A DLTS study of deep levels in n-type CdTe

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We report the results of a DLTS study on the majority carrier deep level structure of three samples of n-type CdTe and the effects on the deep level structure of indium doped CdTe due to H_2 annealing. H_2 annealing did not qualitatively change the deep level structure of the annealed sample. It did cause the shallow level concentration to decrease with a proportional decrease in the deep level concentrations as a result of indium out-diffusion and compensation by native defects. Levels present in all of the materials studied have been characterized and attributed to either native defects or innate chemical impurities. Other levels present in indium doped material require above band gap illumination of the sample before they are observed. A possible model proposes that these levels arise from defect complexes.

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I. INTRODUCTION

The presence of crystal defects has long complicated our understanding of II–VI semiconductors. These defects are a result of the wide phase stability regions of II–VI compounds, and they often dominate the electrical characteristics of the material. The defect structure of CdTe, a II–IV semiconductor which exhibits large deviations from stoichiometry, is recently of great interest because of the use of CdTe in infrared devices. Annealing CdTe at elevated temperatures under fixed partial pressures of its constituent elements, Cd and Te, can modify the material's defect structure.[1,2] Annealing CdTe at a high temperature in an H_2 ambient prior to its use as a substrate for epitaxial growth has been shown to alter the electrical properties of the CdTe in the near surface region through the introduction of crystal defects.[3] Despite the importance of crystal defects in CdTe, they are poorly characterized and understood at present.[4]

We present here a deep level transient spectroscopy (DLTS) study of deep levels in both indium doped and undoped CdTe. The effects on the deep level structure of indium doped CdTe due to H_2 annealing are also presented.

II. EXPERIMENTAL PROCEDURES

Physical and electrical measurements made on three different single crystals of n-type CdTe are reported here. Material IN1, indium doped CdTe obtained from Eagle Picher Ind., was initially on the Cd excess side of the phase stability region. Its indium concentration was $\sim 10^{18}$ cm^{-3}. Materials UN1 and IN2, undoped CdTe from Eagle Picher Ind. and indium doped CdTe from the II–VI Corporation, respectively, were annealed in Cd vapor at 750 °C for between 6 and 12 h to raise their carrier concentrations. The concentration of indium in IN2 was several orders of magnitude less than in IN1.

Electrical measurements were performed on Au Schottky barrier devices. Two methods of sample preparation were used in fabricating devices on IN1. In both methods clean surfaces of CdTe were prepared by cleaving rods of bulk CdTe in air. One set of samples was immediately placed into an ion pumped vacuum system ($< 10^{-6}$ Torr) where 160-μm-diam Au dots were evaporated onto the cleaved CdTe surfaces. A second set of samples was annealed at 350–370 °C for 1 h in Pd purified H_2 ambient before Au dots were deposited onto the annealed, cleaved sample surfaces. Au Schottky devices were also made on air cleaved surfaces of UN1 and IN2. No H_2 annealing treatment was used in these samples.

Capacitance voltage (C–V) profiling of the CdTe samples was carried out at room temperature using a Model 71A Boonton capacitance meter. DLTS spectra were taken on a fast capacitance bridge using a double boxcar integrator as described by Lang.[5]

Secondary ion mass spectroscopy (SIMS) was used to depth profile the indium concentrations at H_2 annealed and unannealed surfaces of IN1.[6]

III. RESULTS

The results of DLTS and capacitance measurements made on the various CdTe structures are summarized below and in Figs. 1, 2, and 3. Since there is negligible minority carrier injection in a Schottky barrier device only majority carrier traps were observed. The shallow level concentrations (N_D–N_A) were determined from measurements of reverse bias capacitance characteristics.

We begin our discussion with the results on the two crystals from Eagle Picher Ind. The shallow level concentrations of samples from IN1 (CdTe originally doped with $N_{\rm In} \sim 10^{18}$cm^{-3}) were 7×10^{17} cm^{-3} for unannealed surfaces and 3×10^{15}–5×10^{16}cm^{-3} for H_2 annealed surfaces. SIMS measurements showed a minor surface buildup of indium followed by a 2–3 μm layer depleted of indium by a factor of two at the H_2 annealed surface. DLTS spectra for unannealed and H_2 annealed surfaces of IN1 did not differ markedly as a result of the two methods of sample preparation. These DLTS measurements probed a region extending 1–2 μm below the surface. Typical DLTS spectra are given in Fig. 1(a) and (c). In the temperature range from 80 to 400 K three main electron traps ($E1$, $E2$, and $E3$) were evident. A shoulder was visible on the low temperature side of $E2$ ($E2a$). Some of the samples also exhibited a level ($E1a$)

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which occurred at a lower temperature than $E\,1$. The activation energies of levels $E\,1$ and $E\,2$, determined from Arrhenius plots shown in Fig. 3, were 0.34 ± 0.06 and $0.77 \pm .05$ eV, respectively, relative to the conduction band. The concentrations of levels $E\,1$ and $E\,2$ tracked the shallow level concentration at approximately 3% and 8% of the shallow level concentration in all of the samples made from IN1. Level $E\,3$ was not studied in detail because, even for rate windows corresponding to long time constants, rapid changes occurred in the Schottky barrier device characteristics at the temperatures where $E\,3$ was observed.[1]

The DLTS spectrum for IN1 was modified by above band gap illumination (HeNe laser) as shown in Fig. 1(b). A spectrum was taken with the sample in the dark as the sample was cooled to 100 K (dashed curve). After exposure to above band gap light, a DLTS spectrum was taken with the sample in the dark as the sample temperature increased (solid curve). Level $E\,1a$ increased in amplitude, a new level ($E\,1b$) appeared, and a background which is visible in the difference spectrum (dotted curve) appeared under $E\,1$ ($E\,1c$). The device capacitance at 100 K also increased by 5%–15 % as a result of illumination. Changes in the device capacitance and DLTS spectrum persisted for at least an hour after the light source was removed, independent of the biasing voltage maintained, provided the sample temperature remained ~ 100 K. After warming to room temperature and waiting ~ 15 min, these light associated effects were not evident in subsequent dark measurements. Activation energies for levels $E\,1a$ and $E\,1b$ were estimated as suggested by Lang to be 0.24 and 0.30 eV.[8] The spectra in Fig. 1 are for H_2 annealed IN1. The same effect was observed in unannealed IN1 although the amplitudes of $E\,1a$ and $E\,1b$ relative to $E\,1c$ were smaller.

We also examined the unintentionally doped crystal from Eagle Picher Ind. Samples from UN1 had shallow level concentrations of approximately $2 \times 10^{15}\mathrm{cm}^{-3}$. Five majority carrier levels are observed, ($E\,2$, $E\,4$, $E\,5$, $E\,6$, and $E\,7$) in a typical DLTS spectrum for UN1 [Fig. 2(a)]. $E\,2a$ was also seen in most samples, and a peak corresponding to level $E\,3$ observed in IN1 was present in a number of UN1 samples. The concentration of $E\,2$ was $\sim 5\%$ of the shallow level concentration. The Arrhenius plot for $E\,2$ in Fig. 3 includes points taken from UN1. $E\,6$ was not observed until the device being studied was mechanically stressed. Subsequent heating to 400 K removed $E\,6$. No optical effects similar to those found in IN1 were observed.

To investigate how much these results depend on the source of the crystals, we have also studied a crystal doped with indium from II–VI Corporation. The shallow level concentration of samples taken from IN2 were approximately $2 \times 10^{17}\mathrm{cm}^{-3}$. This is larger than the reported indium concentration, possibly because of the presence of other impurities or the introduction of native defects during the Cd vapor anneals. A typical DLTS spectrum for IN2 is shown in Fig. 2(b). Three main levels ($E\,2$, $E\,8$, and $E\,9$) can be resolved. In most spectra $E\,2a$ and $E\,3$ are also visible. Illumination at low temperatures did cause a capacitance change and an increase in the low temperature background of a subsequent dark DLTS scan, but no new peaks could be resolved from this background.

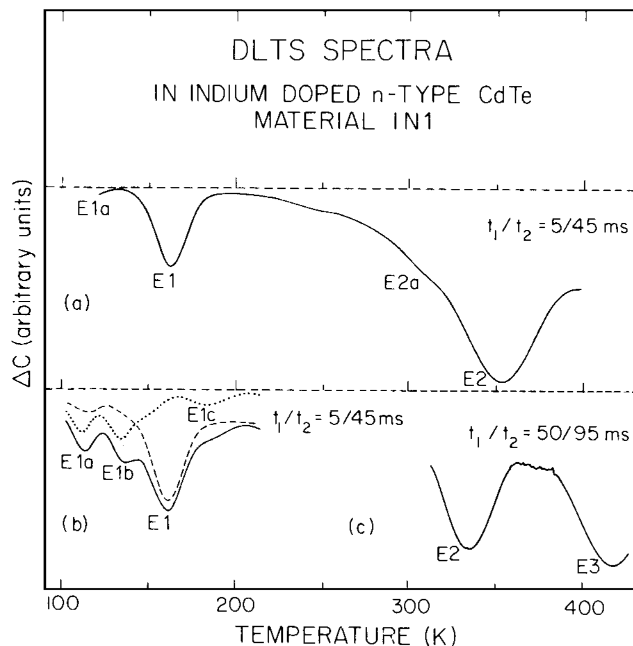

FIG. 1. DLTS spectra of electron traps in indium doped n-type CdTe (material IN1). The positions of the boxcar windows are given by t_1 and t_2. (a) A typical spectrum in IN1. (b) Optical effect in IN1. The dashed scan was made before illumination; solid scan after illumination at 100 K. The dotted curve is the difference. (c) Spectrum in IN1 using a small rate window to show $E\,3$.

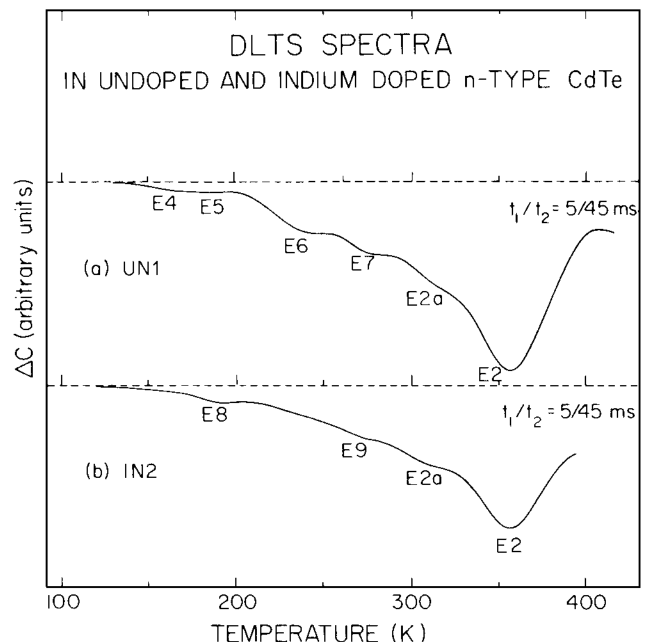

FIG. 2. DLTS spectra of electron traps in undoped and indium doped n-type CdTe (materials UN1 and IN2, respectively). The positions of the boxcar windows are given by t_1 and t_2. (a) A typical spectrum in UN1. (b) A typical spectrum in IN2.

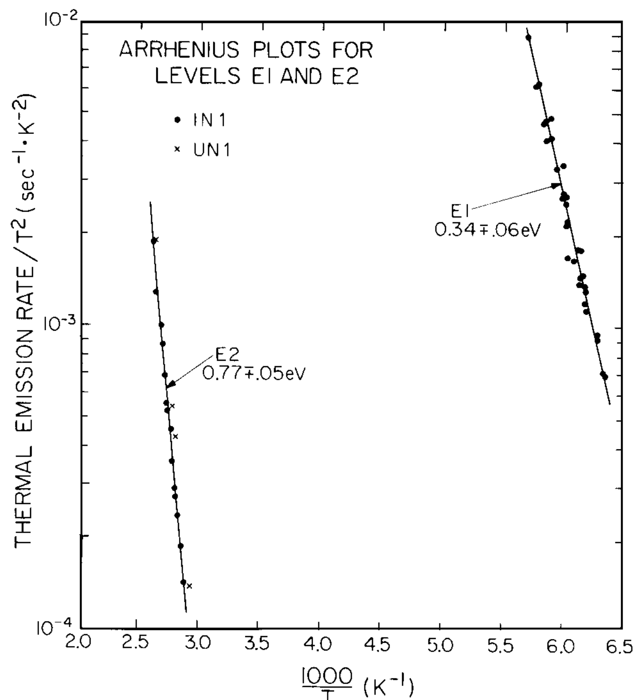

FIG. 3. Arrhenius plots for electron traps $E\,1$ and $E\,2$ present n-type CdTe.

IV. DISCUSSION AND CONCLUSIONS

The predominant effect of H_2 annealing IN1 was the drop in shallow level concentration. The estimated deep level concentrations also fell proportionately, suggesting that the deep and shallow levels are in some way related. An understanding of the effects of H_2 annealing on the shallow levels may lead to a better understanding of the origin and character of the deep levels. The drop in carrier concentration during anneal can be attributed to two main sources, loss of indium through indium evaporation, or the introduction of compensating defects. Such native crystal defects can also lead to the loss of electrically active indium through the formation of indium telluride precipitates. The decrease in indium concentration at annealed surfaces, as measured by SIMS, is not sufficient to account for the observed drop in shallow donor concentration, suggesting that the introduction of native crystal defects is the dominating process.

DLTS spectra for all three samples are strikingly similar near $E\,2$ and $E\,2a$, also, from Fig. 3, we see that the emission rate as a function of temperature is the same for level $E\,2$ in materials IN1 and UN1. From this we conclude $E\,2$ arises from a source present in all of these samples. We suggest that $E\,2$ and $E\,2a$ are associated with impurities or native defects which are either commonly found in CdTe, or easily introduced during the Cd vapor anneals performed on the samples. Although the data are less conclusive, $E\,3$ appears to be present in all of our samples indicating that it has an origin similar to that of $E\,2$. $E\,8$ and $E\,9$ in IN2 are probably the same as some of the levels in UN1 ($E\,4$–$E\,7$). But, all of these levels are buried too deeply in the background to make conclusive measurements on them.

Levels $E\,1$, $E\,1a$, $E\,1b$, and $E\,1c$ are probably indium related. They would be expected to appear in IN2 with concentrations several orders of magnitude less than in IN1. If they did have concentrations which were within the limits of the sensitivity of the DLTS, they were probably buried in the background of the other peaks present in IN2. Electron emission from $E\,1b$, $E\,1c$ and to a certain extent $E\,1a$ only occurs after above band gap illumination. The predominant effect of this illumination is the creation of electron-hole pairs in the depletion region. Since electrons can be introduced electrically, the appearance of these levels in the spectrum can be attributed to the presence of holes in the depletion region. This suggests that there are associated hole traps in the depletion region which must bind holes before these electron traps can be observed. Increased device capacitance following illumination supports this interpretation. Similar conclusions have been drawn from observations of DLTS spectra in InP.[9] Persistent photoconductivity and photocapacitance have been previously observed in CdTe, but this is the first study correlating them with changes in DLTS spectra.[7,10]

Identifying the centers responsible for levels $E\,1a$, $E\,1b$, and background $E\,1c$ is not possible without further study. We can, however, propose a model. Because all of these levels are affected by illumination, it seems likely that the centers responsible for each of these levels are of a similar nature. One possibility is that each center results from a different configuration of a defect complex.

Comparing these results with those previously reported, we find several observations of levels in n-type CdTe approximately 0.6 eV (0.55–0.70 eV) from the conduction band have been made.[4] These could correspond to levels presented in this study, but the variety of samples studied and techniques used do not allow a definite conclusion to be drawn. When comparing the energies presented here to those from other studies, it must be remembered that these are activation energies and have not been corrected for electric field effects or thermally activated capture cross sections.

Huber *et al.*[11] have made DLTS measurements on n-type, indium doped CdTe films grown on BaF_2 and PbTe. Of the six levels they observe between 100 and 300 K, which they attribute to native defects and native defect complexes; none correspond to $E\,2$ presented here. Levels $E\,1$–$E\,4$ in their study are at energies near 0.34 eV and may correspond to $E\,1$, $E\,1a$, or $E\,1b$, but one must be careful in comparing materials grown so differently.

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