1-15-2009

3d transition metal doping of semiconducting boron carbides

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

Orhan Kizilkaya
Louisiana State University at Baton Rouge, orhan@lsu.edu

Jing Liu
University of Nebraska-Lincoln

B. Montag
University of Nebraska-Lincoln

K. Nelson
University of Nebraska-Lincoln

See next page for additional authors

Published in *Materials Letters* 63:1 (January 15, 2009), pp. 72-74; doi: 10.1016/j.matlet.2008.09.004

Submitted August 27, 2008; accepted September 2, 2008; published online September 7, 2008.

3d transition metal doping of semiconducting boron carbides

P. A. Dowben,[a] Orhan Kizilkaya,[b] Jing Liu,[a] B. Montag,[c] K. Nelson,[c] I. Sabirianov,[c] and J. I. Brand [c]

[a] Department of Physics and Astronomy and the Nebraska Center for Materials and Nanoscience, Behlen Laboratory of Physics, University of Nebraska, P.O. Box 880111, Lincoln, NE 68588-0111, USA

[b] The J. Bennett Johnston Sr. Center for Advanced Microstructures and Devices, Louisiana State University, 6980 Jefferson Hwy., Baton Rouge LA 70806, USA

[c] College of Engineering, and the Nebraska Center for Materials and Nanoscience, N209 Walter Scott Engineering Center, 17th and Vine Streets, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0511, USA

Corresponding author – Peter A. Dowben, pdowben@unl.edu

Abstract

The introduction metallocenes, in particular ferrocene ($Fe(\eta^5\text{-}C_5H_5)_2$), cobaltocene ($Co(\eta^5\text{-}C_5H_5)_2$), and nickelocene ($Ni(\eta^5\text{-}C_5H_5)_2$), together with the carborane source molecule *closo*-1,2-dicarbadodecaborane, during plasma enhanced chemical vapor deposition, will result in the transition metal doping of semiconducting boron carbides. Here we report using ferrocene to introduce Fe dopants, and a semiconducting boron-carbide homojunction has been fabricated. The diode characteristics are very similar to those fabricated with Co and Ni doping.

Keywords: boron rich semiconductors, doping, heterojunction diodes, boron carbide

1. Introduction

The ability to generate semiconducting grades of boron carbide films by plasma enhanced chemical vapor phase deposition (PECVD) of carboranes permits the development of corrosion resistant, high temperature devices with many applications including neutron detection [1–4]. It is now clear that these boron carbides, of approximate stoichiometry "$C_2B_{10}H_x$" (where x represents up to ~ 5% molar fraction or more of hydrogen), exhibit a range of electronic properties (i.e. p-type or n-type) presumably as a result of differing electronic structures originating in differences in polytype (molecular structure) [4–6].

A growing number of potential dopants for this PECVD grown semiconducting boron carbide have now been explored, driven by the potential applications of all semiconducting boron-carbide devices [3, 4, 6], rather than a heterojunction device. One possible route for doping is to include a metallocene, $M(C_5H_5)_2$, M = V, Cr, Mn, Fe, Co, Ni, simultaneously with the carborane source molecule during plasma enhanced chemical vapor phase deposition (PECVD). Nickel, via nickelocene, was successfully introduced as a dopant in semiconducting boron carbides grown by PECVD from orthocarborane (*closo*-1,2-dicarbadodecaborane) [7–10]. Cobaltocene has been shown to dope PECVD grown semiconducting boron carbide [11]. Oddly enough, some other common semiconductor dopants, like Hg [12], do not dope PECVD grown semiconducting boron carbide at all.

Successful n-type doping of ß-rhombohedral boron has been accomplished with dopants such as iron [13–16], vanadium [16], chromium [16], nickel [16], and cobalt [17]. For the related boron carbides, nickel is certainly an n-type dopant [7–10] while cobalt may or may not [11] be a p-type dopant of the boron carbides, that depends upon temperature. While ß-rhombohedral boron is very different from PECVD grown semiconducting boron carbide, if iron is a successful dopant of PECVD grown semiconducting boron carbide, then there is a stronger case to be made that the dopants of ß-rhombohedral boron are a guide to what will dope PECVD grown semiconducting boron carbide. At issue is whether the two boron rich semiconductors based on an icosahedral (12 atom) building block dope in a similar fashion, in spite of the many differences between them.

2. Experimental

The doped boron carbide films used for device fabrication and X-ray absorption near edge structure (XANES) measurements were constructed using the process of PECVD (plasma

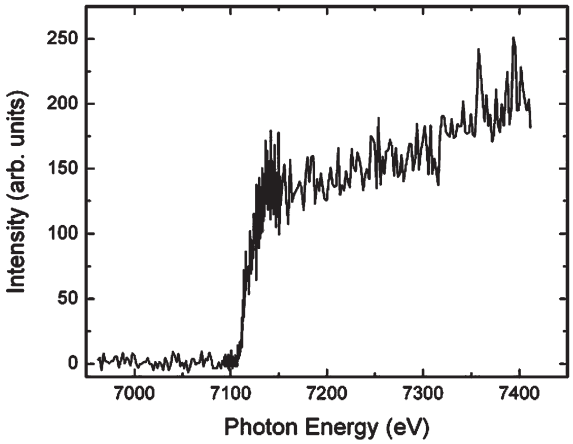

Figure 1. Normalized Fe *K*-edge XANES spectra of Fe-doped boron carbide.

enhanced chemical vapor deposition) as described for the heterojunction [1, 2, 9, 10] and homojunction diodes [7–11] of boron carbide as well as diodes made from two polytypes of boron carbide [3, 4, 6], but with only orthocarborane (*closo*-1,2-$C_2B_{10}H_{12}$), ferrocene and argon as the plasma reactor gases. The X-ray absorption near edge structure (XANES) spectra were collected at the DCM (double crystal monochromator) beamline at the Center for Microstructures and Devices (CAMD). Monochromatic light was obtained by using a double crystal monochromator of Lemonnier type [18], equipped with Ge(220) crystal pair and the overall resolution was ~ 2 eV. The EXAFS and XANES spectra were collected in the fluorescent yield mode, as has proven to be successful in characterizing other doped boron carbides [6, 19, 20].

3. Iron doping

We have performed Fe *K*-edge X-ray absorption near edge structure (XANES) measurements of Fe-doped plasma enhanced chemical vapor phase deposition (PECVD) grown "$C_2B_{10}H_x$" semiconducting boron carbides, using ferrocene. The characteristic signature of iron is evident at a value close to the expected 7112 eV Fe *K*-edge, and we can infer from Figure 1 that ferrocene source gas does result in iron doping of the PECVD grown boron carbides.

Note distinctive features at the absorption edge of the Fe-doped boron carbide, indicating strong hybridization between iron and the inorganic host matrix. This is similar in some respect to that observed with Co-doped plasma enhanced chemical vapor phase deposition (PECVD) grown "$C_2B_{10}H_x$" semiconducting boron carbides, using cobaltocene [11, 19, 20].

4. Comparing homojunction diodes

The transition metals Ni, Co and Fe all share a similar $4s^2$ frontier orbital. Thus not surprisingly, homojunction diodes of PECVD grown semiconducting boron carbide, with Ni, Co and Fe dopants, can be fabricated that are very similar, as seen in Figure 2. The diode characteristics do differ slightly.

Our experience is that Ni seems the most reliable and robust dopant, with the highest device success. On the other hand the forward bias onset voltage is 1–2 V higher in Ni doped homojunctions than was observed with either Co or Fe, as indicated in Figure 2. Yet in all cases, Ni, Co and Fe-doped

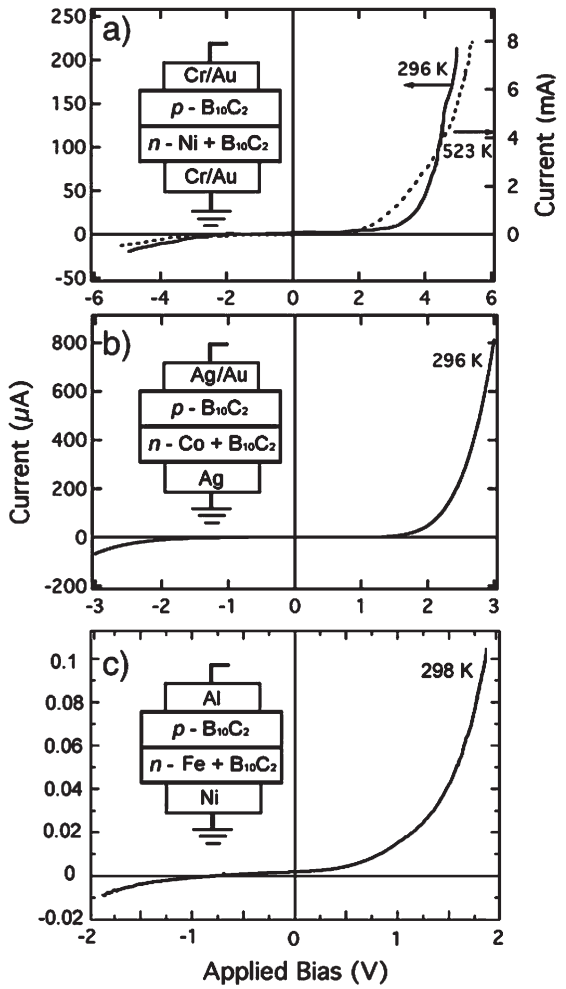

Figure 2. The diode I–V characteristics of a) Ni(*n*)-$B_{10}C_2$/(*p*)-$B_{10}C_2$, b) Co(*n*)-$B_{10}C_2$/(*p*)-$B_{10}C_2$, and c) Fe(*n*)-$B_{10}C_2$/(*p*)-$B_{10}C_2$, formed from the PECVD decomposition of orthocarborane (see text). The insets are schematics of the diodes, as assembled.

PECVD grown semiconducting boron carbides (grown using orthocarborane as a source gas) are more n-type relative to the undoped of PECVD grown semiconducting boron carbide. In this regard, PECVD grown semiconducting boron carbide is in fact similar to ß-rhombohedral boron with Ni, Co and Fe dopants.

Establishing a comparison of the different devices based on the current characteristics requires establishing the doping concentrations, as increased doping does lead to decreased resistivities [8, 11]. Obtaining an absolute measure of the doping concentration has not been established, and has been a challenge. It is clear that similar partial pressure of the different metallocenes do not lead to identical dopant concentrations, though in all cases shown here, the dopant concentrations are less than 1%.

5. Summary

There does appear to be a growing boding of evidence that some material properties of ß-rhombohedral boron do resemble that of PECVD grown semiconducting boron carbide grown using orthocarborane as a source gas. The 3d metals do appear to dope both ß-rhombohedral boron and PECVD grown semiconducting boron carbide in a similar fashion.

While clearly Ni, Co and Fe are successful dopants of PECVD grown semiconducting boron carbide (grown using orthocarborane as a source gas), there is an implicit assumption not supported yet by any experimental data: the polytype of PECVD grown semiconducting boron carbide with Ni, Co and Fe dopants, introduced from a metallocene during PECVD, is the same as the updoped PECVD grown semiconducting boron carbide. While rectifying diodes are readily formed, these are homojunctions if and only if the structural polytypes are similar. Addressing this question has proved to be a very difficult challenge for a decade or more and remains unresolved. An effort must be made to identify the structural polytypes associated with the PECVD grown semiconducting boron carbide with different electronic properties.

Acknowledgments

This work was supported by the Office of Naval Research (Grant No. N00014-06-1-0616), the National Science Foundations (NSF-ECS 0725881), the Chief Technical Officer, Intelligence Technology Innovation Center of the United States Intelligence Community and also the Nebraska Research Initiative. CAMD is supported by the Louisiana Board of Regents.

References

[1] B. W. Robertson, S. Adenwalla, A. Harken, P. Welsch, J. I. Brand, and P. A. Dowben *et al.*, *Appl Phys Lett* **80** (2002), pp. 3644–3646.

[2] E. Day, M. J. Diaz, and S. Adenwalla, *J Phys D Appl Phys* **39** (2006), p. 2920.

[3] A. N. Caruso, P. A. Dowben, S. Balkir, N. Schemm, K. Osberg, and R. W. Fairchild *et al.*, *Mat Sci Eng B* **135** (2006), p. 129.

[4] A. N. Caruso, R. B. Billa, S. Balaz, J. I. Brand, and P. A. Dowben, *J Phys Condens Matter* **16** (2004), pp. L139–L146.

[5] P. Lunca-Popa, J. I. Brand, S. Balaz, L. G. Rosa, N. M. Boag, and M. Bai *et al.*, *J Phys D Appl Phys* **38** (2005), pp. 1248–1252.

[6] S. Balaz, D. I. Dimov, N. M. Boag, K. Nelson, B. Montag, and J. I. Brand *et al.*, *Appl Phys A* **84** (2006), pp. 149–159.

[7] S.-D. Hwang, K. Yang, P. A. Dowben, A. A. Ahmad, N. J. Ianno, and J. Z. Li *et al.*, *Appl Phys Lett* **70** (1997), pp. 1028–1030.

[8] D. N. McIlroy, S.-D. Hwang, K. Yang, N. Remmes, P. A. Dowben, and A. A. Ahmad *et al.*, *Appl Phys A* **67** (1998), pp. 335–342.

[9] S.-D. Hwang, N. B. Remmes, P. A. Dowben, and D. N. McIlroy, *J Vac Sci Technol B* **14** (1996), pp. 2957–2960.

[10] S.-D. Hwang, N. Remmes, P. A. Dowben, and D. N. McIlroy, *J Vac Sci Technol A* **15** (1997), pp. 854–859.

[11] L. Carlson, D. LaGraffe, S. Balaz, A. Ignatov, Ya. B. Losovyj, and J. Choi *et al.*, *Appl Phys A* **89** (2007), p. 195.

[12] Carolina C. Ilie, S. Balaz, L. G. Rosa, J. Zhang, P. Lunca-Popa, and C. Bianchetti *et al.*, *Appl Phys A* **81** (2005), p. 1613.

[13] H. Takizawa, N. Haze, K. Okamoto, K. Uheda, and T. Endo, *Mater Res Bull* **37** (2002), pp. 113–121.

[14] U. Kuhlmann, H. Werheit, J. Pelloth, W. Keune, and T. Lundstrom, *Phys Status Solidi B* **187** (1995), pp. 43–59.

[15] U. Kuhlmann, H. Werheit, T. Dose, and T. Lundstrom, *J Alloys Compd* **186** (1992), pp. 187–200.

[16] H. Werheit, R. Schmechel, V. Kueffel, and T. Lundstrom, *J Alloys Compd* **262** (1997), pp. 372–380.

[17] H. Werheit, R. Schmechel, V. Kueffel, and T. Lundstrom, *J Alloys Compd* **262** (1997), p. 372.

[18] M. Lemonnier, O. Collet, C. Depautex, J. M. Esteva, and D. Raoux, *Nucl Instrum Methods A* **152** (1978), p. 109.

[19] A. Yu. Ignatov, Ya. B. Losovyj, L. Carlson, D. LaGraffe, J. I. Brand, and P. A. Dowben, *J Appl Phys* **102** (2007), p. 083520.

[20] P. A. Dowben, A. Yu. Ignatov, Jing Liu, and R. Skomski, *J Appl Phys* **103** (2008), p. 07D125.