

**DOE/EPSCoR State/Laboratory Partnership Award  
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**FINAL TECHNICAL REPORT**

Title of Project: Correlation of Point Defects in CdZnTe with Charge Transport:  
Application to Room-Temperature X-Ray and Gamma Ray-  
Detectors

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Project Description:

Applications requiring room-temperature x-ray and gamma-ray detectors are rapidly increasing and now include nuclear medicine, space sciences, national security, environmental remediation, nonproliferation inspections, etc. To meet these needs, a new generation of detectors based on single crystals of cadmium zinc telluride ( $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ ) is being developed. This semiconductor material possesses many desirable detector properties, such as constituent atoms with high atomic number (Z), a sufficiently large band gap to minimize leakage currents at room temperature, and high intrinsic mobility-lifetime ( $\mu\tau$ ) products for electrons and holes. However, despite the tremendous promise of this material, problems clearly exist. CdZnTe crystals are difficult to grow in large sizes and with ultra-high purity. There is a need to further lower the leakage currents in detector-grade material and also to increase the efficiency of charge

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collection. In general, all aspects of carrier trapping in this material must be understood and minimized. Point defects are a primary reason CdZnTe crystals have not yet reached their expected levels of performance. Thus, a better understanding of the role of point defects and the larger microstructure defects on the transport of electrons and holes will lead to improved detector-grade CdZnTe.

The primary goal of this project has been to characterize and identify point defects (e.g., impurities, vacancies, vacancy-impurity complexes, etc.) in CdZnTe and determine the mechanisms by which these defects influence the carrier  $\mu\tau$  products. Special attention is given to the role of shallow donors, shallow acceptors, and deeper acceptors. There are two experimental focus areas in the project: (1) liquid-helium photoluminescence (PL) and PL excitation spectroscopy are used to identify and characterize donors and acceptors and to determine zinc molar fraction; and (2) electron paramagnetic resonance (EPR) and photoinduced EPR experiments are performed at liquid-helium temperature to identify paramagnetic point defects and to determine the concentration of these defects. Results from the two experimental focus areas are correlated with detector performance parameters (e.g., electron and hole  $\mu\tau$  products), crystal growth conditions, and microstructure analyses. The project employed one physics graduate student each year and it has served to further enhance the infrastructure for research and education in advanced semiconductor materials at West Virginia University.

#### Accomplishments:

A detailed study of  $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$  crystals with  $0 \leq x \leq 0.14$  has been completed using photoluminescence spectroscopy. In this work, specific experiments were performed with the purpose of: 1) identifying various radiative transitions that are signatures of various point defects in bulk CdZnTe crystals, 2) determining the zinc concentration in these crystals, and 3) identifying the nature of room-temperature PL.

A series of PL spectra were taken at liquid helium temperatures for various doped and undoped CdZnTe crystals. These data allowed us to extract the free exciton energy and hence the sample band gap at low temperatures for each of the samples. Then, using the various expressions proposed in the literature, we determined the zinc concentration of each sample. A more detailed PL study was performed on eleven samples (from the larger set of samples). These particular samples had different zinc concentrations, and were doped and undoped. PL data were taken as a function of temperature to determine the origin of the room-temperature PL from CdZnTe grown for radiation detector/IR substrate applications. The PL measurements were made in the temperature range from 5 K to 300 K. Currently, the typical growth of high-quality bulk CdZnTe produces material that is slightly n-type. However, it is desirable to have high resistivity or highly compensated material. In CdZnTe material grown by state-of-the-art technology, it is common to observe 5-K PL spectra dominated by donor-bound exciton emission ( $D^0, X$ ). Also, a deep acceptor-bound exciton ( $A^0, X$ ) related to a complex associated with Cd vacancies is usually detected. Thus, it was of interest to perform a study and determine whether recent modifications in bulk CdZnTe growth would produce a different conclusion about the

origin of the 300-K PL.

The CdZnTe samples included in the present project exhibited both the upper and lower polariton branches in PL spectra at 5 K. The excited state ( $n=2$ ) free exciton emission could also be resolved in a few cases. The temperature dependence of the PL emission from these crystals was used to determine the nature of the PL at room temperature. The upper polariton branch was resolved up to 125 K. Above 125 K, a single broad band was observed. The origin of this broad PL band is due to a superposition of exciton and phonon-related recombinations. In donor-doped material, the donor-hole recombination was not dominant in PL spectra taken at 300 K. Variations in zinc concentration among the samples leads to shifts in emission energies. This makes it difficult to directly compare PL features from different samples that are due to the same point defects. To overcome this problem, various low-temperature PL spectra from different samples were compared using the energy shift below  $E_g$  as the common reference. Doping with donor impurities (Al, Cl, In) produced a deep acceptor-bound exciton. The thermal quenching behavior of this line at 1.5844 eV (referred to as W line or C line in literature) in CdTe:In was studied and two activation energies of 15.2 meV and 1.75 meV were determined.

We have also used electron paramagnetic resonance (EPR) and photo-induced EPR to evaluate shallow-donor defects in CdZnTe crystals grown by the two different techniques—high-pressure Bridgman and horizontal Bridgman. In this portion of our project, we investigated five samples grown by the high-pressure Bridgman (HPB) technique. One sample was undoped and four were doped with aluminum. Four of these five samples were included in a previous EPR and PL study [C. I. Rablau et al., Materials Research Society Symposium Proc. Vol. 487, pp. 71-76, 1998]. One sample grown by the horizontal Bridgman technique at IMARAD Imaging Systems Ltd. (Israel) and doped with indium was provided to the present investigation for comparison. Prior to the EPR investigations, we performed liquid-helium photoluminescence (PL) in order to examine the radiative recombination paths and identify the presence of other defects in these crystals. Spectra were obtained over the range from the energy gap down to about 0.89 eV. PL spectra showing sharp excitonic lines, shallow and deep DAP emission bands, and a deeper 1.1 eV emission were observed. The PL data were then used to define the optical excitation range used in subsequent photo-EPR measurements. The photo-EPR data from these CdZnTe samples is used to determine a minimum concentration of isolated donor centers, while the EPR signal present under no illumination gives a measure of the net compensation. The excitation wavelength dependence of the isotropic EPR signal from the shallow donors in these different samples was also measured and will be described below.

There is a broad emission band centered near 1.45 eV in all of the samples (although weak in the undoped sample). This band has been attributed to several different defects. In the case of the undoped material, it most likely is donor-acceptor-pair (DAP) recombination between shallow donors and acceptor impurities (e.g., copper, or silver). For the Al- and In-doped samples, this band may also contain a contribution from DAP emission where the acceptor center is a complex point defect referred to as an A center. A centers in II-VI materials have been widely studied. They are present in donor-doped material and are structurally described as a

cation vacancy-donor impurity complex  $(V_{\text{Cd}}-D^+_{\text{Cd}})^0$  with the Group III donor impurity on a next-nearest-neighbor cation site. The unpaired electron from the donor is localized at the vacancy. The overall defect is electrically neutral unless it traps a second electron, in which case it becomes a singly ionized acceptor  $(V_{\text{Cd}}-D^+_{\text{Cd}})^-$ .

In each of the doped samples, there appears an emission at about 24 meV below the band gap energy. This emission in CdZnTe is accompanied by phonon replicas, which suggests it is due to a deep acceptor-bound exciton ( $A^0, X$ ). The origin of this deeper bound exciton in CdZnTe is most likely similar to the "C line" described in high-resistivity CdTe:In and attributed to defect complexes involving the donor impurities and cadmium vacancies. This deep ( $A^0, X$ ) emission was not detected from the undoped CdZnTe sample. A separate emission at about 1.1 eV was weak in most of the samples studied. This deeper PL emission was significantly brighter in two of the samples. The origin of the PL emission near 1.1 eV has been attributed to several different types of defects. One suggestion associates Te vacancies with radiative recombination in CdTe and CdZnTe occurring in this spectral region. The ionization energy of the Te vacancy in CdTe has been suggested to be  $\sim 0.2$  eV. If Te vacancies are present in the samples and acting as deep electron traps ( $V_{\text{Te}}^0$ ), they would be nonparamagnetic. However, if the Te vacancies are singly ionized ( $V_{\text{Te}}^+$ ), the one unpaired spin would allow detection using EPR. In donor-doped material, it is unlikely that these centers would be paramagnetic.

EPR spectra were recorded from each sample in light-off and light-on conditions. The spectrum from a hydrogenic donor ( $S=1/2$ ) defect center could be seen in all cases under illumination. The g-value of the spectrum is obtained using  $h\nu = g\beta H$ , where H is the center magnetic-field value for the spectrum. The g value for shallow donors in CZT is dependent on zinc concentration. In a previous study [C. I. Rablau et al., Journal of Electronic Materials, Vol. 27, pp. 813-819, 1998], we used PL and EPR data to obtain the expression  $g = 1.68 - 1.28x$  which describes the dependence of g on x, the zinc molar fraction. The donor EPR line is located at different magnetic fields for different zinc compositions, and having the x-value determined previously from PL data greatly aids in locating and detecting the EPR signal.

EPR spectra are obtained by modulating the magnetic field, thus the spectra appear as first-derivative line shapes. The shallow-donor EPR signal were taken at 8 K and signal averaging was often used. These signals were best observed when the sample was illuminated with below-band-gap light. Measurements of the wavelength dependence for producing the EPR signal were obtained under excitation at constant laser power. These results showed the greatest efficiency was for wavelengths between 750 and 790 nm, while wavelengths greater than  $\sim 800$  nm show a rapid decrease in efficiency. In this latter case, the EPR signal becomes less intense because the photon energy becomes too small to efficiently pump acceptor-to-donor transitions. The laser-power saturation of the photo-induced EPR signal was also measured. With no illumination, the EPR signal was weak but could still be observed in a few samples. In order to convert the EPR signal to donor concentration, the volume of the sample was taken into account. The "light-off" concentration corresponds to the net uncompensated donor concentration (i.e.,  $N_D - N_A$ ). The maximum intensity of the photo-induced EPR signal (i.e., "light on") provides a

measure of the donor concentration within the crystal. This provides a minimum value for the donor concentration. Because the signal is photo-induced, the number of actual shallow donors may be larger and the observed EPR intensity is only due to the net number that can be maintained in the neutral state by the pump light.

In the previously described work, a reduced sample size was necessary for the liquid-helium EPR experiments, owing to the dimensions of the glassware in the microwave cavity. Nominal sample dimensions of  $3 \times 2 \times 5 \text{ mm}^3$  were used. Prior to the EPR measurements, the sample surfaces were chemically polished and etched with Br/methanol and PL data was collected at liquid helium temperatures. PL excitation was provided by a HeNe laser (632.8 nm), and PL signals were detected using a grating spectrometer and a GaAs(Cs) photomultiplier tube (wavelength cut-off at  $\sim 8850 \text{ \AA}$ ) and a 77-K-cooled Ge detector (wavelength cut-off at  $\sim 14000 \text{ \AA}$ ). All PL spectra were corrected for the wavelength response of the detection system. The spectra recorded using the Ge detector were scaled and matched to the region recorded using the PMT so that relative intensities of the deep-level bands as compared to the near-edge emission could be determined. Zinc molar fractions were determined from the PL data using standard expressions.

The EPR and photo-EPR measurements were then collected using a Bruker spectrometer operating at 9.45 GHz with 100 kHz modulation frequency. The low sample temperatures (near 8 K) were obtained using an Oxford Instruments liquid-helium flow system which extended through a standard TE<sub>102</sub> microwave cavity. Magnetic fields were measured using a Varian proton gaussmeter, and a MgO:Cr crystal was used for correction of the small difference in magnetic field at the sample position and at the position of the gaussmeter. The cavity allows optical access to the sample so that in-situ illumination is possible. The tunable output from a Ti:sapphire laser (pumped by an argon ion laser) was used in the photo-EPR experiments. The wavelength output from the tunable laser was monitored using a Burleigh wavemeter. We used the EPR technique to quantify the concentration of shallow donors in the CdZnTe samples. The detection limit of our EPR spectrometer is approximately  $5 \times 10^{10}$  spins (for a 1 gauss linewidth and a temperature of 8 K). Thus, for the maximum sample size that can be placed in our microwave cavity glassware, the corresponding minimum concentration of paramagnetic defects is in the range of low  $10^{13} \text{ cm}^{-3}$ , in principle. Owing to the linewidth of the donor EPR signal, and many of our samples are smaller than the maximum size, we have been able to quantify donor concentrations as low as the mid- $10^{14} \text{ cm}^{-3}$  level. We estimate the uncertainty in the donor concentrations determined using the EPR technique to be no larger than a factor of 2.

#### Student Participation:

Four students were supported by this DOE/EPSCoR grant. A brief description of each of these students follows. Please note that three of the four are female.

Jessica McChesney was an undergraduate student in our Physics Department. She spent the summer of 1999 working at Sandia National Laboratory in Livermore, CA. While at Sandia,

Science, Engineering, and Instrumentation Symposium, Denver, CO (July 19-22, 1999).

3. "Compensation and Trapping in Semi-Insulating CdZnTe", E.Y. Lee, J. L. McChesney, R. B. James, R. W. Olsen, H. Hermon, and M. M. Schieber, SPIE Optical Science, Engineering, and Instrumentation Symposium, Denver, CO (July 19-22, 1999).

4. "Deep Levels in Semi-Insulating CdZnTe Studied by Time-Resolved PL, TEVS, TSC, and Radiation Measurements", E.Y. Lee, R. B. James, R. W. Olsen, H. Hermon, J. McChesney, and M. Schieber, The 1999 U.S. Workshop on the Physics and Chemistry of II-VI Materials, Las Vegas, NV (October, 1999).

Publications:

1. "Large Volume Imaging Arrays for Gamma-Ray Spectroscopy," T. E. Schlesinger, B. Brunett, H. Yao, J. M. vanSycoc, R. B. James, S. U. Egarievwe, K. Chattopadhyay, X.-Y. Ma, A. Burger, N. Giles, U. El-Hanany, A. Shahar, and A. Tsigelman, Journal of Electronic Materials, vol. 28, pp. 864-878 (1999).

2. "Electron Paramagnetic Resonance Investigation of Donor Impurities in CdZnTe Grown by Different Techniques," N. C. Giles, C. I. Rablau, N. Y. Garces, K. Chattopadhyay, A. Burger, E. Cross, F. P. Doty, and R. B. James, in SPIE Conference on Hard X-Ray, Gamma-Ray, and Neutron Detector Physics, Proceedings Vol. 3768, pp. 472-480 (1999).

3. "Compensation and Trapping in Semi-Insulating CdZnTe," E.Y. Lee, J. L. McChesney, R. B. James, R. W. Olsen, H. Hermon, and M. M. Schieber, in SPIE Conference on Hard X-Ray, Gamma-Ray, and Neutron Detector Physics, Proceedings Vol. 3768, pp. 115-128 (1999).

4. "CZT Detectors Fabricated from Horizontal and Vertical Bridgman-Grown Crystals," H. Hermon, M. Schieber, E. Y. Lee, J. L. McChesney, M. Goorsky, T. Lam, E. Meerson, and H. Yao, and R. B. James, Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Vol. 458, no. 1-2, pp. 503-510 (2001).

5. "Photoluminescence Study of Cadmium Zinc Telluride," Swati Jain, Masters Thesis, Physics Department, West Virginia University (May 2001).