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Thallium Bromide Semiconductor Radiation Materials and Detectors Characterization Studies

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ABSTRACT:

Two overarching requirements of crucial importance for the commercial and scientific establishment of semiconductor radiation detectors are: (1) exceptionally high-purity crystals with impurity concentrations less than 1 part-per-billion and (2) single crystals that are relatively free from subgrain boundaries, secondary phases, dislocations, and other electrically-active defects. We investigated the properties of thallium bromide (TlBr) material that affect its performance with the goal of increasing the material's commercial viability for radiation detection applications. For this purpose, we used beamlines at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL), performing Micron-scale X-ray Detector Mapping, White Beam X-ray Diffraction Topography, and Micron-scale X-ray Fluorescence. These characterization methods improve the industry's understanding of TlBr and lead to the production of improved instrumentation. In this particular study we report electro-migration measurements of positive-ion Cu, Ag, and Au impurities in TlBr detectors under electric field strengths typically used for device operation. BNL improved TlBr detectors with an electrode design that corrects the response non-uniformities caused by crystal defects. This design can achieve improved energy resolution while using typical-grade, commercial crystals with relaxed quality requirements, thus reducing the overall cost of detectors. Additional characterization will be necessary to fully understand the structure and performance of TlBr with the ultimate goal to achieve the highest energy resolution. Our findings from past work will be presented along with our recommendations for additional investigation.

INTRODUCTION:

Thallium bromide (TlBr) is a compound semiconductor with a large bandgap (2.7 eV) making it promising for room temperature detection. The high atomic numbers (81 and 35), and the high density of 7.5 g/cm^3 give it good gamma-ray stopping power [1]. Room temperature resistivity of detector quality TlBr crystals is in the order of 10^{11} Ohm-cm and electron mobility-lifetime product ($\mu_e\tau_e$) values are in the 10^{-3} to 10^{-2} cm^2/V range [2]. TlBr is a cubic material which melts congruently at a relatively low temperature (~480 °C) [3]. The cubic structure makes the growth of high quality single crystals relatively easy using conventional melt growth techniques, such as the Bridgman method. One drawback with TlBr is that it is relatively soft compared to other materials (Knoop hardness = 12 kg/mm^2 as opposed to 45 kg/mm^2 for CdTe and 1150 kg/mm^2 for Si)., This makes TlBr susceptible to pressure-induced structural defects generated by local plastic deformation. Therefore, special caution is needed when connecting the electrodes to the readout circuitry. These factors could collectively explain the poor crystallinity of as-grown TlBr ingots. Radiation Monitoring

Devices (RMD), Inc. provided several TlBr samples to BNL in 2011 for the first part of this work. The typical size of the TlBr detectors used in our experiments was 8 x 8 x 1–1.5 mm^3.

Two overarching requirements of crucial importance for the commercial and scientific establishment of semiconductor radiation detectors are: (1) exceptionally high-purity crystals with impurity concentrations less than 1 part-per-billion and (2) single crystals that are relatively free from subgrain boundaries, secondary phases, dislocations, and other electrically active defects. When these issues are solved, TlBr will become a serious competitor to CdTe and $Cd_xZn_{1-x}Te$ for room temperature radiation detection.

By employing micron-beam X-ray Fluorescence (μ-XRF), White Beam X-ray Diffraction Topography (WBXDT) and micron-scale X-ray detector mapping measurements, available at the LBNL's Advanced Light Source (ALS), NSLS and NSLS-II synchrotron facilities, BNL has helped and plans to continue helping researchers to understand the factors limiting the performance of TlBr detectors and explore the uniformity of their responses by identifying defects, the presence of clusters of dislocations, and possibly, detrimental impurities, and determine their role in the performance of TlBr radiation-detection materials.

DISCUSSION AND RESULTS

We employed White Beam X-ray Diffraction Topography (WBXDT) [4] to assess the degree of perfection of the TlBr samples. WBXDT is a very powerful tool to analyze the crystallinity of material in a fast and non-destructive way. Some crystals exhibited poor crystallinity unlike CZT crystals, as shown in Figure 1. Based on prior observations, BNL clearly demonstrated the importance of crystallinity on the detector performance in CZT, so it is reasonable to assume a similar dependence on the carrier transport properties of TlBr.

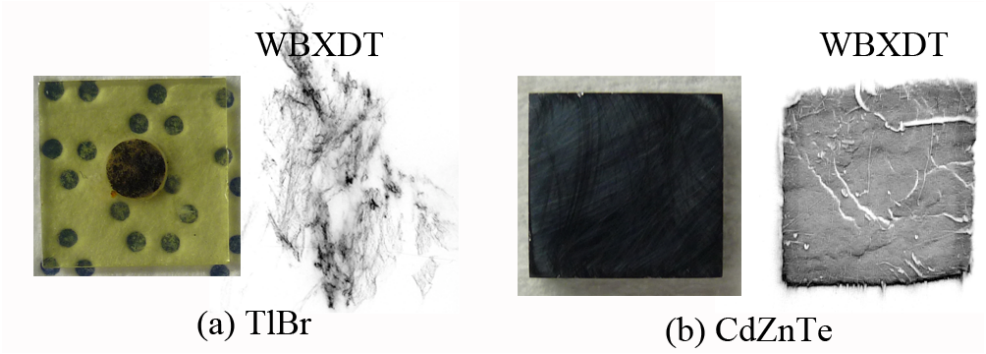

Figure 1. Sample photographs and typical WBXDT images of a (a) TlBr and (b) CdZnTe crystal. The WBXDT images of TlBr are blurry with a shape that barely resembles the geometry of the sample (as expected for a perfect crystal). BNL's experiments indicate poor crystallinity for most of the TlBr produced seven years ago.

Current material-purification technologies for TlBr detectors have been based on the successive distillation and zone-refining treatment. The performance of more recent TlBr detectors was improved by material purification via zone-refining [5].

We deposited on one side of several TlBr samples a 200-A° layer of Cu and Au, Ag and Au, and just Au; e-beam evaporation was used. These metallic layers were used as an electrode. Cr and Au were used as the electrode on the opposite face. The detectors' overall structures were Au/Cr/TlBr/Cu/Au, Au/Cr/TlBr/Ag/Au, and Au/Cr/TlBr/Au. The diameter of the

deposited electrodes was about 3 mm. We applied an electric field of 500–800 V/mm across each TlBr detector with a Keithley 237 source-measure-unit at room temperature, and then recorded the dark current every 15 min. We applied a positive bias continuously on the Au/Cr electrode side until a drastic change in the dark current was observed, caused by the electro-drift of Cu or Ag or Au atoms from one electrode to the other one. It took between 1–4 weeks, depending on the applied bias voltage and the sample's thickness. At the same time, we kept a comparable TlBr detector "control sample" with the same structure in ambient temperature with no bias voltage during the electro-migration experiment, in order to distinguish between electro-drift and the possible diffusion process of Cu, Ag, and Au atoms due to a concentration gradient.

The electro-migration of impurities was identified by micro-beam X-ray fluorescence (μ-XRF) mapping. The μ-XRF system of the X-27A beamline of the NSLS was fast, nondestructive, and able to trace 1 ppm of impurities with a fine step (5 x 5 μm^2). We observed the electro-migration of Cu, Ag, and Au impurities that exist in positive-ion states in TlBr detectors under electric field strengths typically used for device operation. The migration occurred predominantly through bulk and specific channels, which are presumed to be a network of grain and sub-grain boundaries. [6]. Fig. 2 shows the μ-XRF mapping images of the signals from Cr and Cu before and after Cu electro-migration and diffusion. We can trace the Cu signal from the Au/Cr electrode side, highlighting a clear electro-migration. In addition, there is no Cu signal on the Au/Cr electrode side in the diffusion-only TlBr detector used as a control sample. As depicted in Figs. 2(c) and 2(d), the electro-migration of Cu is not uniform through the bulk.

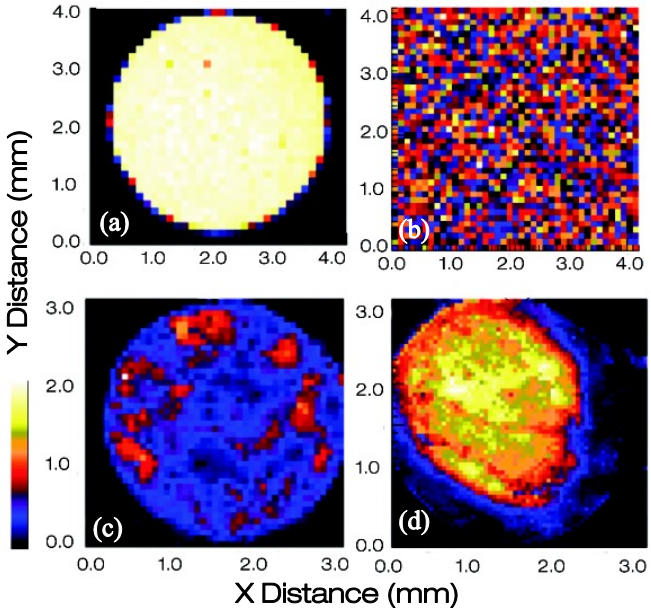

Figure. 2. μ-XRF images of (a) Cr K_α signal on the Cr-electrode side before electro-migration, (b) Cu K_α in TlBr kept in the ambient environment for 30 days, (c) non-uniform Cu K_α signal on the Cr-electrode side after applying an electric field of 500 V/mm for 14 days, and (d) Cu K_α on the Cr electrode side after applying electric field of 800 V/mm for 12 days. The Cr electrode was circular with a diameter of 3 mm.

Applying an electric field to a bulk semiconductor caused electrically charged impurities to drift preferentially in a direction based on the electric field and the impurities' charge state [7,8]. Previously, TlBr and other large bandgap materials such as HgI2 and PbI2, have shown

ionic conductivity [9–11]. It was demonstrated that ionic conduction was a principal cause of polarization in the device, since the internal electric field changed as the charged ions drifted through the detectors. The polarization of a semiconductor radiation detector causes the degradation of its spectroscopic characteristics, such as the counting rate, energy resolution, and photocurrent, and it also shifts the gamma-ray peaks. Usually polarization arises from changes in the local charge-distribution entailing a weak, non-linear electric field in the bulk of the crystal. In summary, from the extensive electro-migration studies that we conducted, the electrically active impurities (Cu, Ni, Fe, and Zn) all drifted along the electric field lines, affecting the long-term stability of operation of the TlBr detectors measured.

Another possible reason for the polarization is the electro-migration of the electrodes' metal element(s) into the bulk TlBr and the formation of unstable intermediate layers. The uniformity and spatial response of the TlBr detector were tested by highly collimated X-ray beam mapping technique at NSLS X27B. We employed mono-energetic synchrotron X-rays with high flux (10^{12} photons/s) and high spatial resolution (10 μm).

The pulse height spectra of the TlBr detector disappeared from the multi-channel analyzer (MCA) while mapping under the high-flux (10^{12} photons/s) condition, indicating the polarization of the detector. However, we could not observe polarization phenomena for the same TlBr detector in low-flux conditions with a high bias of 1500 V/mm. This indicates that the polarization in TlBr might have come from the attenuated electric field caused by accumulated space charge. As shown in Fig. 3(a,b), fairly uniform charge collection was obtained in 1 x 1-cm^2 area, except for the grain boundaries, which appear as dark lines due to the degraded charge collection. The periphery and central area of the TlBr planar detector exhibit improved charge collection (lighter grey-colored areas) compared to the rest of the detector area. The central area corresponds to where the sample holder's pogo pin presses on the sample surface to achieve electrical contact. TlBr is relatively soft compared to other materials, so the pressure induced by the pogo pin generates structural defects by local plastic deformation. This results in higher leakage currents and increased charge trapping. The peak position of the pulse-height spectra around the sample's edges and at the probe pin region are found to be at relatively high channel numbers, but also the width of the peaks is large because of the high leakage current in these regions.

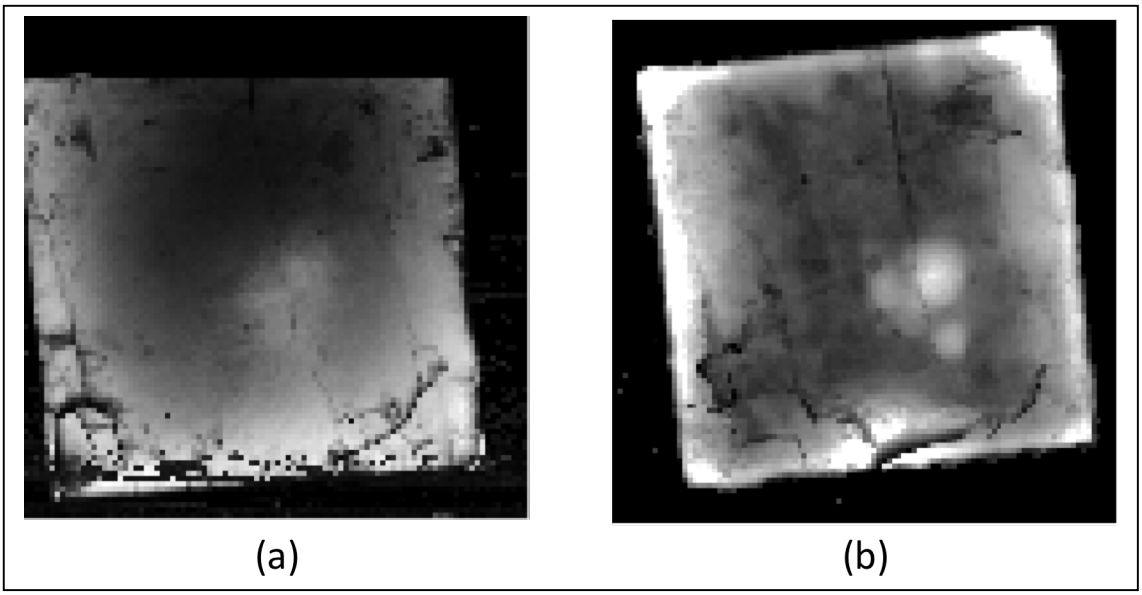

Figure. 3 Low flux electron collection maps of a TlBr sample with 100 μm step and bias applied of (a) 800 V and (b) 1500 V.

The crystal growth of enhanced TlBr material with minimal extended defects, such as subgrain boundaries, secondary phases, dislocations, and other electrically active defects, will lead to TlBr detectors with enhanced performance. In another approach that bypasses the need for these crystal qualities, BNL recently helped the TlBr vendor to apply an electrode design to accurately correct the response non-uniformities caused by crystal defects while using typical-grade, commercial crystals with relaxed quality requirements. Two of BNL's electrode designs were used to improve the energy resolution of the detectors. In most wide band-gap compound semiconductors utilized for room-temperature radiation detection, the mobility-lifetime product of the holes is at least an order-of-magnitude smaller than the electron mobility-lifetime product. Accordingly, holes may be lost to defects before reaching the cathode, thereby resulting in a depth-dependent radiation response that shows up as a distortion (i.e., low-energy tailing) of the photopeak and a degradation of the photopeak's resolution and efficiency. Hence, materials with high stopping power for gamma radiation and good electron transport properties often fail to exhibit a discernable photopeak when configured as a simple planar device, thus precluding their use for isotope identification. To overcome this limitation, researchers developed clever electrode configurations that rely solely on the electron response (single-polarity charge-sensing devices) and thereby mitigate the resolution degradation caused by the lack of hole transport in planar detectors. Such systems include coplanar grid [12], Frisch-grid [13], hemispheric [14], and pixellated detectors [15].

BNL improved TlBr detector performance by implementing an electrode design, similar to the Virtual Frisch Grid (VFG) applied to CdZnTe, that corrects the response non-uniformities caused by crystal defects. This design can achieve improved energy resolution while using typical-grade, commercial crystals with relaxed quality requirements, thus reducing the overall cost of detectors. These techniques primarily sense the flow the electrons rather than both electrons and holes. In addition, an electronic-depth correction has been added to some of these electron-transport-only designs to correct for trapping of electrons. Thus, large-volume TlBr detectors can attain better than 2% energy resolution at 662 keV, making their use feasible for spectroscopic and other photon-counting applications.

The planar detector was wrapped with thin Teflon tape, which acts as an insulating layer. A thin copper foil was cut to size and used as the Frisch grid/collar to cover the entire device length and was connected to the device cathode. The Cs-137 energy spectrum was measured and a FWHM of 2.2% at 662 keV was achieved with no correction. For the second electrode design fabricated to be similar to the position-sensitive VFG electrode design of CdZnTe [16,17], the side electrode's widths are altered and optimized to provide good electrostatic shielding for the anode while leaving the cathode unshielded. All six electrodes are connected to the readout electronics to provide signals. This configuration allows the cathode signals to become sensitive to the depth of interaction and can be employed to correct the charge losses as the electron clouds drift from the point of interaction towards the anode. For the Cs-137 energy spectra measurements, the anode and four sensing side pads are all grounded at the

same potential and the cathode is negatively biased. The corrected energy spectra improved the detector energy resolution to below 2% FWHM at 662 keV

The TlBr bar shaped detectors have not been measured at the beamlines yet and μ-XRF and micron-scale detector mappings are planned for the near future. These measurements will help to identify defects, the presence of clusters of dislocations, and possibly, detrimental impurities and determine their role in the performance of radiation-detection materials. The significance of using highly-collimated, bright X-ray micro beams (from a few microns down to ~0.4 microns) rather than flood illumination is that it allows us to isolate and visualize micro-defects, and therefore, to understand their role on the detectors' performance and stability caused by the crystal non-uniformities that they introduce. Previously, we employed these techniques with a larger (8-25 μm) X-ray beam than the sub-micron beams now available. The new capability offered by the several NSLS-II beamlines and by the ALS BL 3.3.2. could clarify the role of the defects and impurities in detector performance.

The beamline at the ALS is available with 25% of its time allotted for an extensive research program on radiation-detection materials. The following are the three main advantages of this beamline compared to the NSLS' Beamline X27B that we previously used:

(1) The possibility of achieving a ~1x1 μm^2 X-ray pencil beam;
(2) the availability of a large white- beam to undertake X-ray diffraction topography; and,
(3) a large end-station for experiments for testing compound-semiconductor-radiation-detection systems;
(4) Multi readout up to 8 channels, allowing position-sensitive CFG detectors or any multi-anode device to be measured.

CONCLUSIONS

In summary, from the extensive electro-migration studies that we conducted, the electrically active impurities (Cu, Ni, Fe, and Zn) all drifted along the electric field lines, affecting the long-term stability of operation of the TlBr detectors measured. The electro-migration is not uniform in cross-section, but the movement is predominantly along certain paths that we considered connected to the grain- and subgrain-boundaries network. To assure the long-term stable operation of a TlBr detector, it is important to obtain a stable electrode structure and to remove the electrically active metallic impurities, as demonstrated in our experiments.

The uniformity and spatial response of the TlBr detector were evaluated using a highly collimated X-ray beam mapping technique. A fairly uniform charge collection was obtained within the area of the measured detectors, except for the grain boundaries, which appear as dark lines due to the degraded charge collection.

BNL improved TlBr detectors with an electrode design that corrects the response non-uniformities caused by crystal defects. This design can achieve improved energy resolution while using typical-grade, commercial crystals with relaxed quality requirements, thus reducing the overall cost of detectors.

The TlBr bar shaped detectors have not been measured at the beamlines yet; μ-XRF and micron-scale detector mappings will help to identify defects, the presence of clusters of dislocations, and possibly, detrimental impurities, and determine their role in the performance of radiation-detection materials.

Key words: TlBr, NSLS, Thallium Bromide, BNL, X-ray, detectors.

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