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CHEMICAL VAPOR DEPOSITION OF P-TYPE AND N-TYPE SEMICONDUCTING
BORON CARBIDE THIN FILMS

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ABSTRACT

Chemical vapor deposition of boron carbide produces films which are valued for their outstanding hardness, excellent mechanical, thermal and electrical properties. Many film polytypes can be produced, depending on the deposition conditions and the precursors. Some, but not all, of these CVD boron carbide films are semiconducting, a special property giving them micro-electronic applications ranging from low-powered neutron detectors for homeland security to direct power conversion devices. Here, growth parameters for a 13.56 MHz RF argon plasma reactor with both meta- and ortho-carborane precursors are investigated. Orthocarborane consistently produces p-type films, and metacarborane, n-type. Substrate temperatures are varied from 302 C to 321 C and mildly influence growth rates. Deposition times ranging from 10 to 420 minutes influence growth rates significantly. Metacarborane precursors grew at more than theoretically predicted 1.5 times faster than orthocarborane precursors.

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INTRODUCTION

Semiconducting boron carbide is a promising new material with largely untapped potential for applications such as low-power neutron detection and direct electrical power conversion. The material is lightweight and compatible with existing silicon semiconductor devices and could add functionality to high-temperature silicon-based diodes. The potential of this versatile material has far more esoteric applications such as dielectric barrier layers in magnetoresistive junctions or as a silicon-free device with semiconducting properties using the ability of differing isomer precursor molecules to deposit n and p-type boron carbide.

Advantages of boron carbide to the semiconductor industry include: inexpensive production of these robust semiconductor polytypes by plasma enhanced chemical vapor deposition (PECVD); relative absence of toxicity of the precursors (closo-carborane cages); and the low toxicity of the products themselves. The proposed devices lack the heavy metals and solvent processing that require hazardous waste disposal, an increasing concern in the disposal of conventional highly toxic semiconductors and detector devices.

Boron carbide neutron detectors also have advantages over conventional technologies for medical, petroleum extraction and radiation waste monitoring. Presently, radiation detectors for human exposure have limitations such as the atomic number of the detector material being higher than those of the tissues resulting in a displaced neutron response. The boron carbide materials more closely mimic human tissue and will yield a more accurate dosage reading without the use of cumbersome filters and software compensation normally used in attempts to circumvent the previously described problem. The tissue mimicking properties of the boron carbide also make this a good candidate material for in situ medical dosimetry. In addition, preliminary tests have confirmed that, as expected, boron carbide remains semiconducting at temperatures as high as 388°C, making it a likely candidate for electronics for geothermal energy production, oil-well down holes, and groundwater monitoring for environmental contamination and remediation.

The University of Nebraska - Lincoln (UNL) is a world leader in the production and investigation of nanocrystalline semiconducting and high dielectric boron carbide material and devices, as well as a strong effort in magnetic materials. In the years since 1992, when a UNL team first developed the PECVD process for fabricating boron carbide thin films as a highly resistive semiconductor (1-11), using a variety of boron carbide compounds as precursors to produce heterojunction diodes with different boron carbide stoichiometries, we have gone on to make the first boron carbide heterojunctions (5), the first boron carbide transistor (8), the first boron carbide Esaki type tunnel diodes (2-5) and even the first boron carbide homojunction diodes (2,3). Recently, we have made the first boron carbide solid-state neutron detector (10), a diode with a good figure of merit above 300°C (9) and the novel heteroisomeric diode (11), where different isomeric precursors give p-type or n-type semiconduction layers according to the initial carbon placement within the isomers. Each source compound (isomer) in this unique configuration makes use of the semiconductor electronic structure differences similar to the distinction between chiral isomers of the molecule limonene that results in our ability to distinguish between the smell of lemons and oranges or perhaps more appropriately, the different
isomers of the purine alkaloids dimethylated xanthenes of theobromine (found in cacao), paraxanthine (the human metabolite of caffeine, found in coffee) and theophylline (found in tea). Among the other groups which have used “The Nebraska Method” to repeat our success(es) in fabricating semiconducting boron carbide are: A.A. Ahmad, College of Engineering, Univ. of Jordan (12), H. Werheit, Dept. of Physics, Duisberg Univ., Germany (13,14), C.H. Liu, Dept. of Phys., Tsing Hua Univ., Beijing (15).

The best solution for the detecting element in an integrated neutron detecting instrument is a thick solid-state semiconducting device, as well-explained by D. S. McGregor and Shultis (19) who say “self-absorption and particle range problems associated with thin-film-coated diodes are not encountered with a solid-form or bulk semiconductor neutron detector .... In theory, a sufficiently thick (solid-form) device can approach 100% intrinsic efficiency for detecting thermal neutrons.... In a solid form device, both particles generally contribute to the pulse observed for a single interaction.” The heteroisomeric diode meets all these requirements, as it is a true, all-semiconducting, all-boron carbide device.

We have been able to fabricate this all boron carbide p-n junction diode by decomposing two different icosahedral closo-carborane source compounds (11) which fits the bill for a thick solid-state semiconducting inherently efficient thermal neutron detector. We used closo-1,7-dicarbadoxecaborane (metacarborane) for the n-type layer and closo-1,2-dicarbadoxecaborane (orthocarborane) for the p-type layer. The idea for exploiting main group molecular chemical vapor deposition to make the boron carbide film materials, stems from the need to keep “doping” impurities out of the semiconductor material and to make a highly resistive semiconductor over a large area (with few intrinsic carriers). The impetus was to increase the device efficiency by insuring that the entire device was an active solid-state detector as discussed above.

FABRICATING THE HETEROISOMERIC DIODE

The films were deposited by the “Nebraska Method” of plasma enhanced chemical vapour deposition (PECVD) described previously (3,5,9). Briefly, a 13.56 MHz RF argon plasma provides the energy to convert the gaseous precursors, ortho- and metacarborane, to the thin film layers in a parallel plate reactor operated at 200 mTorr. Precursors as purchased (>98% purity) are evaporated by gentle heating and the resulting vapor was carried into the plasma by a flowing stream of argon. Both heteroisomeric diodes and boron carbide on silicon diodes were produced for these studies.

Substrates for single films were silicon wafers, doped n-type for the orthocarborane precursors and p-type for the metacarborane, to obtain p-n junctions for all films. The heteroisomeric diodes are grown on polycrystalline substrates such as Al and 99.9 purity Ni, which were used directly as contacts. After cooling, the diodes were removed from the PECVD 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 0.1 cm in diameter.

In designing experiments to investigate production efficiency for scale-up of
fabrication of the diodes themselves, the rate of deposition (in Angstroms per minute) was a key response variable. Several parameters were identified as independent variables: precursor evaporation temperatures, which were varied to control the partial pressure of the precursors; substrate temperatures; substrate types, including silicon wafers, Au and SiO2; and deposition time, which was varied from 20 to 420 minutes as other conditions remained constant for the orthocarbonates. In a series of 45 minute long runs, substrate temperatures were varied from 579 K to 595 K to investigate the effect of substrate temperatures. Previous studies had indicated that the substrate adhesion could be compromised at higher and lower temperatures.

![Graph](image)

Figure 1 The growth rate, in Angstroms per minute, of PECVD orthocarbonate precursor films, as a function of substrate temperature.

RESULTS AND DISCUSSION

Even though meta- and orthocarbonate differ only by the position of the carbons in the icosahedral cage, there are large differences in the electronic properties of the films from these precursors. Initial deposition rate studies indicate surprising processing differences between the isomers, as well. There were no observed differences in deposition rates with substrate type for Si, Au, and SiO2 for either precursor. The most significant variable for overall deposition rate was the total time of deposition, with the substrate temperature also affecting the run-averaged film growth rate in a non-linear fashion, as shown in Figure 1. These films shown in that figure were all grown at the typical conditions for 45 minutes, but the substrate temperature was varied between runs. Film thickness was measured by profilometry using an AMBIOS XP-2. The apparent optimum for the substrate temperature near 314 C remains to be confirmed, but the uniformity of the growth rates within the reactor are clearly demonstrated.
The partial pressures of the precursors introduced into the argon plasma were controlled by temperatures in the evaporation chambers of the precursors. Ortho- and metacarbon vapor pressures (in atmospheres) have been measured and correlated by the following equations (20), where the temperature is in Kelvin.

\[
\log_{10}(P_{\text{vapor o-carborane}}) = 10.94 - \frac{2897}{T} - 2.095 \log_{10} T \tag{1}
\]

\[
\log_{10}(P_{\text{vapor m-carborane}}) = 38.59 - \frac{4896}{T} - 10.597 \log_{10} T \tag{2}
\]

At a typical processing temperature of 333 K for the precursor introduction, orthocarbon would have a vapor pressure of 0.0009 atmospheres (91 Pa) and metacarbon at 328 K would have a specific vapor pressure of 0.00144 atmospheres (145 Pa) nearly 1.6 times higher. Thus, for the same deposition conditions and flow rates, the metacarbon was predicted to grow films about 1.5 as fast as the orthocarbon precursor. As with so much semiconducting boron carbide processing, such as doping and polytype prediction, conventional logic does not help much.

Figure 2 shows the average deposition rates of the typical PECVD ortho- and metacarbon films. The films grown from the metacarbon precursor were consistently more than the expected 1.5 times the orthocarbon, indicating that the
process is not controlled by the concentration of precursor in the plasma. (The ten values at 45 minutes were substrate temperature variation experiments.) The deposition rates are non-linear, with a higher growth rate for both precursors in the initial few minutes of film growth. These data, when controlled for substrate temperature, can be each fit well with a second-order polynomials:

\[
\begin{align*}
\text{Rate}_{o\text{-carborane}} &= 0.0027x^2 - 1.5278x + 240.79 \\
\text{Rate}_{m\text{-carborane}} &= 0.0019x^2 - 1.5101x + 451.83
\end{align*}
\]

where Rate is in Angstroms per minute and x is time in minutes. The R^2 values were 0.96 for the orthocarborane and 0.88 for the metacarborane. Linear and exponential fits were significantly worse. Further experiments are needed to investigate the physical basis for these empirical fits and to extend the model to account for the differences with varying substrate temperatures. The slower growth rate with longer times may reflect the differential surface layer formation previously observed [5,21] which may indicate preferential orientation on the surface layers, as seen in photoemission experiments. The importance of substrate temperature variations is another indication of the importance of the initial layer formation.

There are nonzero offset currents in many but not all of the light saturated heteroisoemeric diodes at zero bias, as shown in Figure 3. This photocurrent is a reversible effect. In the absence of light, the nonzero offset current diminishes with time. In addition, the photovoltaic aspects of this diode are promising. However, no

![Diagram of Applied Bias vs. Current](image)

Figure 3 A zero bias offset (A,B,C) increases with exposure to increasing light exposure, but diminishes when operated again in the dark (D).

correlation to any processing conditions so far investigated is a good predictor for the existence of the photovoltaic behavior in the diodes. Our experiments show that unlike the standard photovoltaic materials, these all boron carbide diodes absorb and convert a wider range of photons from the near infrared to ultraviolet due to the well-defined midgap states and the relatively small indirect band gap (about 0.7 eV for
the orthocarborane derived material from optical measurements).

Thermal neutrons (from a moderated PuBe source) and alpha particles (\(^{241}\text{Am}\)) will also generate a current in our all boron carbide photodiodes with no voltage applied (zero bias). These boron carbide devices are, however, insensitive to gamma and beta radiation. The neutron and alpha electrical energy conversion process is different from photon conversion in that they are not restricted by the one photon–one electron/hole pair limitation.

CONCLUSIONS

Both n-type and p-type boron carbide layers can be reliably formed without doping. These can be combined reliably to form the all boron-carbide heteroisomeric diode. There can be no question about the boron carbide acting as a conversion layer, as the entire diode is made from the self-doping heteroisomer precursors. This diode is also a photovoltaic and shows promise as a method of efficiently deriving direct power of thermal neutrons.

The successful scale-up from the laboratory scale PECVD fabrication requires further investigation as indicated by the preliminary deposition data so far. The deposition of semiconducting boron carbide from the metacarborane is n-type; the orthocarborane, p-type; growth rates are significantly different between the different precursors, but can be fit empirically with quadratic equations. Non-linear growth rates with sharply faster initial growth indicates that more data are needed for understanding the process. Growth rates are mildly influenced by substrate temperatures and insensitive to substrate type. Notwithstanding the gaps in the understanding of the growth process, the semiconducting boron carbide from PECVD is well on its way to becoming the keystone in a highly efficient, ergonomic, and economical commercial neuron detection product.

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