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Improved p–n heterojunction device performance induced by irradiation in amorphous boron carbide films

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ABSTRACT

Amorphous hydrogenated boron carbide films (a-$B_{10}C_{2+x}$:H_y) on Si p–n heterojunctions were fabricated utilizing plasma enhanced chemical vapor deposition (PECVD). These devices were found to be robust when irradiated with 200 keV He^+ ions. For low doses of irradiation, contrary to most other electrical devices, the electrical performance improved. On the heterojunction $I(V)$ curve, reverse bias leakage current decreased by 3 orders of magnitude, series resistance across the device decreased by 64%, and saturation current due to generation of electron–hole pairs in the depletion region also decreased by an order of magnitude. It is believed that the improvements in the electrical properties of the devices are due to an initial passivation of defects in the a-$B_{10}C_{2+x}$:H_y film resulting from electronic energy deposition, breaking bonds and allowing them to reform in a lower energy state, or resolving distorted icosahedron anion states.

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]:

$$^{10}B + n \rightarrow {}^{7}Li\,(0.84\,MeV) + {}^{4}He\,(1.47\,MeV) + \gamma\,(0.48\,MeV)\quad(94\%)$$

$$^{10}B + n \rightarrow {}^{7}Li\,(1.02\,MeV) + {}^{4}He\,(1.78\,MeV)\quad(6\%)$$

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 explores the electrical properties and structural changes of amorphous hydrogenated boron carbide (a-$B_{10}C_{2+x}$: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 μm 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 vary [8,44,45]. While range of stoichiometry may be represented by a-$B_{10}C_{2+x}$: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 uses an n-type silicon (P doped) substrate (purchased from Silicon Inc.): resistivity 1–10 Ω cm. Substrate

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preparation included sonication in acetone, methanol, and deionized, filtered water followed by a 5 wt% hydrofluoric acid (HF) bath for oxide removal and hydrogen termination [25]. A 30 min Ar plasma etch was performed prior to film deposition. Hong provides a detailed description of film synthesis with annealing [24] of a-$B_{10}C_{2+x}$:H_y. This study employed the deposition parameters outlined by Hong, but did not post-anneal.

The a-$B_{10}C_{2+x}$:H_y films were grown via plasma enhanced chemical vapor deposition (PECVD) utilizing ortho-carborane (closo-1,2 dicarbadodecaborane, $C_2B_{10}H_{12}$) 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} W/cm^2. 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/cm^2 with the He^+ ion beam current density of ∼4.4 μA/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/cm^2) was calculated to result in 0.1 displacements per atom (dpa) in the (a-$B_{10}C_{2+x}$:H_y) films studied, as determined from the SRIM calculated damage events (full cascade mode) and assuming a film atomic density of 5.0×10^{22} atoms/cm^3. The He^+ ion irradiated fluence to dose (dpa) relationship is linear: 2 times the above fluence yields 0.2 dpa in dose, 5 times the above fluence yields 0.5 dpa in dose, etc. One half of each diode was covered with aluminum foil to maintain a portion of the sample in the virgin state for comparison.

Fig. 1 shows the SRIM simulation of energy deposition in a diode comprised of 285-nm thick boron carbide film on semi-infinite silicon. This simulation indicates that the energy transferred to the a-$B_{10}C_{2+x}$:H_y films is dominated by the ionization process, and that within the Si, energy deposition is a function of depth. Note the change in scale of Fig. 1. The energy deposition due to electronic stopping ranges from 0 to 280 eV/nm, while the energy deposition to recoil ranges from 0 to 14 eV/nm. However, recoil events have a higher correlation to displacement damage. Calculations indicate that a fluence sufficient to create 0.1 dpa in the a-$B_{10}C_{2+x}$:H_y creates 5.4 dpa at the ion end of range in Si [26].

Following irradiation, the samples were returned for electrical characterization. Current versus voltage measurements were obtained using a Keithley 2411B SourceMeter to deliver a dc voltage, a Keithley 6485 PicoAmmeter to measure the resulting current, and a HP 3478A Multimeter to measure the voltage across the device under test.

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-$B_{10}C_{2+x}$: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 ^{10}B 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].

Fig. 2 plots the current versus voltage $I(V)$ curve for selected a-$B_{10}C_{2+x}$:H_y heterojunction diodes, as a function of irradiation. The solid black triangles show the current–voltage response for the virgin a-$B_{10}C_{2+x}$: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

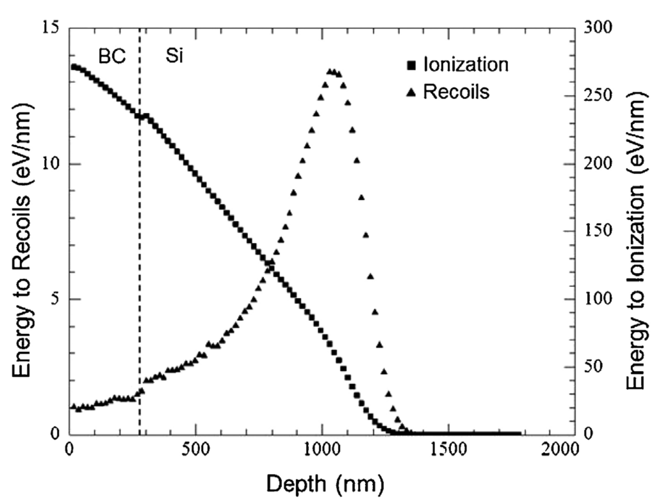

Fig. 1. The SRIM simulation of energy deposition in a-$B_{10}C_{2+x}H_y$-Si device separated into its ionization (electronic stopping) and recoil (elastic collisions) components per ion.

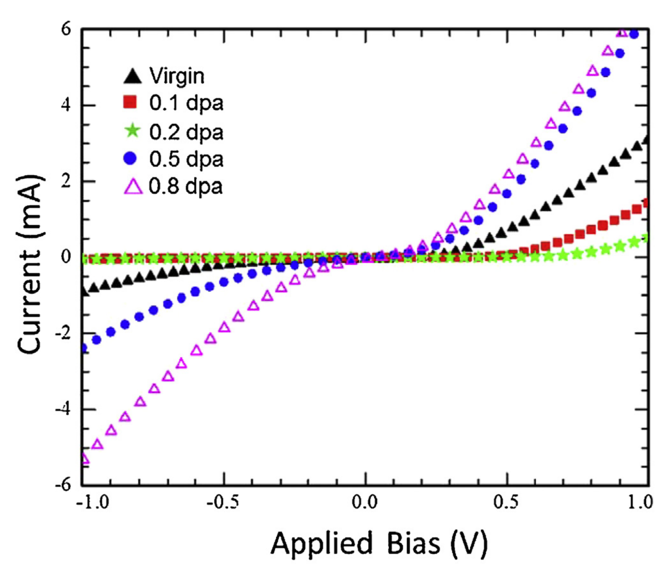

Fig. 2. The current versus voltage curves for boron carbide to silicon heterojunction diodes, following different levels of irradiation.