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The effects of annealing on the distributions of deep and shallow states in CdTe single crystals

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Abstract. Schottky barrier capacitance and DLTS techniques have been employed to study the shallow- and deep-state distributions in bulk-grown CdTe crystals following an annealing treatment designed to convert the samples from semi-insulating to n-type conductivity. Although the annealing conditions (saturated Cd vapour at 800 °C) were chosen to ensure that homogeneity was achieved at the annealing temperature, substantial non-uniformities were observed in the test samples at room temperature. Although n-type conductivity was successfully achieved, this was restricted to a near-surface channel with a width of $\sim$50 μm for undoped samples and $>$400 μm for In-doped samples. These results can be attributed to diffusion and self-compensation processes occurring during cool-down following the anneal, but the DLTS measurements yield no evidence for the generation of new levels arising from these processes. The existing states (with energy levels in the detectable range from $\sim$0.2 to $\sim$0.9 eV below the conduction band) are found to be non-uniformly distributed as a function of depth below the surface, the form of the actual depth profiles being very similar to the corresponding free carrier concentration profile.

1. Introduction

Being the only member of the II–VI group of semiconductors which can be easily prepared in both n-type and p-type forms, much interest has been, and continues to be, focused on CdTe for use in a variety of devices. However, like other members of this group of materials, much still remains to be learned about its defect structure before sufficient control of its properties can be achieved to ensure that high-quality material can be reliably produced and subsequent device processing reproducibly performed.

The problem is well illustrated by the uncertainties which exist relating to some standard annealing procedures. For example, it has been known since the early studies of de Nobel [1] that n-type behaviour is achieved by annealing undoped CdTe in a Cd atmosphere. This effect can be most easily interpreted in terms of native defect formation, but more recent work has established that residual impurities can play an important role. A further complication, in relation to the interpretation of the experimental data, concerns the homogeneity of the material both before and after the annealing process. Bulk-grown II–VI compounds are frequently found to contain precipitates of one or the other of the constituents and these can act as sinks for some of the common residual impurities. These impurities can then be released into the material during a subsequent annealing process in which the precipitates are dissolved. Such a process is thought to be responsible for the non-uniformities observed in ZnTe samples annealed in a Zn atmosphere [2]. For the case of CdTe crystals we have recently reported the observation of depth non-uniformities in samples annealed in excess Cd [3]. However, in this case, the annealing conditions were chosen to ensure complete dissolution of any precipitates and total uniformity at the anneal temperature. The resultant non-uniformities observed at room temperature were, accordingly, attributed to a redistribution of defects in the vicinity of the sample surface during cooling.

In view of the interest in the processes leading to macroscopic inhomogeneities and their importance in relation to interpreting the effects of annealing, a further more detailed study has now been undertaken. In this study, the samples were subjected to a variety of different annealing treatments and the observed effects for both doped and undoped samples grown by the Bridgman technique were compared with those for corresponding samples grown by the travelling heater method (THM). With a view to developing an improved understanding of the observed spatial non-uniformities in the free carrier concentration, deep-level transient spectroscopy (DLTS) measurements have now been made as a function of depth through all these samples. As the previously reported depth profiles in Bridgman samples [3] were attributed to a non-uniform distribution of defects following annealing, these depth-dependent DLTS measurements were intended to identify any trapping states arising from these defects and to determine their spatial distribution.

2. Experimental details

The samples used in this study were taken from two different boules of CdTe, one grown by the Bridgman method and the other by the travelling heater method. The starting material for each boule was taken from a common source which was produced from a stoichiometric mix of high-purity (6 N) cadmium and tellurium. The final boules were sliced into 2 mm thick discs and the test samples were in the form of 5 mm × 5 mm segments cut from these discs. These samples were labelled T type or B type according to whether they were grown by the THM or Bridgman method and they were given a number indicating the position of the disc within the boule from which they were taken, starting with disc number one at the bottom of each boule. All the samples were initially semi-insulating (with resistivities in the range 10^3–10^4 Ω m) and, in order to convert them to n-type conductivity, post-growth annealing of some test samples was carried out for various lengths of time at 800 °C under nearly saturated Cd pressure and some of these samples were doped with In during the annealing process. Other samples were annealed in liquid cadmium at 500 °C.

For initial Hall effect studies, ohmic contacts were formed by soldering with In. For capacitance voltage (C–V) and deep-level transient spectroscopy (DLTS) measurements rectifying contacts were applied to the front of the samples by evaporating gold (in the form of dots of 1 mm diameter) while ohmic back-contacts were formed using evaporated In. It should be noted here that subsequent measurements (described in section 3) revealed that the interior of the samples remained in a semi-insulating condition after annealing. However, this did not impose a high resistance between the front and back contacts; good electrical conduction between the front and rear surfaces was provided by the higher-conductivity regions at the surfaces and edges of the samples, which were all exposed to the Cd environment during the annealing treatment.

The capacitance measurements were made using a Boonton capacitance meter and DLTS measurements were carried out using a double-boxcar method as described by Lang [4]. For depth profiling studies, some use was made of the voltage dependence of the Schottky barrier depletion depth but this has a very limited range. For example, with shallow-donor densities of approximately 10^{16} cm^{-3} in CdTe, a bias voltage of up to 10 V will extend the Schottky depletion depth to less than 1 μm. Thus, for the extensive depths studied in

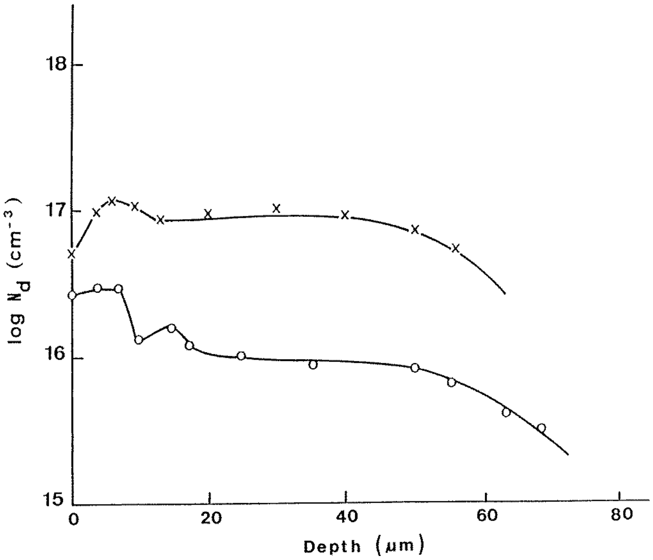


Figure 1. Dependence of effective shallow-donor concentration on depth for undoped samples B2 and T3 annealed at 800 °C for 48 hours. ○ for sample B2 and × for sample T3. (Full lines between data points are included to guide the eye.)

the current work (covering several hundred μm) an alternative, but destructive, technique was necessary. This technique involved the use of a Baty dial gauge to measure the initial thickness of a sample. Similar measurements were made after successive mechanical polishing and chemical etching stages. This allowed the thickness removed to be determined after each stage to within ± 1 μm. New contacts were formed after each polish/etch cycle and, after checking the Schottky barrier characteristics to ensure that low-leakage-current and low-series-resistance conditions were maintained, successive sets of C–V measurements and DLTS measurements were made to enable the required shallow-donor and deep-trap profiles to be gradually built up.

3. Results and discussion

3.1. Carrier concentration profiles

Figure 1 shows the variation of the effective donor density N_d as a function of depth in two undoped samples, one grown by the Bridgman method (sample B2) and the other grown by THM (T3). Both were annealed for 48 hours at 800 °C under saturated Cd pressure. Both curves show an initial increase in N_d to a maximum just below the surface and, after a region of relative uniformity, there is a reduction towards immeasurably small values at depths in excess of 60 μm for sample B2 and 70 μm for sample T3. The overall structure of these curves is similar to that found in the previously reported preliminary work [3] but they differ in two important respects. First of all, the present data provide much more fine detail than the previous work due to the much smaller profiling steps employed here (<7 μm per step compared to >40 μm in the earlier study). Secondly, the depth at which the value of N_d fell to an undetectable value in the earlier work was greater than 200 μm compared to 60–70 μm for the samples in figure 1. The fact that the annealing conditions were the same in both studies suggests that the differences in the depth dependence of N_d can be attributed

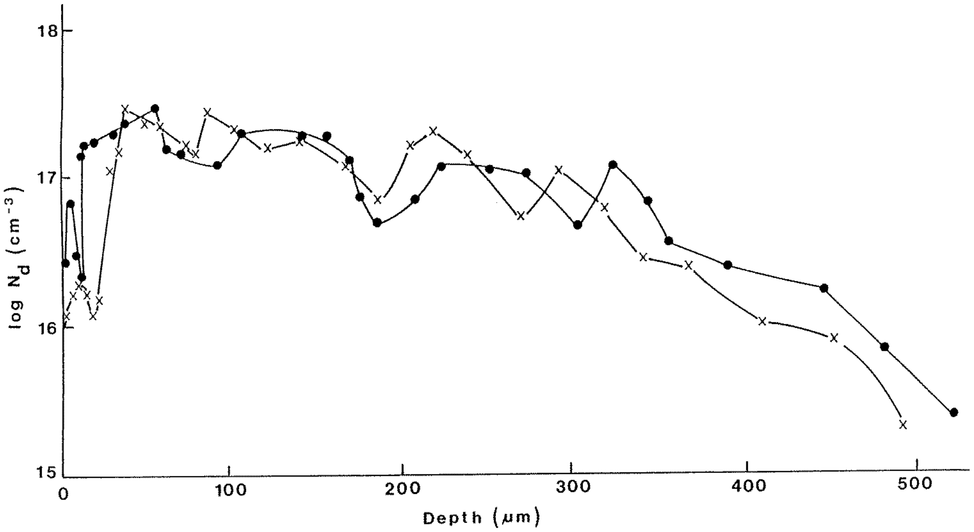


Figure 2. Effective shallow-donor concentration as a function of depth for In-doped Bridgman samples (B30) annealed at 800 °C for 40 hours (×) and 91 hours (●).

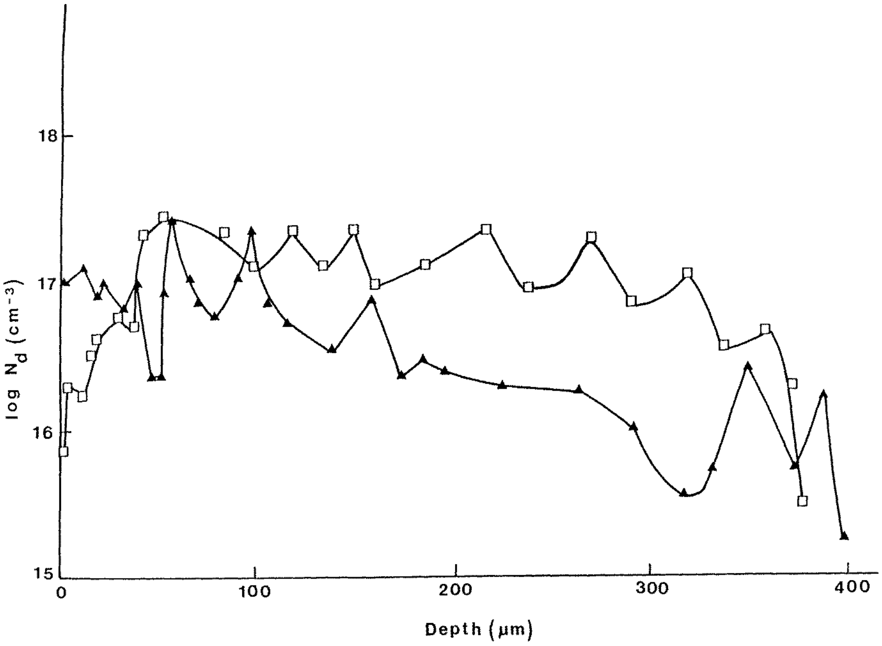


Figure 3. Effective shallow-donor concentration as a function of depth for In-doped THM samples (T37) annealed at 800 °C for 40 hours (□) and 91 hours (▲).

to differences in the properties of the samples involved. This is supported by the results in figures 2 and 3 which show profiles for samples B30 and T37 respectively, taken from the same boules of CdTe as the samples in figure 1. The profiles in figures 2 and 3, like those

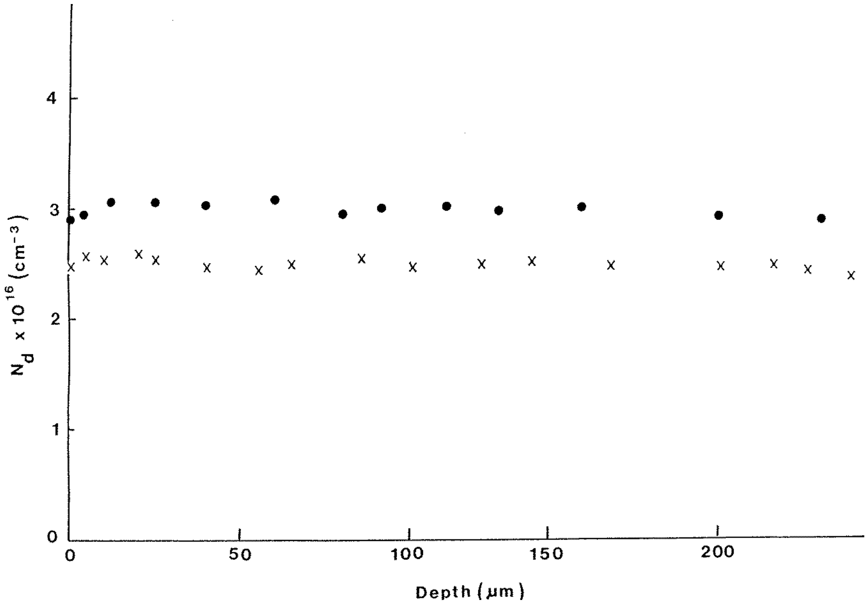


Figure 4. Effective shallow-donor concentration as a function of depth for two samples annealed at 500 °C in liquid Cd for two weeks: ●, THM sample; ×, Bridgman sample.

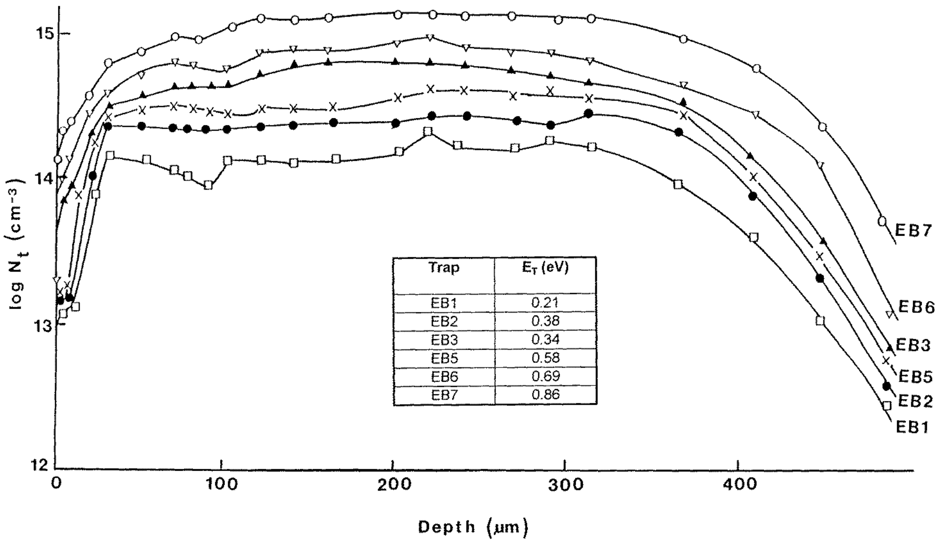
in figure 1, are for samples which were annealed under saturated Cd vapour pressure but, for these samples, In was incorporated in the annealing ampoule. Two different annealing times (40 hours and 91 hours) were employed for each type of material.

There is some significant scatter in the measurements contributing to each profile suggesting a degree of local non-uniformity throughout the samples. Taking account of these variations, the increase in annealing time from 40 to 91 hours appears to have little significant effect on the resultant profiles except for a small increase in the depth of the measurable N_d values. However, the effect of the In doping clearly has a dramatic influence on the profiles, with measurable N_d values reaching nearly 400 μm for the THM samples (figure 2) and approximately 500 μm in the Bridgman samples (figure 3) as compared with <100 μm for the undoped samples (figure 1). However, as the doped samples were from the upper end of the boule and the undoped samples were from the lower end, the possibility existed that the different profiles achieved were associated with properties dependent upon the location of the samples within the boule. In order the check this possibility, two further samples (B4 and T36) were studied. B4, from the lower end of the boule, was annealed for 40 hours and doped with In (the same conditions as previously employed for samples B30 and T37 towards the top of each boule) while T36 was annealed for 48 hours without doping (the conditions used for samples B2 and T3 from close to the bottom of each boule). The results obtained for these samples confirmed the above conclusion that the different profiles were related to the presence of the In dopant. The initial carrier concentration found at the surface of the undoped sample (T36) was 4.2×10^{15} cm^{-3}. This rose to a maximum value of 4.9×10^{16} cm^{-3} before falling to an undetectably low value after reaching a depth of only 64 μm. On the other hand, the doped sample (B4) exhibited an initial carrier concentration of 1.7×10^{16} cm^{-3}, increased to over 10^{17} cm^{-3} at a depth of 109 μm and was still indicating values close to 10^{17} cm^{-3} at a depth of 450 μm. A further variation in the behaviour of these CdTe samples was achieved by annealing in liquid Cd instead of Cd vapour. It is well known that annealing II–VI compounds in the liquid of one of its constituents can remove some of the residual impurities [5] and it has been previously reported that annealing CdTe samples in molten Cd can eliminate some of the initially observed trapping states [6]. In the present study, figure 4 clearly shows that such a process has a significant influence on the N_d depth profile, with a relatively uniform value over a depth in excess of 200 μm as compared to 60–70 μm for the undoped, Cd-vapour-annealed samples.

It is clear from the above results that while the characteristics of bulk-grown CdTe can be manipulated by different annealing treatments, the effect of each treatment is dependent on initial properties of the material. For example, although the Bridgman- and THM-grown samples were seen to behave in the same way with respect to uniformity, it is apparent from figures 1, 2 and 3 that in the case of both doped samples and undoped samples (annealed under similar conditions) the regions of higher carrier concentration extend to greater depths in the B samples than in the T samples. The reason for this may be associated with differences in the quality and purity of the two types of sample. Of course, in this study, care was taken to ensure that the two types of material were of similar purity by growing them from the same source material. However, it is probable that the concentration of residual impurities in the Bridgman samples (B) was greater than that in the THM samples (T) as a result of zone refining purification during the final stage of the THM growth process. Indeed, it has been clearly demonstrated that a reduction in impurity concentration is achieved more effectively by dissolving in molten Te rather than in molten CdTe as in the normal zone refining process [7, 8]. However, although the material grown by THM is expected to be more pure than the Bridgman-grown material, it is possible that the THM technique using Te as the solvent produces a greater concentration of Te precipitates and similarly a large concentration of Cd vacancies which can lead to poor crystal quality [9]. According to our earlier analysis [3], the annealing conditions used in this investigation should be more than sufficient to completely dissolve any Te precipitates and produce a homogeneous distribution of defects and impurities. In fact, with the aid of the radiotracer technique, it was shown that the In dopant incorporated during annealing was, indeed, uniformly distributed [3]. Thus, the spatial non-uniformities in the electrical properties observed here have been attributed to out-diffusion of defects in the vicinity of the surface during the cool-down to room temperature and to an associated self-compensation of donors deep within the sample. However, it is clear from the new results presented here, using a variety of different samples, that the rates at which these processes occur are very dependent on the material quality and purity. This is reflected partly in the differences between THM- and Bridgman-grown samples but is more dramatically demonstrated by the influence of doping (with In). It is well known that impurities can have a significant influence on defect diffusion rates in II–VI compounds. In the case of CdTe, it is believed that the incorporation of donor impurities enhances Cd diffusion as a result of the generation of compensating native defects (Cd vacancies). However, the structure and charge state of the defects finally resulting from such a process have been the subject of much speculation [10]. The DLTS measurements (discussed in the next section) were intended to address this matter by providing information about the nature and spatial distribution of defect-related trapping states in the annealed materials.

3.2. Distribution of trapping states

DLTS studies of all the above samples have revealed the existence of at least 11 different sets of electron traps with activation energies ranging from 0.2 eV to 0.86 eV. Some of these are found in both the THM- and Bridgman-grown materials while others are found in only one of these types of sample depending on the doping and annealing conditions. Full details of the characteristics of all these traps (as determined from DLTS measurements made using the initial contacts on the original (unetched) surfaces) have been published elsewhere [6]. In the course of subsequent measurements made at each stage of the profiling process no new traps have been detected but considerable variations in the densities of existing traps have been found. This is illustrated in figure 5, which gives the trap density profile for sample B30 containing traps labelled EB1, EB2, EB3, EB5, EB6 and EB7 (using the designation previously quoted [6]). Figure 6 shows similar results for sample T37 with traps ET1, ET2, ET3, ET5, ET6 and ET7. By comparing figures 5 and 6 with the corresponding shallow-donor concentration profiles in figures 2 and 3 respectively, it can be seen that, apart from trap ET1, the variation of N_t (trap density) corresponds closely to the form of the associated shallow-donor concentration profile. This indicates that for most of the traps observed here the deep-trap density and shallow-donor concentration tend to maintain an almost fixed ratio as a function of depth and this could be significant in addressing the question of the physical nature of the traps under consideration.



Trap	E_T (eV)
EB1	0.21
EB2	0.38
EB3	0.34
EB5	0.58
EB6	0.69
EB7	0.86

Figure 5. Trap density profiles for sample B30 following annealing at 800 °C for 40 hours. (Inset table gives the activation energy E_T for each set of traps.)

As previously discussed, it is possible to attribute particular traps to the presence of certain impurities or native defects in the light of knowledge about the impurity content and stoichiometry of the material involved but it is likely that some of these traps are complex centres involving, for example, an association between a native defect and an impurity. This could account for the observed close relationship between the trap concentration and effective shallow-donor density referred to above. A linear relationship between trap density and free carrier density has been shown to be a consequence of associate formation in GaP [11] and CdS [12]. The formation of complexes has also been cited to explain the electrical and magnetic resonance properties observed in ZnSe crystals [13]. However, in the case of the CdTe samples under consideration here, it is unlikely that the total defect density diminishes in the surface region and in the deeper interior regions as suggested by the trap

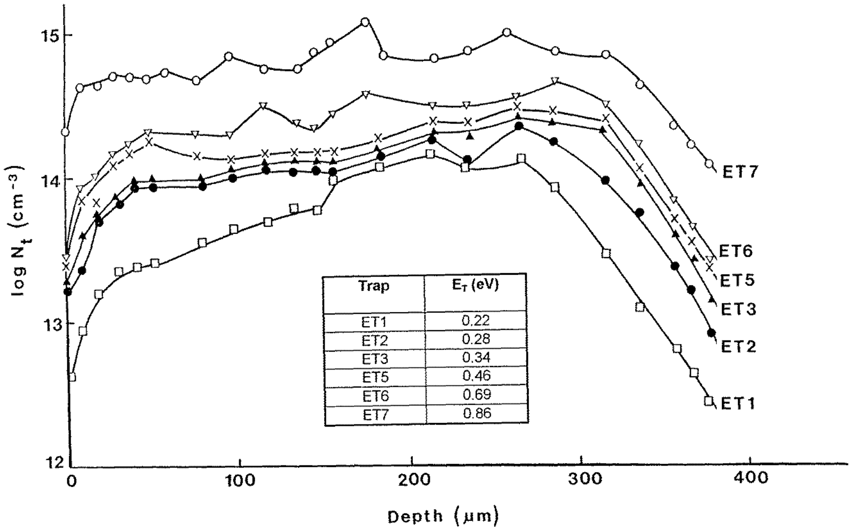


Figure 6. Trap density profiles for sample T37 following annealing at 800 °C for 40 hours. (Inset table gives the activation energy E_T for each set of traps.)

profiles in figures 5 and 6. Accordingly, it was expected that the reductions in the trap densities observed in these regions might be accompanied by the appearance of other traps associated with modifications to the defect structure in these locations. Of course, it is possible that new traps were present but not of sufficient density for their associated DLTS signals to be observed against the existing multifeatured DLTS spectra. A further, likely possibility is that the acceptor states involved lie in the lower half of the bandgap and were, therefore, not accessible with the experimental system used here. Clearly, in any future study of this subject it would be advantageous to employ an additional technique such as optically stimulated DLTS in order to probe states in the lower half of the bandgap.

3.3. Hall effect measurements

In the absence of information about the uniformity of any test sample (as provided by figures 1–3), it is clear that simple conductivity or Hall effect measurements will be open to serious misinterpretation. For example, in the present case, measurements of the carrier concentration made using the Hall effect method have generally been found to be close to those obtained from C–V measurements before profiling. However, this must be considered to be fortuitous, in that the two techniques provide different information about the samples. The data obtained from the C–V measurements relate to a region just below the Schottky contact whereas the Hall method yields a mean density averaged over the full thickness of the sample. Thus, single measurements by either technique give no information about the uniformity of the material. However, the values obtained for the carrier mobility, deduced from Hall effect data, do give an indication of the depth non-uniformities present in these samples. For example, for undoped samples, similar to those in figure 1, Hall effect measurements using the Van der Pauw technique have yielded rather small mobility values ($\sim$0.3 cm^2 V^{-1} s^{-1}). On the other hand, for In-doped samples given the same annealing treatment as for the samples in figure 2, a mobility of $>$400 cm^2 V^{-1} s^{-1} was obtained. The surprisingly small values for undoped samples can be understood in the light of the detailed profiles in figure 1 indicating that the free carriers are confined to a thin near-surface film of 60–70 μm. For the doped samples with a much thicker conducting layer, the mobility is more consistent with previously reported values for bulk CdTe.

4. Summary and conclusions

The distributions of shallow and deep levels in bulk-grown CdTe crystals have been measured as a function of depth following annealing in a Cd atmosphere. Although the annealing conditions were believed to lead to complete homogeneity of the samples at the elevated temperature, this condition was clearly not retained following cooling to room temperature. While conversion to n-type behaviour was successfully achieved by the annealing process, the n-type conductivity was found to be restricted to a near-surface channel, the width of which increased from $\sim$50 μm in undoped samples to $>$400 μm in In-doped samples. These effects have been explained in terms of the diffusion of defects and impurities normal to the surface during the cooling process and it is clear from the above results that the diffusion processes are influenced significantly by doping. DLTS measurements have shown that the densities of the main trapping states (with energies in the range 0.21 to 0.86 eV below the conduction band) vary with depth, keeping a relatively fixed ratio relative to the shallow-donor density and indicating a complex origin. No additional trapping states have been revealed in the regions of the samples where self-compensating defects are believed to be generated. This suggests that the associated trapping levels must lie in the lower half of the bandgap, beyond the range of the DLTS technique as employed in this study.

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