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Point Defects in $CdTe_xSe_{1-x}$ Crystals Grown from a Te-rich Solution for Applications in Detecting Radiation

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ABSTRACT

We investigated cadmium telluride selenide (CdTeSe) crystals, newly grown by the Traveling Heater Method (THM), for the presence and abundance of point defects. Deep Level Transient spectroscopy (I-DLTS) was used to determine the energies of the traps, their capture cross-sections, and densities. The bias across the detectors was varied from (1–30) V. Four types of point defects were identified, ranging from 10 meV to 0.35 eV. Two dominant traps at energies of 0.18 eV and 0.14 eV were studied in depth. Cd vacancies are found at lower concentrations than other point defects present in the material.

INTRODUCTION

II-VI semiconductors are of the major interest for research and technology due to their promising opto-electronic properties. The successful achievement of a controllable band-gap and lattice parameter in these materials assures their application in many different applications, particularly as room-temperature radiation detectors for national security, in monitoring and assuring the non-proliferation of nuclear materials, in imaging devices for medicine and research in space, in light-emitting diodes, and as multilayers, and in hetero-structures in optoelectronic devices[1].

The R&D groups at Brookhaven National Laboratory, Korea University and Fisk University reported previously their significant developments in the field of room-temperature radiation detectors, including CdZnTe, CdMnTe, CdMgTe, and TlBr. The focus of this paper is on detectors made from a different material, i.e., cadmium telluride selenide ($CdTe_xSe_{1-x}$, x=0.90). The In-doped CdTeSe crystals with 10% Se were grown via the Traveling Heater Method (THM) at Brookhaven National Laboratory. The purity level for the starting materials, CdSe and CdTe, was 6N. The parameters of synthesis are described elsewhere[2]. For our research, the

important properties of these crystals are their low density of Te-rich secondary phases (~10^4 cm^{-3}), their high electrical resistivity of the order of 10^9 Ω-cm, and their high electron mobility-lifetime ($\mu\tau_e$) product, along with the near-unity segregation coefficient of Se in the CdTe matrix[3,4]. Furthermore, they display high uniformity in the charge transport, and in their response to X- and gamma-ray radiation. These important structural, optical and electrical properties highlight CdTeSe as an alternative to CdZnTe as a room-temperature radiation-detector material. Our main focus in this paper is on the characterization of newly grown CdTeSe crystals as detectors, considering the point defects within the crystal's band-gap, the cross-section of the traps for capturing the charge carriers (e, h), and the traps' densities. The experimental setup is described elswhere[5]. The main technique we used for characterizing the defects was current deep level transient spectroscopy (I-DLTS).[6]

EXPERIMENTAL DETAILS

The CTS crystals were grown by the Traveling Heater Method (THM) in the crystal-growth facility at Brookhaven National Laboratory. Crystals were cut into pieces with dimensions of 6x6.5x1.8 mm^3. After polishing and etching them, we made planar detectors by fabricating gold contacts and attaching them via electrolysis. The main technique we used for characterizing the point defects was current deep-level transient spectroscopy (I-DLTS); the other technique we employed for this study was photo-induced current transient spectroscopy (PICTS). Electrical characterizations were made to test the resistivity of the crystals for the DLTS experiments, i.e., preferably equal to or greater than 10^8 Ω-cm. The resistivity of the detectors was between 4-5x10^9 Ω-cm. The value for $\mu\tau_e$, 2.6 x 10^{-2} cm^2/V, was calculated using Hecht equation-fitting. After measuring the resistivity and $\mu\tau_e$ product, we characterized the carrier traps in the CTS detectors.

For collecting the DLTS experimental data, we mounted the CTS detector on a cold finger, and took the base-line correction at room temperature. The samples were cooled to 12 K, and then heated up to the room temperature in a step of 1 K. In a complete run from 12-300 K, we acquired about 290 data points; the transients were collected at each individual step. The traps were filled using an 822-nm laser. We obtained the traps' filling time, and the available time for the defects to de-trap from the charge carriers by employing a square pulse-signal with a pulse width and period of 2 ms and 1 s, respectively, which fixes the filling times and the maximum de-trapping times from the traps. The I-DLTS signals, obtained from the transient currents, were plotted against the applied temperature, using the Li model[5]. The DLTS run was made at different applied voltages, between 0.1-30 V, across the detector. We compared the densities of the point defects in the material at 0.1, 0.5, 1, 5, 10, 20, and 30 V Our purpose in using a range of different biases for the repeated DLTS measurements was to distinguish more clearly between the two nearby traps at around 100 K, and to identify the weak signal associated with lower concentrations of Cd vacancies at around 200 K. Additional reasons for our using different applied voltages were to get more precise values for the trap densities and to better understand the possible role of trapping and de-trapping from defects on the current data. Furthermore, we

improved the illumination system by changing laser-pulse frequency and width for the filling and the de-trapping times. These additional steps and modification in illumination system helps in obtaining maximum information about the defects-levels and their densities, and hence minimize the uncertainty in the densities of the defects in these crystals.

RESULTS and DISCUSSION

We analyzed the data on point defects for their energies and types of traps, capture cross-sections, and the density of defects at different applied biases. The energies and the capture cross-sections of the traps were calculated from the slop and intercept of the Arrhenius plots. Trap densities were calculated from the transient time and the maximum peak value of the I-DLTS plots. The analysis model is described in detail by Li (1998)[6]. The DLTS results are plotted in Figs. 1-4, and the results are complied in Table 1, while the PICTS data is compiled in Table 2. To better explain the information obtained from the DLTS experiments, we separately discuss our findings on the energies of traps, their cross-sections, and densities.

Energies of the Traps (E_t)

Table 1, Fig. 1, and Fig. 2 show our data on the energies of the traps. Fig. 1 shows results of the I-DLTS and PICTS measurements for the same detector. There are three main traps in the energy range of 15 meV to 0.40 eV, as measured in the temperature range of 10-300 K. The activation energies calculated from the DLTS data are 0.14 eV, 0.18 eV, and 0.35 eV. There is the possibility of identifying a deep trap between 250-350 K. Due to our desire to avoid significant heating of the samples, we kept the I-DLTS maximum temperature at 300 K, so the deep trap could hardly be identified. There is a shallow trap that is difficult to analyze due to the lower temperature limit (10 K) of the DLTS setup. The energy for the trap was < 20 meV. This trap most probably is related to shallow elemental impurities in the material. The trap related to the cadmium vacancy $(V_{Cd})^{--}$ is located around 200 K. The calculated energy is ~ 0.35 eV, slightly lower than that found in CdZnTe detectors; these comparatively lower peak values indicate a reduced occurrence of $(V_{Cd})^{--}$ compared to typical detector-grade CdZnTe crystals. The lower transient signal makes it hard to identify and to resolve at higher applied biases, > 10 V. At a low bias both the calculation and identification of the DLTS parameters for this trap was possible. Fig. 2 shows the visibility of traps at low- and high-applied voltages (at 1 V and 20 V). The medium energy traps are A-centers and have energies of 0.14 eV and 0.18 eV, and, in the DLTS plots, they are located at around 100 K. It is difficult to separate and analyze these two neighboring traps in a single DLTS run at one applied bias. We determined these two energies and other parameters using data at different biases and a different time windows for transit currents in the DLTS measurements (Fig. 2). We have some other data (unpublished) on CdTeSe detectors grown by other vendors that yielded similar DLTS results, supporting our present deductions. The PICTS plot shown in Fig. 1b shows a shallow and a medium energy trap. The 38-meV trap has approximately the same capture cross-section as calculated by DLTS experiments for the <20 meV trap, so most probably it is the same trap identified by both

techniques. The second trap visible in Fig. 1b has activation energy of 0.27 eV with a capture cross-section of ~ 6.6×10^{-17} cm^2. The value of the capture cross-section is about the same as the one calculated from the DLTS data at 0.14 eV. The primary reason for the different binding energies for traps is unclear and the subject of continued investigations. Presumably, the different techniques and assumptions used to fit the current equations are contributing to some uncertainty in one or both approaches.

Capture Cross-sections (σ)

Capture cross-sections of the defects in the CdTeSe detectors that trap the charge carriers were calculated from the data on the DLTS transient currents (Table 1). In Fig. 3, we plot the capture cross-sections against their energy values. The figure shows that the values vary exponentially with the increase in energy. The 20-meV trap has the lowest value of ~ 10^{-20} cm^2. PICTS determined the same value of capture cross-section for the 38 meV trap. This low value for the capture cross-section suggests that their contribution towards the performance of the detectors operating at room temperature is negligible. The medium-energy traps, 0.14 eV and 0.18 eV, have cross-sections at around 10^{-17} cm^2 and 10^{-16} cm^2, respectively. These two traps accompanied by the Cd vacancies with comparatively higher values of capture cross-sections for the traps (10^{-15} cm^2), differ by one order-of-magnitude in their capture cross-sections, and they are expected to affect the performance of the detectors. There still is a need for quantitative experiments to study the effects of these traps on the electron and hole $\mu\tau$ products and on the detectors' performances.

Densities of Traps (N_t)

The densities of the traps calculated from the DLTS signals are given in Table 1 and Fig. 4. The trap density is a function of the maximum peak current, the depletion width (the thickness of this material), the area of the illuminated part of the sample, and the time window. To identify the optimum applied bias for correcting the density data, we plot the variation in the peak with the applied voltage for a 1-ms time window (see Fig. 4a). To obtain the best information about the density, we repeated the DLTS experiment seven times at different applied biases between 0.1 and 30 V so that due to high electric field, maximum de-trapping takes place. In Fig. 4b, the bar-graph shows the densities of four different traps found in the CTS detectors, taken from the DLTS plots shown in Fig. 4a. The density data indicate that a Cd-vacancies-related trap (at 0.35 eV) yields density information consistent with the variation of the applied bias. The calculated density is ~ (2 - 3) x 10^{13} cm^{-3}, indicating combined lower densities of V_{Cd} for the CTS detectors. Comparing our previous results for the relative densities of V_{Cd} in CZT and CMT with the current measurements for CTS, the concentration of Cd vacancies is found to be lower in CTS detectors, and additionally, a new trap is identified in the A-center region. There is a probability that Cd vacancies are utilized in forming the new trap at around 0.14 eV, seemingly a new type of A-center not observed in CZT- or CMT- detectors. The trap densities for the medium energies, i.e., 0.14 and 0.18 eV, increase with the applied bias within one order of magnitude

(10^{13} -10^{14} cm^{-3}). The values for the maximum density obtained are 5.8 x 10^{14} cm^{-3} for 0.18 eV, and 8.6 x 10^{14} cm^{-3} for 0.14 eV. The calculated density of the shallow trap, <20 meV of energy, is 2 x 10^{14} cm^{-3}.

CONCLUSIONS

We characterized the point defects in CdTeSe detectors fabricated from high-quality crystals grown by the traveling heater method technique at Brookhaven National Laboratory. The concentration of Cd vacancies was comparatively lower than for other traps (3.8 x 10^{13} cm^{-3}). In addition, we identified a new trap in the A-center region. The DLTS results reveal that Cd vacancies are utilized in the formation of two types of A-centers at around 0.14 eV and 0.18 eV. The 0.14-eV trap, which most probably is a new type of A-center, has not been observed in other materials. Comparing our results from CdTeSe material with previous ones from other materials, such as the segregation coefficient of ~1.0 for Se, high resistivity, high $\mu\tau$-product and the lower density of Cd vacancies, we consider that CdTeSe is a very attractive alternative material for radiation-detector applications.

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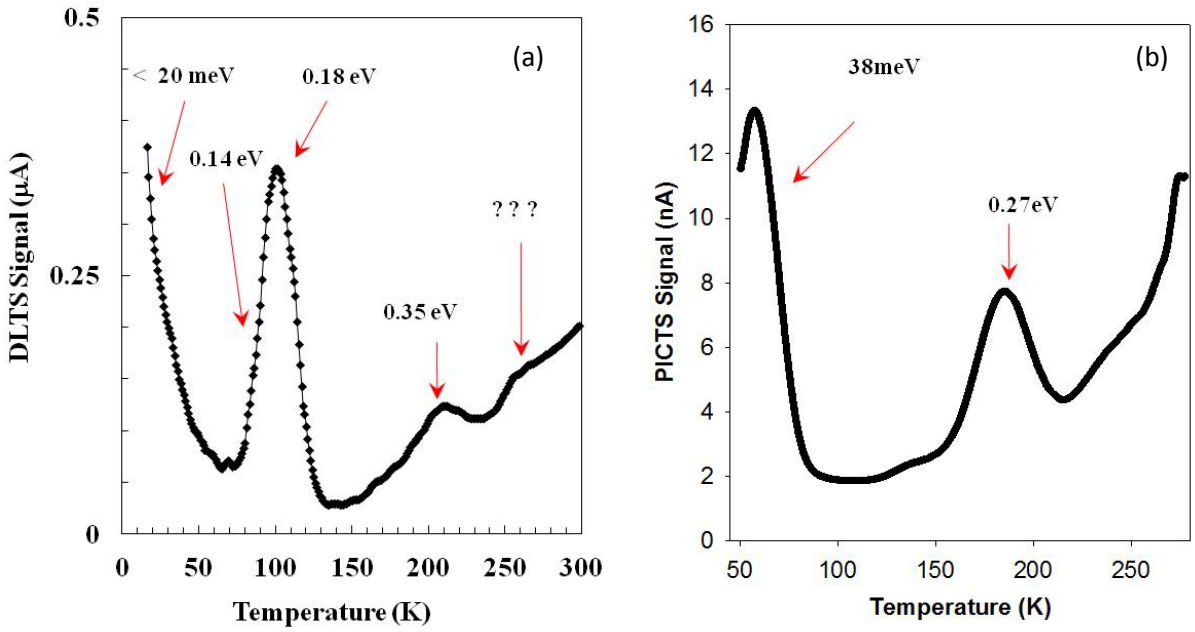

Figure 1. A comparison of the point defects measured by using a) I-DLTS with a time window of 0.2 ms and bias of 1 V and, b) PICTS experiments with a rate window of 504/s and bias of 1 V.

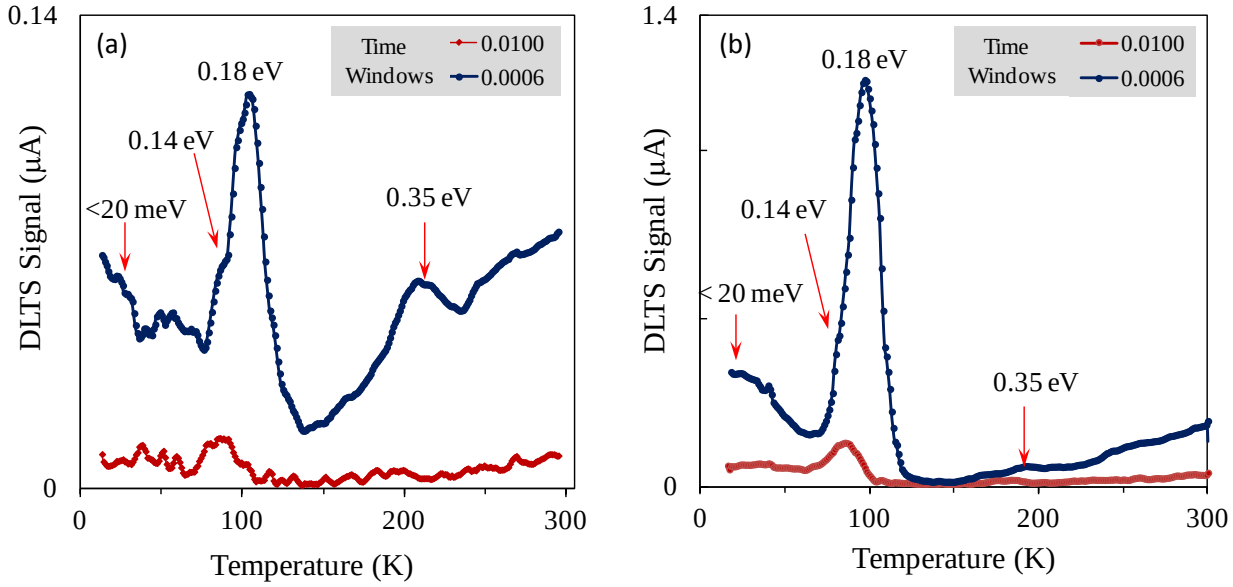

Figure 2. A comparison of the point defects measured by I-DLTS at two time windows of 10ms, and 0.6ms, at two different applied biases; a) 0.1 V and b) 20 V.

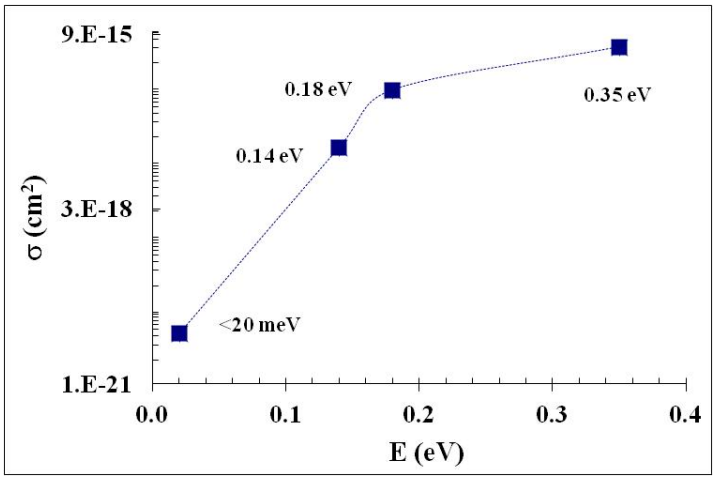

Figure 3. Capture cross-sections of point defects measured by I-DLTS.

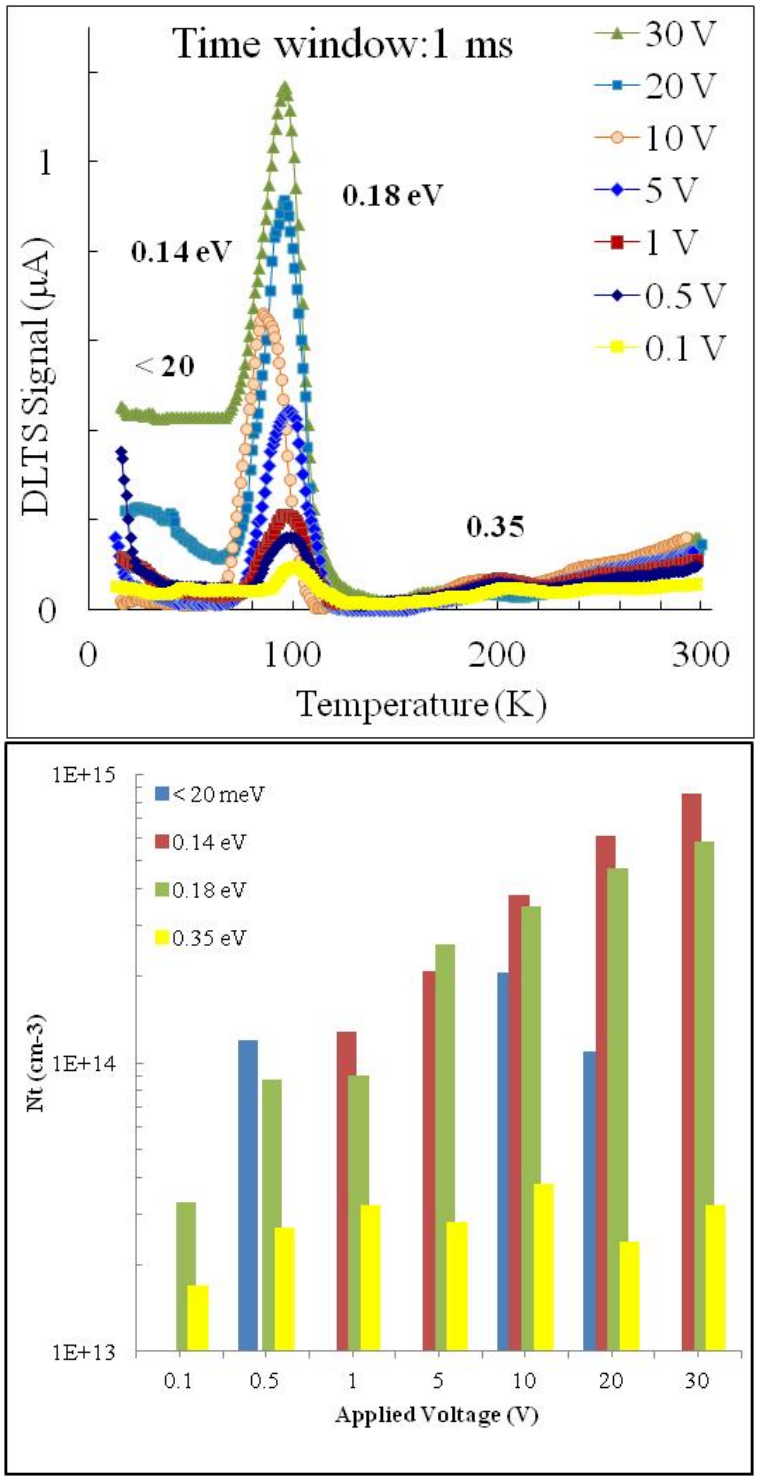

Figure 4. Comparison of the densities of point defects; a) I-DLTS plots at different biases showing the variations in I-DLTS signals with the applied bias and, b) Bar-graph showing the calculated changes in the defect density for different bias voltages.

Table 1. Energy levels of point defects, capture cross-sections, and densities based on I-DLTS measurements taken at different applied voltages.

E_t	σ (cm^2)	Trap Densities (cm^{-3})						
		0.1 V	0.5 V	1 V	5 V	10 V	20 V	30 V
< 20 meV	~ 10^{-20}	---	1.2×10^{14}	---	---	2.1×10^{14}	1.1×10^{14}	---
0.14 eV	5×10^{-17}	--	--	1.3×10^{14}	2.1×10^{14}	3.8×10^{14}	6.1×10^{14}	8.6×10^{14}
0.18 eV	7×10^{-16}	3.3×10^{13}	8.7×10^{13}	9.0×10^{13}	2.6×10^{14}	3.5×10^{14}	4.7×10^{14}	5.8×10^{14}
0.35 eV	5×10^{-15}	1.7×10^{13}	2.7×10^{13}	3.2×10^{13}	2.8×10^{13}	3.8×10^{13}	2.4×10^{13}	3.2×10^{13}

Table 2. Energy levels of point defects, and capture cross-sections based on PICTS measurements.

	E_t	σ (cm^2)
1	38 meV	8.0×10^{-20}
2	0.27 eV	6.6×10^{-17}