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Thermal neutron detection with pyrolytic boron nitride

D.S. McGregor*, T.C. Unruh, W.J. McNeil

S.M.A.R.T. Laboratory, Department of Mechanical and Nuclear Engineering, 3002 Rathbone Hall, Kansas State University, Manhattan, KS 66506-2503, USA

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Abstract

Commercially acquired samples of pyrolytic boron nitride (pBN) were tested as potential thermal neutron detectors. The pBN material has a high content of ^{10}B (19.9% natural abundance), allowing for the excitation of charge carriers from the ^{10}B(n,α)^{7}Li reaction. Samples 5 mm × 5 mm × 1 mm thick with conductive contacts applied to both sides were operated as traditional planar semiconductor detectors. Being a solid, the material is attractive as a possible solid-state neutron detector. The devices were tested in a diffracted neutron beam from a nuclear reactor. Experimental results from the prototype devices are reported.

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Keywords: Semiconductor neutron detectors; Solid-state neutron detectors

1. Introduction

There has long been interest in the development of solid-state neutron detectors. Although neutron-sensitive scintillators such as LiI(Eu) and neutron-sensitive thermoluminescent dosimeters (TLDs) such as LiF are solid-state materials, it is the development of semiconductor materials for neutron detection that is usually meant when considering solid-state neutron detectors. There are two basic types of semiconductor neutron detectors, those being thin-film-coated diodes and solid form devices [1,2]. Thin-film-coated devices are configured as junction diode detectors, often from Si or GaAs, with a conversion film of neutron-reactive material attached to the rectifying junction surface (details on the basic operation found elsewhere [1]). Solid form semiconductor detectors consist of a compound semiconducting material, fashioned into a detector, with one or more constituents being a neutron-reactive material.

The most popular neutron reaction of interest is the ^{10}B(n,α)^{7}Li reaction, which yields two possible de-excitation branches from the excited ^{11}B compound nucleus, namely

$$ {}^{1}_{0}\mathrm{n} + {}^{10}_{5}\mathrm{B} \rightarrow \begin{cases} {}^{7}_{3}\mathrm{Li}^{*}(1.4721\ \mathrm{MeV}) + {}^{4}_{2}\mathrm{He}(0.8398\ \mathrm{MeV})\ (93.7\%) \\ {}^{7}_{3}\mathrm{Li}(1.7762\ \mathrm{MeV}) + {}^{4}_{2}\mathrm{He}(1.0133\ \mathrm{MeV})\ (6.3\%) \end{cases} $$

where the Li ion in the 93.7% branch is ejected in an excited state, which de-excites through the prompt emission of a 480 keV gamma ray. For thermal neutrons, the two charged particle reaction products are ejected in opposite directions. Fully enriched ^{10}B has a microscopic absorption cross-section for thermal neutrons (2200 m s^{-1}) of 3840 b. With a mass density of 2.15 g cm^{-3}, the solid structure of ^{10}B has a macroscopic thermal neutron absorption cross-section of 500 cm^{-1}. The absorption cross-section for ^{10}B follows a $1/v$ dependence [3,4].

Solid-state neutron detectors based on boron semiconductors are attractive as compact high-efficiency devices. Boron-based compounds that have been studied include boron monophosphide (BP), boron arsenide (BAs), boron nitride (BN) and various forms of boron carbide (B_xC) [5–10], with patents for such devices dating back decades [11,12], as well as being recently allowed [13–16]. Cubic BP

*Corresponding author. Tel.: +1 785 532 5284; fax: +1 785 532 7057
E-mail address: mcgregor@ksu.edu (D.S. McGregor).
URL: http://https://www.mne.ksu.edu/research/centers/SMARTlab (D.S. McGregor).

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has been researched extensively, having been grown by various bulk and thin film methods [17]. There are only a few reports on neutron measurements with boron-based semiconductor materials, and most report small changes in leakage current when irradiated with neutrons or alpha particles [6,7,10]. Reports claiming that boron-based thin films detected neutrons as pulse mode counters are less convincing since they were grown upon n-type Si substrates [8,9]. As pointed out in the literature [18], such configurations will most likely produce pn junction diodes at the B film/Si interface, hence becoming nothing more than thin-film-coated diode detectors, as explained elsewhere [2,19]. Described in the following work are neutron detection results from tests on solid form pyrolytic boron nitride (pBN) samples fashioned as detectors.

2. Theory

Samples of pBN can be acquired commercially in a pure bulk form, rather than as a thin film on a supporting substrate. pBN is grown through high temperature chemical vapor deposition and can be grown in a variety of shapes and sizes. Quite often pBN is grown on a graphite substrate or mold, and after growth subsequently released from the substrate or mold. Hence, the resulting material is a highly pure solid of pBN. Most manufacturers quote the total metallic trace impurity concentration at less than 10 ppm. The material is fairly inert and can withstand temperatures up to 1800 °C (in vacuum). pBN is often used for furnace components and crystal growth crucibles.

pBN forms in a hexagonal lattice, and as a result, has anisotropic electrical properties. Those bonds that form along the *a* lattice direction are covalent, thereby forming strong bonds. However, the bonds along the *c* direction are weaker van der Waals bonds. At room temperature, the material resistivity is approximately $10^{15}\,\Omega\,\mathrm{cm}$ in both the *a* and *c* directions. The dielectric constant, at room temperature, is 4.97 along the *a* direction and 3.67 along the *c* direction. The bandgap of hexagonal BN is less understood. Recent results indicate that hexagonal single-crystal BN is a direct bandgap semiconductor with a bandgap energy of 5.971 eV [20]. Yet, considering that pBN is not necessarily a single-crystal material, although ordered, it is difficult to assign such a bandgap value. Regardless, consensus indicates that the bandgap is wide, with measured bandgap values on various hexagonal BN samples ranging from 3.6 to 7.1 eV [see Refs. within [20]]. The mass density of pBN is $2.185\,\mathrm{g\,cm^{-3}}$. As a result, when considering that the natural abundance of $^{10}\mathrm{B}$ is 19.9%, yields a macroscopic thermal neutron cross-section of $40.52\,\mathrm{cm^{-1}}$. Hence, a 1-mm-thick piece of pBN would absorb 98.26% of thermal neutrons perpendicularly intersecting the sample.

3. Device design and fabrication

To avoid possible misinterpretations from BN thin films deposited upon Si or other semiconductor substrates, solid pBN samples were acquired from advanced ceramics to study their properties as potential neutron detectors. Hence, the devices had no substrate, which could be inadvertently doped to produce a *pn* junction. The samples were 5 mm × 5 mm in area and 1 mm thick. Samples were prepared by cleaning them in a series of solvents, those being acetone, isopropyl alcohol, and methanol, followed by a cascade de-ionized water bath. Each sample was blown dry with nitrogen. The samples were inserted into a multi-pocket shadow mask with 4.5 mm diameter circular patterns. The shadow mask and samples were then placed in an electron beam evaporator and metal contacts consisting of a 600 Å Ti layer followed by a 10,000 Å Au layer were deposited upon the samples through the shadow mask. The evaporation procedure was repeated for the opposite side, thereby producing simple planar devices. The pBN devices were mounted onto aluminum oxide (Al_2O_3) substrates with Ag epoxy (see Fig. 1). Each Al_2O_3 substrate mount had a hole centered and aligned with the pBN detector to eliminate any possible interference from the substrate.

4. Characterization and results

The pBN devices were tested for *IV* characteristics, as shown in Fig. 2. The leakage currents for the pBN detectors averaged only a few nanoamps in either the

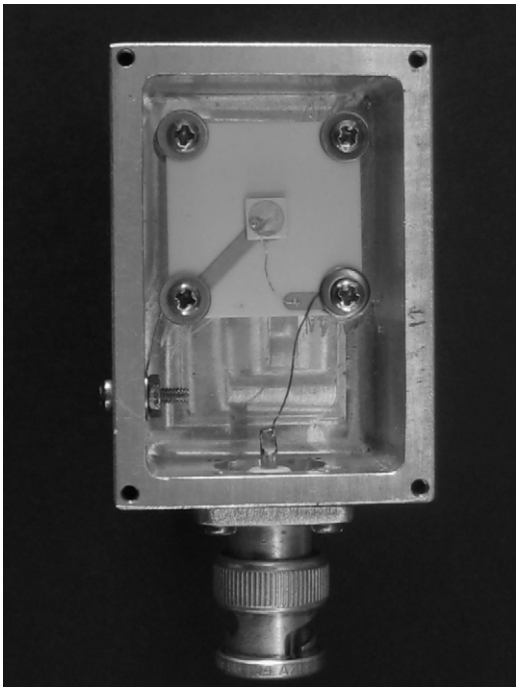

Fig. 1. A pBN device (BN-1) mounted onto an aluminum oxide (Al_2O_3) substrate inside the testing box. The detector alignment hole is directly behind the pBN device and cannot be seen.

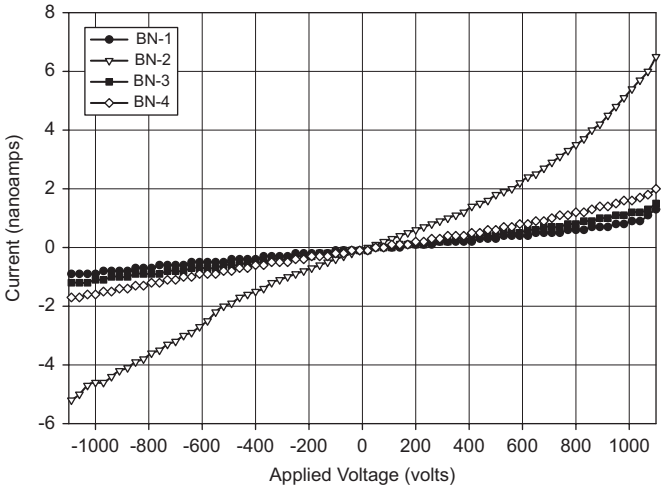

Fig. 2. The *I–V* curves for pBN samples 1–4. The results indicate that the devices are simple low-leakage resistors.

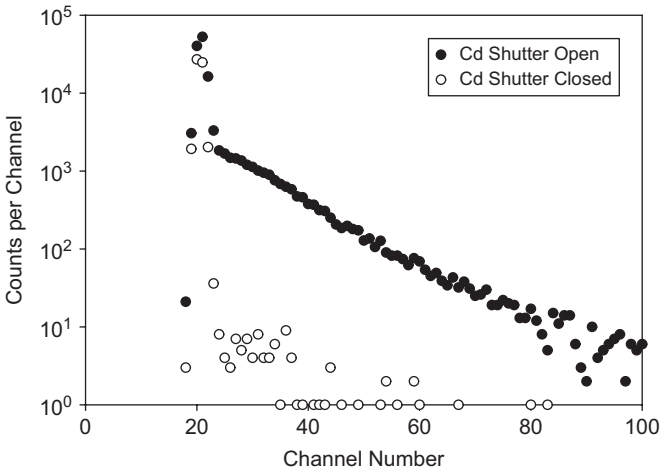

Fig. 3. Pulse height spectra from a pBN detector exposed to a thermal neutron beam showing results from measurements with the Cd shutter open and closed. The LLD was set at channel 20, and the duration of each measurement was 1 h.

forward or reverse bias direction at voltages exceeding 1000 V. The graph in Fig. 2 indicates that devices are non-rectifying, hence are simple resistors with a bulk resistivity of approximately $10^{12}\,\Omega\,\mathrm{cm}$.

Each mounted device was connected into a lightproof aluminum test box (Fig. 1) that was indexed to align detectors with a diffracted neutron beam from the Kansas State University TRIGA Mark II nuclear reactor. The thermal neutron flux, as measured with a ^{3}He detector, was $1.2\times10^4\,\mathrm{n\,cm^{-2}\,s^{-1}}$. The pBN device was operated at biases ranging up to 500 V. Prolonged operation above 500 V resulted in electronic noise that masked all of the neutron pulses. Most of the tests were performed with the bias stabilized at 400 V. Basic NIM counting electronics and an MCA were used for data collection.

With the detector outside of the neutron beam, the lower-level discriminator (LLD) was set slightly above the electronic noise level. With the detector in the beam, a Cd shutter was placed in front of the detector to absorb and block thermal neutrons from entering the device. When the shutter was opened, neutron-induced pulses were observed as shown in Fig. 3. When the shutter was closed, the pulses no longer appeared, except for electronic noise and perhaps some background gamma-ray interactions, as can be seen in Fig. 3. The device appeared to yield symmetric results, in that reversing the voltage and detector direction yielded a similar pulse height spectrum in all cases.

Counting efficiency of detectors was calculated by using an active detection area of $0.159\,\mathrm{cm^2}$ with the total net counts being the difference between the counts observed with the Cd shutter open and Cd shutter closed. The thermal neutron counting efficiency was found to vary from 1.18% to as high as 7.2%. This variation was likely caused by the fact that in all pulse height spectra over 70% of the total counts were in the first four channels above the LLD setting. With a slightly higher LLD setting, all detectors were below 1% efficient. Unfortunately, these results do not compare well to the anticipated absorption efficiency of 98.26%, in which each neutron absorption was expected to produce a neutron count. An explanation is provided elsewhere, in which non-uniform electric fields were reported in similar pBN devices [21]. Hence, it is believed that most of the pulses produced are so small that they are masked by the electronic noise and are below the LLD setting, similar to results found elsewhere [21]. This would also mean that the charge carrier transport in the device is poor.

Further testing was performed to determine the effective useful lifetime of the pBN detectors. Initial response testing over a period of several weeks resulted in irradiating detector samples with a total thermal neutron fluence of $1.5\times10^9\,\mathrm{cm^{-2}}$. To achieve higher levels of irradiation in a reasonable amount of time, the detector was removed from the test box and placed in the middle of the nuclear reactor core and irradiated to a thermal neutron level 10 times greater ($1.5\times10^{10}\,\mathrm{cm^{-2}}$) than from the response testing. After removal from the reactor core, the detector was again mounted in the test box and response testing was repeated, in which case no observable response change was witnessed. In fact, no change in response was observed for neutron fluences up $1.5\times10^{12}\,\mathrm{n\,cm^{-2}}$. A 5% decrease in count rate was observed at $1.5\times10^{13}\,\mathrm{n\,cm^{-2}}$, a 22% decrease in count rate was observed at $1.5\times10^{14}\,\mathrm{n\,cm^{-2}}$, and a 98% decrease in count rate was observed at $1.5\times10^{15}\,\mathrm{n\,cm^{-2}}$ (catastrophic damage), all mainly due to decreasing charge carrier transport properties which caused the pulses to fall into the electronic noise.

The authors wish to point out that previous experiments conducted on other pBN samples from the same sample batch demonstrated inferior radiation hardness, having shown increases in leakage current noise at fluences as low as $10^9\,\mathrm{n\,cm^{-2}}$. The detector performance degraded and the

leakage current increased within only 1 day of irradiation for either bias direction. Further, the degradation appeared to be permanent, a result observed elsewhere on chemically vapor-deposited BN samples [10]. Hence, there are obvious differences in the material characteristics between the various pBN samples, regardless of the fact that they were acquired from the same pBN fabrication batch produced by the vendor. The reasons for these differences are not understood, yet observations are consistent with the polarization effects reported elsewhere with similar pBN samples [21].

5. Conclusions and future work

Commercially available pBN requires very few processing steps to convert it into a neutron detector that can be used with basic NIM counting electronics. However, neutron measurements indicate that the majority of the neutron events in the pulse height spectrum are near or below the electronic noise level, thereby resulting in low and varied counting efficiencies. These results indicate that charge carrier transport in the device is poor, and that a small increase in the electronic noise, caused by a loose electrical connection for instance, can have an adverse affect on the observed efficiency. There is indication elsewhere that non-uniform electric fields in the devices may be responsible for the small pulses and low efficiencies [21], an effect that may be a consequence of polarization.

The ease of construction initially makes pBN a good candidate for simple-to-manufacture neutron detectors, however, this benefit is overshadowed by the unreliable performance, poor carrier transport properties inherent to the material (and devices), and the need for high-bias voltages. The polarization mechanisms need to be investigated and understood. Further, the charge carrier transport in the material must be understood and improved such that reasonably larger pulses, well above the electronic noise, can be observed. Future work will include testing of various thicknesses of pBN samples to determine if sample volume has an effect on the observed pulse height spectrum. However, with recent advances in high-efficiency perforated semiconductor neutron detectors [22–24], further research on pBN has become less interesting.

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