The Band Offsets of Isomeric Boron Carbide Overlayers

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ABSTRACT

Semiconducting boron carbide overlayers, formed from the decomposition of orthocarborane and metacarborane have been studied by angle resolved photoemission. The incurrence of surface photovoltage and the photovoltaic process, from the photoemission experiment, reveal band offsets in the orthocarborane multilayer configurations that are inverted relative to single layer configurations. Defect induced gap states which trap charge at the heterostructure interface is used as one explanation of these results. The role of defects is also used to help illuminate why opposite semiconducting type materials are formed from the decomposition of isomer carborane molecules.

INTRODUCTION

Recent experimental results [1,2] demonstrated that boron carbide fabricated from the precursor molecules closo – 1,2 dicarbododecaborane (orthocarborane) and closo – 1,7 dicarbododecaborane (metacarborane) form p-type and n-type semiconducting thin films. Based on these results an all boron carbide p-n junction diode [3] was constructed. These “heteroisomeric” diodes also demonstrated both photovoltaic [3,4] and neutronovoltaic [3] responses. The fundamental question arising from this discovery is why thin films composed of isoelectronic molecules, with the same chemical makeup and differing only by carbon position (Figure 1), would form opposite semiconducting types? To begin providing answers to this observed phenomenon, a systematic photoemission study of surface photovoltage and photovoltaic accumulation was completed with boron carbide overlayers. This experiment is a study of the electronic structure created at the metal/semiconductor and semiconductor/semiconductor interface.

Figure 1. (LEFT) closo – 1,2 dicarbododecaborane or metacarborane and (RIGHT) closo – 1,7 dicarbododecaborane or orthocarborane. Both molecules are isoelectronic with the constituents C2B10H12.
Figure 2. Photoemission based rectification of p-type (a) and n-type (b) semiconductors through the accumulation of surface photovoltage. The dotted lines represent the final band position upon rectification. The initial band bending is caused by the space charge layer at the vacuum interface.

EXPERIMENTAL DETAILS

The electronic structure studies were undertaken by angle resolved photoemission. Photoemission extracts a quantity which is proportional to the electron density of states (photoemission intensity) as a function of binding energy; we treat the Fermi level as zero binding energy. The photoemission experiments were completed at the Center for Advanced Microstructures and Devices synchrotron radiation facility in Baton Rouge, Louisiana.

Deposition of orthocarborane and metacarborane was completed through vapor adsorptions. The vapor was generated by sublimation from commercially purchased powder (Aldrich), leaked into the UHV characterizing chamber and adsorbed on a cooled (105K) polycrystalline silver substrate. Film thicknesses were approximately 30 molecular layers. Semiconducting boron carbide from the precursor molecules, indicated above, is formed by removing the exopolyhedral hydrogen from the icosahedral cage. The hydrogen removal is typically accomplish by PECVD (plasma enhanced chemical vapor deposition), however electron bombardment or zero order diffracted light (white light) from the synchrotron may be used [5]. For the studies described herein, the synchrotron light provided the foundation for both decomposition and characterization.

The Fermi level was calibrated by tantalum foil in intimate contact with the sample surface and the measurements described herein represent photoelectron collection normal to the substrate surface (k∥=0) such that only the center of the Brillouin Zone was being probed. The spectra presented below were completed using p-polarized light (70º off normal) with a photon energy of 45 eV.

DISCUSSION

The accumulation of holes or electrons due to the incurrence of surface photovoltage and/or photovoltaic effects shifts the binding energy of the molecular orbitals (band offset). During the photoemission process a photon is absorbed and energy is conserved elastically by the ejection of a photoelectron (above \(E_{\text{vac}}\)) or by some inelastic process in which an interband transition can occur or any number of secondary electron effects. When an electron is ejected from the surface region of a film with poor electron conductivity, a depletion of electrons occurs...
so that there is a net concentration of holes. To satisfy neutrality, the holes migrate by diffusion (rather than electron replacement by earth ground). For a surface concentration of holes in a material that has a p-type bulk, but n-type space charge surface, a rectification occurs, so that the surface band moves toward the Fermi level (Figure 2a). For a material with an n-type bulk, but p-type space charge surface, the surface band moves away from the Fermi level (Figure 2b). There also exists a high probability [6] of photoelectron yield from and to surface or defect states as well as secondary electrons (inelastic). A more extensive description of these phenomena and the types of band bending they may produce can be found elsewhere [7-9]. We will use these band bending phenomena to describe the charging effects incurred during photoemission to overlayers of orthocarborane and metacarborane in their pristine and decomposed forms.

The spectra below (Figure 3) represent the molecular and decomposed forms of metacarborane deposited on silver, with molecular and decomposed forms of orthocarborane as overlayers. For the first decomposition of metacarborane, the common molecular orbital binding energies moved away from the Fermi energy as would be expected for a material with an n-type bulk. Without moving the sample position, a second layer of equal thickness (30 monolayers) was deposited. The binding energy of this fresh layer and its decomposed form, exist at a higher binding energy than the original film of the same carborane precursor. We attribute this shift to the locality of synchrotron induced decomposition and the inability for the photovoltage to reach equilibrium. Further evidence to support this claim is found by moving the sample position to a region which has not been irradiated, finding that the binding energy of the pristine and decomposed film matches the original deposition.

![Figure 3](image-url)

**Figure 3.** Photoemission spectra (LEFT) of metacarborane, boron carbide formed from the decomposition of metacarborane, with overlayers of orthocarborane and decomposed orthocarborane. An exaggeration of the common molecular orbital shifts of the carboranes due to the accumulation of photovoltage is shown right.
An overlayer of orthocarborane is then adsorbed on the decomposed metacarborane resulting in binding energies positions concurrently farther away from $E_F$. Although this result seems odd, it may be explained by the excess donor states which have been made available to this fairly intrinsic molecular state and follows the result obtained for depositing metacarborane on decomposed metacarborane. However, the decomposition of orthocarborane on decomposed metacarborane leads to a state where the common molecular orbitals exist at even higher binding energies. This observation is inverted with respect to the decomposition of a thin layer of orthocarborane on a metal in which the molecular orbital binding energies decrease or move toward the Fermi level [2,3] as expected of a p-type material.

A case of comparison is made, to help understand the above phenomena, for metacarborane and decomposed metacarborane overlayers on orthocarborane and decomposed orthocarborane (Figure 4). During the initial deposition and decomposition, the orthocarborane molecular orbital binding energies shift toward lower binding energies as would be expected for a bulk p-type material using the zeroth order model of Figure 2. This same behavior (Figure 4 bottom two spectra) has been observed for orthocarborane decomposition by itself in previous studies [2,5]. But, a further deposition and decomposition of orthocarborane reveals a shift of the common molecular orbitals toward higher binding energy, counter to the simple model and counter to the original orthocarborane deposition and decomposition. We again find an “inverted” charging effect with orthocarborane just as in the first scenario. Then the sample position is moved to a location undisturbed by radiation wherein the binding energy of the pristine molecule and its decomposed form repeat the original binding energy positions. That is, the molecular orbitals shift toward the Fermi level.

Figure 4. Photoemission spectra (LEFT) of orthocarborane, boron carbide formed from the decomposition of orthocarborane, with overlayers of metacarborane and decomposed metacarborane. An exaggeration of the common molecular orbital shifts of the carboranes due to the accumulation of photovoltage is shown right.
Hence, we feel confident that the charging is localized to the region of synchrotron irradiation and the sample surface and bulk have very poor conductivity, due to the re-establishment of binding energy position for both new orthocarborane and metacarborane overlayers (moved positions). This moved position for orthocarborane is key because it reflects the fact that an interface was not constructed and therefore no interface induced states were formed to cause a shift toward higher binding energy. The deposition and decomposition of metacarborane on decomposed orthocarborane reveal the result, analogous to the first overlayer scenario, that the molecule exists at higher binding energy than its underlayer and the decomposed molecular orbitals exist at even higher binding energy.

Thus, we may summarize the above findings as follows: the molecular orbital binding energies of one carborane molecular layer only and their decomposition result in surface photovoltage accumulation which can be described within the simple model provided by Figure 2, consistent with prior work [2,3]. What is novel is that with either the orthocarborane derived boron carbide on the metacarborane derived boron carbide, or vis versa, shifts the common molecular orbitals toward larger binding energies. We attribute these larger binding energies to accumulation of donors which most probably exist at the interface between layers where secondary electrons from photoemission are accumulated.

Furthermore, both metacarborane adsorbed on decomposed metacarborane and orthocarborane adsorbed on decomposed orthocarborane demonstrate a shift of the common molecular orbitals toward higher binding energy. When either of the carborane molecules is decomposed, the space charge layer at the vacuum interface is more greatly pronounced from the accumulation of donor states. Upon adsorption of the pristine molecule, that space charge layer is compensated where any prior surface states now turn into interface states. These interface states are opposite in character (free carrier density) to the surface states for a standard p-type material (decomposed orthocarborane) but analogous to the surface states formed from an n-type material (decomposed metacarborane). Thus, for the orthocarborane on metacarborane an accumulation layer is formed at the interface, whereas for the metacarborane on orthocarborane and inversion layer is formed [7]. In either case, donor states prevail. For orthocarborane on decomposed orthocarborane it is not clear which phenomenological layer is formed.

CONCLUSIONS

Photovoltage studies of orthocarborane and metacarborane overlayers, in their pristine and decomposed forms have been studied by ultraviolet photoemission spectroscopy. As sole layers, the metacarborane (n-type) and orthocarborane (p-type) films respond to photovoltage accumulation as would be expected; the metacarborane density of states shift away from the Fermi energy whereas orthocarborane density of states shift toward the Fermi energy. However, upon forming any overlayer structures, whether by orthocarborane on itself or on metacarborane, the spectra show a shift of the carborane molecular orbitals toward higher binding energies (away from the Fermi energy). We interpret these results through the accumulation of donor states, formed as a function of creating the carborane/carborane interface, regardless of the bulk semiconducting type found for sole carborane layers. With regard to the problem of isomer dependent semiconducting type, we find only more questions. It will be of interest to find if paracarborane (closo - 1,12 dicarbadodecaborane) forms donor states at any carborane based interface.
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REFERENCES

8. H.C. Gatos and J. Lagowski, J. Vac. Sci. Tech. 10 (1973) 130