SEMICONDUCTING BORON CARBIDE THIN FILMS: STRUCTURE, PROCESSING, AND DIODE APPLICATIONS

by

Ruqiang Bao

An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Materials Engineering

The original of the complete thesis is on file
In the Rensselaer Polytechnic Institute Library

Examining Committee:

Douglas B. Chrisey, Thesis Adviser

Daniel Gall, Member

Ishwara B. Bhat, Member

Minoru Tomozawa, Member

Rensselaer Polytechnic Institute
Troy, New York

June 2010
(For Graduation August 2010)

ABSTRACT

The high energy density and long lifetime of betavoltaic devices make them very useful to provide the power for applications ranging from implantable cardiac pacemakers to deep space satellites and remote sensors. However, when made with conventional semiconductors, betavoltaic devices tend to suffer rapid degradation as a result of radiation damage. It has been suggested that the degradation problem could potentially be alleviated by replacing conventional semiconductors with a radiation hard semiconducting material like icosahedral boron carbide.

The goal of my dissertation was to better understand the fundamental properties and structure of boron carbide thin films and to explore the processes to fabricate boron carbide based devices for voltaic applications. A pulsed laser deposition system and a radio frequency (RF) magnetron sputtering deposition system were designed and built to achieve the goals. After comparing the experimental results obtained using these two techniques, it was concluded that RF magnetron sputtering deposition technique is a good method to make B_4C boron carbide thin films to fabricate repeatable and reproducible voltaic devices. The B_4C thin films deposited by RF magnetron sputtering require *in situ* dry pre-cleaning to make ohmic contacts for B_4C thin films to fabricate the devices. By adding another RF sputtering to pre-clean the substrate and thin films, a process to fabricate B_4C / n-Si heterojunctions has been established. In addition, a low energy electron accelerator (LEEA) was built to mimic beta particles emitted from Pm^{147} and used to characterize the betavoltaic performance of betavoltaic devices as a function of beta energy and beta flux as well as do accelerated lifetime testing for betavoltaic devices. The energy range of LEEA is 20 - 250 keV with the current from several nA to 50 μA. High efficiency Si solar cells were used to demonstrate the powerful capabilities of LEEA, i.e., the characterization of betavoltaic performance and the accelerated lifetime test of betavoltaic devices.

Structural analysis by X-ray diffraction and high resolution transmission electron microscopy showed that the prepared B_4C thin films are amorphous. The presence of icosahedrons, which account for the radiation hardness of icosahedral boron rich solids, in the amorphous B_4C thin films was supported by Fourier transform infrared

spectroscopy. The pair distribution functions derived from selected area diffraction pattern of amorphous B_4C thin films showed that the short range order structure of amorphous B_4C thin films is similar to β-rhombohedral boron but with a shorter distance. The investigation of electrical properties of B_4C thin films showed that the resistivity of B_4C thin films ranges from 695 Ω-cm to 9650 Ω-cm depending on the deposition temperature; the direct and indirect bandgaps for B_4C thin films are 2.776 - 2.898 eV and 1.148 - 1.327 eV, respectively; the effective lifetime of excess charge carrier is close to 0.1 ms for B_4C thin film deposited at room temperature and approximates to 1 ms for those deposited at 175 °C to 500 °C. Based on structural characterization and electrical properties of B_4C thin films, a structural model of B_4C thin films was proposed and supported by nanoindenter experiments, i.e., the hardness of thin films deposited at temperature in the range of 275 °C to 350 °C is lower than that of the films deposited at RT and 650 °C.

Heterojunctions of B_4C / n-Si (100) possessing photovoltaic response have been fabricated. The suitable deposition temperature for B_4C thin film to fabricate photovoltaic device is from 175 °C to 350 °C. When the Si substrate surface was not pre-cleaned before depositing B_4C thin film, the B_4C / n-Si (100) heterojunction has better photovoltaic responses, presumably because there were no sputter-produced defects on the surface of Si (100) substrate. Until now, the best achievable photovoltaic performance is B_4C / n-Si (100) heterojunction with 200 nm thick B_4C thin film when the Si (100) substrate surface was not pre-cleaned by RF sputtering. When this heterojunction was characterized using solar simulator with air mass 1.5 spectra, the short circuit current density is 1.484 mA/cm^2, the open circuit voltage is about 0.389 V, and the power conversion efficiency is about 0.214 %. In addition, B_5C thin films deposited by plasma enhanced chemical vapor deposition were used to make some of the devices studied in this dissertation. It was found that the Si-doped B_5C / n-Si (111) heterojunctions also demonstrates their photovoltaic and betavoltaic responses. Even after irradiated by a 120 keV electron beam to a fluence of 4.38×10^{17} electrons/cm^2, the heterojunctions still posses betavoltaic behavior and their responses to the incident irradiance density are similar to that before irradiation.