LiInSe$_2$ for Semiconductor Neutron Detectors

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Lithium indium selenide (LiInSe$_2$) is being developed for use as a room temperature semiconductor detector for thermal neutrons. The material has been studied for a number of applications including non-linear optics such as parametric oscillators, as anode material for lithium ion batteries, piezoelectrics, as a scintillation detector material, and as a semiconductor detector material. The recent advances of the crystal growth, material processing, and detector fabrication have led to semiconductor neutron detectors with up to 100 mm$^2$ active area. The theoretical thermal neutron detection sensitivity and gamma rejection ratio (GRR) are comparable to 10 atm, $^3$He tubes of similar size. Detector fabrication and characterization are described and the results are discussed.

Keywords: enriched Li, $^6$Li, thermal neutron detection, detector, LiInSe$_2$, semiconductor and lithium indium selenide

INTRODUCTION

Semiconductors with one or more constituent neutron sensitive isotopes have potential for compact, efficient thermal neutron detection [1]. Table 1 shows neutron sensitive isotopes with relatively high thermal neutron interaction cross sections along with reaction products and energies. Reactions that yield charged particles with ranges much shorter than the semiconductor dimensions are desired for neutron detection. Unlike conversion layered devices, the detection efficiency of semiconductor devices that incorporate thermal neutron sensitive isotopes as a constituent would not be limited by the short range of charged particle reaction products in the converter layer. In this paper, we report on LiInSe$_2$ semiconductors for thermal neutron as well as its capability for pulse height gamma-ray rejection.

LiInSe$_2$ has a wide bandgap and high resistivity, allowing for detectors for room-temperature operation with low noise (low leakage current) [2]. Several crystals of LiInSe$_2$ with varying conditions were grown and characterized. The optical transmission spectroscopy measurement along with resistivity measurement were performed on many LiInSe$_2$ samples and the results are reported for one representative sample. A moderated $^{241}$AmBe fast neutron source was used as the source for thermal neutrons to investigate the device neutron response. Further, the gamma-ray response to $^{60}$Co source was measured and the results of the neutron/gamma-ray response are reported.

CALCULATED ABSORPTION

The reactions used in traditional neutron detectors are listed in Table 1. Considering the Q-value listed in Table 1, the $^6$Li$(n,\alpha)^3$H reaction gives off charged particles with higher energy, resulting in better neutron-gamma ray discrimination. $^6$Li has the highest thermal neutron absorption...
cross section (940 barns) in $^{6}$LiInSe$_2$ composition, which makes the macroscopic thermal neutron absorption cross section of $^{6}$LiInSe$_2$ composition relatively high. This cross section can be evaluated from the basic relations (labeled as Equation 1) as:

$$\Sigma = \frac{\rho N_a \sigma_{\text{tot}}}{A}$$  \hspace{1cm} (1)$$

where for a given material composition, $\Sigma$ is the macroscopic thermal neutron absorption cross section of the composition in cm$^{-1}$, $\sigma_{\text{tot}}$ is the summation of microscopic thermal neutron absorption cross sections of all elements in the composition in barns ($\sigma_{\text{tot}} = \sigma_{\text{li}} + \sigma_{\text{in}} + 2\sigma_{\text{se}}$), $\rho$ is the density of the composition in grams per cm$^3$, $N_a$ is the Avogadro's number and $A$ is the molecular weight of the composition in grams per mole. If 100% of lithium atoms are $^6$Li in $^{6}$LiInSe$_2$ compound, $\Sigma$ can be evaluated as 11.2 cm$^{-1}$ [3, 4], given density of 4.47 g cm$^{-3}$ for the compound and the microscopic thermal neutron absorption cross section of the elements, $\sigma$, as: 940 barns for $^6$Li atoms, 193.8 barns for indium atoms and 11.7 barns for Se atoms. Note that, only the $^6$Li(n,$\alpha$)$^3$H reaction gives off charged particles for the detection application and has the highest absorption cross section among all elements of the composition. The thermal neutrons that interact with In and Se atoms are absorbed in the composition but are not detected. Based on the 11.2 cm$^{-1}$ absorption cross section, a 2.0 mm thick $^{6}$LiInSe$_2$ crystal absorbs 89% of the thermal neutrons (intrinsic absorption efficiency) based on the following relation (labeled as Equation 2), where $t$ is the thickness of the crystal in cm:

$$\text{Intrinsic absorption efficiency} = 1 - e^{-\Sigma \cdot t}$$  \hspace{1cm} (2)$$

The contribution from $^6$Li to the absorbed thermal neutrons is: $\sigma_{\text{li}} / \sigma_{\text{tot}}$ (≈ 0.82). In other words 82% of the total absorbed thermal neutrons will experience the $^6$Li(n,$\alpha$)$^3$H reaction, and can be detected. In comparison, a 2.0 mm thickness of $^3$He at 10 atm absorbs only 32% of thermal neutrons, which is based on macroscopic thermal neutron absorption cross section of 1.9 cm$^{-1}$ for $^3$He at 10 atm based on Equation (1) or Scattering Length Density Calculator [3].

**EXPERIMENTAL PROCEDURE**

**Crystal Growth**

$^{6}$LiInSe$_2$ crystals were grown by the Vertical Bridgman (VB) technique, following methods described in the literature [2, 5–7]. Semiconductor grade high-purity indium and selenium were purchased from Sigma-Aldrich. Enriched $^6$Li was obtained from the Y-12 Isotope office at Oak Ridge National Laboratory in Oak Ridge Tennessee. The LiInSe$_2$ was synthesized in two steps: first by reaction of lithium metal with indium metal in the melt at 1,000$^\circ$C contained in a pBN crucible, which is sealed under vacuum in a larger quartz ampoule along with selenium beads at the bottom of the ampoule. Selenium vapor reacts with lithium-indium molten alloy to form LiInSe$_2$. LiInSe$_2$ crystals are then grown in the same pBN crucible using the vertical Bridgman crystal growth method in a 2-zone Mellon furnace. Figure 1 shows an ingot removed from the growth ampoule. As can be seen in the figure, the crystal has a chartreuse-yellow color. Note that the voids, on the surface of the ingot, are due to bubbles that form on the surface during the melting of the Li and In metals.
Detector Fabrication

Once the LiInSe$_2$ crystals were taken out of the ampoule, they were cut, and polished. The polished crystals had average final thickness of 0.7 mm. The samples were cleaned with cyclohexane prior to contact deposition. Optical transmission measurements were performed at this stage on the samples, as will be discussed later. Iron was deposited as the metal contacts (typical thickness of 500 angstroms and 8 mm in diameter) on both sides of each

### TABLE 2 | Characteristics of LiInSe$_2$ crystals and devices.

| Growth # | Enriched Li-6 | Optical transmission data | Name of detector(s) tested | Contacts material | Resistivity ($\Omega \text{ cm mm}$) | Ohmic behavior | Neutron response (AmBe) | Gamma ray response |
|----------|---------------|---------------------------|---------------------------|------------------|-----------------------------------|----------------|-------------------------|-------------------|
|          | Samples prepared | Wavelength (nm) | bandgap (eV) | |
| G50      | No             | G50-1                      | Cr/Au                     | 1.6 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G50-4    |                | G50-4                      | Pt                        | 1.2 $\times 10^{12}$ | Yes | Yes (Co-60) |
| G50-6-2  |                | G50-6-2                    | Polymer                   | 2.1 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G50-6-3-1|                | G50-6-3-1                  | Cr/Au                     | 6.2 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G52      | No             | G52-7-3                    | Cr/Au                     | 3.8 $\times 10^{11}$ | Yes |                        |
| G52-7-4  |                |                            | Cr/Au                     | 3.3 $\times 10^{11}$ | Yes |                        |
| G54      | Yes            | G54-1,2,5,7                | Cr/Au/Pt                  | 1.2 $\times 10^{11}$ | Yes | Yes | Yes (Co-137) |
| G54-5    |                |                            | Pt                        | 1.2 $\times 10^{12}$ | Yes |                        |
| G54-6-1  |                |                            | Polymer                   | 5.2 $\times 10^{12}$ | Yes | Yes (Co-60) |
| G54-6-2  |                |                            | Polymer                   | 5.6 $\times 10^{12}$ | Yes |                        |
| G54-6-3-2|                |                            | Polymer                   | 8.7 $\times 10^{11}$ | Yes |                        |
| G54-5-Fe-Polymer |                |                            | Fe / Polymer              | 1.5-1.7 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G55      | No             | G55-1,3,5                  | Cr/Au                     | 2.6 $\times 10^{11}$ | Yes |                        |
| G58      | No             | G58-4                      | Cr/Au                     | 8.7 $\times 10^{11}$ | Yes |                        |
| G65      | Yes            | G65-2                      | Cr/Au                     | 6.2-7.8 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G65-3    |                |                            | Cr/Au                     | 4.3-6.7 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G66      | Yes            | G66-2                      | Fe / Au                   | 1.6 $\times 10^{11}$ | Yes |                        |
| G67      | Yes            | G67-1,2                    | Fe / Au                   | 2.1 $\times 10^{11}$ | Yes |                        |
| G68      | Yes            | G68-1                      | Fe / Au                   | 1.4 $\times 10^{11}$ | Yes |                        |
| G68-2    |                |                            | Fe / Au                   | 1.4 $\times 10^{11}$ | Yes |                        |
| G68-4    |                |                            | Fe / Au                   | 1.7 $\times 10^{11}$ | Yes | No (Co-60) |
| G68-Tip  |                |                            | Fe / Au                   | 1.7 $\times 10^{10}$ | Yes |                        |
| G68-T1   |                |                            | Fe / Au                   | 1.5 $\times 10^{10}$ | Yes |                        |
| G68-T4   |                |                            | Fe / Au                   | 1.5 $\times 10^{10}$ | Yes |                        |
| G70      | Yes            | G70-8                      | Fe/ Au                    | 7.0 $\times 10^{10}$ | Yes |                        |
| G70-9    |                |                            | Fe/ Au                    | 1.8 $\times 10^{11}$ | Yes |                        |
| G70-10   |                |                            | Fe/ Au                    | 0.1 $\times 10^{11}$-7.4 $\times 10^{1}$ | Yes |                        |
| G70-11   |                |                            | Fe/ Au                    | 4.6 $\times 10^{11}$ | Yes |                        |
| G70-14   |                |                            | Fe/ Au                    | 0.2 $\times 10^{11}$-1.2 $\times 10^{1}$ | Yes |                        |
| G70-15   |                |                            | Fe/ Au                    | 0.0 $\times 10^{11}$-2.1 $\times 10^{1}$ | Yes |                        |
| G70-16   |                |                            | Fe/ Au                    | 3.3 $\times 10^{11}$ | Yes |                        |
| G70-17   |                |                            | Fe/ Au                    | 0.5 $\times 10^{11}$-1.7 $\times 10^{1}$ | Yes |                        |
| G70-18   |                |                            | Fe/ Au                    | 0.3 $\times 10^{11}$-1.8 $\times 10^{1}$ | Yes |                        |
| G70-12   |                |                            | Fe/ Au                    | 7.9 $\times 10^{11}$ | Yes |                        |
| G77      | Yes            | G77-2,4,11                 | Fe/ Au                    | 4.7 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G77-4    |                |                            | Fe/ Au                    | 3.9 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G77-5-1  |                |                            | Fe/ Au                    | 3.9 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G77-5-2  |                |                            | Fe/ Au                    | 3.9 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G77-6    |                |                            | Fe/ Au                    | 3.0 $\times 10^{11}$ | Yes | Yes (Co-60) |
| G77-7    |                |                            | Fe/ Au                    | 4.5 $\times 10^{11}$ | Yes | No | No |
sample through thermal evaporation. Carbon paste was used to attach 0.05 mm (2 mil) Pd wires to the Fe contacts. Note that Au, Cr, and Pt have also been previously used and all metals have shown good performances. Fe, however, was the most stable of the metals for the longevity of the LiInSe₂ detectors. In other words, the detector was not degraded over time. The samples were then mounted on ceramic substrates using RTV Si based glue for further characterization. Figure 2 shows the detector, labeled as 6LiInSe₂-G77-6, fabricated from ingot G77. Thirty-eight samples were fabricate and tested from different ingots; data for one representative 6Li enriched detector is reported in this paper.

Table 2 shows data from 38 devices fabricated from wafers cut from eleven LiInSe₂ crystal ingots. The data include the optical transmission spectra, resistivity, and the neutron and gamma-ray response. The bandgap was estimated from the transmission spectra for five samples to be 2.82–2.86 eV. All 38 eight samples were similar in color. Devices were tested with a variety of electrode materials including Cr/Au, Fe, Fe/Au, conducting polymer, and Fe/Polymer. Iron electrodes provided the best stability. Resistivity calculated from IV data ranged from about $1 \times 10^{11}$ to $6 \times 10^{12} \Omega \cdot \text{cm}$. Thirty-six of the detectors detected both gamma rays and neutrons.

**Detector Characterization**

Three measurements were employed for characterization of the samples: current-voltage (I-V) measurements, optical transmission measurements, and pulse height spectrum measurements (neutrons and gamma rays). Optical transmission from 400 to 800 nm was conducted at room temperature using a Cary spectrometer. The results of the optical transmission spectroscopy measurements are presented in Results section. A programmable Keithley current-voltage (I-V) characteristic measurement system was used to monitor and record the current at different biases. A linear behavior was observed for both forward and reverse bias, indicating ohmic behavior of Fe/LiInSe₂ interface. The values for the resistivity along with the I-V characteristic curve for one of the samples is presented below.

A Tennelec high voltage power supply (HVPS), a CR-110 Cremat preamplifier, a CANBERRA 2022 amplifier and a multi-channel analyzer (MCA) were used to monitor and acquire pulse height. The top contact of the detectors was grounded and the bottom contact was positively biased at $+300 \text{ V}$ through the preamplifier. The amplifier gain was set to $210 \times$, 8 µs shaping time and positive polarity. The test box with detector, connections, and sources for neutron/gamma-ray counting measurements is shown in Figure 3. With the above mentioned setup, pulse height spectra were collected from all samples with a moderated $^{241}$AmBe neutron source and $^{60}$Co gamma-ray source. Note that the $^{241}$AmBe neutron source has a custom designed casing as illustrated in Figure 4 to facilitate the thermalization of neutrons leaving the bottom of the casing. The schematic of the measurement setup is shown in Figure 5. The results of device response to neutrons and gamma rays are reported below.
RESULTS

Optical Transmission and Spectroscopy Results
The results of the optical transmission measurements for three samples of ingot G77 are presented in Figure 6. The absorption edge was observed at about 434 nm, which corresponds to an energy bandgap of 2.86 eV for LiInSe$_2$ crystals.

Resistivity Results
The current-voltage (IV) characteristic curve obtained from one of the planar devices in Table 2 ($^6$LiInSe$_2$-G77-6 fabricated from G77 ingot) is presented in Figure 7. Note that, this is one of the representatives of the 38 fabricated devices listed in Table 2, and one of the 17 devices fabricated with Fe contacts on both sides of the device. As shown, the resistivity of the $^6$LiInSe$_2$-G77-6 sample was determined to be $3.0 \times 10^{11}$ $\Omega$ cm. Note that the IV curve shows a very linear ohmic behavior. It is known that formation of ohmic contact for a metal-semiconductor interface depends on, the work function WF of metal (Fe in this case being 4.5 eV) and the bandgap of semiconductor (2.86 eV for LiInSe$_2$), the electron affinity of semiconductor and the position of Fermi level within the bandgap (p-type of n-type semiconductor). This ohmic behavior was also observed for other metals applied to LiInSe$_2$ material. Those metals are Au (WF = 5.3 eV), Pt (WF = 5.5 eV) and Cr (WF = 4.5), all forming ohmic contacts on LiInSe$_2$ materials, based on the RMD database summarized in Table 2.

Neutron and Gamma-Ray Counting Results
Figure 8 shows spectra for background, $^{241}$AmBe neutron source and $^{60}$Co gamma-ray source with $^6$LiInSe$_2$-G77-6 detector. The spectra were taken in 1 h increments with the detector under continuous bias for 21 h to examine the stability over time.

DISCUSSION
Gamma Rejection Ratio (GRR) is defined as the difference of the gamma-ray ($\gamma$) counts and background (BG) above the cut off energy line, over the total counts of gamma rays. Thus, GRR can be written as:

$$GRR = \frac{\gamma_{>\text{cut off}} - \text{BG}_{>\text{cut off}}}{\gamma_{\text{total}}}$$

(3)

The cut off energy line was chosen to be around channel 150, close to the endpoint of $^{60}$Co gamma ray energy...
line. The line is shown for the combined spectra for the $^{241}$AmBe/$^{60}$Co neutrons and gamma-rays, and the background for 21 h, as shown in Figure 8. By integrating the counts and using the equation above, the GRR was estimated to be around $6.7 \times 10^{-6}$ for $^6$LiInSe$_2$-G77-6 sample. The GRR is an important ratio for thermal neutron devices since it indicates the device capability in rejecting the gamma rays, while still detecting the thermal neutrons above the cut off energy line.

CONCLUSION

LiInSe$_2$ semiconductor devices were successfully fabricated and tested for thermal neutron detection purposes. The devices showed response to neutrons emitted from a thermalized $^{241}$AmBe source, with decent Gamma Rejection Ratio (GRR) of $6.7 \times 10^{-6}$. A compact solid state neutron detection system based on LiInSe$_2$ would be a major breakthrough over conventional thermal neutron detectors, such as $^3$He tubes that are currently in short supply. This is the long term goal for this study at RMD Inc. Other goals for this research are improving the crystal quality and scaling up the device size. It should be noted that in recent years, other groups have conducted research on Li-based semiconductor devices for thermal neutron detection applications [8–11].

DATA AVAILABILITY STATEMENT

The datasets analyzed in this article are not publicly available. Requests to access the datasets should be directed to Dr. Kanai Shah (kshah@rmdinc.com), since they may contain proprietary information.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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**Conflict of Interest:** The authors of this article were employed by company Radiation Devices Inc. (RMD).

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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