PHYSICAL REVIEW B VOLUME 62, NUMBER 24 15 DECEMBER 2000-II

Electrical compensation in CdTe and $Cd_{0.9}Zn_{0.1}Te$ by intrinsic defects

N. Krsmanovic, K. G. Lynn, M. H. Weber, R. Tjossem, and Th. Gessmann
Center for Materials Research, Washington State University, Pullman, Washington, 99163

Cs. Szeles and E. E. Eissler
eV PRODUCTS a division of II-VI Inc., Saxonburg, Pennsylvania 16056

J. P. Flint and H. L. Glass
Photonic Materials, Honeywell Electronic Materials, Spokane, Washington 99216-1895
(Received 7 April 2000; revised manuscript received 28 September 2000)

The effects of two *intrinsic* deep levels on electrical compensation in semi-insulating CdTe and Cd-Zn-Te crystals are reported here. These levels were found in samples grown by conventional Bridgman and high-pressure Bridgman techniques. The levels were observed with thermoelectric effect spectroscopy at distinct temperatures corresponding to thermal ionization energies of $E_{d1}=E_v+0.735\pm0.005$ eV and $E_{d2}=E_v+0.743\pm0.005$ eV. The first level is associated with the doubly ionized Cd vacancy acceptor and the second level was tentatively identified as the Te antisite (Te_{Cd}), which is thought to be complexed with a vacancy. The second level was found to electrically compensate CdTe and Cd-Zn-Te to produce high resistivity crystals, provided that the Cd vacancy concentration is sufficiently reduced during crystal growth or by post-growth thermal processing.

The relatively wide band gap, large atomic numbers, and good carrier mobility render CdTe and Cd-Zn-Te (Refs. 1 and 2) as promising materials for room-temperature radiation sensor applications. High resistivity is necessary but not sufficient for production of CdTe and Cd-Zn-Te radiation detectors. To realize the maximum resistivity of CdTe and Cd-Zn-Te crystals allowed by the band gap a net carrier concentration of $10^8\ \mathrm{cm}^{-3}$ or lower has to be achieved. Early attempts to produce high resistivity CdTe and Cd-Zn-Te crystals by common growth techniques resulted in materials with native defect or impurity concentrations on the order of $10^{15}\ \mathrm{cm}^{-3}$ and carrier concentrations orders of magnitude in excess of the requirements for intrinsic resistivity. Recently, high resistivity CdTe and Cd-Zn-Te crystals have been grown with both high-pressure Bridgman[3] (HPB)[4] and vertical Bridgman with overpressure control (VBOC) techniques. In this paper we show that intrinsic defects compensate CdTe and Cd-Zn-Te resulting in semi-insulating materials in spite of a total impurity concentration of $\sim10^{15}\ \mathrm{cm}^{-3}$, which is achievable with current technologies.

Samples of CdTe and Cd-Zn-Te were characterized with current-voltage measurements (I-V), glow discharge mass spectroscopy (GDMS), and thermoelectric effect spectroscopy (TEES).[5] The electrical transport properties of the samples including bulk electrical resistivity were studied by I-V measurements. The thermal activation energies of the various defect levels were extracted from TEES data. Results on four different representative CdTe and Cd-Zn-Te crystals are presented in this paper. The samples were grown by eV PRODUCTS using the HPB technique and by Johnson Matthey Electronics (JME, now Honeywell Electronic Materials) using the VBOC technique. The eV samples included $Cd_{0.9}Zn_{0.1}Te$ and CdTe samples, as well as an Al-doped CdTe sample.[6] The JME samples were all $Cd_{0.85}Zn_{0.15}Te$. The total residual impurity concentration was on the order of $10^{15}\ \mathrm{cm}^{-3}$ for all samples studied. Glow-discharge mass spectroscopy (GDMS) data for selected elements, which are discussed in the literature as candidates for midgap trap, are shown in Table I. Samples of $10\times10\times2\ \mathrm{mm}^3$ size were cut and polished by the suppliers. All samples were etched in a methanol-bromine solution and cleaned in methanol before the deposition of the electrodes. Uniform Au electrodes were sputtered on the $10\times10\ \mathrm{mm}^2$ surfaces of the samples.

Figure 1 shows the thermoelectric current versus the temperature for the four samples studied. The energy levels of the detected traps were calculated using

$$E_{\mathrm{th}}=k_bT_{\max}\ln\left(\frac{Cm^*\sigma T_{\max}^4}{\beta E_{\mathrm{th}}}\right)\quad\text{with}\quad C=\frac{4k_b^3\sqrt{6\pi^3}}{h^3},\tag{1}$$

where for each trap σ is the trapping cross section $T_{\max}$ the temperature of the current peak, k_b is Boltzmann's constant, m^* is the effective mass of the electron or hole. In CdTe, $m^*=0.14\,m_0$ for electrons and $m^*=0.37\,m_0$ for holes, with m_0 being the electron rest mass.[7] Planck's constant is noted as h.

We focus on the two deep levels which generate thermoelectric current peaks at $T_{\max}=245\pm1$ K and 266 ± 1 K, respectively. Since the measured thermoelectric current is positive, the peaks are the result of hole emission and the corresponding energy levels are 0.735 ± 0.005 eV and 0.743 ± 0.005 eV above the valence band. The trapping cross sections of the levels, $6\times10^{-13}\ \mathrm{cm}^2$ and $4\times10^{-14}\ \mathrm{cm}^2$, respectively, were chosen based on cross-section data of similar levels reported in the literature.[8]

The first deep level at $E_{d1}=E_v+0.735\pm0.005$ eV is associated with the doubly ionized acceptor level of Cd vacancies ($V_{Cd^{2-}}$).[8,9] This assignment is consistent with the behavior of the level as a function of Al doping. It is well

 ©2000 The American Physical Society

TABLE I. GDMS results for the ingots from which the studied samples were taken. The Li in the VBOC Cd-Zn-Te sample is most likely coming from the quartz ampoule used in this growth process. The concentrations of transition metals like V, Fe, Ti, Co, Cr, and elements like Sn and Ge are close or below the detection limit of GDMS which is below 5 ppb.

Sample	Li (ppb)	Na (ppb)	O (ppb)	Mg (ppb)	Al (ppb)	Cu (ppb)	Ni (ppb)	Zn
HPB CdTe (eV)	<1	3	91	18	13	2	<0.3	12 ppb
HPB Cd-Zn-Te (eV)	<1	ND	76	78	18	<0.2	<0.7	10%
VBOC Cd-Zn-Te (JME)	450	8	530	50	25	10	<1	10%
Al-doped HPB CdTe (eV)	<1	12	93	19	1000	3	25	17 ppb

Sample	Cl (ppb)	Ga (ppb)	Si (ppb)	N (ppb)	K (ppb)	P (ppb)
HPB CdTe (eV)	2	1	5	55	<20	2
HPB Cd-Zn-Te (eV)	<2	<0.8	2	<17	<25	<0.5
VBOC Cd-Zn-Te (JME)	7	<1	2	35	25	0.7
Al-doped HPB CdTe (eV)	37	<0.2	8	12	4	<0.2

known that the addition of shallow donors such as Cl, Al or In to CdTe causes the pairing of Cd vacancies with the donor atoms to form *A* centers.[7] Upon Al doping the expected decrease in signal intensity from the 0.735 eV level was observed, hence its association with $V_{Cd^{2-}}$ level. Emanuelsson *et al.* and Szeles *et al.* also observed the first of the two levels of V_{Cd} by EPR (0.47 eV) and TEES (0.43 eV), respectively.[10,11] We observed this level at 0.43 eV as well in the undoped samples. We also note that in the undoped Cd-Zn-Te HPB sample that a shallow level was also observed which is consistent with Emanuelsson *et al.* and this level could not be associated with an impurity in the sample.

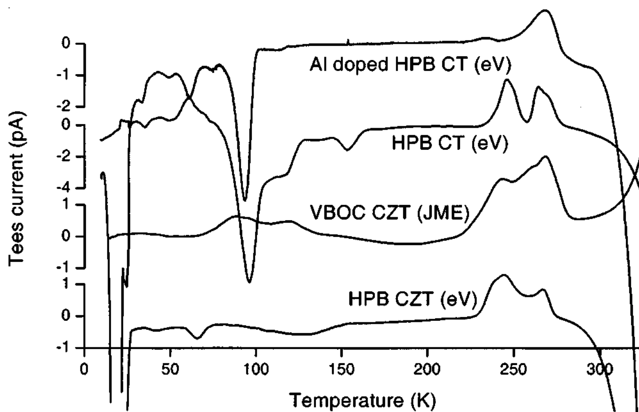

FIG. 1. Thermoelectric current as a function of the sample temperature at a constant heating rate. A small temperature gradient across the samples is the driving force for the current in these experiments. The peaks occur when previously charged traps thermally release their charge. The measurement is polarity sensitive, thus allowing the distinction of electrons from holes. Positive currents indicate hole transport and negative currents indicate electron transport.

The second deep level at $E_{d2}=E_v+0.743\pm0.005\,\mathrm{eV}$ could not be associated with any impurities based on the GDMS data (some of the elemental concentrations are shown in Table I). We associate this level with an intrinsic defect. Chibani *et al.*[12] were among the first to suggest the existence of an intrinsic deep level in CdTe but did not identify a specific defect. We explore the possibility of a Te antisite (Te_{Cd}) which it thought to be complexed with a vacancy, which has been suggested to exist in both CdTe and Cd-Zn-Te.[13–15] According to theory (Berding[16]) the Te_{Cd} is a double donor with the doubly ionized donor level 0.4 eV below the conduction band edge. The calculations show that Te_{Cd} can be present in significant concentrations in CdTe if the crystal is solidified or annealed under Te-rich conditions. In the HPB growth technique typically a Te-rich mixture is used.[3] More than 90% of the Te excess is expected to form Te precipitates during the cool down of the crystals.[14] Te_{Cd} consists of a group of 5 neighboring Te atoms; which might be considered as the early stage of a growing Te precipitate and appears to complex with a vacancy in the early stages. This deep level appears as a hole trap, rather than an electron donor state in the TEES data because it lies below the Fermi level. ''Normal'' donors with shallow levels are ionized when the sample is cooled. Photoexcitation will fill the level with electrons. In this case, however, the trap holds on to the electron until photoexcitation removes it electron into the conduction band. In subsequent TEES runs the trap appears as a hole trap. Positron annihilation studies are currently under way in order to obtain direct evidence for Te_{Cd} complex.

The electrical resistivities obtained from *I-V* curves, are summarized in Table II. The resistivity is calculated from the

TABLE II. Resistivity of the samples studied.

Sample	Resistivity (Ω cm)	Maximum achievable resistivity (Ω cm)
HPB CdTe (eV)	$5.75\pm0.07\times10^{9}$	1.0×10^{10}
HPB Cd-Zn-Te (eV)	$1.79\pm0.13\times10^{9}$	3.0×10^{10}
VBOC Cd-Zn-Te (JME)	$1.06\pm0.04\times10^{9}$	3.0×10^{11}
Al-doped HPB CdTE (eV)	$1.58\pm0.009\times10^{9}$	1.0×10^{10}

I-V curves at low bias (in the range of ±0.5 V) conditions where the series resistance of the material dominates the charge transport across the device. Note that, although all four samples studied here were semi-insulating, none of them approached the theoretical maximum resistivity allowed by the band gap of the material, indicating that the samples are not fully compensated.

Considering the concentration of impurities in the samples of $\sim10^{15}\,\mathrm{cm}^{-3}$, much larger than the $<10^{8}\,\mathrm{cm}^{-3}$ required for intrinsic material, the high resistivity of the crystals is due to electrical compensation. One-to-one compensation between shallow donors and acceptors cannot be achieved in practice with a precision that would produce the high resistivity of these samples. Instead, electrical compensation results from deep levels close to the middle of the band gap. A model for such a compensation scheme was presented by Neumark.[17] An excess of shallow acceptors (N_a) over shallow donors (N_d), $\Delta N_s=(N_a-N_d)>0$ can be compensated by deep donors $N_{dd}>\Delta N_s$, to achieve high resistivity. Similarly, an excess of shallow donors $\Delta N_s=(N_d-N_a)>0$ can be compensated by deep acceptors if $N_{da}>\Delta N_s$.

This model was invoked by Fiederle *et al.*[13] to describe the behavior of Cd-Zn-Te grown by physical vapor transport. Figure 2 shows our calculated electrical resistivity of CdTe and $\mathrm{Cd}_{1-x}\mathrm{Zn}_x\mathrm{Te}$ ($x=0.1$) as a function of deep donor concentration N_{dd} for a net acceptor excess of $\Delta N_s=8.8\times10^{15}\,\mathrm{cm}^{-3}$ (300 ppb). Results are shown for three different deep acceptor concentrations $\Delta N_{da}=0,10,100$ ppb ($0,3\times10^{14}\,\mathrm{cm}^{-3}$, $3\times10^{15}\,\mathrm{cm}^{-3}$). Since all but the VBOC sample shows *n*-type conductivity at room temperature, the electrical compensation of the samples is due to a deep donor. The measured resistivity of the studied samples is between $1.06\times10^{9}\,\Omega$ cm and $5.57\times10^{9}\,\Omega$ cm (Table II) corresponding to a deep donor concentration range of 200 ppb ($5.9\times10^{15}\,\mathrm{cm}^{-3}$) to 600 ppb ($1.8\times10^{16}\,\mathrm{cm}^{-3}$) (Fig. 2). No impurities with known deep donor levels were found in the samples at such a high concentration. We suggest that the deep donor level of an intrinsic defect is responsible for the compensation.

Our results show that semi-insulating CdTe and Cd-Zn-Te are compensated by intrinsic defects that satisfy the Neumark model. The resistivity is sensitive to the concentration of the intrinsic defects that we tentatively assigned to $\mathrm{Te}_{\mathrm{Cd}}$ and Cd vacancies. Due to the retrograde solubility of Te in CdTe and Cd-Zn-Te,[14] and potential Cd losses during growth,[14] solid CdTe and Cd-Zn-Te contain excess Te even if grown from stoichiometric melt. This excess Te can be accommodated as Cd vacancies, Te precipitates[14] and Te antisites.[15] Among these, typically Cd vacancies are the dominant defects. Their acceptor state controls the electrical conductivity of the material. As a result undoped CdTe and Cd-Zn-Te are typically low-resistivity and *p* type.[18] When the formation of Cd vacancies is suppressed, such as in HPB growth, or their concentration is reduced by annealing in Cd vapor, the electrical conductivity is controlled by the second deep level, the deep donor level at $E_{d2}=E_v+0.743\pm0.005$ eV, which we have tentatively attributed to $\mathrm{Te}_{\mathrm{Cd}}$ or complex W*V*Cd. This deep donor compensates CdTe and Cd-Zn-Te crystals, however, for radiation detector applications it is essential that the deep level does not affect the charge transport in the material. Further studies are in progress to investigate the effects of this deep level on charge transport.

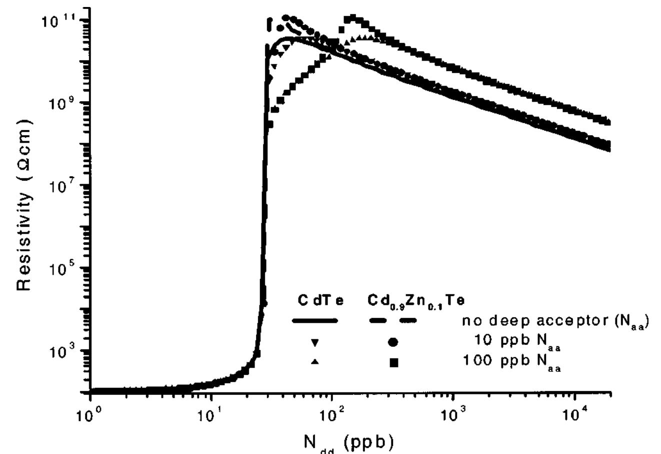

FIG. 2. Resistivity vs the concentration of deep donor at $E_{d2}=E_v+0.743\pm0.005$ eV is shown for CdTe and Cd-Zn-Te with 10% Zn, respectively. In addition to deep donor the presence of deep acceptors N_{da} at $E_{d2}=E_v+0.735\pm0.005$ eV was also considered (0, 10, and 100 ppb). When the Neumark conditions are satisfied, i.e., the concentration of deep donors exceeds the number of uncompensated acceptors the resistivity rises sharply.

We demonstrated that high-resistivity CdTe and Cd-Zn-Te material can be grown from high-purity materials with the high-pressure Bridgman technique as well as by annealing Cd-Zn-Te grown with the modified vertical Bridgman method. Either method reduces the Cd vacancy concentration to a level at which it can be compensated by the second observed intrinsic defect with a deep level at $E_{d2}=E_v+0.743\pm0.005$ eV. We tentatively associate it with the deep donor level of a complexed Te antisite. The identification as a $\mathrm{Te}_{\mathrm{Cd}}$ is not positive, but that has little consequence on the compensating nature of this intrinsic defect.

The authors would like to thank Alan W. Hunt for his interest in this work and valuable discussions. The authors acknowledge NSF financial support under Grant No. 9802712.

[1] T. E. Schlesinger and R. B. James, *Semiconductors for Room Temperature Nuclear Detector Applications*, *Semiconductors of Semimetals* (Academic Press, San Diego, 1995), Vol. 43, p. 238.

[2] U. El-Hanany, A. Shahar, and A. Tsigelman, Proc. SPIE **3768**, 2 (1999).

[3] E. Raiskin and J. F. Butler, IEEE Trans. Nucl. Sci. **NS-35**, 85 (1988).

[4] K. G. Lynn, M. H. Weber, H. L. Glass, J. P. Flint, and Cs. Szeles, in *Semiconductors for Room-Temperature Radiation Detector Applications II*, edited by R. B. James *et al.*, MRS Symposia Proceedings No. 487 (Materials Research Society, Pittsburgh, 1998), p. 229.

[5] B. Santic and U. V. Desnica, Appl. Phys. Lett. **56**, 2636 (1990).

[6] Z. C. Huang, E. Eissler, and C. R. Wie, Nucl. Instrum. Methods Phys. Res. B **100**, 507 (1995).

[7] H. F. Wolf, *Silicon Semiconductor Data* (Pergamon, Oxford, 1969), p. 6.

[8] A. Castaldini, A. Cavallini, B. Fraboni, P. Fernandez, and J. Piqueras, J. Appl. Phys. **83**, 2121 (1998).

[9] M. Hage-Ali and P. Siffert, Nucl. Instrum. Methods Phys. Res. A **322**, 313 (1992).

[10] P. Emanuelsson, P. Omling, B. K. Meyer, M. Wienecke, and M. Schenk, Phys. Rev. B **47**, 15 578 (1993).

[11] Cs. Szeles, Y. Y. Shan, K. G. Lynn, A. R. Moodenbaugh, and E. E. Eissler, Phys. Rev. B **55**, 6945 (1997).

[12] L. Chibani, M. Hage-Ali, and P. Siffert, J. Cryst. Growth **161**, 153 (1996).

[13] M. Fiederle, C. Eiche, M. Salk, R. Schwartz, K. W. Benz, W. Stadler, D. M. Hofmann, and B. K. Meyer, J. Appl. Phys. **84**, 6689 (1998).

[14] P. Rudolph, M. Neubert, and M. Muhlberg, J. Cryst. Growth **128**, 582 (1993).

[15] D. M. Hofmann, W. Stadler, P. Christmann, and B. K. Meyer, Nucl. Instrum. Methods Phys. Res. A **380**, 117 (1996).

[16] M. A. Berding, Phys. Rev. B **60**, 8943 (1999); the author's result of 0.4 eV for Te_{Cd} depends on assumptions which are not necessarily true for the samples studied here, M. A. Berding (private communication).

[17] G. F. Neumark, Phys. Rev. B **26**, 2250 (1982).

[18] Cs. Szeles, Y. Y. Shan, K. G. Lynn, and E. E. Eissler, Nucl. Instrum. Methods Phys. Res. A **380**, 148 (1996).