Effects of surface recombination on the charge collection in h-BN neutron detectors

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INTRODUCTION

Neutron detectors are indispensable for the detection of fissile materials such as Plutonium-239 (239Pu). They are also needed in applications of geothermal and well-logging for the determination of porosity and water content of the rocks. Presurized Helium-3 (3He2) tubes are the most developed and widely deployed technology due to which He-3 has a high thermal neutron capture cross section of ∼3840 b. However, being gas-filled detectors, He-3 detectors have low atomic densities corresponding to long absorption lengths for thermal neutrons, making these detectors inherently bulky. Other disadvantages of He-3 detectors include the need for high pressurization and high voltage operation (>1000 V), slow response speed (∼ms), low Q value (∼0.764 MeV), and high ionization energy of gas. Moreover, the price of He-3 gas has increased dramatically in recent years. Therefore, extensive efforts have been devoted to the development of solid-state neutron detectors. Hexagonal boron nitride (h-BN) has emerged as an important wide bandgap (6.0 eV) semiconductor for its applications in deep ultraviolet photonics and solid-state neutron detectors. Recent development of epitaxial growth processes for producing thick (∼50 μm) B-10 enriched h-BN (h-10BN) films using metal organic chemical vapor deposition (MOCVD) has led to the attainment of thermal neutron detectors with a 58% detection efficiency, which is the highest among all solid-state detectors. This opens up the possibility of realizing solid-state neutron detectors which offer comparable performances but with more flexibilities in design as well as in form factors and lower manufacturing and maintenance costs compared with He-3 detectors.

The isotope B-10 has a large thermal neutron capture cross section of σ ∼ 3840 b (=3.84 × 10−21 cm²), whereas the density of B-10 atoms in h-10BN is N [10B] = 5.5 × 1022 cm−3, which is about 550 times higher than that in He-3 gas pressurized at 4 atm. These together afford a relatively large absorption coefficient (Σ = Nσ = 5.5 × 1022 cm−3 × 3.84 × 10−21 cm² = 211 cm−1) and a short absorption length (λ = 1/Σ = 47.3 μm) for thermal neutrons. The theoretical detection efficiency (η) of neutron detectors based on h-10BN as a function of the detector’s thickness, L, can be expressed in terms of the interaction probability as

\[ \eta = P(L) = 1 - e^{-L/\lambda}, \]  

where λ = 47.3 μm. As such, an h-10BN detector with a layer...
thickness of \( L = 3\lambda \) (\( \sim 140\,\mu\text{m} \)) can attain an intrinsic detection efficiency of 95%, and with a layer thickness of \( L = 5\lambda \) (\( \sim 250\,\mu\text{m} \)), it can attain an intrinsic detection efficiency approaching 100%. However, the total detection efficiency also depends on the charge collection (or charge extraction) efficiency, which is highly correlated with the material quality and carrier transport properties.

The capture of a thermal neutron (\( \sim 25\,\text{MeV} \)) by a \( ^{10}\text{B} \) atom initiates the following nuclear reaction inside h-\( ^{10}\text{BN} \) detectors:

\[
^{10}\text{B} + \gamma = ^{7}\text{Li}^* (0.84\,\text{MeV}) + ^{4}\alpha (1.47\,\text{MeV}) \quad [94\% \text{ excited state}], \quad (2a)
\]

\[
^{10}\text{B} + \gamma = ^{7}\text{Li} (1.015\,\text{MeV}) + ^{4}\alpha (1.777\,\text{MeV}) \quad [6\% \text{ ground state}], \quad (2b)
\]

\[
\text{Li}, \quad \alpha \rightarrow N (e^-) + N (h^+), \quad N \sim 10^5. \quad (3)
\]

The high energy daughter particles (\( ^{7}\text{Li}, ^{4}\alpha \)) generated by the nuclear reaction of Eq. (2) decelerate through an h-\( ^{10}\text{BN} \) detector material by depositing their energies, which create a cloud of electrons and holes inside h-\( ^{10}\text{BN} \), as described in Eq. (3). With the aid of an external applied electric field \( (E_x) \), these electrons and holes move across the detector toward anode and cathode and are then collected by the electrodes to serve as a detection signal of absorbed thermal neutrons.

It is well known from prior works on radiation detectors that the mobility-lifetime (\( \mu\tau \)) product which characterizes the process of bulk trapping is a key parameter that determines the detector performance.\textsuperscript{24,25} This is because to the first order the condition for collecting the radiation-generated charge carriers is that the charge carrier drift length \( (=\mu\tau E_x) \) must be larger than the carrier transit distance (or the distance between the two electrodes, \( L \)), i.e., \( \mu\tau E_x > L \), or \( \mu\tau > L^2/V \) or \( \mu\tau < L/V \), where \( V \) is the external voltage applied to the two electrodes. The relationship between \( \mu\tau \) and \( V \) reveals that a material with a higher \( \mu\tau \) product requires a lower applied bias voltage for sweeping out charge carriers, whereas the \( \mu\tau \) product is correlated with the bulk material properties of the detector, including crystalline quality as well as the density of charge carrier traps.

Since the development of BN neutron detectors is in its early stage, all previous works conducted on BN neutron detectors have been primarily concentrated on increasing the film thickness to provide a reasonable intrinsic detection efficiency as well as on improving the \( \mu\tau \) products with the aim of enhancing the charge collection efficiency at a reasonable bias voltage. For instance, the \( \mu\tau \) products of our h-BN films have been improved from \( \sim 10^{-8}\,\text{cm}^2/\text{V} \) to \( \sim 10^{-5}\,\text{cm}^2/\text{V} \), whereas the film thickness has been increased from less than 1 \( \mu\text{m} \) to 50 \( \mu\text{m} \) over the last several years.\textsuperscript{17,19} Subsequently, a detection efficiency of 58% has been achieved for 50 \( \mu\text{m} \) thick vertical detectors biased at 200 V.\textsuperscript{21} However, the highest efficiency of 58% attained so far for 1 \( \text{mm}^2 \) detectors fabricated from 50 \( \mu\text{m} \) thick films is still lower than the theoretical efficiency of 64%, as expected from Eq. (1). This discrepancy is attributed to the less than perfect charge collection efficiency. In this work, we aim to investigate the mechanisms that limit the charge collection efficiency. By evaluating a set of 11 detectors, we demonstrate that the surface effects (charge carrier trapping and recombination at surfaces) are a key factor that prevents a further increase in the charge collection and hence limits the total detection efficiency of h-\( ^{10}\text{BN} \) neutron detectors.

EXPERIMENTS

\( ^{10}\text{B} \) enriched h-BN epilayers were grown using MOCVD on c-plane sapphires of 4-in. in diameter. Precursors for the chemical reaction were 99.9% \( ^{10}\text{B} \)-enriched trimethylboron and ammonia (\( \text{NH}_3 \)), and \( \text{H}_2 \) was used as a carrier gas.\textsuperscript{21-23,26} One of the unique properties of h-BN epilayers is the ability of obtaining freestanding wafers without invoking techniques such as the laser lift-off as for other III-nitrides. Due to the difference in thermal expansion coefficients between h-BN and sapphire substrate and the layer structure nature of h-BN, thick h-\( ^{10}\text{BN} \) epilayers with a sufficient thickness (\( >30\,\mu\text{m} \)) naturally separate from the sapphire substrate during cooling down after growth, providing freestanding h-\( ^{10}\text{BN} \) wafers as schematically depicted in Fig. 1(a). An image of a freestanding h-\( ^{10}\text{BN} \) wafer of 4-in. in diameter is shown in Fig. 1(b).

The electron-beam evaporation technique was used to deposit Ohmic contacts consisting of the Ni (10 nm)/Au (20 nm) bilayer on both sides of the freestanding h-\( ^{10}\text{BN} \) to form a vertical photoconductive type of detectors, as schematically represented in Fig. 1(c). Detectors consisting of the Ti (10 nm)/Al (20 nm) bilayer were also fabricated for the purpose of conducting comparison studies on the effects of different metal contacts on the surface recombination. The use of these metals as Ohmic contacts was adopted from GaN devices. Figure 1(d) shows a dark current-voltage (I-V) characteristic of a 50 \( \mu\text{m} \) thick vertical detector with a detection area of 1 \( \text{mm}^2 \) incorporating Ni (10 nm)/Au (20 nm) bilayer as electrodes, revealing an Ohmic behavior. As shown in Fig. 1(d), the typically leakage current densities of h-\( ^{10}\text{BN} \) detectors are very low, around \( 1 \times 10^{-10} \,\text{A/cm}^2 \) at a bias voltage of 200 V (or at an applied electric field of \( 4 \times 10^4\,\text{V/cm} \)) due to the large bandgap of h-BN, rendering these materials highly resistive. In contrast to conventional III-nitride wide bandgap semiconductors, the as-deposited metal contacts on h-BN exhibit Ohmic behavior without additional thermal annealing.

The mobility-lifetime (\( \mu\tau \)) products and the surface recombination velocities for electrons and holes were obtained by measuring the photocurrent-voltage (I-V) characteristics with either the anode or the cathode of the detector surface irradiated with a UV light (a deuterium UV lamp consisting of a continuum spectrum from 190 to 350 nm) and analyzed using the classical Many’s equation.\textsuperscript{24}

RESULTS AND DISCUSSION

In h-BN, above bandgap photons have a very high optical absorption coefficient (\( \sim 7 \times 10^5\,\text{cm}^{-1} \)), corresponding to a short optical absorption length \( (\lambda) \) of 14.5 nm.\textsuperscript{25,27} Therefore, the penetration depth of the above bandgap photons is within \( \sim 70\,\text{nm} \) from the irradiated surface, which is much smaller than the thickness (\( \sim 50\,\mu\text{m} \)) of the detectors. As such, the applied voltage polarity can be set up as to either inject electrons or holes from the illuminated surface into the bulk, as depicted in Fig. 1(c), so that the transport properties of electrons and holes can be separately...
probed. The photocurrent as a function of the applied voltage under UV excitation for a set of 11 detectors of 1 mm² in size was measured and analyzed based on the classical Many’s equation for insulating semiconductors under strongly absorbed illumination by taking into consideration of both effects of surface recombination and bulk trapping\(^{24}\)

\[
I_i(V) = I_{0i} \left[ \eta_{ci}(V) \right] = I_{0i} \left[ \frac{V \mu_i \tau_i \left( 1 - \frac{1}{e^{\frac{V}{L \mu_i \tau_i}}} \right)}{L^2 \left( 1 + \frac{s_i L}{\mu_i V} \right)} \right] , \quad (i = e, h), \tag{4}
\]

where \(\eta_i(V)\) defines as the charge collection efficiency at an external bias voltage \(V\) applied between the two electrodes, \(I_0\) is the saturation current, \(\mu_i \tau_i\) and \(s_i\) (\(s_e\)) denote, respectively, the mobility-lifetime product and surface recombination velocity for holes (electrons), and \(L\) is the thickness of the detector (or the carrier transit length). For the purpose of illustration, I-V characteristic for the hole transport under UV excitation for a representative 50 μm thick detector is shown in Fig. 2. Fitting with Eq. (4) yields values of \(\mu_h \tau_h\) and \(s_h/\mu_h\) of \(1.0 \times 10^{-4} \text{cm}^2/\text{V}\) and \(9.6 \times 10^3 \text{V/cm}\), respectively.

By examining Eq. (4), one can see that other than the condition of \(\mu_\text{r}E_0 > L\) or \(\frac{L}{\mu_\text{r} \tau} < 1\) appeared in the numerator, another condition for attaining a high charge collection efficiency contained in the denominator is \(\frac{s \mu}{\mu} \leq s_i < 1\), which is governed by the surface recombination velocities. By defining \(s_i/\mu\) as the “surface recombination field,” \(E_0\), we can rewrite this condition as \(s \mu < s_i L < 1\), where \(E_0 \left( = \frac{s_i L}{\mu} \right)\) is the external applied electric field. Introducing \(E_0\) is useful for understanding the effects of surface recombination on the charge collection efficiency. Not only the ratio of the surface recombination velocity to mobility is a measure of an “effective electric field” at the surfaces, but also it provides a direct way for quantifying the necessary charge collection condition with respect to the applied electric field, that is, \(E_0 \gg E_0\). In other words, other than the charge transport processes occurring in the bulk as described in the numerator of Eq. (4), photo- or neutron-generated charge carriers must also overcome the surface trap induced potential barriers or surface recombination fields at both surfaces in order to be extracted by the electrodes. This scenario is schematically illustrated in Fig. 3. As such, the external applied electric field must be much greater than the surface recombination field, \(E_0 \gg E_0\) in order to effectively sweep out charge carriers.

FIG. 1. (a) Schematic diagram of a freestanding h\(^{10}\)BN wafer formed by self-separation from the sapphire substrate during cooling down after MOCVD growth. (b) Photo of a freestanding h\(^{10}\)BN epilayer wafer of 4-in. in diameter. (c) Schematic diagram of a h\(^{10}\)BN vertical detector with its anode bottom surface irradiated with UV radiation, allowing the probe of the hole transport properties in the detector material. (d) Dark (leakage) current vs applied voltage (or I-V characteristic) of a 1 mm² neutron detector fabricated from a 50 μm thick h\(^{10}\)BN epilayer.
Surface trap states are formed due to the presence of impurities at both surfaces, which act as recombination centers for neutron- or photo-generated charge carriers in addition to bulk traps. To the first order, the surface recombination rate can be written as 
\[ \frac{R_s}{s/\mu N_t} \], where \( \sigma_t \) and \( N_t \) denote the recombination cross section and density of the surface traps, respectively. Hence, the surface field, \( E_s = s/\mu \), is also proportional to the surface trap density and inversely proportional to the carrier mobility, whereas its direction is always opposite to the applied electric field, \( E_a \), as indicated in Fig. 3.

To investigate the dominant factors which are limiting the charge collection efficiency, following Eq. (4), we plot in Fig. 4 the calculated values of (a) \( L^2 V/\mu \tau \) and (b) \( sL/\mu \) as functions of the applied voltage (V) up to 200 V for several different values of \( \mu \tau \) products between \( 10^{-6} \) and \( 10^{-4} \) cm\(^2\)/V and \( s/\mu \) between \( 10^2 \) and \( 10^5 \) V/cm. To achieve a high charge collection efficiency (\( \eta_c \)), it is preferable that both conditions of \( L^2 V/\mu \tau \) and \( sL/\mu \) are satisfied. Plots shown in Fig. 4(a) are predominantly determined by the bulk trapping as represented by the numerator of Eq. (4), which provide a useful guidance on the attainable \( \eta_c \) at a certain bias voltage for a given material (with a fixed \( \mu \tau \) product value). Plots shown in Fig. 4(b) are dominated by the surface effects contained in the denominator of Eq. (4).
and represent achievable \( \eta \) at a certain bias voltage at a given surface condition (or a surface recombination field).

As most of our thick h-BN samples possess \( \mu \tau \) products of about \( 10^{-5} \text{cm}^2/\text{V} \) or greater, the condition for overcoming the bulk trapping of \( \frac{\tau_i}{\mu_i} \ll 1 \left( < 10^{-2} \right. \) below) is already satisfied at a bias voltage of 200 V, as shown in Fig. 4(a). This implies that further improvement in the \( \mu \tau \) products will not increase significantly the charge collection efficiency as the values of the numerator \( \frac{V_{\mu_i \tau_i}}{L_2} (1 - e^{-\frac{L}{\mu \tau}}) \) in Eq. (4) for most of our detectors are already approach \( > 99\% \). The high values of this term helped to bring down the required bias voltage for retaining relatively high efficiencies for our detectors. However, the measured values of \( E_s = \frac{s}{\mu} \) of our thick h-BN samples are between \( 10^3 \) and \( 10^4 \text{V/cm} \), providing values of \( \frac{E_s}{\mu} = \frac{L_2 \tau}{(1 + \frac{L}{\mu \tau})} < 25\% \) at a bias voltage of 200 V, as depicted in Fig. 4(b). The results thus indicate that presently the charge collection efficiency of our h-BN neutron detectors is limited by the surface recombination.

This point is further illuminated in Fig. 5, where the values of the numerator of Eq. (4), \( \frac{V_{\mu_i \tau_i}}{L_2} (1 - e^{-\frac{L}{\mu \tau}}) \), are plotted against those of the denominator of Eq. (4), \( \frac{1}{1 + \frac{L}{\mu \tau}} \) or \( \frac{1}{1 + \frac{L}{\mu \tau}} \), using the measured \( \mu \tau \) product and \( s/\mu \) values obtained from a set of 11 h-BN neutron detectors fabricated from various samples. Ideally, both terms need to approach \( 100\% \) in order to achieve a perfect charge collection efficiency. The majority of detectors have \( \mu \tau \) product values of \( \sim 10^{-5} \text{cm}^2/\text{V} \) or greater and are clustered together where values of \( \frac{V_{\mu_i \tau_i}}{L_2} (1 - e^{-\frac{L}{\mu \tau}}) \) are mostly greater than \( > 99\% \). This means that the charge collection efficiency approaches \( > 99\% \) if we consider the bulk transport alone. However, the values of the surface related term, \( 1/(1 + \frac{L}{\mu \tau}) \), have a much larger variation, ranging from \( 70\% \) to \( 90\% \). For instance, the measured \( \mu_i \tau_i \) and \( \mu_e \tau_e \) products for device \#7 with a thickness of \( 35 \mu \) are \( 1.5 \times 10^{-3} \) and \( 0.7 \times 10^{-3} \text{cm}^2/\text{V} \), which provide values of \( 99.8\% \) and \( 99.6\% \) at a bias voltage of 200 V for \( \frac{V_{\mu_i \tau_i}}{L_2} (1 - e^{-\frac{L}{\mu \tau}}) \) for holes and electrons, respectively. However, the measured “surface recombination fields” for the same device are \( 2.1 \times 10^4 \) and \( 1.8 \times 10^4 \text{V/cm} \) for holes and electrons, respectively, giving values of \( 72.7\% \) and \( 76.5\% \) at a bias voltage of 200 V for \( 1/(1 + \frac{L}{\mu \tau}) \) for holes and electrons, respectively. These lead to overall charge collection efficiencies for holes and electrons in device \#7 of \( 72.6\% \) and \( 76.1\% \), respectively. Therefore, the results again confirm that the overall charge collection efficiencies are largely limited by the surface recombination fields. Consequently, minimizing the surface recombination velocities or equivalently minimizing the ratio of \( E_s/\mu \) is necessary to further improve the charge collection efficiency. On the other hand, increasing the applied voltage (or \( E_s \)) can help to thrust the charge carriers to overcome the surface recombination fields and push the term of \( 1/(1 + \frac{L}{\mu \tau}) \) close to \( 100\% \), but is less practical for applications.

In Fig. 6, the “surface recombination fields” for holes are plotted against those of electrons for the same set of 11 h-BN neutron detectors fabricated from various samples. The dotted line indicates \( s/\mu = e/\mu_e \).
detectors. The dotted line represents the case $E^h_s = \frac{1}{\mu_e} = \frac{1}{\mu_h} = E^e_s$. It is apparent that values of $E^h_s$ for holes are above this line, whereas those of electrons are below this line for the condition shown in Fig. 1(c) with the bottom surface being irradiated. This implies that $E^h_s$ is larger than $E^e_s$. The results not only suggest that h-BN surfaces contain traps for both types of charge carries, but the surfaces contain more traps for holes than for electrons.

Figure 7 plots the "surface recombination fields," $s/\mu$, for neutron detectors of two different sizes, 1 and 9 mm$^2$ fabricated from a 50 μm thick sample. The "surface recombination field" appears to increase with increasing detector size. It is well known in the radiation detector field that enlargement of detection area is a key to achieve highly sensitive neutron detectors. Therefore, reducing $E_s$ is not only important for attaining neutron detectors with higher detection efficiencies but is also necessary for achieving detectors with higher sensitivities.

As Ni/Au and Ti/Al bilayers were widely used, respectively, as Ohmic contacts for p-type and n-type GaN devices, we have also examined Ti/Al bilayers as Ohmic contacts for h-BN detectors aimed at reducing the surface recombination effects. A recent calculation revealed that the Schottky barrier heights of Ni and Ti on p-type (n-type) h-BN were 2.2 eV (4.3 eV) and 2.34 eV (4.16 eV), respectively.28 However, our undoped h-BN epilayers are highly insulating, which makes examination of Ti/Al bilayer as another possible Ohmic contact on h-BN a worthy study. Figure 8 compares the "surface recombination fields" of electrons between two 1 mm$^2$ neutron detectors fabricated from a 50 μm thick h-BN wafer using metal contacts of Ni/Au (10 nm/20 nm) and Ti/Al (10 nm/20 nm) bilayers. We found that Ni/Au bilayer produces a smaller $E_s$ than that of Ti/Al bilayer. Hence, Ni/Au bilayer is preferred over Ti/Al bilayer for the fabrication of h-10BN detectors, which corroborates our previous measurement results on leakage currents and overall thermal neutron detection efficiencies.23

Surface traps on h-BN surfaces could form due to the presence of intrinsic defects such as nitrogen vacancy $V_N$ (donor) and boron vacancy $V_B$ (acceptor) or impurities like oxygen occupying nitrogen site $O_N$ (donor) and carbon occupying nitrogen site $C_N$ (acceptor).26 There is also a possibility that impurities tend to attach to the surfaces of h-BN from air. Thus, apart from enhancing the material purity and crystalline quality through epitaxial growth, surface protection of h-BN films needs to be investigated along with the development of effective surface cleaning and surface treatment techniques.

In summary, considering the results from bulk trapping ($\tau_B$) and surface recombination ($\tau_S$), we have identified that the surface effects are the primary factor that prevents further improvement in the charge collection efficiency in our current vertical h-10BN detectors. At the current stage of development, as most of our detectors exhibit charge collection efficiencies of greater than 99% at a bias voltage of 200 V by considering the bulk transport alone, bulk trapping appears to be a less serious issue. It is the surface recombination that limits the overall charge collection efficiency to below 90%. Experimental data also revealed that the surface recombination effects will hamper the development of large neutron detectors as the surface recombination field increases with the detector size. Our results also showed that the surfaces of our current h-BN samples contain more traps for holes than for electrons. We have also identified that the Ni/Au bilayer is more suitable than the Ti/Al bilayer as an Ohmic contact for h-10BN neutron detectors as it yields a lower "surface recombination field."
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