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Awardee Name: Washington State University

Project Title: Improvement in compensation and crystal growth of cadmium zinc telluride radiation detectors

Project Director/Principal Investigator: Dr. Kelvin Lynn

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Comparison of actual accomplishments with goals and objectives:

Goal #1: Growth of 12 ingots. Washington State University (WSU) more than met this goal for the project by growing 12 final ingots for the year. Nine of the twelve crystal growth ingots resolved gamma radiation at room temperature. The other three ingots where resistivity of $\sim 3 \times 10^8 \text{ Ohm}\cdot\text{cm}$ for CG32a, CG36, and CG42 lower than expected, however none of these were tried with blocking contacts. All ingots were evaluated from tip to heel. In these three cases, the group III, dopant Aluminum (Al) was not detected to a level to compensate the Cd vacancies in the cadmium zinc telluride (CZT) thus the ingots were lower resistivity. The nine ingots that were successful radiation detectors averaged a bulk resistivity of $1.25 \times 10^{10} \text{ Ohm}\cdot\text{cm}$ and with a average $\mu\tau$ product for electrons of $\sim 2.2 \times 10^{-4} \text{ cm}^2/\text{V}$ with a $\frac{1}{4}$ microsecond shaping time with samples $\sim 2 \text{ mm}$ in thickness.

Goal #2: Attempt new compensations techniques. WSU also met this goal. Several doping schemes were attempted and investigated with various amounts of excess Tellurium added to the growth. The combination of Al and Erbium (Er) were first attempted for these ingots and subsequently CG34 was grown with Al, Er and Holmium. These compensation techniques produced radiation detectors and are currently under investigation. These growths were made with significant different doping levels to determine the affect of the dopants. CG43 was doped with Indium and Er. Indium was introduced instead of Al to determine if Indium is more soluble than Al for CZT and was less oxidized. This may decrease the amount of low resistivity ingots grown by doping with Indium instead of Al.

Goal #3, grow large single crystals. Several changes in approach occurred in the crystal growth furnace. Steps were taken to maximize the crystal growth interface during growth by modifying liners, quartz, heat sinks, crucibles and various growth steps and temperature profiles. CG39 ingot was a single crystal except on the edges. We consider that single crystals are necessary but are not yet the key to the best radiation response. Starting this with very few changes we were unable to reproduce the single crystal in CG40.

Goal #4: CZT Defect characterization. Upgraded defect characterization techniques and tools were implemented as well improving the cutting process to reduce damage. An automated thermoelectric effect spectroscopy (TEES) and thermally stimulated current (TSC) machine was modified and tested.. Infrared transmission

microscopy was improved to better analyze the role of these inclusions. These three devices improved defect analysis capabilities and helped produce a presentation.

Discussion:

CG32a was a reused charge material from a previous growth. The charge material was already pre-compounded CZT, but contained no Al. The growth was prepared and Al was added to the crucible. The growth was about 2 weeks. After the growth the ingot was examined and tested. The ingot had lower resistivity and Glow Discharge Mass Spectroscopy (GDMS) showed low Al concentration which confirmed the reason for the low resistivity. CG33 had high resistivity and functioned as a radiation detector. The Al concentration in 33 was lower than intended but was high resistivity. CG33, 34 and 35 were grown in two steps. The charge was initially melted in a tall crucible and mixed in the liquid for 24 hours. After cooling the ingot was transfer into a shorter crucible and grown for a period of 12 days. The shorter crucible reduced the ampoule open volume. This process reduced vapor loss during the growth resulting in fewer intrinsic defects, specifically cadmium vacancies. However, impurities in the resulting ingots started to rise because of the increase in handling the material, due to transferring crucibles. This process was also considerably more time consuming and costly. CG35 was doped with a very large amount of Er. It was designed to match the amount of excess Tellurium rejected from the CZT lattice during the retrograde solubility. Er and Tellurium forms Er telluride within the CZT lattice minimizing the effects of Tellurium inclusion and precipitates. CG35 had high resistivity and performed well as a radiation detector. CG36 was another reused charge from CG32a. Again, additional Al was added along with excess Tellurium. The resulting ingot had low resistivity and the GDMS results showed a very low Al concentration. CG37 and 38 were similar in dopants and excess Tellurium. CG37 had impurities such as Chromium, Manganese, and Copper in the heel of the ingot and did not produce good radiation detectors. The tip and middle was comparable to CG38 properties. CG39 ingot was a single crystal. This was largely due to changing the crystal growth temperature profile resulting in less turbulent flow from the melt and creating a more stable and optimal growth interface. CG40 and CG41 ingots were grown with less excess tellurium than CG39. This was to optimize detector properties by attempting to decrease the amount of tellurium inclusions and increasing electron charge collection properties of the detectors. An interesting result was the decrease in resulting doping levels found in the ingots from GDMS analysis. CG39, CG40 and CG41 all had high resistivity, $1-3 \times 10^{10} \text{ Ohm*cm}$. CG39 and CG41 had good $\mu\tau$ electron values and CG40 had good energy resolution from gamma spectroscopy measurements at room temperature on standard sources. CG42 had low resistivity because of the low Al concentration. Again, the Al failed to be soluble in the ingot. CG43 was doped with Indium and Er. Indium was introduced instead of Al to determine if Indium is more soluble than Al for CZT. This may decrease the amount of low resistivity ingots grown by doping with Indium instead of Al. CG43 was also grown using a zone leveling process to minimize the vapor loss during the growth. The Indium was soluble and the ingot had high resistivity, but the Er dopant was not incorporated into the matrix. This was because of the high melting temperature of Er and the zone leveling

Comment [r1]: Kelly, is "was" normal usage? Could we say "had"

Comment [r2]: Again, "had"?

Comment [r3]: "had"?

Comment [r4]: "had"?

Comment [r5]: "performed" ?????

Comment [r6]: "had"?

Comment [r7]: "had"?

Comment [r8]: "had"?

technique attempted did not allow for adequate time of the Er to mix with the CZT. Indium has been determined to be the preferred dopant for solubility into CZT.

Thermoelectric effect spectroscopy (TEES) and thermally stimulated current (TSC) experiments were conducted on the following samples: a. samples CG32a-AC-C2, b. CG33-AB-AD-G2, and c. CG34-AB-H3. From the TEES/TSC current vs. average temperature curves, the energy and thermal ionization cross-section of some prominent peaks were calculated. The analysis of the observed current peaks for all the three samples with their corresponding was consistent with GDMS data. The GDMS data revealed low Al on CG32a, a high Er on CG33 and CG34, and Ho in sample CG34.

TEES current peaks uniquely occurring in sample CG34-AB-H3 at 213K ($E_{th}=0.61[05]$ eV; $\sigma_{th}=1.3[5] \times 10^{-13}$ cm²), 229K ($E_{th}=0.67[05]$ eV; $\sigma_{th}=4.8[5] \times 10^{-13}$ cm²) and 268K ($E_{th}=0.82[05]$ eV; $\sigma_{th}=1.25[5] \times 10^{-12}$ cm²) were compared with sample CG33-AB-AD-G2. It is possible the peaks at temperatures about 213K and 229K could be a transition to one of the charge states of Al-Tellurium antisite-Cd vacancy complex (Al-Te_{cd}-V_{cd}). In high purity CdTe samples, the deep levels at about 245K and 260K have been attributed to the higher order transition of the Tellurium antisite-double Cd vacancy complexes. In this sample, the deep level was observed at a higher temperature (268K) and the value of energy and cross-section were also high. Further research is required to determine if this is a higher order transition of the (antisite-double Cd vacancy pair) or if it is a deep level of Holmium.

The peak at ± 173 K ($E_{th}=0.47[05]$ eV; $\sigma_{th}=8.2[5] \times 10^{-14}$ cm²) in sample CG32a-AC-C2 was unique. Since the charge used to produce the CG32a boule was originally from a failed CG32 run, the analysis of the TSC current peaks was complicated.

TEES and thermally stimulated current (TSC) experiments were conducted on samples from CG39 ingot to extract information on the thermal ionization energy (E_{th}) and cross-section (σ_{th}) of the various intrinsic and/or extrinsic impurity, and impurity complex levels in the band gap. Variable heating rate TSC experiments on annealed CG39 samples have revealed a very prominent level with $E_{th} : 0.26[05]$ eV and $\sigma_{th}=7.7[5] \times 10^{-18}$ cm², which was identified as the donor level of Te-antisite (Te_{Cd})^{0/+}.

Schedule Status for the first year:

WSU completed tasks on schedule with desired milestones.

Changes in Approach:

No major changes in approach occurred during this reporting period.

Actual or Anticipated Problems:

Reproducibility in the single crystal growth process remains a challenge.

Learning about the growth interface has been a challenging issue.

Changes of Key Personnel:

None.

Technology Transfer:

Kelly Jones and Kelvin Lynn attended SORMA XI conference at the University of Michigan 5/22-26/2006 and two presentations were given. Dr. Lynn's was "Crystal Growth and Characterization of Cd_{1-x}Zn_xTe Radiation Detectors" (5/23/06) and the other presentation by Kelly Jones was "Vertical Bridgman Growth of Cd_{1-x}Zn_xTe Room Temperature Radiation Detectors" (5/23/06).

Comment [r9]: Financial reports already have been filed.

C. CZT samples were given to Pacific Northwest National Laboratory (PNNL) for IR transmission microscopy studies and incident gamma ray spectroscopy analysis. Crucibles from CZT crystal growth were also given to PNNL for SIMS analysis.

Results from samples previously given to Lawrence Berkeley National Laboratory Semiconductor Detector Group were provided with characterization of Infrared transmission microscopy and mutau products for electrons. Paul Luke reported results from samples grown at WSU of $3.17 \times 10^{-3} \text{ cm}^2/\text{V}$.

Samples were also given to the Kansas State's semiconductor materials and radiological technologies (S.M.A.R.T.) laboratory for Frisch grid detectors. They were able to record 2.5% resolution at 662keV from a sample also grown at WSU.

From the university of Dr. Jeffery Derby and Graduate Student Lisa Lun visited the CMR. Presentations and a laboratory tour were given to develop knowledge of both research teams and capabilities. Goals and research tasks were assigned for the collaboration.

E. A provisional patent was filed entitled, Compositions of Doped, Co-Doped and Tri-Doped Semiconductor Materials. The field of the invention was Semiconductor materials for radiation detectors. Inventors are Dr. Kelvin Lynn, Kelly Jones and Guido Ciampi. The invention described herein concerns a bulk II-VI type semiconductor material. It is especially applied for CdTe, CdZnTe, CdZnSe or CdZnTeSe crystals (collectively referred to herein as CZT). Such ingots may be used in the manufacture of elementary or matrix detectors for radiation detection. The charge supplied in the crucible for heating and crystal growth includes members from group II (e.g. Cd, Zn) and group IV (e.g. Te, Se) along with doping impurities selected from Group III (e.g. Al, In, Ga) and/or Group VII (e.g. Cl, Br) and/or the rare earth elements (e.g. Er, Yb, Eu).

Comment [r10]: "applicable" maybe?