Trapping properties of cadmium vacancies in $Cd_{1-x}Zn_xTe$

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The trapping and thermal emission of holes were studied from a deep acceptor level created during thermal annealing of a $Cd_{1-x}Zn_xTe$ ($x=0.12$) crystal grown by the high-pressure Bridgman (HPB) technique using thermoelectric-effect spectroscopy and thermally stimulated current experiments. The deep level, which is usually absent in as-grown HPB $Cd_{1-x}Zn_xTe$ crystals, is assigned to the $2-/-$ acceptor level of Cd (Zn) vacancies. The thermal ionization energy of the level is $E_{th}=(0.43\pm0.01)$ eV, and the trapping cross section of holes was found to be $\sigma=(2.0\pm0.2)\times10^{-16}$ cm^{-2}. [S0163-1829(97)03111-1]

I. INTRODUCTION

The use of II-VI semiconductors such as CdTe and $Cd_{1-x}Zn_xTe$ as room-temperature x-ray and γ-ray detectors is severely limited by trapping of electrons and holes at defects and the resulting incomplete charge collection.[1,2] Both native defects and residual impurities are known to introduce localized levels to the band gap of these materials, influencing electrical compensation and carrier trapping. Recent improvements in the purity and growth techniques enable more reliable growth of bulk semi-insulating CdTe and $Cd_{1-x}Zn_xTe$ crystals. Crystals with resistivity close to the intrinsic resistivity ($\rho>10^{10}$ Ω cm) are now routinely grown by the high-pressure Bridgman (HPB) technique.[3,4] Little progress has been achieved, however, in understanding the underlying mechanism of electrical compensation and the role of native and impurity defects in carrier trapping, severely hampering the further progress of applications.

It is long believed that cation (group-II element) vacancies and vacancy-impurity complexes play an important role in electrical compensation and carrier trapping in II-VI semiconductors. Isolated cation (Cd, Zn) vacancies introduce a double-acceptor level to the band gap of II-VI compounds, [CdTe,[5], CdS,[6] ZnS,[7] ZnSe (Ref. 8)]. Among the variety of possible vacancy-impurities complexes, *A* centers are often observed.[9–11] The *A* centers consist of a cation vacancy and a group-III (Al, Ga, In) donor impurity on the group-II element (Cd, Zn) site or a group-VII (F, Cl) donor impurity on the nearest-neighbor anion (Te) site in $Cd_{1-x}Zn_xTe$. *A* centers contribute an acceptor level to the band gap about 0.12–0.15 eV above the valence-band maximum.

In a recent paper, Emanuelsson *et al.* reported the identification of the Cd vacancy in CdTe by electron paramagnetic resonance (EPR) experiments.[5] They found that the defect has a trigonal symmetry which they explained by a Jahn-Teller distortion. They argued that the level observed in photo-EPR measurements corresponds to the $2-/-$ acceptor level of the Cd vacancy. The optical excitation energy of the defect is less than 0.47 eV.

In this paper we report the thermal ionization energy (E_{th}, i.e., the binding energy of the hole) and the hole capture cross section of the $2-/-$ acceptor level of Cd (Zn) vacancy in the $Cd_{1-x}Zn_xTe$ ($x=0.12$) compound. The value of the thermal ionization energy, $E_{th}=(0.43\pm0.01)$ eV, is somewhat smaller than the reported optical ionization energy, $E_{op}\leq0.47$ eV in CdTe, possibly reflecting the Jahn-Teller distortion of the vacancy. We also find that isolated Cd (Zn) vacancies are not present in as-grown samples of HPB CdTe and $Cd_{1-x}Zn_xTe$ crystals in substantial concentrations in this study. This was attributed to the complexing of vacancies with residual impurities forming *A* centers and other vacancy-impurity complexes. Isolated Cd (Zn) vacancies are, therefore, not the dominant defects that control electrical compensation and carrier trapping in semi-insulating HPB-grown $Cd_{1-x}Zn_xTe$.

II. EXPERIMENT

The $Cd_{1-x}Zn_xTe$ ($x=0.12$) material was grown from melt by the high-pressure Bridgman technique in a vertical furnace and graphite crucible using high-purity starting materials. The Zn composition of the sample was measured by energy dispersive spectroscopy using a scanning electron microscopy setup. A sample with dimensions $2\times10\times10$ mm^3 was saw cut from the 90-mm-diameter ingot and etched in 5% Br-MeOH solution. For the electrical measurements Au electrodes, 8×8 mm^2, were sputtered onto the opposite surfaces.

The energy levels of the carrier traps were studied by thermoelectric effect spectroscopy (TEES) (Refs. 12 and 13) and thermally stimulated current (TSC) (Ref. 14) experiments. Thermally stimulated spectroscopies use the thermal excitation of trapped charge carriers, from the localized energy levels to the conduction or valence band, to determine the ionization energies, densities, and capture cross sections of carrier traps. The charge emanating from the traps is determined by the trap density and the temperature of trap emptying is related to the thermal ionization energy and carrier capture cross section of the localized levels. In TSC the charge emitted by the traps modulates the dark current (dc) produced by an external bias while in TEES experiments the thermoelectric current induced by a temperature difference

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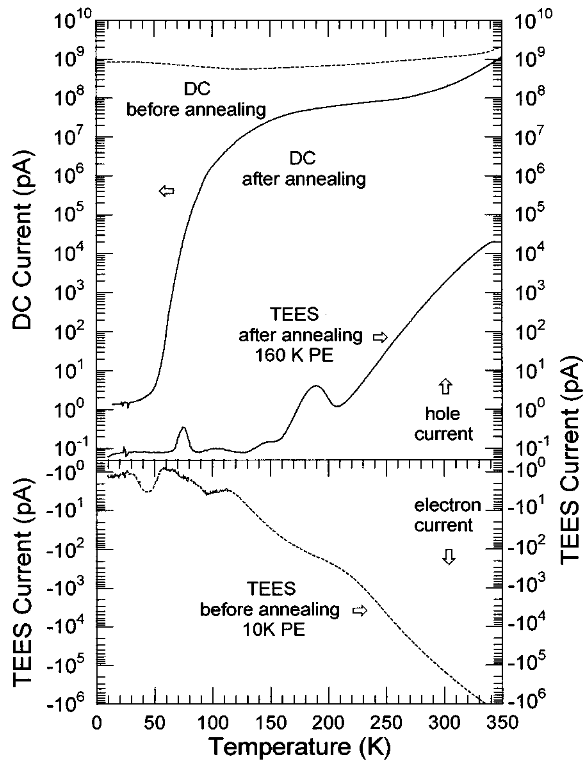

FIG. 1. TEES spectra and the temperature dependence of the dark current (dc current) of the $Cd_{1-x}Zn_xTe$ ($x=0.12$) sample before and after annealing. For the TEES experiments the crystal was photoexcited (PE) at 9 K by 1.33-eV photons for 1000 s. The TEES spectra were taken at an average heating rate of 0.42 K/s.

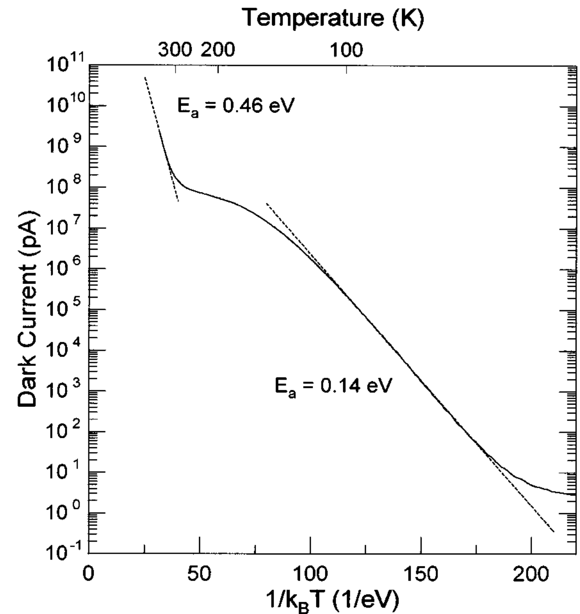

FIG. 2. Arrhenius plot of the dark current (dc) and the fitted activation energies in the low ($T<150$ K) and high temperature ($T>300$ K).

across the sample is measured. TEES has three advantages over TSC: (1) it has a higher sensitivity to deeper levels, (2) it directly distinguishes between electron and hole traps in the absence of internal electric fields, and (3) provides the conductivity type of the material.[15] The experiment setup consists of a sample holder enclosed in a cryostat operating in the 10–400-K temperature range, a temperature controller, a Keithley 617 electrometer and a control and date acquisition system. The samples are cooled in the absence of light to ~9 K, where the traps are filled by optical excitation using subband gap 1.33-eV photons from an infrared light-emitting diode. The TEES and TSC experiments were performed with a heating rate of 0.42 K/s.

III. RESULTS AND DISCUSSION

The as-grown material was n type, as shown by the negative thermoelectric current in Fig. 1. The carrier concentration estimated from the conductivity at 300 K was $n\approx\times10^{11}$ cm^{-3}. The conductivity of the material before annealing was nearly independent of temperature (see the dc current in Fig. 1) indicating that the Fermi level is pinned in the band gap by deep levels. Purity analysis of the material showed that C, N, O, Al, and Se were the major impurities. Al was the dominant impurity with concentration of $\approx5\times10^{16}$ cm^{-3}. The total impurity concentration was less than 3×10^{17} cm^{-3}. The n type of the material indicates that the shallow donor state of substitutional Al_{Cd}, located 14 meV below the conduction band,[16] governed the conductivity of the as-grown material.

The sample was annealed under Ar atmosphere for 4 h at 583 °C to produce Cd (Zn) vacancies. The formation of Cd (Zn) vacancies (V_{Cd}, V_{Zn}) is signaled by the conversion of the material from n to p type (Fig. 1) and the appearance of a deep level at 188 K (Fig. 3). This level was not observed before annealing of the sample (no peak in the TEES spectrum in Fig. 1), and we found this to be a general trend in all HPB-grown semi-insulating $Cd_{1-x}Zn_xTe$ crystals we studied. The positive thermoelectric current above 210 K indicates that holes are the majority carriers and the material is p type after annealing. The carrier concentration in the annealed sample was $p\approx4\times10^{11}$ cm^{-3} at 300 K. The conversion of the sample n to p type indicates that formation of acceptor levels, and presumably the diminution of donor levels, takes place during annealing of the sample. Due to the difference in the vapor pressures of Cd and Te,[17] annealing at 583 °C without Cd overpressure facilitates Cd loss from the sample and the formation of Cd vacancies. Isolated single Cd vacancies are double acceptors in CdTe.[5] A fraction of the diffusion Cd vacancies is presumably captured at donor impurities forming donor-V_{Cd} pairs (A centers), which are also known single acceptors.[9–11] The capture and complexing of Cd vacancies with isolated donor impurities decreases the donor and increases the acceptor concentration in the sample facilitating the conversion from n to p type. The temperature dependence of the conductivity (Fig. 2) showed a behavior typical of an extrinsic semiconductor with two activation energies $E_a=0.14$ and 0.46 eV dominating at low and high temperatures, respectively. The lower activation energy is close to the ionization of the acceptor levels of A centers in CdTe.[10,11] The $E_a=0.14$ eV ionization energy presumably corresponds to the ionization of the aluminum A centers (V_{Cd}-Al_{Cd} pairs) (Refs. 10 and 11) that are formed by the capture of vacancies (V_{Cd}, V_{Zn}) at Al_{Cd} atoms during

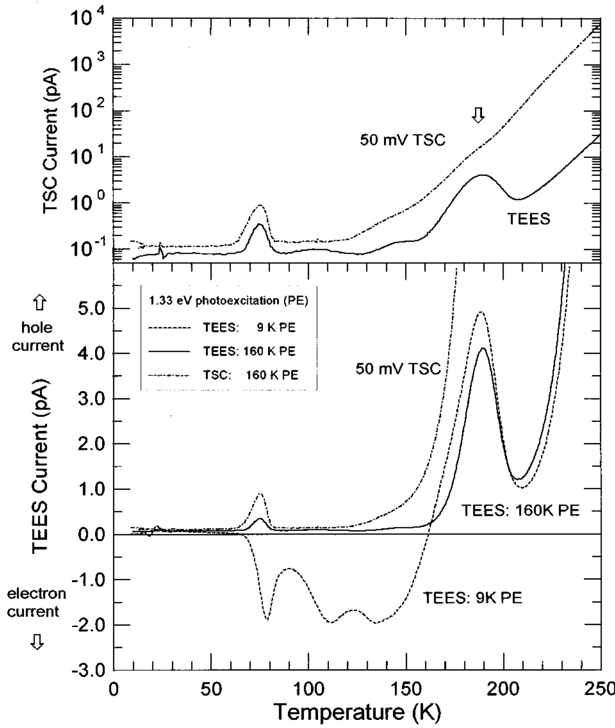

FIG. 3. TEES and TSC spectra of the annealed $Cd_{1-x}Zn_xTe$ ($x=0.12$) sample photoexcited (PE) at 9 and 160 K by 1.33-eV photons for 1000 s taken at an average heating rate of 0.42 K/s. The hole trap at 188 K is indicated by an arrow in the TSC spectrum.

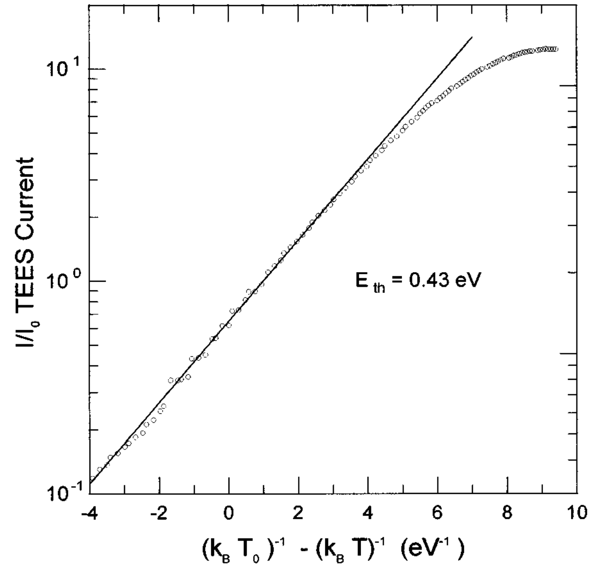

FIG. 4. The initial-slope fit to the current peak at 188 K associated with Cd vacancies. The parameters $T_0=164$ K and $I_0=0.3$ pA were chosen on the exponential slope to avoid distortion from the background. The error introduced by improper background correction could be as much as 0.2 eV.

annealing. The higher activation energy most likely corresponds to the double-acceptor level of Cd (Zn) vacancies. These acceptor levels render the material p type after annealing.

The level at 188 K cannot easily be revealed in TSC experiments. Due to the low resistivity of the annealed sample, $\rho=2.3\times10^5$ Ω cm, the current under normal bias conditions ($E_b=10$ V) is orders of magnitude higher than the corresponding peak amplitude. Even in a low-bias TSC experiment ($E_b=50$ mV) the corresponding peak is superimposed on the semiexponentially increasing current from the ionization of deep levels (see the arrow in Fig. 3). The peak can, however, be clearly resolved in the TEES spectra, where the thermoelectric current from the thermal ionization of acceptors is of much smaller amplitude.

To extract the thermal ionization energy (E_{th}) of the trap level at 188 K, the initial slope method was used.[18] The method is based on the observation that the early stage of trap emptying is a thermally activated process with an activation energy equal to the thermal ionization energy of the trap, and is independent of the subsequent fate of the emitted charge. The thermal ionization energy of the trap can be extracted by fitting an exponential to the initial slope of the peak

$$\ln\left(\frac{I}{I_0}\right)=E_{th}\left(\frac{1}{k_BT_0}-\frac{1}{k_BT}\right), \tag{1}$$

where I and I_0 are the current values at temperatures T and T_0, respectively.[19] To prevent the distortion of the initial rise of the current peak, levels at temperatures below the studied level should be emptied. The deep level observed at 188 K is preceded by a complex band of more shallow levels. The origin of these levels will not be discussed here. When the deep levels are filled at 9 K, emptying of electron traps takes place right below the 188-K peak, and the resulting slope is subexponential. In order to avoid the effect of carrier emission from these traps on the shape of the 188-K peak, the trap was filled by optical excitation at 160 K. The Arrhenius plot of the initial slope of the peak and the fitted model using Eq. (1) is shown in Fig. 4. The ionization energy of the deep level (binding energy of the hole) was found to be $E_{th}=(0.43\pm0.01)$ eV. This value is somewhat smaller than the reported optical ionization energy, $E_{op}\leq0.47$ eV, in CdTe reflecting the Jahn-Teller distortion of the vacancy.[5]

Provided retrapping of the liberated carriers is negligible and the recombination rate is high relative to the emission rate and a slowly varying function of temperature, the ionization energy and carrier capture rate of localized levels is related to the peak maximum temperature (T_m) by the expression[15]

$$E_{th}=k_BT_m\left[\ln\left(\frac{T_m^4}{\beta}\right)+\ln Cm_d\sigma-\ln E_{th}\right], \tag{2}$$

where σ is the carrier capture rate, $m_d=0.4m_0$ is the effective mass of the charge carries,[20] β is the heating rate, and $C=4(6\pi^3)^{1/2}k_B^3/h^3$ is a constant. The capture rate of the traps was calculated from Eq. (2) using $E_{th}=(0.43\pm0.01)$ eV, and was found to be $\sigma=(2.0\pm0.2)\times10^{-16}$ cm^{-2}.

Positive current indicates hole emission in our TEES experiments. As hole emission can only be observed for levels in the bottom half of the band gap, the deep level observed at 188 K corresponds to a hole trap located between the intrinsic Fermi level and the valence-band maximum. The observed hole trap, in principle, can be either an acceptor level

or a very deep donor level with thermal ionization energy greater than half of the band-gap energy $E_{th} > E_g(188\text{ K}) \approx 0.8$ eV.[21] The donor level would be located about $E_g - E_{th} \approx 1.17$ eV below the conduction band. Metallic impurities occupying Cd sites such as Fe (1.0 eV),[22] Ti (1.1 eV),[23] and Pb (1.28 eV) (Ref. 24) exhibit donor levels in this range in CdTe. The formation of the hole trap would then indicate the activation of the deep donors during annealing. However, the hole trap cannot be associated with deep donors as it contradicts the conversion of the conductivity from n to p type. The conversion clearly indicates the increase of the acceptor concentration relative to the donor concentration during annealing.

We attribute the trap to an *acceptor* level located in the lower half of the band gap. Acceptor levels below the Fermi level (E_F) are filled in thermal equilibrium and can be readily ionized by photoexcitation of the electron to the conduction band. The resulting state is a trapped hole which is stable in p-type material at low temperatures. The thermal emission of the localized holes produces current peaks in thermally stimulated experiments. The band gap of our sample is estimated to be $E_g = 1.674$ at 9 K,[21] and only acceptor levels with optical ionization energies greater than $E_{op} = E_g - h\nu = 0.434$ eV can be effectively photoexcited with $h\nu = 1.33$ eV photons. This threshold effect is clearly visible in our TEES experiments, where no carrier emission is observed from levels below 65 K. It should be mentioned, however, that the optical excitation energy of deep levels can be significantly larger than the thermal ionization energy due to Jahn-Teller distortion of the defects. As a result the threshold effect observed in thermally stimulated experiments may appear at lower energies (lower temperatures) than in optical experiments.

In conclusion, the hole trap observed at 188 K is an *acceptor* level with a thermal ionization energy of $E_{th} = (0.43 \pm 0.01)$ eV. Thermally stimulated experiments unfortunately give no information about the charge state of the defects. The measured thermal ionization energy is, however, consistent with the $2-/-$ transition of the Cd vacancy with $E_{op} < 0.47$ eV observed by EPR experiments.[5] We therefore assign the observed acceptor level to the $2-/-$ transition of the isolated Cd (Zn) vacancy. The vacancy is doubly ionized $(2-)$ in thermal equilibrium at 9 K. During photoexcitation an electron is excited to the conduction band, and a transition takes place to a singly ionized state $(-)$. The state is equivalent to a trapped hole. Although the $2-/-$ level is below E_F, the singly ionized state has a very long lifetime at low temperatures in compensated p-type material due to the low concentration of free electrons. Upon heating the sample to elevated temperatures, thermal hole emission takes place around 188 K from the localized level that can be observed by TEES experiments. Thermally stimulated experiments give no information on the atomic configuration of the defects. Thus we cannot exclude the possibility that vacancy-impurity pairs also contribute to the observed deep level beside isolated single vacancies. However, the impurities that bind strongly to Cd (Zn) vacancies, such as Al, perturb the electronic levels of the vacancy significantly. These vacancy-impurity pairs exhibit their own electronic levels such as that of the aluminum A centers observed at $E = 0.14$ eV (the peak at 75 K in Fig. 3) in this study. In addition, we found no evidence of weakly interacting impurities that would shift the ionization level of the Cd (Zn) vacancy. Thermal annealing performed in the 400–650 °C range showed the gradual increase of the $E_{th} = 0.43$ eV peak in the thermally stimulated spectra with no shift in the peak position. It is therefore most likely that a single defect, namely, the isolated Cd (Zn) vacancy, makes the predominant contribution to the observed deep level.

IV. CONCLUSIONS

We observed hole trapping and thermal emission from a deep acceptor level created during thermal annealing of a $Cd_{1-x}Zn_xTe$ ($x = 0.12$) sample by thermoelectric effect spectroscopy. The deep level was assigned to the $2-/-$ acceptor level of isolated Cd (Zn) vacancies. The thermal ionization energy of the level is $E_{th} = (0.43 \pm 0.01)$ eV, and the trapping cross section of holes was found to be $\sigma = (2.0\text{-} \pm 0.2) \times 10^{-16}$ cm^{-2}.

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