A New Class of Solar Cells: Isomeric Boron Carbide Semiconductors with Fourth Quadrant Conductivity

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ABSTRACT

Previously, we have made diodes[1,2] and transistors [3] as well as very effective real-time solid state neutron detectors [4] out of semiconducting boron carbide deposited on silicon or silicon carbide..

In this work the recent fabrication of a new class of highly photosensitive boron carbide diodes is discussed. These diodes exploit the electronic behavior differences of the isomers of film precursors, the closo-dicarbododecaboranes. These differences were observed in photoemission and inverse photoemission studies where the HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) gap variations upon deposition varied strongly with the isomeric configuration. Based on these results, p-n junctions were formed by plasma enhanced chemical vapor of ortho and meta carborane, respectively, on both nickel and aluminum substrates. These diodes exhibit fourth-quadrant conductivity, making them exciting new photovoltaic conversion devices.

KEYWORDS: boron carbide, photovoltaic diode, photoemission spectroscopy.

INTRODUCTION

Semiconducting boron carbide was first proposed in 1958 and realized in 1991. Homojunctions, heterojunctions, transistors, high-temperature diodes, and real time solid state neutron detectors have been fabricated from this in the ensuing years[1-5]. Recently, a pure boron carbide (heteroisomeric device) photovoltaic device was formed from this material in a unique way, by exploiting the bandgap differences.

Semiconducting boron carbide is not a single identified compound, but belongs to the complex molecular family sometimes referred to as the “borane, carborance, carbocation continuum” [7]. Composed of varying numbers of boron and carbon atoms (with a few terminal and bridging hydrogens) and arranged in arachno and nido open structures and the closed cage (closo) forms, compounds sharing the same stoichiometry can exhibit different chemical reactivity and local electronic distributions [7,8]. Theoretical calculations from semiempirical modified neglect of differential overlap (MNDO) calculations of the isolated molecules [9,10], indicate that the isoelectronic carboranes should be very similar in HOMO-LUMO gap (highest occupied molecular orbital - lowest unoccupied MO). These calculations predicted 10.97 eV for the orthocarborane and 10.87 eV for the metacarborane. Since the two carboranes differ only in the positions of the two included carbon atoms and theory predicted the electronic
Figure 1 shows the experimental results which led to the postulation of the diode. Ortho and meta carborane were individually adsorbed and then decomposed and the shift toward the Fermi level (ortho) or away from the Fermi level (meta), typical of p and n type semiconductors, was noted. The molecular films were prepared by adsorption from vapour on substrates (Ag, Au, or Co) cooled to 105 K. The metal surfaces were cleaned before each adsorption by argon ion sputtering. Decomposition of the source molecules was completed using unmonochromated (zero order) synchrotron light white light [2,11] or electron bombardment [12] noting that both methods yielded the same results. All binding energies are referenced to the Fermi level, and were calibrated by a tantalum foil in intimate contact with the sample surface, and the gold substrate. Decomposed films showed additional shifts, with the metaborane shifting toward the higher binding energies and the orthoborane shifting toward the lower binding energies. Thus, the two isomers decompose to make slightly p-type acceptor (orthocarborane) and strongly n-type donor state dominated (metacarborane) semiconducting materials.

Figure 1 Photoemission (PES) and inverse photoemission (IPES) of molecular films of ortho and meta carborane.
The shifts in the photoemission spectra, with decomposition of metacarborane and orthocarborane and formation of semiconducting boron-carbides, are characteristic photovoltaic charging of n-type and p-type semiconductors respectively [13-15]. n-type semiconductors will incur a surface photovoltage shifting the molecular orbitals toward higher binding energy (valence band shifts away from the Fermi level) and for p-type, the molecular orbitals shift toward lower binding energy (valence bands shifts towards from the Fermi level) [13-15]. For thicker molecular/boron-carbide films, the shifts in the photoemission features due to the photovoltaic charging are larger than the expected closure of the HOMO-LUMO gap, evident for metacarborane. For the alloy compositions of B_{10}C_{2}, an indirect band gap of well under 1 eV is expected [16-17].

DEVICE FABRICATION

The films were deposited by the “Nebraska Method” of plasma enhanced chemical vapour deposition described previously [3,5,6]. Briefly, a 13.56 MHz argon plasma provides the energy to convert the gaseous precursors, ortho- and meta-carborane, to the thin film layers. Based on previous operational data, the layers were estimated to be on the order of xxx microns each. Two polycrystalline substrates were chosen: Al and 99.9 purity Ni, which were used directly as contacts. First the ortho layer was deposited and then the meta. After cooling, the diodes were removed from the reactor, silver epoxy contacts were made and a contact compatible protective coating was added to prevent oxidation in the humid Nebraska summer. Diodes were then stored in ambient conditions, but in closed containers to prevent dust contamination. Contact area was roughly 0.01 cm in diameter. The inset in Figure 2 shows the diode configuration. A total of 16 diodes were created in this way. Results are typical,

DEVICE CHARACTERIZATION AND DISCUSSION

I(V) characteristics were measured with a Keithley-6517A electrometer. A typical curve is shown in Figure 2. All diodes, of varying thicknesses from 70 to 2000 nm show these clear breakdown voltages (from -5 to -20 V), and turn-on voltages (from 3 to 25), with individual diode properties varying with process conditions, and layer thicknesses. Leakage currents were of the order of 10^{-9} amps or better and resistivities were on the order of 10^{10}.
The most remarkable feature of the I(V) characterization is shown in expansion of a typical I(V) curve near the origin, figure 3, where the fourth quadrant conductivity is clearly seen. These curves result from a series of I(V) characteristics taken in the dark, and then with alternating light and dark exposures to where light exposure time was increased in each iteration. As can be seen from the Figure 3, the fourth quadrant conductivity is reproducible and reversible, as the I(V) characteristics returned to as the dark current curve, D, after approximately 30 seconds of darkness. This non-zero dark current is not surprising, given the highly resistive and capacitive nature of boron carbide films grown by the Nebraska method. Curves A, B, and C are responses to light after exposure to about 30 seconds, 60 seconds and 90 seconds of light, respectively. Thus, the photovoltaic behavior is reversible and light saturation was not yet reached. There was no significant difference among the silver or nickel substrates in either the nature or the magnitude of the diode responses.

CONCLUSION

In conclusion, we have clearly demonstrated that the ability to create photovoltaic diodes from closely related isomers. This is the proof of the concept suggested by the experimental PES-IPES data, suggesting the possibility of producing a p-n junction from isomers of the starting precursor. The photovoltaic performance of these new boron carbide devices fulfill the promise of early, sporadic and weak photoeffects observed in some early work.

Future work will include development and optimization of this diode, which is clearly a more environmentally friendly photovoltaic than some popular alternatives, such gallium arsenide. Demonstrating the extent that these photovoltaics share the robustness of typical boron carbide diodes to harsh environments is also scheduled. Nevertheless, this new class of diodes is a promising alternative for solar cells, and an intriguing prototype for future electronic materials, built on isomeric differences.

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