



BNL-93953-2010-CP

***Detector Performance of
Ammonium-Sulfide-Passivated CdZnTe and
CdMnTe Materials***

**K.H. Kim, A.E. Bolotnikov, G.S. Camarda, L. Marchini, G. Yang,
A. Hossain, Y. Cui, L. Xu, and R.B. James**

*Presented at the 2010 SPIE Optics + Photonics Conference
San Diego, California
August 1-5, 2010*

August 2010

Nonproliferation and National Security Department

Brookhaven National Laboratory

P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

This preprint is intended for publication in a journal or proceedings. Since changes may be made before publication, it may not be cited or reproduced without the author's permission.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Detector Performance of Ammonium-Sulfide-Passivated CdZnTe and CdMnTe Materials

K. H. Kim^{*a}, A. E. Bolotnikov^a, G. S. Camarda^a, L. Marchini^{a,b}, G. Yang^a, A. Hossain^a, Y. Cui^a,
L. Xu^{a,c}, and R. B. James^a

^aBrookhaven National Laboratory, Upton, NY 11973, USA

^bIMEM-CNR, Parma 43100, Italy

^cNorthwestern Polytechnical University, Xi'an, Shaanxi 710072, China

ABSTRACT

Dark currents, including those in the surface and bulk, are the leading source of electronic noise in X-ray and gamma detectors, and are responsible for degrading a detector's energy resolution. The detector material itself determines the bulk leakage current; however, the surface leakage current is controllable by depositing appropriate passivation layers. In previous research, we demonstrated the effectiveness of surface passivation in CZT (CdZnTe) and CMT (CdMnTe) materials using ammonium sulfide and ammonium fluoride. In this research, we measured the effect of such passivation on the surface states of these materials, and on the performances of detectors made from them.

Keywords: Passivation, CdZnTe, CdMnTe, ammonium sulfide, leakage current

1. INTRODUCTION

Passivation technology is a very important approach for improving the efficiency of gamma-ray detectors. Chemically etching CZT crystals with Br-MeOH (bromine methanol) leaves a Te-rich surface due to the differential etching rate of the bulk material. These Te-rich layers are highly conductive compared to the bulk and thus, surface leakage current increases. Most surface-passivation processes focus on removing such conductive layers, and returning the electrically active surface-state to a neutral one. The criteria for successful passivation for semiconductor devices fall into two categories: The semiconductor/passivant interface properties, such as interface potential, density of interface traps, and surface recombination velocity; and, the bulk characteristics of the passivant itself, such as insulation, dielectric properties, adhesion, stability, deposition technology, and radiation hardening. Our previous research demonstrated the efficacy of sulfide passivation on CMT (CdMnTe) and CZT (CdZnTe) crystals [1,2]. Passivation with aqueous sulfide solutions encompasses both chemical- and electronic- processes. This highly alkaline medium removes the oxide layer from the Cd(Zn,Mn)Te surface, and forms a thin (practically mono-atomic) sulfide coating on it. [3,4] This procedure noticeably decreases the surface recombination and its velocity, along with lowering the density of the surface-state, thus bettering the device's performance. In this research, we measured the efficiency of sulfide passivation on the performance of detectors made from these materials, and identified the changes in their surface states.

2. EXPERIMENTS

The CZT:In (Zn=10%) and CMT:In (Mn=5%) crystals used in this experiment were grown by the vertical Bridgman method at BNL (Fig. 1). We prepared twelve CZT and CMT samples of two different sizes; one is 5×5×2 mm², and the other is 5×5×9 mm³. In determining the selected samples, we excluded those containing extended defects, such as sub-grain- or grain-boundaries. Fig. 2 shows typical X-ray diffraction topographic images of CZT- and CMT-samples. This technique frequently is used to visualize growth- and process-induced defects, such as dislocations, twins, domains, and inclusions. [5]

*khkim@bnl.gov; phone 1 631 344-4168

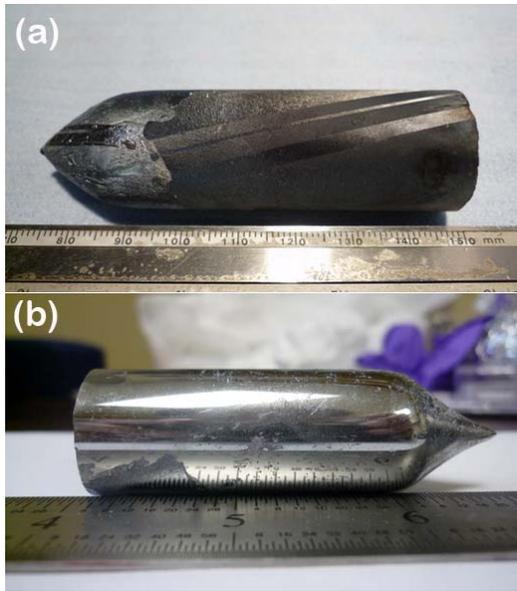


Figure 1. Photograph of as-grown (a) CZT- and (b) CMT-ingots grown by the vertical Bridgman method. They are about 1 inch in diameter and 3.5 inches long.

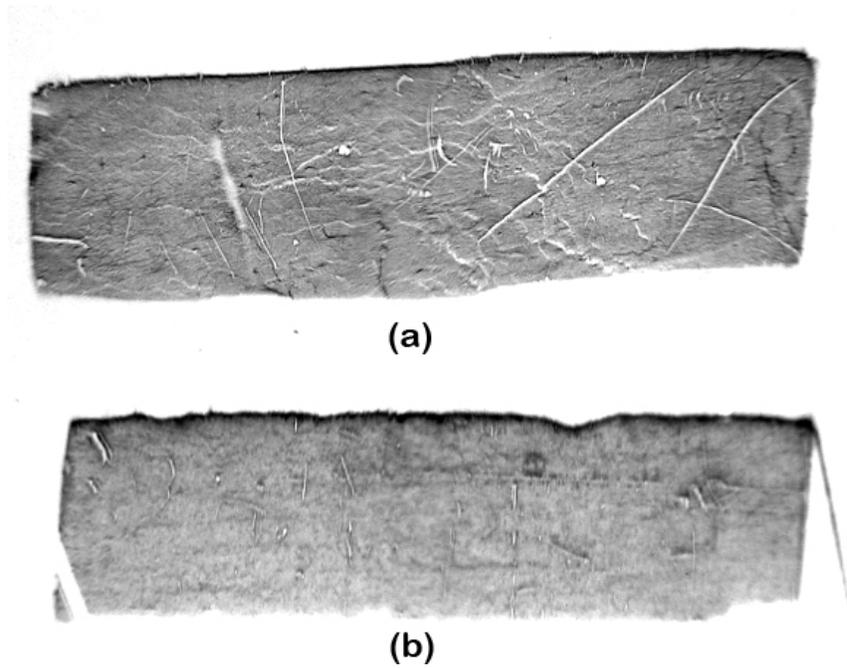
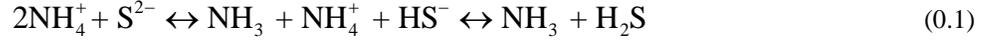


Figure 2. X-ray diffraction topography image of $5 \times 5 \times 9 \text{ mm}^3$ samples: (a) CZT, and (b) CMT detector. The lines in the images indicate random scratches generated during the polishing process.

Before passivation with ammonium sulfide ((NH₄)₂S), we etched the samples with 2% Br-MeOH for 30 sec. The electrode was prepared by an electroless method with 5% AuCl₃. The resistivity of both CZT- and CMT-crystals was more than 2×10¹⁰ Ω–cm. Sulfide treatment consisted of dipping the detector material into the solution for 90 sec at room temperature, while keeping the solution around 70 °C. The remaining sulfide solution on the sample’s surface after passivation was cleaned off with de-ionized water. During the process, we covered the top and bottom electrodes with photo-resistor to prevent chemical reactions there.

Ammonium-sulfide solution is a highly alkaline medium of pH > 11; the hydroxides and peroxides of Te on the detector’s surface dissolve completely in it. [3] The dissolution of ammonium sulfide gives rise to protolytic reactions of the type [4]



Depending on the fraction of H₂S molecules in the total sulfide content, it exhibits different chemical reactions with CZT and CMT. In an aqueous solution of (NH₄)₂S, the fraction of H₂S in the total sulfide content is relatively small, and therefore, the following reaction is dominant.



The solvent does not participate in this reaction. Further, since ions are not involved in this reaction, electrostatic interactions should not affect it noticeably. Tellurium sulfide (TeS) and manganese sulfide (MnS) are moderately soluble in water and acid.

We employed a standard eV Microelectronics preamplifier to read the ²⁴¹Am gamma-ray signals, which were further shaped and amplified with a standard research amplifier, while keeping the temperature around 20 °C. The ²⁴¹Am source was not collimated, and the shaping time was set at 6 μsec for complete charge collection. In addition, the change of surface states was observed by PL (photoluminescence) measurements at 4.2 K.

3. RESULTS AND DISCUSSION

We measured the gamma-response of twelve detectors before and after sulfide passivation: There were three 2-mm-thick and three 9-mm-thick CZT detectors, and three 2-mm-thick and three 9-mm-thick CMT detectors. Fig. 3 plots the ²⁴¹Am gamma-ray response taken for the 2-mm-thick CZT and CMT detectors. Both detectors clearly reveal a 59.6-keV peak and another escape peak. The FWHM (Full width at half maximum) of the 59.6-keV peak was improved, and the peak channel numbers rose in both types of detectors after passivation. We cannot observe deterioration in the gamma-response with time in both CZT and CMT detectors.

Fig. 4 shows a typical plot of the peak channel number of the 59.6-keV peak vs. bias voltage for a 2-mm CZT, and a 9-mm CMT detector. For 2-mm thick detectors of both types, the peak channel number at 59.6 keV shifted to a higher number at the same bias voltage, although the increase was small, as seen in Fig. 4 (a). The shift of peak channel number to a higher one indicates an enhancement of electron charge collection. Fitting the experimental data with the Hecht equation yields the mobility-lifetime product, one of most important parameters used in judging a detector’s properties. The apparent mobility-lifetime product of the 2-mm thick CZT detector improved from 1.1 × 10⁻³ V/s to 1.4 × 10⁻³ V/s after passivation. However, a notable difference was observed for 9-mm thick CZT and CMT detectors, as is evident in Fig 4(b). Also, the mobility-lifetime product was remarkably enhanced from 4.8 × 10⁻⁴ V/s to 1.0×10⁻³ V/s in CMT detectors. A common feature of both the 2-mm and 9-mm thick CZT- and CMT-detectors is that the gap between the peak channel number before and after passivation at same bias voltage declines as the electric field (bias voltage) increases. Passivation is known to improve energy resolution by reducing the dark current and 1/f noise. However, the change in channel number indicates an alteration in the electrons’ drift-time from cathode to anode reflecting the change of the effective electric field. The distribution of the electric field is determined by the boundary conditions, i.e., by the dispersion of electrostatic potential on the device’s side surface that, in turn, is set by surface conductivity. If the surface potential decrease between the cathode and the anode is faster than the potential along the device’s axis, then a “defocusing field” is generated inside of the device, thereby diminishing the detector’s performance. In the opposite case, a “focusing” drift-field forming within the device steers the electrons toward the anode. [6]

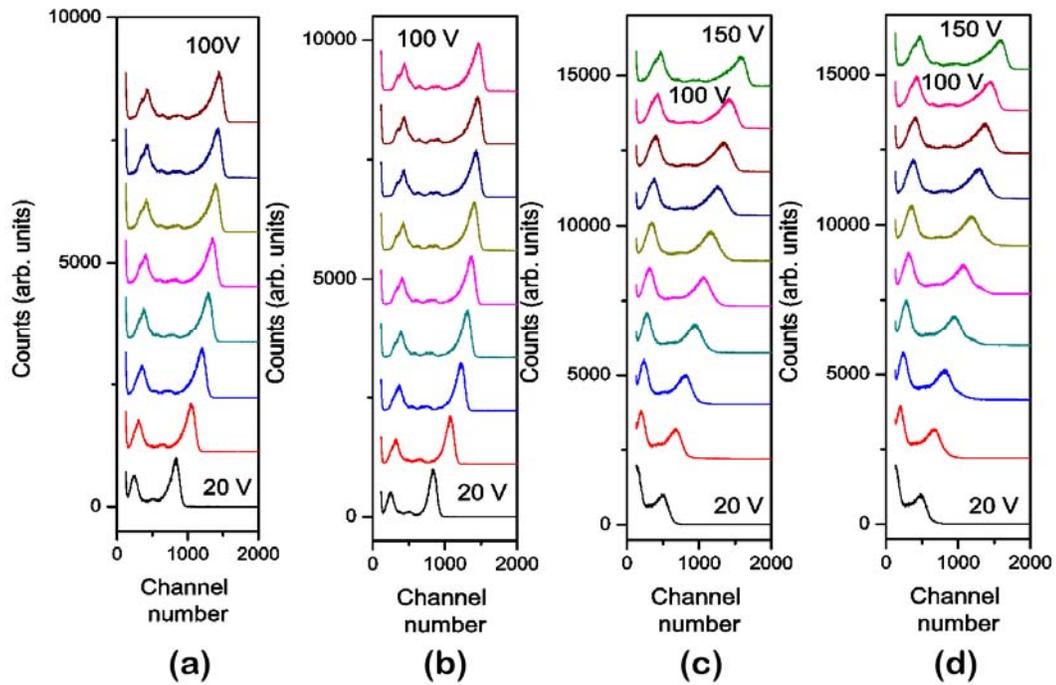


Figure 3. The evolution of the ^{241}Am gamma response of a 2mm-thick CZT detector (a) before and (b) after passivation, and for a 2mm-thick CMT detector (c) before and (d) after passivation. The shaping times were fixed at 6 μs throughout the measurements.

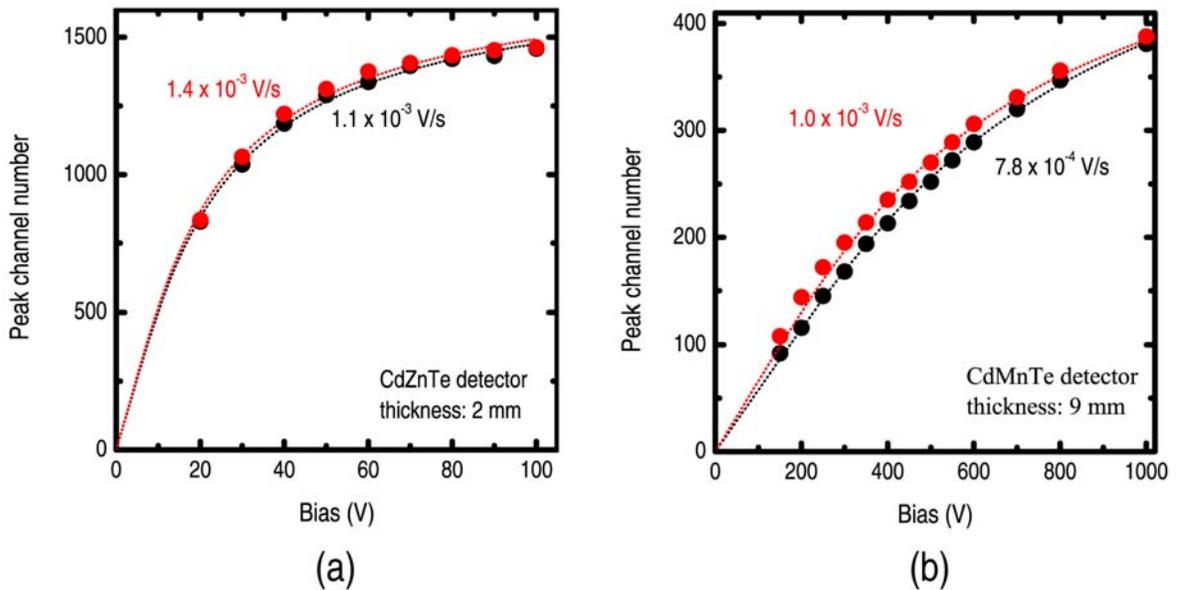


Figure 4. Efficiency of charge collection of (a) 2-mm-thick CdZnTe detector, and (b) 9-mm-thick CdMnTe detector. After passivation, the apparent mobility-lifetime product rose in all twelve detectors tested.

Fig. 5 plots the PL spectra showing the change of space-charge accumulated on the surface of a 9-mm-thick CMT sample. We ascribe the low-energy broad band around 1.49 eV to the A-center formed consequent upon indium doping and the large concentration of cadmium vacancies, that is $(V_{Cd}-In_{Cd})^-$. This band was evident in all compensated CZT and CMT materials. Comparing the A-center intensities before and after passivation, we note the reduction in the densities of defects. Also, in XPS (X-ray photoelectron spectroscopy) measurements, such changes of surface states, especially for Te, were observed before and after sulfide passivation in both CZT [6] and CMT [1].

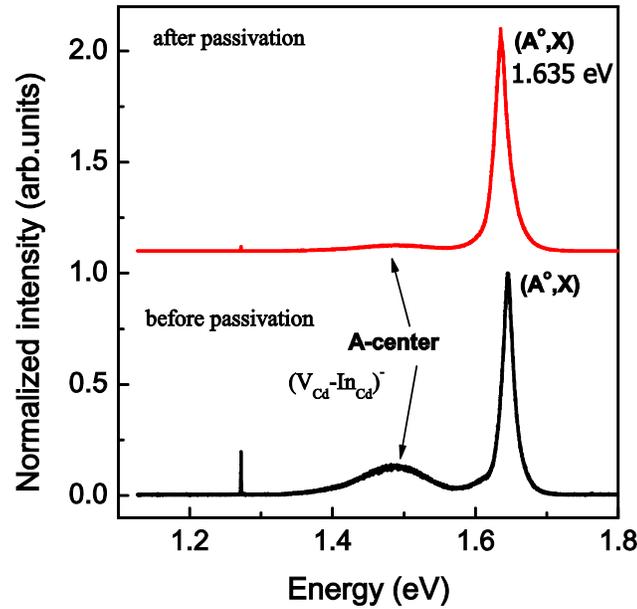


Figure 5. PL spectrum of 9-mm-thick CdMnTe crystal before and after passivation with ammonium sulfide. The intensity of acceptor bound exciton ($A^{\circ}X$) peak located at 1.635 eV was normalized to compare the changes in the A-center peak.

Our finding of the formation of positive space-charge in CZT detectors was consistent with analyses of I-V curves measured for 2-mm thin planar detectors with a small geometrical-aspect ratio (thickness-to-width ratio). We estimated the concentrations of the positive ions as $\sim 10^{10} \text{ cm}^{-3}$, while that of the free carriers in high-resistivity material is only $\sim 10^5 \text{ cm}^{-3}$. For example, at such space-charge densities, the expected reduction of the electric field is 15% in a 2-mm thick detector biased at 200 V. In CZT and CMT detectors with large aspect ratio > 1 , it is very likely that the variations of the electric field may not be described by a simple linear function because of the possibility of the non-uniform accumulation of space charge [7]. A large-volume detector, that is the 9-mm-thick detector, has much more side surfaces, so it might well be more affected by space charge than are thin detectors. These explanations might account for the larger variation of peak channel number in thick detectors than thin detectors, both CZT and CMT ones. In a strong enough electric field, most of the generated charge is collected, but in low electric fields, there is a greater chance that generated electrons become trapped or recombined with traps due to their longer drift-time. Therefore, the shift of the peak channel number is lesser in a high electric field. The ability to maintain a desired electric field inside CZT and CMT detectors is important for assuring their expected performance and functionalities. If the actual distribution of the field lines differs from the anticipated one based on the electrode's configuration, then the charges generated by incident particles might be driven towards the wrong electrodes, or become trapped near the side surfaces.

4. CONCLUSIONS

Passivation of CZT and CMT crystals with ammonium sulfide efficiently removes the oxide layer, and deposits an electronic mono-atomic sulfide coating on their surfaces. Sulfide passivation also results in a noticeable decrease of the leakage current and surface-state densities, thus improving the device's performance. For a large-volume detector, 9-mm-thick, passivation also aids in establishing a "focusing field" by removing the space-charge accumulated on the side surfaces.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Office of Nonproliferation Research and Development, NA-22, and the Defense Threat Reduction Agency (DTRA). The manuscript has been authored by Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH1-886 with the U.S. Department of Energy.

REFERENCES

- [1] Kim, K. H., Carcelén, V., Bolotnikov, A. E., Camarda, G.S., Gul, R., Hossain, A., Yang, G., Cui, Y., and James, R. B., "Effective Surface Passivation of CdMnTe Materials", *J. Electronic Materials* 39, 1015-1018 (2010).
- [2] Kim, K. H., Camarda, G. S., Bolotnikov, A. E., James, R. B., Hong, Jinki, Kim, SunUng, "Improved carrier-transport properties of passivated CdMnTe crystals", *J. Appl. Phys.* 105(9), 093705-093705-4 (2009).
- [3] Dremlyuzhenko, S. G., Zakharuk, Z. I., Rarenko, I. M., Srtebegev, V. M., Voloshchuk, A. G., and Yuriychuk, I. M., "State of Cd_{1-x}Zn_xTe and Cd_{1-x}Mn_xTe surface depending on treatment type", *Semicond. Phys. Quant. Electron. Optoelectron.* 7, 52-55 (2004).
- [4] Bessolov, V. N., Konenkova, E. V., and Lebedev, M. V., "A comparison of the effectiveness of GaAs surface passivation with sodium and ammonium sulfide solutions", *Phys. Solid State* 39(1), 54-57 (1997).
- [5] Carini, G. A., Camarda, G. S., Zhong, Z., Siddons, D. P., Bolotnikov, A. E., Wright, G. W., Barber, B., Arnone C., and James, R. B., "High-energy X-ray diffraction and topography investigation of CdZnTe", *J. Electronic Materials* 34(6), 804-810 (2005).
- [6] Bolotnikov, A. E., Camarda, G. S., Cui, Y., Hossain A., Yang, G., Yao, H. W., and James, R. B., "Internal Electric-Field-Lines Distribution in CdZnTe Detectors Measured Using X-Ray Mapping", *IEEE Trans. Nuclear Science* 56(3), 791-794 (2009).
- [7] Kim, K.H., Won, J. H., Cho, S. H., Cho, P. K., J. Hong, Kim, S. U., and Han. Y. R, "Passivation of semi-insulating polycrystalline CdZnTe films", *J. Korean Phys. Soc.* 53(1), 317-321 (2008).
- [8] Bolotnikov, A. E., Boggs, S. E., Hubert Chen, C. M., Cook, W. R., Harrison, F. A., and Schindler, S. M., "Properties of Pt Schottky type contacts on high-resistivity CdZnTe detectors", *Nucl. Instr. Meth.* 482, 395-407 (2002).