University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Peter Dowben Publications | Research Papers in Physics and Astronomy

4-11-1994

Heterojunction fabrication by selective area chemical vapor deposition induced by synchrotron radiation

Dongjin Byun
University of Nebraska - Lincoln

Seong-don Hwang
University of Nebraska - Lincoln

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

F. Keith Perkins
Electronic Science Technology Division, Naval Research Laboratory, Washington, DC

F. Filips
University of Nebraska - Lincoln

See next page for additional authors

Follow this and additional works at: http://digitalcommons.unl.edu/physicsdowben

Part of the Physics Commons

Byun, Dongjin; Hwang, Seong-don; Dowben, Peter A.; Perkins, F. Keith; Filips, F.; and Ianno, N.J., "Heterojunction fabrication by selective area chemical vapor deposition induced by synchrotron radiation" (1994). *Peter Dowben Publications.* Paper 97.
http://digitalcommons.unl.edu/physicsdowben/97

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Peter Dowben Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors
Dongjin Byun, Seong-don Hwang, Peter A. Dowben, F. Keith Perkins, F. Filips, and N.J. Ianno

This article is available at DigitalCommons@University of Nebraska - Lincoln: http://digitalcommons.unl.edu/physicsdowben/97

Heterojunction fabrication by selective area chemical vapor deposition induced by synchrotron radiation

Dongjin Byun,[a] Seong-don Hwang,[a] and P. A. Dowben[b]
Center for Materials Research and Analysis, Department of Physics, University of Nebraska, Lincoln, Nebraska 68588-0111

F. Keith Perkins[c]
Electronic Science Technology Division, Code 6864, Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, DC 20375-5320

F. Filips and N. J. Ianno
Center for Materials Research and Analysis, Department of Electrical Engineering, 209 N. W. Scott Engineering Center, University of Nebraska, Lincoln, Nebraska 68588

(Received 10 November 1993; accepted for publication 4 February 1994)

We have fabricated a B_5C, boron-carbide/Si(111) heterojunction diode by the synchrotron radiation-induced decomposition of orthocarborane. This diode can be compared with similar boron-carbide/Si(111) heterojunction diodes fabricated by plasma enhanced chemical vapor deposition. The synchrotron radiation induced chemical vapor deposition is postulated to occur via the decomposition of weakly chemisorbed species and the results suggest that "real-time" projection lithography (selective area deposition) of boron-carbide devices is possible.

Synchrotron radiation-based lithography has long been known to be a means for obtaining high resolution pattern transfer. Similarly, synchrotron radiation assisted selective area deposition offers the promise of far, far better feature resolution than ultraviolet (UV) photoassisted chemical vapor deposition because of the shorter available wavelengths. Boron thin films and delta-doping layers have been fabricated using this approach.[1–4] While there are a few other synchrotron radiation-induced chemical vapor deposition studies,[5–15] this is the first demonstration that a heterojunction can be fabricated by this technique.

Unfortunately, the selective chemistry possible with UV photon initiated decomposition of organometallic or cluster source molecules has not been achieved with soft x-ray synchrotron radiation, partly because decomposition of complex molecules by synchrotron radiation is due to secondary electrons.[1,16] This limits the choice of source molecules and thin film materials that can be fabricated by synchrotron radiation.

Fortunately, the icosahedral closo-1,2-dicarbadodecarborane cluster molecule (orthocarborane; $C_2B_{10}H_{12}$) is close to the B_{12} icosahedral "building block" of the rhombohedral boron carbides. Orthocarborane and similar molecules represent potential single source precursors for the fabrication of a semiconductor form of boron-carbides;[17,18] a process that has failed with other carborane source molecules.[16]

The synchrotron radiation assisted deposition was carried out in a white light beam line previously described[12] at the Synchrotron Radiation Center in Stoughton, Wisconsin. The broad band synchrotron radiation, with a 545 eV critical energy, was focused on the sample with a fluence of 5×10^{13} photons$\cdot$s^{-1} mA^{-1} mm^{-2} and typical beam currents ranged from 80 to 180 mA. The photoemission experiments were undertaken in a separate angle resolved photoemission system as described in detail elsewhere.[19,20]

To establish that synchrotron radiation could initiate decomposition of a chemisorbed orthocarborane species, orthocarborane was molecularly adsorbed on Cu(100) at 180 K (to ensure a well defined Fermi level) and exposed to 25–30 eV photon energy light dispersed by a 4 m normal incidence monochromator. As seen in Fig. 1 following an exposure eight langmuirs (1 langmuir$=1\times10^{-6}$ Torr$\cdot$s) orthocarborane to Cu(100) at 180 K, several sharp photoemission features are observed. Based on modified neglect of differential overlap (MNDO) calculations[21–25] and gas phase spectra,[26] these photoemission features have been assigned to the molecular orbitals of orthocarborane.[20] The feature at 5.7 eV is a mixture of the $6b_2$, $6b_1$, $10a_1$, $9a_1$, $5b_2$, and $5b_1$ orbitals. The other orthocarborane photoemission features at 6.3 eV ($8a_1$ orbital), 8.25 eV ($4b_1$, $4b_2$ and $7a_1$ orbitals), 11.2 eV ($3b_1$, $6a_1$, and $3b_2$ orbitals), 12.3 eV ($5a_1$ orbital) and 14.7 eV ($2b_1$, $4a_1$, and $3a_1$ orbitals) exhibit light polarization dependence indicating that molecules bond to copper with a preferential orientation.[20] With exposure to synchrotron radiation at 25–30 eV, these molecular orbitals become less distinct, i.e., the photoemission features exhibit increasing half-widths as seen in Fig. 1. In particular, even with modest exposure to synchrotron light, the 5.7 and 6.3 eV binding energy features cannot be distinguished. This effect of synchrotron radiation is suggestive of fragmentation and has been observed in photoemission with other chemisorbed molecular overlayers.[4,13–15,27]

Consistent with this evidence of synchrotron radiation-induced decomposition of orthocarborane is the decrease in binding energy of the residual molecular orbital features. This is most clearly seen in the binding energy shift of the valence band edge established from highest occupied molecular orbital (HOMO) of orthocarborane (or $6b_2$ orbital) as seen in the insert to Fig. 1. The HOMO to lowest unoccupied

[a]Also at the Solid State Science and Technology Program, Syracuse University.
[b]Address correspondence to this author.
[c]Naval Research Council/Naval Research Laboratory Cooperative Research Associate.

 0003-6951/94/64(15)/1968/3/$6.00 © 1994 American Institute of Physics

Downloaded 01 Nov 2006 to 129.93.16.206. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

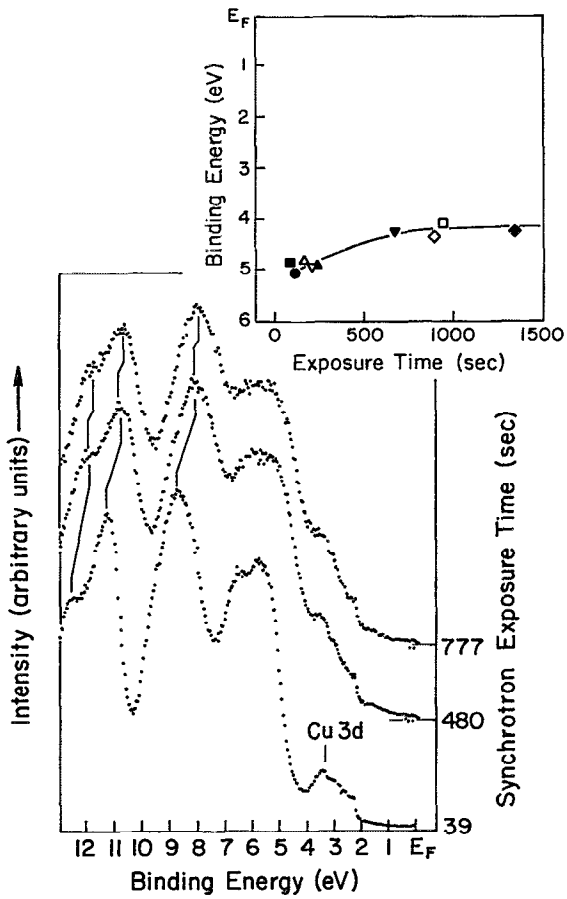

FIG. 1. Photoemission spectra of 8 langmuirs of orthocarborane adsorbed on Cu(100) at 180 K. The photon energy is 25 eV, and the light incidence angle is 65° off normal. All photoelectrons were collected normal to the surface. Note the binding energy shifts and increased full widths of the photoemission features with increased exposure to the synchrotron light. The insert shows the binding energy shift of the highest occupied molecular orbital of orthocarborane as the valence band edge is established with the formation of a boron-carbide.

molecular orbital (LUMO) gap is expected to be about 11 eV based upon MNDO calculations[21,22] for orthocarborane. Thus, for the initial molecular film, we see that the Fermi level (chemical potential) is roughly midgap. As the orthocarborane dissociates, the HOMO develops into the valence band edge. Since boron-carbide is generally accepted to be a *p*-type material[17] the binding energy of this level must therefore decrease until it is very close to the Fermi level. Furthermore, this apparent binding energy shift occurs because the band gap of B_5C is close to 0.9 eV.[17,18] Near edge x-ray absorption spectroscopy (NEXAFS) studies of orthocarborane[4] have noted the similarity between the local electronic structure of orthocarborane and boron carbide. We postulate that the similar NEXAFS spectra obtained for boron carbide and orthocarborane is, in part, an artifact of the partial dissociation of orthocarborane induced by the high-energy photons used in that experiment.[4] Reactions of diborane with graphite induced by synchrotron radiation result in a boron carbide phase[4] indicating that this is a thermodynamic "sink."

It is important to realize that the molecular chemisorbed state observed at 180 K on Cu(100) is not the precursor state to dissociative adsorption.[22] This precursor state to dissociative adsorption, as yet, remains unidentified. Nor should we expect the rate of synchrotron radiation-induced decomposition of the observed molecular orthocarborane species at one wavelength (25 eV) to be representative of the synchrotron radiation induced chemical vapor deposition (CVD) rate with white light that includes higher (and lower) photon energies. As is indicated by the data discussed below (Fig. 2), the rate of synchrotron white light induced CVD of boron-carbide is much faster than is induced by the single wavelength (25 eV) induced decomposition results of Fig. 1.

With white light induced decomposition of orthocarborane on *n*-type silicon, deposition of boron and carbon are observed to occur in white light Auger electron spectroscopy as seen in Fig. 2. The area of deposition is visibly restricted to only the area illuminated, an indication that the deposition is, at least partly, a selective area deposition process and surface mediated (as indicated by photoemission).

The Auger electron spectroscopy intensities of the B (180 eV) and C (272 eV) lines (Fig. 2) suggest that the growing boron-carbide film is homogeneous and of a composition close to B_5C following deposition of the first 12 Å. The orthocarborane dissociates without the loss of carbon or boron atoms unlike the carbon loss observed in the synchrotron radiation-induced decomposition of another carborane: *nido*-2,3 diethyl-2,3-dicarbahexaborane.[16] [The initial stage of growth appears to be carbon rich up to 12 Å film thickness, due to boron insertion selvedge Si(111) sites.]

Under our experimental conditions, synchrotron white light irradiation results in the deposition of roughly one "hexagonal" *c*-axis oriented unit cell (12 Å) of boron-carbide for every 90 langmuirs of orthocarborane exposure. This is based upon the attenuation of the Si(111) substrates signal as seen in Fig. 2.

In order to ascertain whether the boron-carbide material made from the synchrotron radiation induced dissociation of orthocarborane is similar to the boron-carbide fabricated by plasma enhanced CVD,[17,18] we fabricated a heterojunction diode. A 1000 Å B_5C/Si(111) diode fabricated by synchrotron light-induced CVD is very similar to the $B_{4.7}C$/Si(111) heterojunction diodes fabricated through the plasma enhanced CVD of boron-carbide from *nido*-pentaborane(B_5H_9) and methane[17,18] as seen in Fig. 3. The very small onset voltage (the approximate voltage at which there is appreciable current in the forward direction) for the synchrotron radiation fabricated diode is a consequence of the very thin B_5C layer formed. Plasma enhanced CVD fabricated diodes exhibit a rapidly decreasing onset voltage with decreasing film thickness as seen in the insert to Fig. 3. The small onset voltage of the synchrotron radiation-induced CVD diode is consistent with a 1000 Å thick B_5C layer.

Differences in the magnitude of the currents for the different diodes is solely a consequence of the differences in the relative sizes of the diodes. The plasma enhanced CVD fabricated diodes are, in fact, four times the size of the synchrotron radiation assisted CVD diodes. The resistivity of the boron-carbide diodes fabricated by either plasma assisted

Downloaded 01 Nov 2006 to 129.93.16.206. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

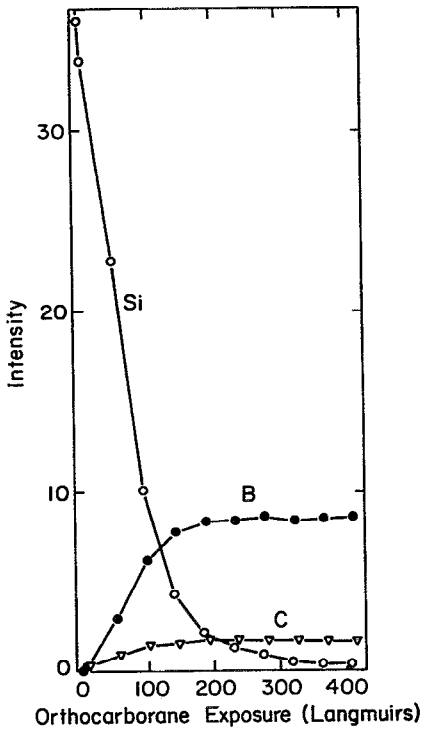

FIG. 2. The Auger electron spectra peak intensities of silicon, denoted by open circles (○), boron, denoted by filled circles (●) and carbon, denoted by open triangles (▽) as a function of orthocarborane exposure to Si(111) at room temperature. The sample was irradiated with synchrotron radiation white light throughout the experiment to assist in the orthocarborane decomposition.

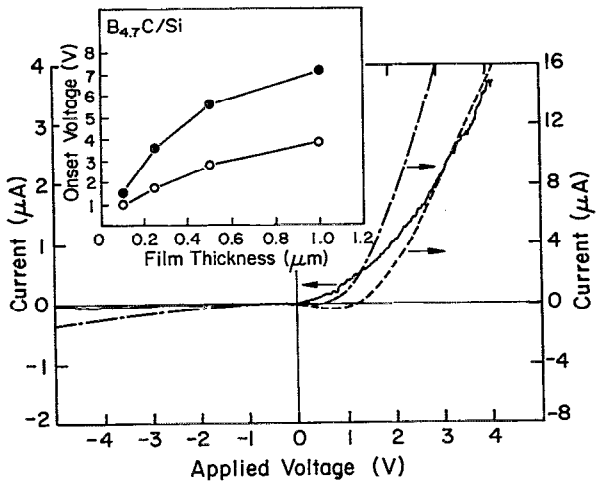

FIG. 3. The I-V curves for synchrotron radiation assisted CVD fabricated diodes identified by solid line (——) and plasma enhanced CVD fabricated diodes without illumination, identified by the dashed line (----), and with illumination, identified by the dot-dashed line (-·-·-). The insert show the onset voltage for $B_{4.7}C$ on Si(111) heterojunction diode fabricated by PECVD, as a function of boron-carbide film thickness.

CVD or synchrotron radiation assisted CVD is very similar and about 10^{12} Ω cm.

Clearly, we can conclude that synchrotron radiation induced decomposition of orthocarborane results in the formation of a boron-carbide similar in properties to that obtained by plasma enhanced CVD. This boron-carbide is sufficiently resistive to be able to be used for the fabrication of heterojunctions. The "direct" writing of a boron-carbide on a variety of substrates is now possible and given the short wavelengths of light available in synchrotron radiation, submicrometer resolution should be possible.

This work was funded by the AFOSR, the Naval Research Laboratory, the NSF(DDM 92-22880, and DDM-93-45686) and the Research Institute of Industrial Science and Technology (RIST). This work was undertaken at the Synchrotron Radiation Center in Stoughton, Wisconsin, which is supported by the NSF. The authors would like to thank S. Lee, H. Zeng, J. Zhang, M. Onellion, J. Simons, S. P. Frigo, and R. A. Rosenberg for their technical support.

[1] F. K. Perkins, R. A. Rosenberg, S. Lee, and P. A. Dowben, J. Appl. Phys. **69**, 4103 (1991).
[2] R. A. Rosenberg, F. K. Perkins, D. C. Mancini, G. R. Harp, B. P. Tonner, S. Lee, and P. A. Dowben, Appl. Phys. Lett. **58**, 607 (1991).
[3] R. A. Rosenberg, S. P. Frigo, S. Lee, and P. A. Dowben, J. Appl. Phys. **71**, 4795 (1992).
[4] M. W Ruckman, M. F. Murray, J. K. Mowlem, and D. R. Strongin, J. Vac. Sci. Technol. A **11**, 2477 (1993).
[5] T. Urisu and H. Kyuragi, J. Vac. Sci. Technol. B **5**, 1436 (1987).
[6] T. Urisu, T. Akutsu, and K. Kuchitsu, Appl. Phys. Lett. **62**, 2821 (1993).
[7] Y. Utsumi, J.-i. Takahashi, H. Akazawa, and T. Urisu, Jpn. J. Appl. Phys. **30**, B **11**, 3195 (1991).
[8] Y. Utsumi, H. Akazawa, M. Nagase, T. Urisu, and I. Kawashima, Appl. Phys. Lett. **62**, 1647 (1993).
[9] J.-i. Takahashi, Y. Utsumi, H. Akazawa, I. Kawashima, and T. Urisu, Appl. Phys. Lett. **58**, 2776 (1991).
[10] T. Urisu, J.-i. Takahashi, Y. Utsumi, and H. Akazawa, Appl. Organometallic Chem. **5**, 229 (1991).
[11] J.-i. Takahashi, Y. Utsumi, H. Akazawa, I. Kawashima, and T. Urisu, Thin Solid Films **218**, 40 (1992).
[12] D. C. Mancini, S. Varma, J. K. Simons, R. A. Rosenberg, and P. A. Dowben, J. Vac. Sci. Technol. B **8**, 1804 (1990).
[13] F. Cerrina, B. Lai, G. M. Wells, J. R. Wiley, D. G. Kilday, and G. Margaritondo, Appl. Phys. Lett. **50**, 533 (1987).
[14] B. Lai, R. Nachman, A. K. Ray-Chandhuri, and F. Cerrina, Solid State Commun. **71**, 721 (1989).
[15] F. Bozso and Ph. Avouris, Phys. Rev. B **38**, 3943 (1988).
[16] F. K. Perkins, M. Onellion, Sunwoo Lee, Dongqi Li, J. Mazuroski, and P. A. Dowben, Appl. Phys. A **54**, 442 (1992).
[17] Sunwoo Lee, J. Mazurowski, G. Ramseyer, and P. A. Dowben, J. Appl. Phys. **72**, 4925 (1992).
[18] Sunwoo Lee, Thuong Ton, D. Zych, and P. A. Dowben, Mater. Res. Soc. Symp. Proc. **283**, 483 (1993).
[19] P. A. Dowben, D. LaGraffe, and M. Onellion, J. Phys. Cond. Mat. **1**, 6571 (1989).
[20] H. Zeng, D. Byun, J. Zhang, G. Vidali, M. Onellion, and P. A. Dowben, Surface Sci. (in press).
[21] A. P. Hitchcock, A. T. Wen, S. Lee, J. A. Glass, J. T. Spencer, and P. A. Dowben, J. Phys. Chem. **97**, 8171 (1993).
[22] D. Byun , S. D. Hwang, P. A. Dowben, A. P. Hitchcock, J. A. Glass, and J. T. Spencer, J. Electron Spectrosc. Rel. Phenom. (to be published).
[23] M. F. Guest and I. H. Hillier, Mol. Phys. **26**, 435 (1973).
[24] M. J. S. Dewar and M. McKee, Inorg. Chem. **19**, 2662 (1980).
[25] C.-C. Chung, R. A. Beaudet, and G. A. Segal, J. Am. Chem. Soc. **92**, 4158 (1970).
[26] P. Brint, B. Sangchakr, M. McGrath, T. R. Spalding, and R. J. Suffold, Inorg. Chem. **29**, 47 (1990).
[27] P. A. Dowben and M. Grunze, Ber. Bunsenges. Phys. Chem. **85**, 728 (1981).

Downloaded 01 Nov 2006 to 129.93.16.206. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp