. However, the actual band alignment at B/Si and BX/Si interfaces has received relatively little attention.

In this regard, we have utilized X-ray photoelectron spectroscopy (XPS) to determine the valence band offset and Schottky barrier for a-B:H and a-BX:H (X = C, N, P) interfaces with Si(1 0 0) and polished polycrystalline Cu substrates. Our results for a-B:H, a-BP:H, and a-BN:H interfaces with Si(1 0 0) and a-BN:H/Cu interfaces have been previously reported [18–20]. In this article, we summarize our previous results, and we present new results on the band alignment for a-B_{4-5}C:H/Si and a-B:H/Cu interfaces. We show that the valence band offset for the a-B_{4-5}C:H/Si interface is relatively small at 0.2 ± 0.2 eV and the Schottky barrier for the a-B:H/Cu interface is more significant at 0.8 ± 0.16 eV.

2. Experimental

2.1. Film deposition and property characterization

The amorphous boron and boron carbide films were deposited on 4″ square (1 0 0) Si double side polished substrates cleaved from larger 300 mm diameter wafers. Prior to deposition, the Si substrates were given a clean in dilute buffered HF to remove the native surface oxide and produce a hydrogen terminated, hydrophobic surface [21–23]. Prior extensive research has shown that buffered HF cleans of (1 0 0) Si results in an unreconstructed surface for which each surface Si dangling bond is terminated by a hydrogen atom [24]. Furthermore, the hydrogen termination of HF treated (1 0 0) Si surfaces has been shown in numerous studies to be stable against oxidation in air for several hours to days [25,26] and thermally stable to temperatures exceeding 400 °C [24,27]. Oxygen and carbon contamination of buffered HF prepared Si(1 0 0) surfaces has been generally shown to be <0.05 monolayer [24].

The a-B_5C:H thin films were deposited at temperatures on the order of 350 °C by plasma enhanced chemical vapor

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Table 1
Summary of properties for the PECVD a-$B_{4-5}C$:H and a-B:H thin films investigated in this study.

Film	RBS-NRA % B, C, O, H (±5%)	RBS B/C	Mass density (g/cm^3)	Young's modulus (GPa)	Hardness (GPa)	Resistivity (Ω cm)
a-B_4C:H	52.3, 19.1, 8.5, 20.1	2.74	1.9 ± 0.1	145 ± 15	5.6 ± 0.5	2.5×10^9
a-B_5C:H	42.9, 11.8, 7.1, 38.1	3.63	1.5 ± 0.1	46 ± 5	1.9 ± 0.2	5.9×10^9
a-B:H [20]	86.8, 4.2, 0, 9	20.6	2.0 ± 0.1	311 ± 30	13 ± 1	3.8×10^9

deposition (PECVD) using a mixture of argon and orthocarborane (o-$B_{10}C_2H_{12}$) [11,28,29]. The a-B_4C:H films were deposited at temperatures on the order of 350 °C via sputter deposition using a poly-crystalline B_4C target and an Ar working gas [30]. The a-B:H films were deposited by PECVD using diborane at temperatures on the order of 400 °C [20]. For investigation of a-B:H/Cu interfaces, a polycrystalline Cu substrate was prepared utilizing industry standard physical vapor deposition methods to deposit a thin film of Cu on a previously prepared Ta/SiO_2/Si(1 0 0) film stack. Prior to a-B:H deposition, the Cu surface was given a short chemical mechanical polish (CMP) to produce a mirror finish [31,32]. An industry standard corrosion inhibitor [33] was added to the CMP finishing step to prevent corrosion and oxidation of the Cu surface in air [34]. This corrosion inhibitor was removed in situ just prior to a-B:H deposition by an NH_3 plasma treatment [31,32] that has been previously shown to effectively remove the corrosion inhibitor, atmospheric organics, and reduce surface oxygen/(Cu oxides) to <0.05 monolayer [35,36].

Table 1 summarizes some of the key material properties for the a-$B_{4-5}C$:H and a-B:H films investigated in this study including Rutherford backscattering (RBS) and nuclear reaction analysis (NRA) atomic composition, RBS B/C ratio, X-ray reflectivity mass density, nano-indentation Young's modulus and hardness, and resistivity. These measurements were all performed utilizing 500 nm thick films. Additional details concerning the PECVD processing and thin film measurements have been previously reported elsewhere [20,28–32,37].

2.2. XPS, valence band offset, and Schottky barrier

After PECVD deposition, the a-$B_{4-5}C$:H/Si and a-B:H/Cu samples were transferred ex situ to a VG Theta 300 XPS system equipped with a 300 mm diameter hemispherical analyzer and a monochromated Al anode X-ray source (1486.6 eV) [31]. The emitted photoelectrons were detected using a pass energy of 80 eV that generated a full width half maximum (FWHM) of <0.55 eV for the $Ag3d_{5/2}$ core level from a Ag reference sample. The same Ag reference sample and the above Cu substrate were utilized to calibrate the system Fermi level. The B1s, Si2p, C1s, O1s, and Cu3p core levels were scanned at an energy resolution of 0.05 eV [20]. Removal of surface contamination and oxidation (< 1 nm) from ex situ transfer was achieved using a 2 keV Ar^+ ion sputtering beam operating at 1 mA.

The method of Kraut [38] was utilized to determine the valence band offset (VBO) at the a-$B_{4-5}C$:H/Si interface and has been previously described in detail [39–43]. The method relies on individually referencing distinct core levels (CL) in the bulk of both dielectric materials with respect to their valence band maxima (VBM), and then measuring the relative position of these core levels with respect to one another at their interface (ΔCL_{int}). Specifically, the valence band offset at the interface between two materials (ΔE_v) can be determined using Eq. (1):

$$\Delta E_v \left(\frac{BC}{Si}\right) = (\text{CL-VBM})_{Si} - (\text{CL-VBM})_{BC} + \Delta CL_{int}, \quad (1)$$

where $(\text{CL-VBM})_{Si}$ and $(\text{CL-VBM})_{BC}$ are the positions of a core level in Si and BC with respect to their bulk valence band maxima (i.e. $(\text{CL-VBM})_{bulk}$), and $\Delta CL_{int} = (CL_{BC} - CL_{Si})_{int}$. Values for $(\text{CL-VBM})_{bulk}$ are typically measured at least 10 nm away from the interface. In our case, we determined $(\text{CL-VBM})_{bulk}$ for a-$B_{4-5}C$:H using the B1s core level detected from 25 nm thick films deposited on (1 0 0) Si p-type substrates (0.8 Ω cm). Likewise, Si2p-VBM was determined from a bare/uncoated Si substrate. To determine ΔCL_{int}, we deposited 5 nm of a-$B_{4-5}C$:H on an HF cleaned Si wafer and measured the relative position of the B1s and Si2p core levels.

The Schottky barrier at the a-B:H/Cu interface was determined utilizing the method of Grant and Waldrop [44]. Similar to the VBO measurement, this method relies on referencing a core level in the bulk of the dielectric material to the dielectric VBM and then measuring the position of that core level at the interface with the metal (CL_{int}). Specifically, the Schottky barrier (Φ_B) can be determined using Eq. (2):

$$\Phi_B = E_g - CL_{int} + (\text{CL-VBM})_{bulk}, \quad (2)$$

where E_g is the bandgap of the dielectric material. The values of E_g and B1s $(\text{CL-VBM})_{bulk}$ utilized in this study were previously determined and reported in our investigation of the a-B:H/Si interface [20]. The value of CL_{int} was determined by depositing 3 nm of a-B:H on the polished poly-crystalline Cu substrate as has been previously described in detail [31,32].

3. Results

3.1. a-$B_{4-5}C$:H film properties

As shown in Table 1, the two a-$B_{4-5}C$:H films differ significantly in their material properties with the a-B_5C:H film showing significantly reduced properties. In particular, the a-B_5C:H film shows a reduced mass density, Young's modulus and hardness relative to the a-B_4C:H film. The lower density for a-B_5C:H is consistent with the higher hydrogen content detected via NRA. RBS measurements for both films also showed significant oxygen content and reduced B/C ratios with respect to the expected stoichiometry based on the precursor/target material. The latter has been observed previously in RBS measurements of PECVD a-B_5C:H films [28]. For the former, the oxygen was found to be uniformly distributed across the entire thickness of the 500 nm film and is believed to be a result of moisture/oxygen diffusion into the film due to a low mass density [45]. More details regarding the oxygen content in the films and the differences in a-$B_{4-5}C$:H materials properties were gained by additional transmission Fourier transform infra-red (FTIR) spectroscopy measurements.

FTIR spectra acquired from 500 nm thick a-$B_{4-5}C$:H films are shown in Fig. 1. The most prominent feature in the a-B_5C:H FTIR spectrum is the B—H stretching mode at ≈2570 cm^{-1}, whereas for the a-B_4C:H film, the B—B and B—C inter and intra-icosahedral stretching modes at 700–1500 cm^{-1} are more prominent [20,35,46]. Both films show a significant O—H stretching band at 3300–3500 cm^{-1} that is consistent with the RBS measurements and can be attributed to moisture in-diffusion due to the low density of these films [47]. The sharp peak at 1100 cm^{-1} is an artifact and arises due to differences in the amount of interstitial oxygen in the Si substrate and the reference Si substrate used for background subtraction [48].

To eliminate any possible substrate artifacts, the a-$B_{4-5}C$:H films were also investigated using grazing angle, attenuated total