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CZT DTRA final report

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Grant/Award #: HDTRA1-08-10-BRCWMD
PI Name: Stephen A. Payne and Lars F. Voss
Organization/Institution: Lawrence Livermore National Laboratory
Project Title: Bandgap Engineering of CZT Contacts for Radiation Detectors

What are the major goals of the project?

The objective of the project is to understand the physical origin of electronic noise injected by the electrical contacts in CZT and CdTe, and moreover to understand how it impacts the current- voltage (IV) relationships of these materials. This understanding is critical to enabling the next crucial enhancement in the performance of CZT radiation detectors, as there have recently been impressive advancements in the growth of CZT crystals, particularly at our commercial partner Redlen Technologies. Redlen scientists have successfully reduced the size of the transport-inhibiting tellurium precipitates to be <3 micrometers, such that, with sufficiently high fields, it is possible to achieve resolution of <1% at 662 keV using suitable electrode geometries. In contrast to the excellent progress in crystal growth, practitioners in the field of radiation detection have been fabricating rather routine contacts on CZT for nearly two decades; there is no basic understanding of the semiconductor physics of the contacts, and consequently no breakthrough progress in this area. Our objective is to resolve this inadequacy in CZT diode fabrication on the basis of a science-based study, such that CZT detectors can achieve their full promise in performance as superior contacts will enable use of higher fields with lower leakage current – thereby enhancing the resolution that is possible while eliminating the well-known “tailing” effect suffered by the photopeak.

Our approach is to develop methods that reduce or eliminate leakage currents in CZT devices through “engineering” the surfaces with novel treatments and structures. This includes using high density plasma etching, doping via ion implantation and metal diffusion, rapid thermal annealing, amorphous semiconductor and dielectric films, and controlled oxide growth. Using these methods, sources of injected and generated noise at the surface can be eliminated via plasma etching and film deposition or oxide growth, while advanced junctions (both homo- and heterojunctions) can be created to eliminate current injection from the metal contacts. The work involves the fabrication and characterization of CZT having a variety of contact structures. Tools capable of evaporating and sputtering metals, together with the usual lithographic and chemical processing methods, are employed. The CZT material employed will be of the highest quality available (Redlen Technologies), and we are engaging Prof. Burger of Fisk University, who is internationally recognized as one of the most accomplished materials physicists in the field on radiation detectors. We have also begun collaborating with Prof. Nicholas Kioussis of Cal State Northridge, Srivananthan Labs (Bolingbrook, IL), and Mark Amman of Lawrence Berkeley National Laboratory, all funded separately by DTRA.

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What was accomplished under these goals?

During this project, we have succeeded in reducing the surface leakage current by >90% and the bulk leakage current by >50% relative to state-of-the-art devices, which have surfaces that are finely polished (not etched) through the use of plasma etching and ion implanted doped junctions. We have demonstrated what we believe is the first CZT pn junction via both ion implantation and metal diffusion doping. In addition, the use of amorphous semiconductors (a-Si and a-Se) was explored as a potential avenue to decreasing both surface and bulk leakage current. It was shown the surface leakage current can be reduced by ~10x using the amorphous semiconductors, if the surface preparation is done appropriately. Each of the major activities being pursued can be combined or used individually to achieve low noise detectors. Figure 1 shows a potential future device with minimal electronic noise.

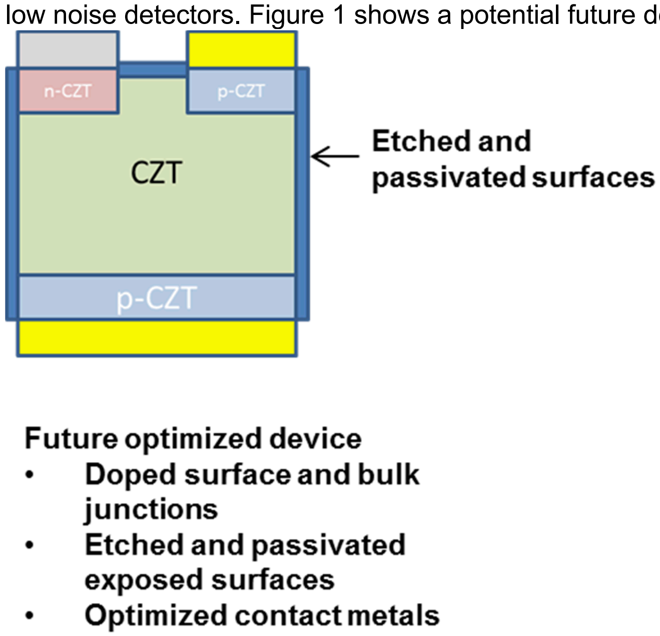

Figure 1: Potential future low-noise device

1) Major Activities

Our activities for this project can be grouped into three major areas, described below.

a) Plasma etching: We have explored plasma etching of CZT using a gas chemistry of Ar, H_2, and CH_4. Under the right conditions and power levels, a mixture of these gases has been shown to produce a CZT surface with very smooth morphology (Fig 2). These plasmas have been used to treat the inter-grid surfaces of co-planar grid CZT detectors.

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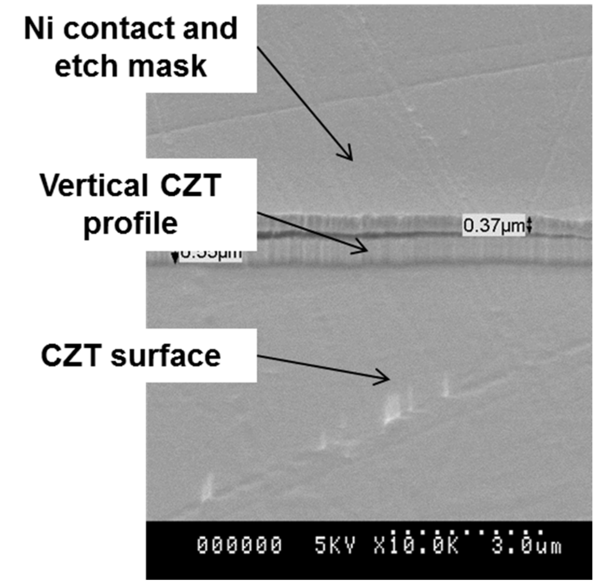

Figure 2: Plasma etched CZT surface with Ni contact/etch mask.

b) Passivating films: During this work, we have explored the use of passivating films for the plasma etched surfaces. We have examined amorphous semiconductors including a-Si and a-Se as well as chemical oxidation (via 30% H_2O_2 or ambient oxidation) on plasma treated surfaces. These approaches have resulted in quenching of leakage current relative to both the polished surface and the as etched plasma surface. In addition, high field breakdown of the surface has been shown to improve with passivation of the surface relative to the plasma treated surfaces. Figure 3 shows various surface leakage currents for CZT passivated by amorphous semiconductor films.

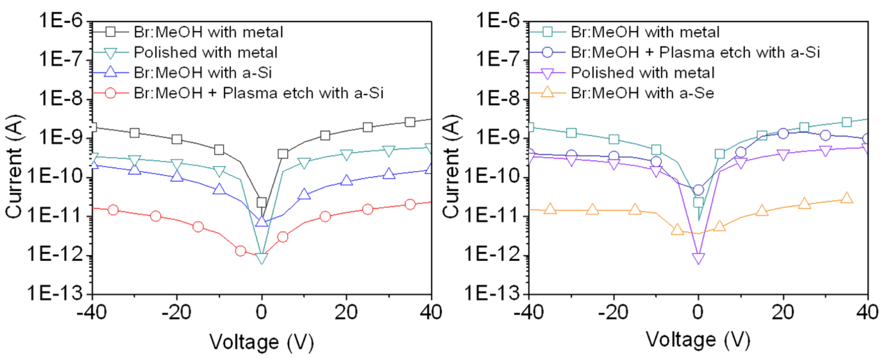

Figure 3: Surface leakage current for (left) a-Si films and (right) a-Se films with various surface preparations

c) Doping: Our third area of work during this project is the use of ion implantation and metal diffusion doping to produce p- and n-type conduction regions on the CZT surface based on implantation of Al and P atoms, respectively. Diffusion of Al and Bi contacts to produce n-type doping, as an alternate technique, has also been explored. Finally, using the recipes we fabricated the first surface pn junctions and bulk p-i-n junctions based on these techniques, to our knowledge. Finally, we have demonstrated pixelated detectors using bulk p-i-n junctions with good resolution (1.3% FWHM @ 662 keV vs XX% for control) on medical grade material.

2) Specific Objectives
Each of our described activities above is being pursued with a specific objective in mind. These are described below.

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a) Plasma etching: The goal of plasma etching the inter-grid surface regions of CZT is to remove damage from this area, thus reducing generated noise while leaving the state-of-the-art low injection blocking contacts formed by the metal/damage interface intact. In this way, we believe that we can minimize surface noise while maintaining low bulk injected current. Figure 4 shows a schematic of the objective.

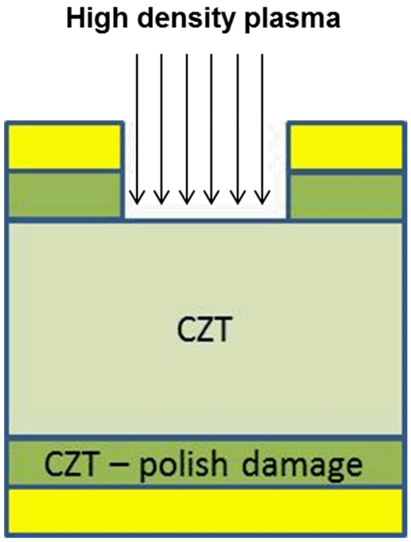

Figure 4: Plasma etching schematic

b) Passivating films: Growth of oxide films or deposition of amorphous semiconductor films on the plasma etched surface is required in order to achieve the lowest leakage current possible while also improving the breakdown strength of the surface. The goal of this activity is to determine the optimum method and conditions for growing these films in order to enable the plasma etched surface to reach its full potential in having low leakage current.
c) Doping: The major objective of this activity is the achievement of surface pn and bulk p-i-n junctions, which in reverse bias will enable extremely low leakage currents, limited to generation from within the CZT itself.

3) Significant Results
a) Plasma etching: We have demonstrated that plasma etching of the inter-grid surface of co-planar grid detectors can reduce the surface leakage current by >90%. For co-planar grid detectors, this has been manifested in a decrease in electronic noise, as measured by the electronic pulsar, from a typical value of 1.8 keV FWHM to 0.9 keV FWHM under a variety of biasing conditions. Figure 5 shows data from a co-planar grid detector that has been fabricated with state of the art polishing (black) and LLNL developed plasma etching and passivation (red). Note the improvement in the full width half maximum when plasma etching is used. This can be understood as a direct result of decrease in the electronic noise, as measured by the pulser. In addition to the leakage current reduction, we have demonstrated the utility of Ni contacts as both an electrical contact to CZT and as an etch mask to enable plasma etching. We recently procured high-quality spectroscopic grade CZT in order to better demonstrate the improvement in resolution. Finally, plasma etching of the surface enables isolation between co-planar electrodes (for instance in either a co-planar grid or pixelated detector) after surface doping and activation. This isolation is critical in order to ensure that each electrode functions independently instead of as one blanket electrode.

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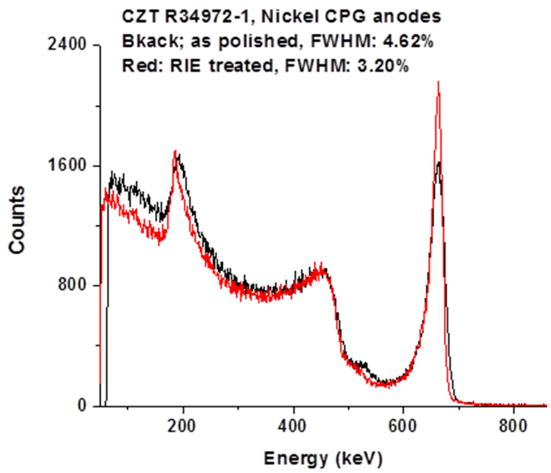

Figure 5: The same crystal measured with plasma-etched and polished surfaces shows a significant improvement in performance for the plasma etched surface.

b) Passivating films: We have demonstrated that, after plasma etching, growth of oxide films using 30% H_2O_2 reduces the surface leakage current to the minimum value achieved thus far. In addition, it improves the breakdown strength of the plasma etched surface. Figure 6 shows the current-voltage curves for the etched surface before and after chemical passivation.

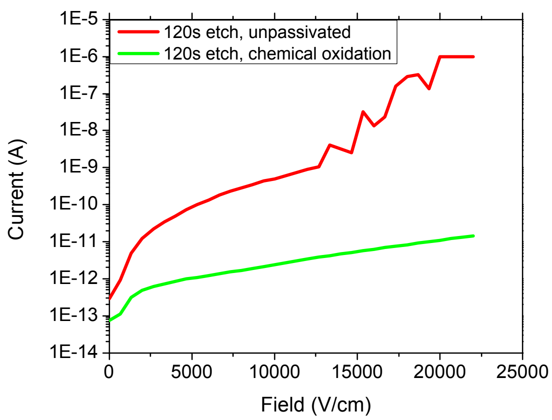

Figure 6: Current-voltage curves for the plasma etched surface before and after chemical oxidation.

It was observed that, after plasma etching, breakdown occurred at fields as low as 15 kV/cm. Oxidation in ambient conditions improved the breakdown characteristics but did not eliminate them. However, after chemical passivation in 30% H_2O_2, no breakdown was observed under measured conditions, with a maximum surface field of 22.5 kV/cm.

c) Doping: We have demonstrated doping and activation for both implanted Al and P species. Further, we have demonstrated metal diffusion doping using both Al and Bi metal contacts. Most significantly, we have fabricated pn junctions formed by ion implantation of Al and P on the same surface. Figure 7 shows the current-voltage characteristics after activation of this sample. We believe this is the first time anyone has demonstrated an ion-implanted CZT pn junction.

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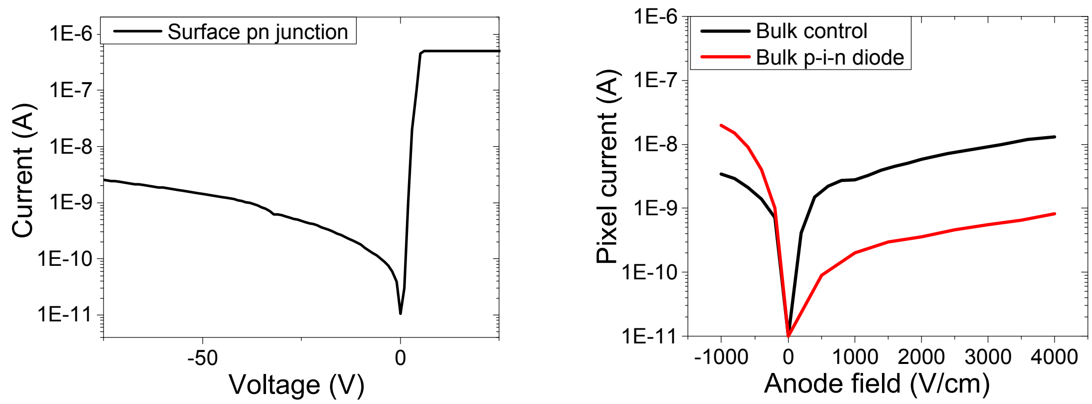

Figure 7: Current-voltage characteristics for CZT (left) surface pn junction and (right) bulk p-i-n diode formed by doping with Al and P ions.

In addition, we have fabricated pixelated detectors on medical grade CZT that show a FWHM of 1.3% at 662 keV using ion implanted bulk p-i-n diodes. To achieve this, shortened anneal time at higher temperature was required in order to reduce the total thermal load on the CZT crystal. Our initial anneal temperatures (275ºC – 325ºC) and times (total time above 200C >3 minutes) had to be modified. These conditions were too much for the CZT crystals to handle and, in spite of improved electrical characteristics, the transport properties were degraded to the point that no clear peak was visible. By using higher temperatures for shorter dwell times (400C, 1s + 450C, 1s), an excellent peak was achieved on medical grade CZT. Figure 8 shows the gamma response of the initial detectors, which were "overcooked" and the detector with the modified anneal cycle.

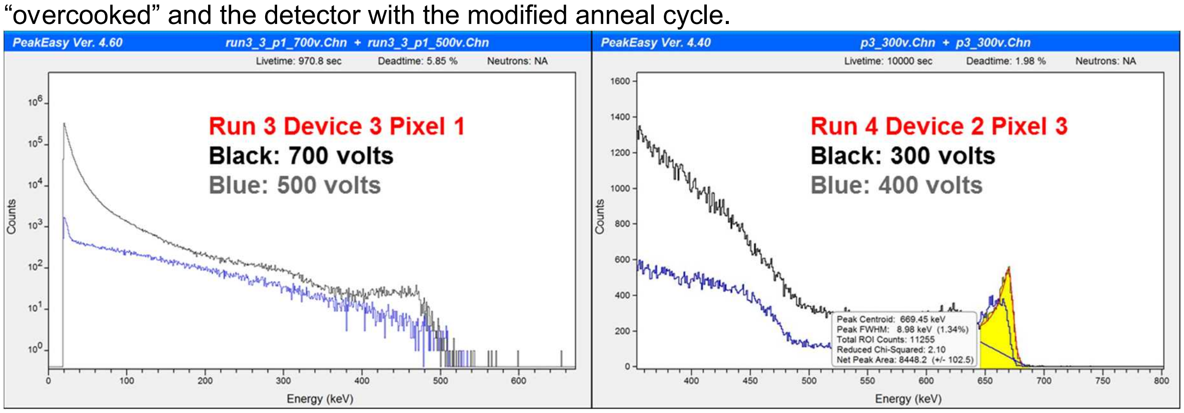

Figure 8: (left) "Overcooked" detector with long activation time (right) detector with short activation time

We believe that the activation is still not complete on this detector, as the leakage current was still elevated compared to our previous rounds (60 pA @ -200V vs 6-8 pA @ -200V for 1 mm^2 pixel). Improved activation is expected to improve both resolution and increase the bias that can be applied (through the elimination of surface defects). However, further annealing would also potentially degrade the transport characteristics.

Due to the difficulty of achieving activation of the doped surface without overheating the bulk of the crystal using a rapid thermal annealer (RTA), we have also begun exploring laser spike activation of the surface and devised a new rapid contact heating method. Laser spike activation is used in other semiconductors and devices with very low thermal budget and uses an intense, short pulse above gap laser that enables heating only of the doped region. The first experiments have been performed in order to determine the safe flux for a 193 nm laser pulsing at 100 Hz for 15-20 ns per pulse. It was determined that <75 mJ/cm^2 is required in order to avoid ablation and cracking of the surface. Figure 9 shows the CZT surface for fluences of 75, 50, and 60 mJ/cm^2.

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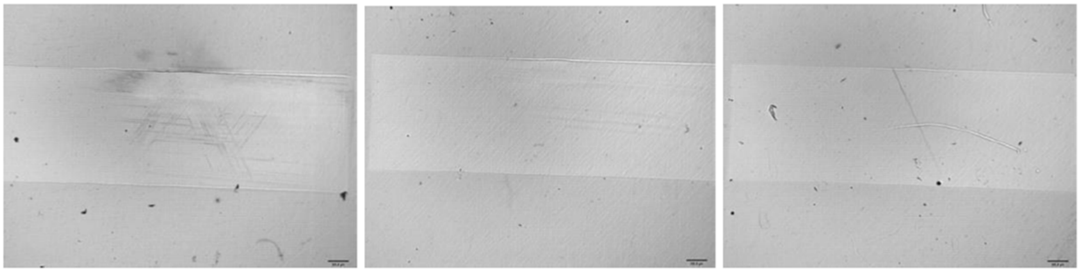

Figure 9: Surface of CZT crystals after (left to right) 75, 60, and 50 mJ/cm^2 fluences using 193 nm laser.

Medical grade CZT material has been implanted and activated using both the 60 and 50 mJ/cm^2 fluences and was fabricated into detectors to evaluate the performance. The 50 mJ/cm^2 part showed no gamma response; however, the 60 mJ/cm^2 part showed good gamma response with a FWHM of 3.5% at 662 keV under a bias of 100 V/cm, shown in Figure 10. This performance is comparable to that of control detectors fabricated from the same material. Large sidewall currents prevented higher biasing of this detector. Clearly further optimization is required.

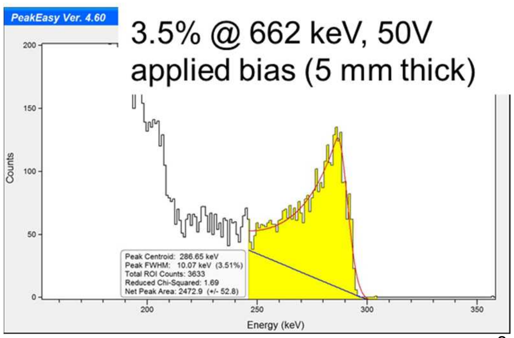

Figure 10: Gamma response of 60 mJ/cm^2 part.

In addition, we have performed simulations of a new technique we have termed Rapid Contact Heating. In this method, a heating material is brought to temperature in a furnace or on a hot plate, for example 450^{o}C or higher, and then removed and brought into contact with the CZT surface. By using a substrate with both a low thermal mass and thermal conductivity, the amount of thermal energy transferred to bulk of the CZT is limited while at the same time the surface heats up for a short period. Finite element simulations using COMSOL have been performed using an SiO_2 wafer that is 0.5 mm thick and the same lateral dimensions of the CZT surface. The simulation set up and temperature profile through the center of the CZT surface are shown in Figure 10 below.

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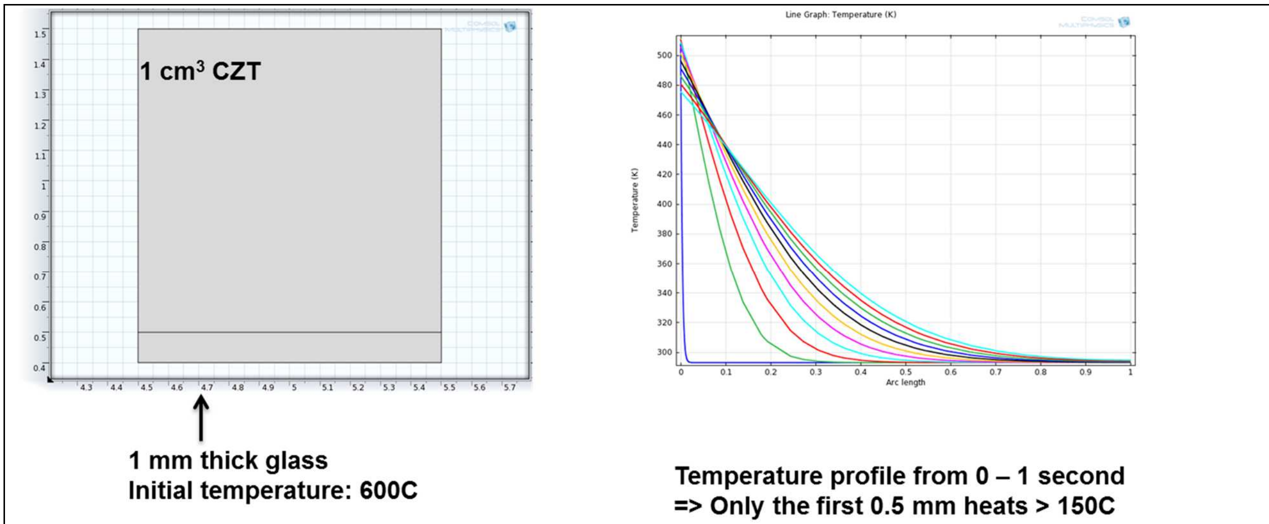

Figure 10: COMSOL problem set up and temperature profile over first second for rapid contact heating.

We expect that with repeated treatments, full activation can be achieved using this method without deleteriously affecting the bulk.

4) Key outcomes and achievements

We have achieved significant results in our three major activity areas during this project. The most significant are:

1) Reduction of >90% in surface leakage current and concurrent improvement in detector performance through the use of surface plasma etching and chemical oxidation.

2) Demonstration of the first CZT p-n and p-i-n junctions formed through doping with ion implantation and metal diffusion doping, ultimately resulting in good gamma detection performance.

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What opportunities for training and professional development has the project provided?
During this project, we have hosted numerous summer interns from Fisk University including Michael Johnson, David Hill, Terreka Hart (twice), and Stephanie Morris. All students received a great deal of experience in the areas of fabrication, and electrical/radiation testing, and interpreting her data while at LLNL. In addition, the co-PI (Lars Voss) is an early-career scientist, and this project is his first programmatic activity for which he bares the main responsibility of directing, executing, reporting, and managing the work. Lars reports to Steve Payne, who is serving as his mentor.

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How have the results been disseminated to communities of interest?

We have held semi-regular teleconferences with other DTRA-funded parties on the subject of CZT fabrication, electrical/radiation testing, and theory of operation (including Fisk University, Cal State Northridge, and Srivananthan Labs). In addition, we have had two meetings with the team at LBNL led by Mark Amman on CZT co-planar grid detectors and have collaborated on some work together. Our objective is to collaborate with the DTRA-funded CZT activities to the maximum extent possible. During the course of the project, we have also presented posters and talks at IEEE NSS, SORMA, and an invited seminar at the University of Alabama and have published our work in IEEE TNS. We have submitted an abstract for the 2015 IEEE NSS conference on our work on ion implanted junction detectors.

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What do you plan to do during the next reporting period to accomplish the goals?
This is a final report

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