

## The heteroisomeric diode

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 L139

(<http://iopscience.iop.org/0953-8984/16/10/L04>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

### Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 12:48

Please note that [terms and conditions apply](#).

## LETTER TO THE EDITOR

## The heteroisomeric diode

Anthony N Caruso<sup>1</sup>, Ravi B Billa<sup>2</sup>, Snjezana Balaz<sup>1</sup>, Jennifer I Brand<sup>2</sup>  
and P A Dowben<sup>1,3</sup>

<sup>1</sup> Department of Physics and Astronomy and the Center for Materials Research and Analysis,  
Behlen Laboratory of Physics, University of Nebraska—Lincoln, Lincoln, NE 68588-0111, USA

<sup>2</sup> College of Engineering and Technology and Center for Materials Research and Analysis,  
University of Nebraska—Lincoln, Lincoln, NE 68588, USA

E-mail: pdowben@unl.edu

Received 4 December 2003

Published 27 February 2004

Online at [stacks.iop.org/JPhysCM/16/L139](http://stacks.iop.org/JPhysCM/16/L139) (DOI: 10.1088/0953-8984/16/10/L04)

### Abstract

We have fabricated a new class of diode from two different polytypes of boron carbide. Diodes were fabricated by chemical vapour deposition from two different isomers of *closo*-dicarbadodecaborane: *closo*-1,2-dicarbadodecaborane (orthocarborane, C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>) and *closo*-1,7-dicarbadodecaborane (metacarborane, C<sub>2</sub>B<sub>10</sub>H<sub>12</sub>), differing only by the carbon placement within the icosahedral cage. We find that the electronic structure (molecular orbitals) of these two isomer molecules and the resulting decomposition reflect the tendency of metacarborane to form an n-type semiconductor while orthocarborane is an effective source compound for a slightly p-type semiconducting boron carbide. The diodes of this novel class are effective solid state neutron detectors, and have a number of unique applications.

(Some figures in this article are in colour only in the electronic version)

Semiconductor polytypes that do not differ in constituents but vary in atomic arrangement are well known. Examples include hexagonal versus cubic boron nitrides, graphite versus diamond and the numerous polytypes of silicon carbide whose electronic properties vary (i.e. bandgap, carrier mobility, breakdown field etc). We have found and have been able to conclusively demonstrate that the use of different polytypes, one material acting as the effective p-type layer and the other as the n-type layer, creates a diode that is neither a heterojunction diode (made of two different semiconductors) nor a homojunction diode (a semiconductor device made of one material, but doped, in different regions, with minute amounts of controlled impurities to make the material p-type or n-type). We have developed diodes from source compounds which differ only by carbon location within the icosahedral cage, as shown inset to figure 1.

<sup>3</sup> Address for correspondence: 116 Brace Laboratory, University of Nebraska, PO Box 880111, Lincoln, NE 68588-0111, USA.

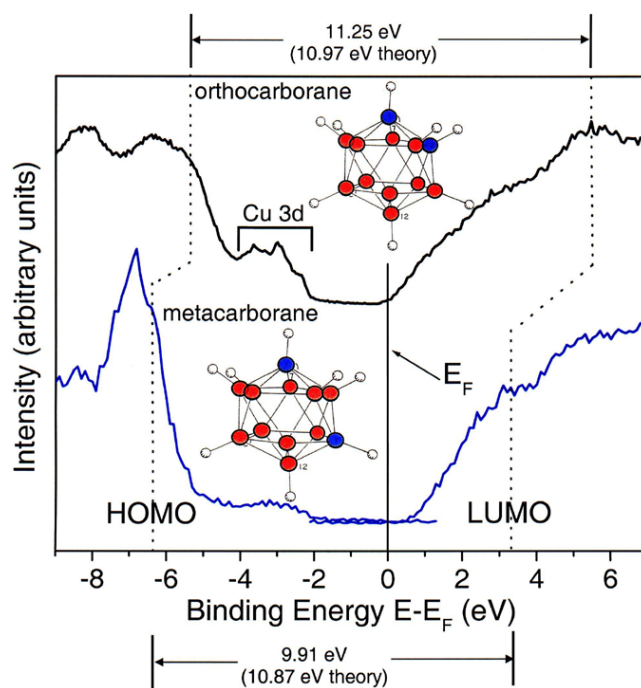
Each source compound (isomer) makes use of the semiconductor electronic structure differences, similar to the distinction between chiral isomers of the molecule limonene that results in our ability to distinguish between the smell of lemons and oranges, or, perhaps more appropriately, the different isomers 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). These heteromorphic diodes are distinct from the reported heterojunction [1–3] and homojunction diodes [4] formed from the semiconducting boron carbide  $B_{10}C_2$ .

Combined photoemission and inverse photoemission spectroscopies were undertaken to study the molecular orbital placement of both occupied and unoccupied orbitals of the adsorbed molecules on metal surfaces. The adsorbed molecular films were prepared by adsorption from vapour on substrates cooled to 105 K. Both orthocarborane and metacarborane were admitted to the vacuum system through a standard leak valve. The metal substrates include polycrystalline Ag, a Cu(100) surface, a 1000 Å Au(111) surface grown on Si(111), and Co prepared by physical vapour deposition on gold coated silicon wafers. The metal surfaces were cleaned before each adsorption by argon ion sputtering. For the photoemission experiments, decomposition of the source molecules was completed using unmonochromated (zero order) synchrotron white light [1, 5] or electron bombardment [6] noting that both methods yielded the same results. The photoemission spectra were taken using a He I line source (21.2 eV) or in the case of the photodecomposition studies were obtained from polarized synchrotron radiation (30 or 32 eV incident energies) dispersed by a 3 m toroidal grating monochromator, at the Center for Microstructures and Devices. All the photoelectrons were energy analysed with a hemispherical electron energy analyser, with photoelectrons collected normal to the sample surface. The He I (21.2 eV) ultraviolet photoemission, inverse photoemission, and x-ray photoemission (XPS) were undertaken in a single UHV chamber. The inverse photoemission studies were performed using a Geiger–Müller detector with a  $SrF_2$  window, with a pass energy of 9.5 eV. The overall energy resolution was approximately 500 meV. All IPES spectra were collected with the electron gun at normal incidence and the detector positioned at 35° off the surface normal, as described elsewhere [7]. 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.

The diodes were constructed using the process of PECVD (plasma enhanced chemical vapour deposition) as described for both heterojunction [2, 3] and homojunction diodes [4] of boron carbide, but with only carboranes and argon as the plasma reactor gases. The neutron studies were undertaken at a reverse bias of 5 V and at no bias. Thermal neutrons were taken from a paraffin moderated plutonium–beryllium source.

Orthocarborane and metacarborane, as shown in figure 1, can be molecularly adsorbed on solid surfaces [7–9]. Photoemission spectra of the occupied molecular orbitals, and inverse photoemission spectra of the unoccupied molecular orbitals, indicate the features characteristic of the molecular orbitals of both molecules [7–9], as shown in figure 1. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were identified from detailed coverage dependent studies and compared with the theoretical expectations from semiempirical modified neglect of differential overlap (MNDO) calculations of the isolated molecule [7, 9]. Surprisingly, considering the two carboranes are isoelectronic, the resulting molecular films show different band offsets.

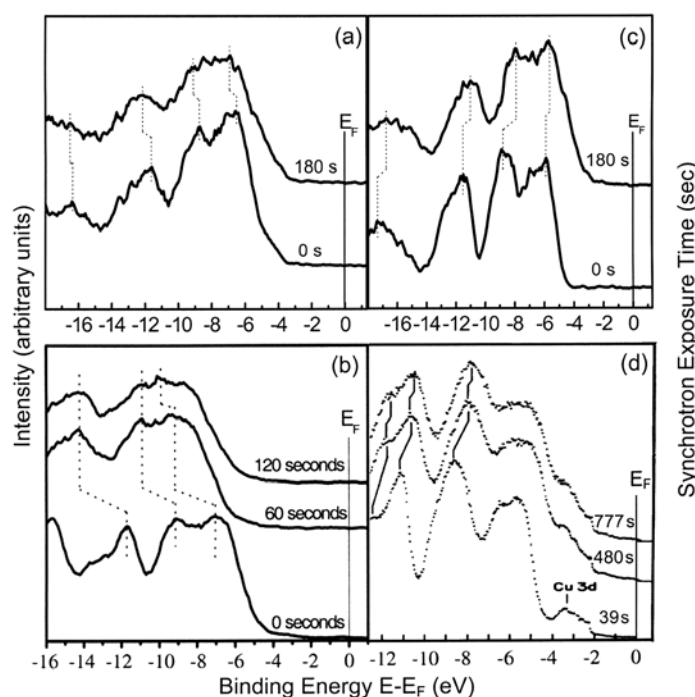
The adsorbed molecular films show band offsets of the highest occupied molecular orbital and lowest unoccupied molecular orbital that are the characteristic positions of valence band and conduction band edges for slightly p-type (orthocarborane) and more strongly n-type (metacarborane) semiconductors. Although the HOMO–LUMO gaps and molecular orbitals



**Figure 1.** The HOMO–LUMO gap of orthocarborane ( $C_2B_{10}H_{12}$ ) or *closo*-1,2-dicarbado-decaborane (top) and metacarborane ( $C_2B_{10}H_{12}$ ) or *closo*-1,7-dicarbado-decaborane (bottom). Shown are the combined photoemission (left) and inverse photoemission (right) spectra of the molecular thin films on gold and copper for metacarborane and orthocarborane respectively. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are identified from detailed coverage dependent studies [7, 9] and compared with the theoretical expectations for the isolated molecule [7, 9]. Blue atoms are carbon and red are boron. The HOMO to LUMO gaps are indicated and the spectra are referenced to the Fermi level of the substrate. As indicated, the Fermi level is closer to the binding energy of the highest occupied molecular orbitals for orthocarborane and closer to the lowest unoccupied molecular orbitals for metacarborane.

of orthocarborane and metacarborane are similar, the corresponding molecular levels are placed differently in binding energy with respect to the substrate Fermi level (electron chemical potential). For orthocarborane, the Fermi level exists closer to the HOMO or valence band states than to the LUMO. Thus orthocarborane molecular films are slightly p-type (acceptor state dominated) when adsorbed on copper, silver, gold, and cobalt. For metacarborane, the Fermi level placement is closer to the LUMO or conduction band states, thus the metacarborane molecular films are n-type (donor state dominated) when adsorbed on gold, silver, and cobalt. This is contrary to the expectation that orthocarborane and metacarborane should exhibit similar placements of the chemical potential and HOMO band edge [7, 10, 11].

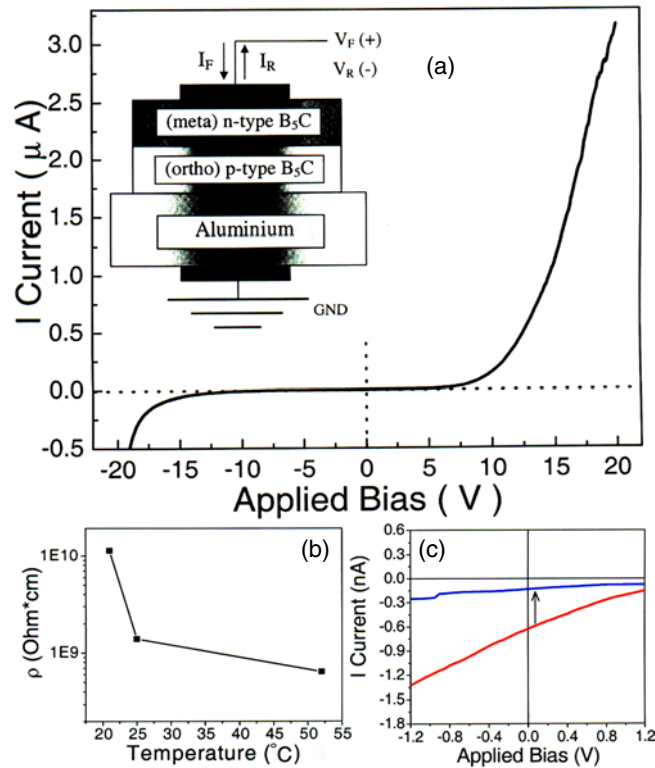
Under exposure to synchrotron white light, an effective route for decomposition [1, 12], the photoemission features are observed to shift toward higher binding energies in the case of metacarborane (on Ag and Au substrates) and lower binding energies in the case of orthocarborane (on Cu and Ag substrates), as both seen in figure 2. Semiconducting boron carbides form when the exopolyhedral hydrogen is lost from these source molecules, placing the icosahedral building blocks in more intimate contact and reducing the HOMO–LUMO band gap [1, 5]. The two isomers decompose to make slightly p-type acceptor (orthocarborane) and strongly n-type donor state dominated (metacarborane) semiconducting materials.



**Figure 2.** Surface photovoltage effects of the source molecules metacarborene and orthocarborene. Shown as a function of exposure to zero order (white) synchrotron light at film temperatures of approximately 105 K. Metacarborene adsorbed on polycrystalline Ag (a) and on Au(111) (b) provides an increase in the binding energies of the icosahedral cage photoemission features (a shift away from the Fermi level) with decomposition (left). Orthocarborene adsorbed on polycrystalline Ag (c) and Cu(111) (d) exhibits a decrease in the binding energies of the icosahedral cage photoemission features (a shift toward the Fermi level) as decomposition occurs (right).

The shifts in the photoemission spectra, with decomposition of metacarborene and orthocarborene and formation of semiconducting boron carbides, are characteristic of 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 band shifts towards 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 metacarborene. For the alloy compositions of  $B_{10}C_2$ , an indirect bandgap of well under 1 eV is expected [16, 17].

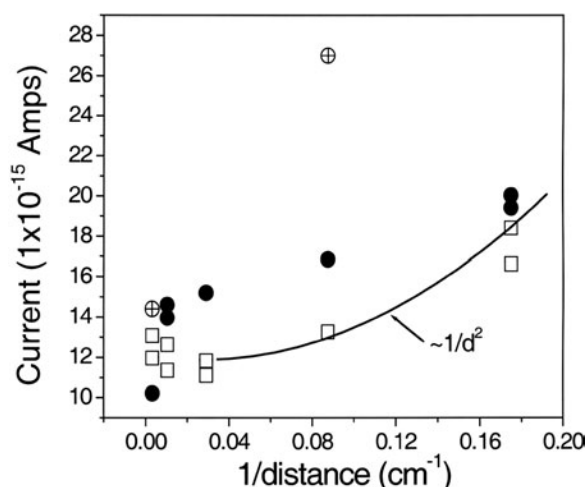
A heterogeneous mixture of carborane species is not formed with decomposition as the photoemission features characteristic of the molecular species, although shifted, remain with exposure to the synchrotron white light (figure 2). This indicates that the decomposition process leaves the icosahedral cage of the carboranes intact and decomposition is dominated by exopolyhedral hydrogen loss. Both the molecular films and the boron carbide semiconductor films formed after decomposition are clearly self-doping materials, since the deposition and decomposition involves only the metacarborene and orthocarborene source molecules (n-type and p-type respectively). In fabricating diodes (discussed below), no transition metal impurity dopants were introduced as was necessary for the more conventional homojunction boron carbide based diodes [4].



**Figure 3.** The  $I(V)$  characteristic curve of the p-type boron carbide/n-type boron carbide isomeric diode at 295 K is shown in (a). The diode resistivity, in reverse bias, is quite large for various temperatures in the vicinity of room temperature (b). A zero-bias offset (c) is observed in a light saturated diode but diminishes when operated again in the dark. Inset is a schematic diagram of the diode construction.

We have fabricated a number of diodes by plasma enhanced chemical vapour deposition or PECVD [2, 3] in a further demonstration that n-type and p-type boron carbides are formed from the decomposition of metacarborene and orthocarborene respectively. Diodes formed by plasma assisted decomposition compare favourably with devices fabricated by synchrotron radiation assisted decomposition and have the advantage that thicker semiconductor films can be readily fabricated by PECVD [1, 5, 16]. The geometry of these new diodes is shown inset to figure 3(a). These diodes are highly resistive, as indicated by the hysteresis in the diode characteristics and as in figure 3(b). In the  $I(V)$  curve of figure 3(a), the diodes show very small leakage currents. This is also summarized by the resistance at 1 V reverse bias (figure 3(b)). There are nonzero offset currents in many of the light saturated diodes at zero bias, as shown in figure 3(c). This photocurrent is a reversible effect. In the absence of light, the nonzero offset current diminishes with time, as indicated in figure 3(c). This fourth quadrant conductivity is a common characteristic of photodiodes [18] indicating photovoltaic applications are possible.

Heteroisomeric boron carbide diodes, formed from metacarborene and orthocarborene decomposition, are sensitive to neutrons, as seen in figure 4. The signal was observed above background for both reverse bias (5 V) and no bias in the absence of light but in the presence of a low incidence neutron flux (on the order of  $120 \text{ neutrons s}^{-1}$  on our diodes at closest placement to the source). Increasing the amount of neutron moderator (paraffin), as expected, increases



**Figure 4.** The heteroisomer diode current response to a low neutron fluence. Current is plotted as a function of inverse distance from the source for two different weakly moderated diodes at 5 V reverse bias (●) and zero bias (□), with a strong neutron response shown for one of the diodes, as expected, when strongly moderated at 5 V reverse bias (⊕). All data follow the expected  $\frac{1}{d^2}$  dependence.

sensitivity (figure 4). Indications of direct power conversion arise from our observation of a zero-bias current from these diodes in the presence of a small neutron fluence.

The potential of boron-rich semiconductors as solid-state neutron detectors has received serious consideration [19–21]. Based on the  $^{10}\text{B}(n, \alpha)^7\text{Li}$  neutron capture reactions



or



boron carbide to silicon heterojunction diodes have been shown to detect neutrons [19] while boron phosphide (BP) heterojunction diodes with silicon [20, 21] were successfully tested as alpha radiation detectors, but failed to work as neutron detectors. Diodes of boron deposited on GaAs [22–27] and silicon [28] have also been shown to work as effective neutron detectors. Such neutron detector devices rely on a conversion layer material of high neutron capture cross-section and, from intrinsic geometry considerations, have lower ultimate efficiencies than solid state neutron detectors where the active semiconductor region is a boron-rich semiconductor. Our heteroisomeric diodes are *not* conversion layer solid state neutron detectors as all of the contributing semiconductor components to our device only contain a boron-rich boron carbide.

There are many advantages to carborane heteroisomer diodes over the previously fabricated heterojunction and homojunction diodes. Since it is the isotope  $^{10}\text{B}$  which has the large neutron capture cross-section, the diodes reported herein should exhibit vastly improved sensitivity by increasing the isotopic abundance of  $^{10}\text{B}$  from its natural abundance of about 20% of the boron in our boron carbides, with the remaining 80% being  $^{11}\text{B}$ , to 100%  $^{10}\text{B}$ . Since the diodes are made by chemical vapour deposition,  $\text{B}^{10}$  enrichment of the carborane source molecules can be efficiently undertaken without introducing contaminants. Boron carbides have been shown to exhibit wide depletion regions [16] and film thickness can be increased to make these devices opaque to epithermal neutrons. These improvements will add further detection efficiencies, possibly in excess of 80% detection. In addition, since



the heteroisomeric diodes are formed without transition metal dopants, activatable transition metals can be eliminated (not possible in the conventional homojunction diode [4]), leading to increased reliability and fewer false positive signals.

This new class of boron carbide diodes is distinct from both the heterojunction diodes and homojunction diodes that exploit semiconducting boron carbides. Neutron detection efficiencies have yet to be measured, and much remains in the characterization of these diodes. These diodes have not, as of yet, exhibited the insensitivity to high temperature found with the silicon carbide/boron carbide heterojunction [3] and the boron carbide homojunction [4] diodes. Nonetheless, the heteroisomeric diodes packaged in organic polymers (that also act as a neutron moderator) are more efficient and subject to fewer false positives than some recent schemes for detecting fissile materials [29, 30]. Even without isotopic enrichment, since the depletion regions and both sides of the p–n junction contain a boron-rich semiconductor, the heteroisomeric diodes represent a potentially far more efficient (and hence sensitive) solid state neutron detector than any conversion layer or heterojunction layer device.

This research was supported by the National Science Foundation through grants Nos ECS-0300018 and EPS-0091909, the Nebraska Research Initiative, and the US Department of Energy National Nuclear Security Administration Office of Nonproliferation Research and Engineering (NA-22) through Pacific Northwest National Laboratory. The authors are grateful to Bo Xu, D N McIlroy, A S McMullen-Gunn, and Walter Hancock for assistance with some of these measurements and D N McIlroy, T C Caruso, S I Webb, and H Batelaan for their comments.

## References

- [1] Byun D, Hwang S-D, Dowben P A, Perkins F K, Filipis F and Ianno N J 1994 *Appl. Phys. Lett.* **64** 1968–70
- [2] Hwang S-D, Byun D, Ianno N J, Dowben P A and Kim H R 1996 *Appl. Phys. Lett.* **68** 1495–7
- [3] Adenwalla S, Welsch P, Harken A, Brand J I, Sezer A and Robertson B W 2001 *Appl. Phys. Lett.* **79** 4357–9
- [4] Hwang S-D, Yang K, Dowben P A, Ahmad A A, Ianno N J, Li J Z, Lin J Y, Jiang H X and McIlroy D N 1997 *Appl. Phys. Lett.* **70** 1028–30
- [5] Byun D, Spady B R, Ianno N J and Dowben P A 1995 *Nanostruct. Mater.* **5** 465–73
- [6] Bernard L, Caruso A N, Xu B, Doudin B and Dowben P A 2003 *Thin Solid Films* **428** 253–6
- [7] Caruso A N, Bernard L and Dowben P A 2003 *J. Phys. Chem.* **107** 9620–3
- [8] Zeng H, Byun D, Zhang J, Vidali G, Onellion M and Dowben P A 1994 *Surf. Sci.* **313** 239–50
- [9] McIlroy D N, Zhang J, Dowben P A and Heskett D 1996 *Mater. Sci. Eng. A* **217/218** 64–8
- [10] Aflatooni K, Gallup G A and Burrow P D 2002 *J. Phys. Chem. A* **106** 4703–8
- [11] Salam A, Deleuze M S and Francois J P 2003 *Chem. Phys.* **286** 45–61
- [12] Byun D, Hwang S-D, Zhang J, Zeng H, Perkins F K, Vidali G and Dowben P A 1995 *Japan. J. Appl. Phys. Lett.* **34** L941–4
- [13] Demuth J E, Thompson W J, DiNardo N J and Imbihl R 1986 *Phys. Rev. Lett.* **56** 1408–11
- [14] Alonso M, Cimino R and Horn K 1990 *Phys. Rev. Lett.* **64** 1947–50
- [15] Stiles K and Kahn A 1988 *Phys. Rev. Lett.* **60** 440–3
- [16] Lee S, Mazurowski J, Ramseyer G and Dowben P A 1992 *J. Appl. Phys.* **72** 4925–33
- [17] Ahmad A A, Ianno N J, Snyder P G, Welipitiya D, Byun D and Dowben P A 1996 *J. Appl. Phys.* **79** 8643–7
- [18] Perez-Albuern E A and Tyan Y-S 1980 *Science* **208** 902–7
- [19] Robertson B W, Adenwalla S, Harken A, Welsch P, Brand J I, Dowben P A and Claassen J P 2002 *Appl. Phys. Lett.* **80** 3644–6
- [20] Lund J C, Olschner F, Ahmed F and Shah K S 1990 *Mater. Res. Soc. Symp. Proc.* **162** 601–4
- [21] Viles T P, Brunnett B A, Yoon H, Lund J C, Hermon H, Buchenauer D, McCarty K, Clift M, Dibble D and James R B 1998 *Mater. Res. Soc. Symp. Proc.* **487** 585–90
- [22] McGregor D S, Hammig M D, Yang Y H, Gersch H K and Klann R T 2003 *Nucl. Instrum. Methods A* **500** 272–308
- [23] McGregor D S, Klann R T, Gersch H K, Ariesanti E, Sanders J D and van der Elzen B 2002 *IEEE Trans. Nucl. Sci.* **49** 1999–2004



- 
- [24] Gersch H K, McGregor D S and Simpson P A 2002 *Nucl. Instrum. Methods A* **489** 85–98
- [25] McGregor D S, Klann R T, Gersch H K and Yang Y H 2001 *Nucl. Instrum. Methods A* **466** 126–41
- [26] McGregor D S, Vernon S M, Gersch H K, Markham S M, Wojtczuk S J and Wehe D K 2000 *IEEE Trans. Nucl. Sci.* **47** 1364–70
- [27] McGregor D S, Lindsay J T, Brannon C C and Olsen R W 1996 *IEEE Trans. Nucl. Sci.* **43** 1357–64
- [28] Sato N, Ishiwata O, Seki Y and Ueda A 1990 *Japan. J. Appl. Phys.* **29** 2526–30
- [29] Fetter S, Cochran T B, Grodzins L, Lynch H L and Zucher M S 1980 *Science* **248** 828–34
- [30] Borozdin K N, Hogan G E, Morris C, Priedhorsky W C, Saunders A, Schultz L J and Teasdale M E 2003 *Nature* **422** 277