Thallium Bromide Gamma-Ray Spectrometers and Pixel Arrays

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Thallium bromide (TlBr) is a compound semiconductor with a band gap of 2.68 eV making it ideal for room temperature radiation detection. The high atomic numbers, 81 and 35, and the high density of 7.56 g/cm³ give it excellent gamma-ray stopping power. TlBr is a cubic material that melts congruently at a relatively low temperature (~480°C). These properties make it relatively easy to grow good quality crystals with high yield. As a result of improvements in the purification of TlBr mobility-lifetime product of electrons, μτₑ, is now on the order of 10⁻² cm²/V, which is similar to that of CZT. High μτₑ enables the fabrication of thicker detectors with good charge collection and energy resolution. The properties of TlBr make it ideal for use in room temperature gamma radiation operation [1]. Single carrier devices such as small pixel arrays [2] and Frisch collar devices [3] which were developed for CZT can also been applied to TlBr. For example, better than 1% FWHM at 662 keV has been obtained for single pixel events with small (e.g., 3 x 3 pixels, 1-mm pitch, 5-mm thick) arrays.

Keywords: Thallium bromide, TlBr, room temperature, semiconductor detector, gamma ray spectroscopy, capacitive Frisch grid, strip detector, small pixel effect

INTRODUCTION

Thallium bromide (TlBr) is a compound semiconductor with a band gap of 2.68 eV making it ideal for room temperature detection. The high atomic numbers, 81 and 35, and the high density of 7.56 g/cc give it excellent gamma-ray stopping power [4]. Room temperature resistivity of detector quality TlBr crystals is on the order of 10¹¹ Ohm-cm and electron mobility-lifetime product (μτₑ) values are in the 10⁻³ to 10⁻² cm²/V range [5]. TlBr is a cubic material which melts congruently at a relatively low temperature (~480°C) [6]. The cubic structure makes the growth of high quality single crystals relatively easy using conventional melt growth techniques, such as the Bridgeman-Stockbarger technique.

These properties combine to make TlBr a serious competitor to CdTe and CdₓZn₁₋ₓTe for room temperature radiation detection. The attenuation length of 662 keV gamma rays in TlBr is 1.4 cm, while in CZT it is 2.3 cm [7]. Thus, 1 cm of TlBr has the same stopping efficiency of about 1.6 cm of CZT at 662 keV. As is the case of CZT the mobility-lifetime (μτᵣ) product of electrons is significantly higher than that of holes, and thus unipolar device configurations like small pixel arrays and capacitive Frisch grids (CFG), which were originally developed for CZT to improve the energy resolution, also work for TlBr.

Research on TlBr has been ongoing for decades [8–15]. Applications include homeland security, astrophysics [16, 17] and medical x-ray imaging [18, 19]. The use of TlBr, however, had been limited by its relatively poor charge transport properties. Recently, Hitomi et al.,
demonstrated that multi-pass zone refining of commercially available material improves the charge transport in TlBr [20–22]. Hitomi demonstrated a strong correlation between $\mu \tau$ product and purity. By purifying the TlBr raw material using multiple zone passes they obtained a two-order increase in the $\mu \tau$-product.

**EXPERIMENTAL**

**Purification and Crystal Growth**

To purify the material multiple passes of zone refining were used on commercially available 5N purity TlBr powder (EMD Performance Materials item number 1.893579999) in a horizontal furnace. In the zone refining process the heater was passed over the material at 50 mm/hr for 50–200 passes. The molten zone width was maintained at 20–25 mm.

In zone refining, purification is achieved by segregating impurities at a liquid-solid interface. Figure 1 shows sketches of the zone refining process. For most materials impurities have differing solubility in the solid and liquid phases. To utilize this technique, a solid-liquid interface is moved from one end to the other along the length of a horizontally oriented ingot. The solubility-difference then “sweeps” impurities in one direction, typically most impurities are more soluble in the melt than in the solid. A small portion (or zone) of the solid host ingot is melted and swept along toward the end of the ampule by the movement of a heater. The impurities migrate, generally with the zone toward one end of the ingot. To increase the efficiency, the process is repeated resulting in highly purified material toward one end (or possibly in the center). Figure 2 shows a TlBr ingot being purified in a zone refiner.

Figure 3 shows a TlBr ingot grown by horizontal zone melting. In this figure, the impurities have been swept to the right end of the ingot, which is clearly darker. The purest material is in the center. The ingot shown underwent 100 zone refining passes. Final crystal growth was performed in the same ampoule using a slow zone melting pass.

GDMS trace element analyses show significant improvement in purity with 100 passes [23]. The concentration of all measured impurities decreased by an order of magnitude or more, some to below the detectable limit. In particular, calcium, aluminum, and chlorine were initially present in high concentrations. Zone refining resulted in a significant reduction in most impurities. Impurities including lithium, sodium, sulfur, calcium, copper, zinc, strontium, and silver were swept to the tail end of the ingot. This is expected for impurities where segregation coefficient $k_0 < 1$.

Crystals up to 34 mm in diameter have been grown by this process. Detailed information about the purification and crystal growth has been given in a previous paper [24].

A wire saw with a cutting slurry was used to cut the boule into wafers. These wafers were lapped, polished (final polish with a slurry using 3 micron $\text{Al}_2\text{O}_3$ grit in water) and chemically etched (Br-MeOH or HCl) prior to contact deposition. Several different fabrication methods are used depending on the device configuration. After contact deposition, devices are mounted to carrier boards and wired up.
Device Fabrication

TlBr detectors have been fabricated as planar, pixelated, strip or CFG (capacitive Frisch Grid) devices. Each has advantages depending on the application.

Most of the basic fabrication steps for the various devices are the same: (1) cut wafer from ingot, (2) lap wafer to obtain flat and parallel surfaces, (3) polish the surfaces to be contacted, (4) chemically etch the wafer, (5) deposit (by either thermal or e-beam evaporation) metal electrodes (either Au/Cr or Pt) and (6) mount to detector carrier board and wire up device for testing. Note that the CFG devices require additional steps (e.g., apply insulating collar and metal foil).

Planar devices are simplest to fabricate and read out (Figure 4A). Typically, planar devices fabricated from compound semiconductor material exhibit “hole tailing” due to poor hole mobility. Various approaches can reduce hole tailing such as selecting a short shaping time (i.e., short relative to carrier drift time).

The crossed strip electrode device structure is basically similar to planar device except that strips make the detector position sensitive (Figure 4B). The strips may be different widths in different pitch on the two sides. The advantage of the structure is you get many pixels with fewer readout channels. The Figure shows a 0.5 mm thick orthogonal strip detector (∼12 × 12 mm)
with 0.5 mm pitch for the top strips and 2.5 mm pitch for the bottom strips.

Small pixel arrays (i.e., the pixel dimension is small relative to the device thickness) are unipolar charge sensing devices [25] where signal induction occurs primarily when the electrons drift in the vicinity of the anodes and therefore minimize the hole tailing effect [26] (Figure 4C). In addition, the ratio of the cathode-to-anode signal can be used as a depth parameter and signals can be corrected for depth dependence due to electron trapping and variations in weighting potential [27].

CFG detectors have several advantages. The fabrication is straightforward and reading them out requires only one channel (Figure 4D). Figure 5 shows a schematic of the detector configuration and principle of operation. The crystal is wrapped with thin film of an insulating material, such as Teflon tape. A metal foil, such as copper tape, is then wrapped around the insulator and grounded. This grounded foil has an effect similar to that of a Frisch grid ionization chamber. Positive bias voltage was applied to the anode and the cathode is grounded. This grounded foil has an effect similar to that of a Frisch grid ionization chamber. Positive bias voltage was applied to the anode and the cathode is grounded. Reading out both cathode and anode allows depth correction to be applied.

RESULTS AND DISCUSSION

Detector Testing

Planar Detector

Figure 6 shows a $^{137}$Cs spectrum obtained from a $20 \times 20 \times 8$ mm planar detector biased to 700 V and operated at room temperature (24°C). This spectrum was recorded with standard NIM electronics, including charge sensitive preamplifier (Cremat CR110), spectroscopy amplifier (Canberra #2020), and an Amptek 8000A pulse height analyzer. The spectra were recorded with standard NIM electronics, including charge sensitive preamplifiers (Cremat CR110), spectroscopy amplifier (Canberra #2020), and an Amptek 8000A pulse height analyzer. The bias voltage was 2000 V and the shaping time was 12 $\mu$s. The energy resolution (% FWHM at 662 keV) was determined to be 2.2%.

Frisch Grid Detector

Figure 7 shows a raw $^{137}$Cs spectrum obtained from a TlBr capacitive Frisch grid device with dimensions of $5 \times 5 \times 12$ mm and an insulated (with Teflon) copper ring $\sim$ 10 mm long. The ring was connected to the cathode. The spectrum was recorded at room temperature with standard NIM electronics, including charge sensitive preamplifier (Cremat CR110), spectroscopy amplifier (Canberra #2020), and an Amptek 8000A pulse height analyzer. The bias voltage was 2000 V and the shaping time was 12 $\mu$s. The energy resolution (% FWHM at 662 keV) was determined to be 2.2%.

Crossed-Strip Detector

Figure 8 shows $^{241}$Am pulse height spectra acquired from nine of the narrow strips of a 0.5 mm thick orthogonal strip detector ($\sim$ 12 $\times$ 12 mm) with 0.5 mm pitch for the top strips and 2.5 mm pitch for the bottom strips. The spectra were recorded with standard NIM electronics, including charge sensitive preamplifiers (Cremat CR110), spectroscopy amplifier (Canberra #2020), and an Amptek 8000A pulse height analyzer. The spectra shown in the figure were recorded at two bias voltages (140 and 200 V). Note that the response is fairly similar for each of the strips. Also, the spectra recorded at the two bias voltages basically overlap.

Small Pixel Arrays

Figure 9 shows a depth corrected $^{137}$Cs spectrum from a single pixel of a 13-mm thick, $3 \times 3$ array with 2 mm pixel pitch. The detector was biased to 2600 V and operated at $-18^\circ$ C. This spectrum was acquired with discrete electronics designed and built at Cremat. Using the cathode-to-anode ratio as a depth parameter, the detector data was separated into 18 depth bins. The photopeaks at each depth were then aligned. The energy resolution was optimized at 2 $\mu$s. The energy resolution after depth correction was determined to be 1.5%.

Figure 10 shows a depth corrected $^{137}$Cs spectrum for single-pixel events from a full 9-pixel 5 mm thick $3 \times 3$ array with 1 mm pitch operated at $-20^\circ$ C and biased to 1000 V. The energy resolution was 0.97%. The data were acquired with eV
FIGURE 8 | $^{241}$Am pulse height spectra acquired from nine of the narrow strips (0.5 mm pitch).

FIGURE 9 | Depth corrected $^{137}$Cs spectrum from a single pixel of the 13mm thick array.

FIGURE 10 | Depth corrected $^{137}$Cs energy spectrum from a 3 × 3 TlBr array (5 mm thick, 1 mm pitch).

Products (Cremat Cr110) charge sensitive preamplifiers and GAGE Octopus Comuscope [28]. Larger arrays have been flip chip bonded to substrates for testing. Figure 11 (top row) shows a 5 mm thick 11 × 11 array (1.0 mm pitch) with guard ring and depth corrected $^{137}$Cs spectrum from single pixel events from the full array. The depth corrected energy resolution for single pixel events from the full array (excepting pixels from which peaks could not
FIGURE 11 | Top left: 11 × 11 array (+ guard ring) (5 mm thick, 1 mm pitch). Top right: depth corrected $^{137}$Cs spectrum from single pixel events for the full array. Bottom left: energy resolution (% FWHM at 662 keV) for the raw spectra. Bottom right: raw, uncorrected $^{137}$Cs spectra for each pixel of the array.

accurately be determined) was determined to be 2.55%. Figure 11 (bottom row, right) shows raw, uncorrected $^{137}$Cs spectra for each pixel of the array. Note that the pixels corresponding to the two green boxes were not connected to preamplifier channels. Figure 11 (bottom row, left) shows energy resolution (% FWHM at 662 keV) for the raw spectra. Note “0.00” indicates that the software could not accurately fit the peak. The average raw energy resolution was 2.85% with a standard deviation of 0.88%. The variation in response from pixel to pixel is due to variations in the detector, not the electronics. The array was biased to 1000 V and operated at room temperature ($\sim 24^\circ C$). Note that

Detector Stability

Research on the properties of TlBr has shown that ionic conduction contributes to deterioration of TlBr device performance at room temperature [30]. Methods have been developed involving crystal growth, surface processing, and electrode deposition that have enabled TlBr detectors to operate [31–33] for many months under continuous bias. Figure 12 shows photo peak channel and $^{241}$Am pulse height spectra vs. time under 100 V bias for a 1 mm thick planar detector. The detector was operated at room temperature ($\sim 24^\circ C$). Note that
while the photopeak position is quite constant, the spectral shape does change. It is not clear whether this change is due to bulk or surface properties.

**DUAL MODE SEMICONDUCTOR AND OPTICAL DETECTION**

Because of its very high stopping power and good energy resolution TlBr has great potential for use in medical imaging [34]. Unfortunately the charge carrier transit time in TlBr is too long for applications like positron tomography (PET) due to relatively low mobility (∼30 cm²/Vsec). Because of its wide band gap, however, TlBr is transparent in the blue. This makes it possible to detect Cherenkov light generated by high energy photoelectrons generated by the positron annihilation 511 keV gamma rays. This light pulse can be used to generate a very fast timing signal. In a recent study a 4 × 4 × 5 mm thick TlBr planar semiconductor detector was modified by coupling a SiPM photodetector to one side of the device to simultaneously measure the Cherenkov radiation with the photodetector and the energy resolution with the semiconductor electronics. The coincidence timing resolution from two coincident annihilation gamma rays was measured to be ∼330 ps, much faster than is possible with semiconductors [34]. A dual mode (i.e., electronic and optical) readout combined with a pixelated configuration could provide fast timing, high resolution and position sensitivity.

**APPLICATIONS**

High gamma-ray absorption, photopeak efficiency, and room temperature operation make TlBr an ideal semiconductor detector material for a wide variety of gamma ray detection applications where room temperature operation, good energy resolution and high efficiency are needed. For example, spectroscopic personal radiation dosimeters (SPRDs) and radioisotope identifying detectors (RIIDs). Figure 13 shows a photograph of a TlBr-based SPRD. Pulse height spectra for various isotopic sources recorded with the SPRD are shown in Figure 14.

Single photon emission computed tomography (SPECT) is another application ideally suited to TlBr. The absorption length for 140 keV photons is <2 mm compared with ∼5 mm for CZT leading to reduced parallax errors.

**CONCLUSION**

Due to advances in material purification, crystal growth, detector fabrication and signal processing, TlBr spectrometers with better than 1.5% energy resolution at 662 keV at room temperature are now possible. In addition, utilizing Cherenkov photons from interaction of gamma-rays allows fast timing resolution for high energy gamma-rays (>500 keV). TlBr detectors that operate for many months at room temperature under a continuous applied electric field are now possible.

CZT remains the main competing room temperature material for room temperature operation. CZT can have energy resolution
better than 1% FWHM at 662 keV using 3D charge collection correction [35]. The detectors are stable at room temperature for long periods of time. The energy resolution of TlBr detectors using single carrier techniques is expected to continue to improve with further research. Even at the present performance TlBr is a superior option in applications where size and stopping power are criteria parameters.

**DATA AVAILABILITY STATEMENT**

The datasets generated for this study are available on request to the corresponding author.

**AUTHOR CONTRIBUTIONS**

HK assisted in fabricating devices and did much of the testing. YO grew TlBr crystals. AK helped design the TlBr CFG devices and fabricated them. LC analyzed and collated the data and wrote most of the article. MS managed several of the TlBr projects reported here and wrote much of the article. KS developed research plans and oversaw the TlBr research. ZH at oversaw the research at University of Michigan. CT, WK, and SO’N assisted ZH in University of Michigan in designing and testing pixel array devices and designing and building the readout ASIC. SP at LLNL oversaw the research and crystal processing procedures and electrode structures, and developed methods for achieving long term stability ES assisted SP in device fabrication and testing.

**FUNDING**

This work has been supported by the US Department of Homeland Security, Countering Weapons of Mass Destruction Office, under competitively awarded contracts HSHQDN-16-C-00024 and 70RDND18C0000019. This support does not constitute an express or implied endorsement on the part of the Government.
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Conflict of Interest: HK, YO, AK, LC, MS and KS are employees of Radiation Monitoring Devices, Inc.

The remaining 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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