Improved p-n hetero-junction device performance induced by irradiation in amorphous boron carbide films.

Authors

George Peterson¹, Qing Su², Yongqiang Wang³, Peter Dowben^{4, 5}, Michael Nastasi^{1, 2, 4}

Affiliations

¹Department of Mechanical and Materials Engineering, University of Nebraska-Lincoln, Lincoln, NE 68583-0857, USA

²Nebraska Center for Energy Sciences Research, University of Nebraska-Lincoln, Lincoln, NE 68583-0857, USA

³Materials Science and Technology Division, Los Alamos National Laboratory, PO Box 1663, Los Alamos, NM 87545, USA

⁴Nebraska Center for Materials and Nanoscience, University of Nebraska, University of Nebraska-Lincoln, Lincoln, NE, 68588-0298, USA

⁵Department of Physics and Astronomy, University of Nebraska-Lincoln, Lincoln, NE 68588-0299, USA

Abstract

Amorphous hydrogenated boron carbide films ($a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$) on Si p-n heterojunctions were fabricated utilizing plasma enhanced chemical vapor deposition (PECVD). These

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5 devices were found to be robust when irradiated with 200 keV He⁺ ions. For low doses of
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7 irradiation, contrary to most other electrical devices, the electrical performance improved.
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10 On the heterojunction I(V) curve, reverse bias leakage current decreased by 3 orders of
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12 magnitude, series resistance across the device decreased by 64%, and saturation current due
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14 to generation of electron-hole pairs in the depletion region also decreased by an order of
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16 magnitude. It is believed that the improvements in the electrical properties of the devices
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18 are due to an initial passivation of defects in the a-B₁₀C_{2+x}:H_y film resulting from electronic
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20 energy deposition, breaking bonds and allowing them to reform in a lower energy state, or
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22 resolving distorted icosahedron anion states.
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30 *Keywords*

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33 Semiconducting boron carbides

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35 Hydrogenated boron carbides

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37 p-n heterojunction

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39 Radiation hard

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50 Corresponding Author: Mike Nastasi

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52 Telephone: (402) 472-3852 (Office)

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54 e-mail: mnastasi2@unl.edu
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Main Text

1. Introduction

Semiconducting boron carbide icosahedral materials have been investigated for solid state neutron detection [1–12]. *What makes the boron-rich icosahedral based boron carbide [13–17], icosahedral based boron nitride and icosahedral based boron phosphide [18,19] materials advantageous is their ability to heal neutron [13] and electron [17,18] radiation damage. Although, damage to the cross-linking chains within the unit cell and volumetric swelling from helium bubble formation is known [14–16] with extensive neutron irradiation.* This is important because ^{10}B neutron capture leads to the loss of boron and creation of daughter fragments with significant kinetic energy [1,10,20]:

For devices where the goal is solid state neutron detection, this radiation hard aspect is extremely important. A radiation hard neutron detector is much more effective and more widely applicable if the devices could be placed in radiation harsh environments.

Traditional p-n junction diodes experience immediate device degradation [21–23] in such environments.

This study seeks to explore the electrical properties and structural changes of amorphous hydrogenated boron carbide ($a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$) films as a function of exposure to alpha particle radiation, one obvious byproduct of the ^{10}B neutron capture process. Since the alpha particle daughter fragment has considerable translational kinetic energy, with a mean range of roughly 5 microns through boron carbide, 200 keV He^+ ions were chosen for irradiation, to examine the effects of high-energy alpha radiation.

Reported stoichiometric compositions of amorphous hydrogenated boron carbide films synthesized by CVD and PECVD are wide ranging [8,44,45]. This is represented by $a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$ with $0 < x < 3$ and $0 < y < 12$. For this study, according to elastic recoil detection measurements, x is approximately 0 and y is approximately 4.

2. Experimental Details

Device fabrication began with an n-type silicon (P doped) substrate (purchased from Silicon Inc.): resistivity 1-10 $\Omega\cdot\text{cm}$. Substrate preparation included sonication in acetone, methanol, and de-ionized, filtered water followed by a 5% wt hydrofluoric acid (HF) bath for oxide removal and hydrogen termination [25]. A 30 minute Ar plasma etch was performed prior to film deposition. Hong provides a detailed description of film synthesis with annealing [24] of $a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$. This study employed the deposition parameters outlined by Hong, but did not post-anneal.

The $a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$ films were grown via plasma enhanced chemical vapor deposition (PECVD) utilizing ortho-carborane (closo – 1,2 dicarbadodecaborane, $\text{C}_2\text{B}_{10}\text{H}_{12}$) as the precursor (purchased from Sigma Aldrich). Plasma environment was 200 mTorr of Ar with a substrate temperature of 350° C, and a power density of 6.479×10^{-3} Watts/cm².

Boron carbide films grown under these conditions were determined to be amorphous by high-resolution transmission electron microscopy (HRTEM) and electron diffraction.

Irradiation was completed at the Center for Integrated Nanotechnologies (CINT), within Los Alamos National Laboratory (LANL) using a 200 kV Danfysik implanter. 200 keV He⁺ ions were implanted to a fluence of 6.5×10^{16} ions/cm² with the He⁺ ion beam current density of $\sim 4.4 \mu\text{A}/\text{cm}^2$. Air-cooling was applied to ensure that the sample temperature remained below 40° C during irradiation.

When an ion enters a material, there are 2 main means of energy deposition. The first is due to electronic stopping (ionization). The incident ion represents a sudden perturbation to the system resulting in a transfer of energy from the projectile to the electrons of the target material [26]. The second form of deposition is due to energy transfer through the elastic collisions (recoil) between the projectile ion and the atoms of the target material. An ion range of ~ 1400 nm was projected for 200 keV He⁺ ions through application of the Monte Carlo SRIM simulation (stopping and range of ions in matter code) [26]. One aliquot fluence above (i.e. 6.5×10^{16} ions/cm²) was calculated to result in 0.1 displacements per atom (dpa) in the ($a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$) films studied, as determined from the SRIM calculated

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5 damage events (full cascade mode) and assuming a film atomic density of 5.0×10^{22}
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7 atoms/cm³. The He⁺ ion irradiated fluence to dose (dpa) relationship is linear: 2 times the
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9 above fluence yields 0.2 dpa in dose, 5 times the above fluence yields 0.5 dpa in dose, etc.
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11 One half of each diode was covered with aluminum foil to maintain a portion of the sample
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13 in the virgin state for comparison.
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20 Figure 1 shows the SRIM simulation of energy deposition in a diode comprised of 285 nm
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22 thick boron carbide film on semi-infinite silicon. This simulation indicates that the energy
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24 transferred to the a-B₁₀C_{2+x}:H_y films is dominated by the ionization process, and that within
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26 the Si, energy deposition is a function of depth. Note the change in scale of Figure 1. The
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28 energy deposition due to electronic stopping ranges from 0 to 280 eV/nm, while the energy
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30 deposition to recoil ranges from 0 to 14 eV/nm. However, recoils have a higher correlation
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32 to displacement damage. Calculations indicate that a fluence sufficient to create 0.1 dpa in
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34 the a-B₁₀C_{2+x}:H_y creates 5.4 dpa at the ion end of range in Si [26].
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42 *Following irradiation, the samples were returned for electrical characterization. Current*
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44 *versus voltage measurements were obtained using a Keithley 2411B SourceMeter to deliver*
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46 *a dc voltage, a Keithley 6485 PicoAmmeter to measure the resulting current, and a HP*
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48 *3478A Multimeter to measure the voltage across the device under test.*
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Figure 1: The SRIM simulation of energy deposition in a-B₁₀C_{2+x}:H_y-Si device separated into its ionization (electronic stopping) and recoil (elastic collisions) components per ion.

3. Results

Current versus voltage I(V) curves are used for traditional p-n junction devices, as a “Figure of Merit”: a characterization of how well a device performs. In this study, it is also appropriate as a Figure of Merit for a-B₁₀C_{2+x}:H_y/Si as a neutron voltaic because the current produced by a device from neutron radiation is a function of the charge separation capabilities of the junction. After neutron capture by a ¹⁰B atom, and fragmentation into the Li atom and alpha particle, they create electron/hole pairs as they translate through the film. The ability of the device to separate the pairs to create both an electron current and a hole current will determine its effectiveness as a neutron voltaic. Caruso *et al.* showed that

when a device does not have good charge separation, the device becomes a less effective neutron voltaic (shown in the pulse height spectra) [8].

Figure 2 plots the current versus voltage $I(V)$ curve for selected $a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$ heterojunction diodes, as a function of irradiation. The solid black triangles show the current - voltage response for the virgin $a\text{-B}_{10}\text{C}_{2+x}\text{H}_y$ to silicon heterojunction diode. Initial He^+ ion irradiation, equivalent to a 0.1 dpa (squares), results in a sharp decrease in the magnitude of the reverse bias current as well as some decrease in the forward bias current. Further He^+ ion irradiation, to the equivalent of 0.2 dpa (stars), results in an additional decrease of forward bias current. Irradiation to the equivalent of 0.5 dpa (circles) results in a sharp *increase* in the current density surpassing that of the virgin heterojunction diode $I(V)$ curve under both forward and reverse bias. Further significant increases in the heterojunction diode reverse bias current density is observed with irradiation to the equivalent of 0.8 dpa (hollow triangles).

Figure 2: The current versus voltage curves for boron carbide to silicon heterojunction diodes, following different levels of irradiation.

To better quantify the improvement of the overall device performance, as well as device degradation, we have examined the differential diode conductance (g_d) = dI/dV in forward bias divided by the differential diode conductance with reverse bias [27]. This ratio of the derivative of the forward current with respect to voltage by the derivative of the reverse current with respect to voltage $\left(\frac{dI}{dV}\right)_F / \left(\frac{dI}{dV}\right)_R$ from the range 0.75 to 1.00 volts, has been plotted in Figure 3. A good figure of merit for a p-n junction is a small leakage current, i.e. very low magnitude reverse bias current density compared to a significant forward bias current density, resulting in a large ratio of differential current with bias. Larger leakage currents, resulting in a lower ratio, are indicative of device degradation. The error bars in Figure 3 represent the standard deviation from the mean of the ratio

calculated for each level of irradiation. Significant improvement in device performance is seen in the samples with the equivalent of 0.1 and 0.2 dpa. Further irradiation to the equivalent of 0.5 dpa results in degradation of the heterojunction diode figure of merit to levels near what was seen for the virgin a-B₁₀C_{2+x}:H_y to silicon heterojunction diode. With irradiation to the equivalent of 0.8 dpa, the heterostructure begins to resemble a bad resistor.

Figure 3: The ratio of the derivative of forward bias current with respect to voltage by the derivative of reverse bias current with respect to voltage derived from I(V) data taken between 0.75 and 1.00 applied volts. The higher the ratio, the better the heterojunction diode performance (figure-of-merit). The error bars are the standard deviation of the calculated mean values.

Transmission electron microscopy (TEM), including high resolution (HRTEM), images were taken to examine the structural changes within the device in an attempt to further understand the source of the changes in the electrical properties of the device. Cross-

sectional TEM samples were prepared from the virgin, 0.2 dpa, 0.4 dpa, and 0.6 dpa equivalent He^+ ion irradiated $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ to silicon heterojunction specimens. All cross-section TEM samples were prepared from $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ films using standard gluing, mechanical grinding and polishing procedures, followed by a low energy (3.7 keV) ion milling. Images were acquired with an FEI Tecnai Osiris (S)TEM electron microscope. Figure 4 shows the HRTEM image of the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y/\text{Si}$ interface after He^+ ion irradiation equivalent to 0.6 dpa, with an inset of the selected area electron diffraction (SAED) pattern of the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ film. The image and SAED clearly show that the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ film remains amorphous, and just as clearly shows that the Si near the interface remains crystalline. However, it should be noted that this image would not indicate the presence or absence of point defects in the Si. Figure 4 does show that the metallurgical junction (the physical interface between the p-type material and n-type material) remains abrupt and well defined. Figure 4 indicates that changes in device performance may not be dictated by structural changes in the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ films or at the p-n heterojunction interface, rather damage to the silicon, not the boron carbide, is implicated as the cause of device degradation.

Figure 4: The HRTEM image of a-B₁₀C_{2+x}:H_y film - Si(001) interface after irradiation (0.6 dpa equivalent) and shows that the Si substrate remains crystalline near the interface and the a-B₁₀C_{2+x}:H_y film - Si(001) junction interface remains abrupt. The insert is a selected area electron diffraction pattern of the boron carbide film, showing the boron carbide remains amorphous.

The TEM cross-section image of the a-B₁₀C_{2+x}:H_y film and the silicon substrate, to a significant depth, is shown in Figure 5. The image shows the device, after irradiation equivalent to 0.6 dpa in the boron carbide film, from the outer edge of the a-B₁₀C_{2+x}:H_y film to the undamaged quasi-neutral Si region. Also plotted in Figure 5 are the vacancy profile and He distributions, as determined by SRIM. The irradiated Si has three discernable regions. Region (a) is the area near the interface with a-B₁₀C_{2+x}:H_y film. At this junction, the Si appears to remain crystalline, and point defects remain isolated from each other. Region (b) exhibits signatures of point defect agglomeration: these are the dark areas adjacent to bright(er) areas in this TEM image. The larger dark areas are attributed to a large concentration of vacancies, while the bright area is attributed to self-interstitials [28]. The vertically oriented white striations of region (c) are indicative of He bubbles. To the

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5 right of region (c) is the undamaged bulk Si. The black lines represent bend contours, most
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7 likely a result of the TEM sample preparation, although sample swelling due to helium
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9 deposition is not unknown [14–17]. Stress/strain fields from such swelling could also yield
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11 similar TEM features. Figure 5 clearly shows a direct correlation between the vacancy
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13 profile and the damage to the Si substrate, as well as a direct correlation between He
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15 bubbles of region (c) and the peak of the He distribution profile. Such helium bubble
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17 formation is not seen in boron carbides until extremely high fluences are reached
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19 corresponding to more than 1 dpa [14–17], well outside the range of this work. The point
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21 defect agglomeration and He bubbles also give a visual indication that di-vacancy states
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23 (V_2) formed by the combination of vacancies created in close proximity to each other, and
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25 other vacancy complexes, are the result of the structural change in the Si substrate.
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27 Changes in the device behavior are not related to structural changes in the boron carbide
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29 film or at the p-n heterojunction interface. This becomes important in our following
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31 discussion of heterojunction leakage currents under reverse bias.
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Figure 5: The TEM image of an a-B₁₀C_{2+x}:H_y to Si heterojunction after irradiation equivalent to 0.6 dpa in the boron carbide film. The red line represents vacancies introduced into the silicon, and the dashed yellow line represents the helium concentration in the silicon substrate. Region (a) is a crystalline region near the metallurgical junction. Region (b) displays signatures of point defect agglomeration. Region (c) is the ion end of range with the highest concentration of He deposition. To the right of (c) is undamaged Si.

4. Discussion

The improvement seen for a-B₁₀C_{2+x}:H_y to silicon heterojunction diode devices, with small amounts of irradiation is very likely occurring in an environment where competing phenomena are in play. We propose that the improvements seen here are a combination of the electronic stopping energy deposited in the a-B₁₀C_{2+x}:H_y film by the alpha particle, breaking strained bonds which reform in lower energy states, or restoring distorted icosahedron cages resultant from mono-anion or di-anion states [29]. Both events may reduce the number of defects in the film, although a direct confirmation for this has not

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5 been ascertained from work reported here and remains an open speculation until definitely
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11 According to Gill *et al.* [30], the reverse bias leakage current density (J_v) arises from a
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13 carrier emission/generation process. Any capture reactions are minimized due to the
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15 reduction in the carrier concentration under reverse bias. The rate of generation (G) is
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18 proportional to the trap concentration (N_t) and electron and hole capture cross-sections (σ).
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$$J_v = e G \quad (1)$$

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$$G = \frac{N_t \sigma v n_i}{2 \cosh(\beta)} \quad (2)$$

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$$\beta = \frac{E_t - E_i}{kT} \quad (3)$$

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39 Where v is the thermal carrier velocity, n_i is the intrinsic carrier concentration, E_t is the
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41 trap energy level, E_i is the intrinsic Fermi level, k is the Boltzmann Constant, and T is
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49 As mentioned above, Figure 5 provides visual evidence that there should be an anisotropic
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51 distribution of trap energy states available for carrier generation as well as a distribution in
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53 the concentration of those states. MacEvoy *et al.* [31] notes that several complexes are
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created in irradiated Si. We note that one expects a proportionality of N_t to the reverse bias current density, which is proportional to the irradiation level.

Figure 6 indicates that two major changes in the reverse bias leakage current of the a-B₁₀C_{2+x}:H_y to Si p-n heterojunctions occurs with increasing He⁺ ion irradiation. Among these changes, surprisingly, the data suggests an initial reduction in the concentration of traps with discrete energy levels, especially with increasing He⁺ ion irradiation near a fluence of 0.1 dpa equivalent irradiation level. Since the Si substrate is single crystal, the amorphous film is the most logical medium to account for the reduction in the concentration of traps with discrete energy levels. The reduction in trap concentration reduces the number of acceptors in the film, increases the effective carrier lifetime, with the experimental observation that the series resistance of the film decreases by over half (175 Ω to 62 Ω). Additionally, it is possible that the decrease in trap concentration for a discrete level(s) is such that the effective distribution of trap states is reduced: i.e. some $G_i \rightarrow 0$, where i indicates an individual component of G , which must be summed. The contribution to the current density of such a G_i is so small as to be completely dominated by the other discrete trap state components. The reverse bias currents are seen to be $\propto N_t \propto dpa$ only at large irradiation fluences. This shows that the trap concentrations likely decrease due to modification of the a-B₁₀C_{2+x}:H_y film via electronic energy deposition, and then increase due to damage accumulation in the Si by nuclear energy deposition.

Figure 6: The reverse bias leakage current (-0.5 volts) versus irradiation level.

For increasing He^+ ion irradiation beyond a 0.1 dpa to 0.2 dpa equivalent, as calculated for the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ film, the damage in the Si begins to degrade the device as fast as the changes in the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ film improves it, and a decrease in device performance is indicated by Figure 3. It is expected that the energy trap levels of the Si will be of different complexes and concentrations than the $\text{a-B}_{10}\text{C}_{2+x}\text{H}_y$ films. This creates new, additional G_i components, increasing the generation current density, though at this point, the concentration of traps is still low enough to be dominated by other radiation induced discrete trap state components, as noted in equation 4.

For irradiation equivalent to 0.5 dpa and 0.8 dpa, device behavior is dominated by the changes in the Si. It is well understood that radiation damage significantly reduces charge carrier lifetimes in silicon [18,32]. It is also known that bulk radiation damage has a

significant effect on charge carrier concentration profiles in silicon [30,33–38], resulting in carrier inversion of n-type silicon to p-type silicon. For light particles (pions, protons, and neutrons), the inversion point occurs at a particle fluence between 10^{13} and 10^{14} cm⁻². The initial particle fluence of this study is 3 orders of magnitude greater than this. If true, this will change the initial charge distribution of the device, creating an exponentially graded decrease in n-type carrier concentration moving from the device interface to ion end of range, as well as creating scattering centers which reduce carrier lifetime. After which the carrier concentration returns to equilibrium levels in the undamaged area. The calculated edge of the depletion region in the virgin Si (with an applied bias of 0.4 volts) is 610 nm [39], just inside of the highest recoil damage region. As point defects accumulate in the Si, the depletion region extends outward exponentially, following the change in carrier concentration grading. While this cannot be confirmed from the data presented here, it is suspected that the n-type silicon near ion end of range type inverts between 0.2 dpa and 0.5 dpa, creating a graded homojunction that is now in series with the heterojunction. If accurate, this creates an electrostatically coupled p-p+ heterojunction / p+-n graded homojunction (grading referring to carrier concentration not metallurgical grading), with a large reverse bias generation current for the reasons discussed previously.

If the electronic energy deposition is breaking bonds, and allowing them to reform in a lower energy state, it is important to perform a cursory thermodynamic examination to determine if the energy deposition per atom is of sufficient magnitude to encourage this. The SRIM simulation of Figure 1 predicts that the majority of the energy deposition in the a-B₁₀C_{2+x}:H_y film will be electronic, and of a magnitude around 270 eV/nm per ion, or at a

fluence of 6.5×10^{16} ions/cm² which is equivalent to 0.1 dpa, 3510 eV/atom in electronic energy deposition. According to Glockler [40] and Feng *et al.* [41], the B-B bonds within an icosahedron have an energy range of 1.3 to 2.6 eV/atom, and B-H bonds an energy range of 1.73 to 3.04 eV/atom. The heat of formation for ortho-carborane is -1.82 eV/atom [29]. Therefore, the electronic energy deposition, within the a-B₁₀C_{2+x}:H_y film is more than enough, within the ion track and secondary ion tracks (delta-ray tracks) [42], to break bonds, and re-form them, reducing N_t of equation (2) as discussed, and as demonstrated for isolated closo carborane icosahedra [41]. The bond energy of Si-Si is 2.25 eV/atom [43], so both electronic and recoil energy deposition in the Si have enough energy to create defects, and increase N_t, nearly right up to the end of the ion deposition range.

5. Conclusions

In conclusion, a-B₁₀C_{2+x}:H_y on Si p-n heterojunctions, synthesized utilizing PECVD, show a robust insensitivity to radiation damage. These heterojunction devices were irradiated with 200 keV He⁺ ions to examine the effects of radiation on the electrical properties of the devices. For low doses of radiation, unlike most other solid state electrical devices, the heterojunction diode performance improved, as illustrated by the ratio of forward bias current to reverse bias or leakage current. A possible origin for the device performance, with modest irradiation, may be due to an initial passivation of defects in the a-B₁₀C_{2+x}:H_y films. Such defect passivation could result from electronic energy deposition, bond breakings and re-formation of the local bonds with a lower total free energy, possibly

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5 resolving distorted icosahedron anion states. As observed by SAED, this is not a re-
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8 crystallization process, but an easing of strain/stress fields.
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12 With sufficient 200 keV He^+ ion irradiation of the a- $\text{B}_{10}\text{C}_{2+x}\text{H}_y$ to silicon heterojunction
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15 devices, we find significant device degradation. It is the fragility of the crystalline Si that
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18 causes device degradation and failure as opposed to any interaction of the He^+ with the a-
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20 $\text{B}_{10}\text{C}_{2+x}\text{H}_y$ films. Devices fabricated solely from boron carbide [2,6–8], might prove to be
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23 even more insensitive to irradiation, until sufficient helium accumulates to create voids and
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26 bubbles [14–16] (representing charge carrier barriers), or the damage is significant enough
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29 to destroy the interface junction, preventing charge separation.
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