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THE DEFECT STRUCTURE OF CdTe (*)

F. A. KRÖGER

David Packard Professor of Electrical Engineering
Departments of Materials Science and Electrical Engineering
University of Southern California, Los Angeles, California 90007, U. S. A.

Résumé. — Dans cet article de revue on s'intéresse aux défauts physiques existant dans le tellurure de cadmium, l'accent étant mis sur les conditions produisant des cristaux de haute résistivité.

Abstract. — Evidence concerning the defect structure of CdTe is reviewed with particular reference to the conditions producing high resistivity material.

1. Introduction. — Recently, results from self-diffusion experiments [1] and of high-temperature Hall effect measurements on pure and donor-doped CdTe [2, 3] have been used to arrive at the defect structure of CdTe. The structure found is rather complicated, involving both interstitial defects and vacancies, each ionized to various degrees. The species believed to be present are $\text{Cd}_i^{\bullet\bullet}$, $\text{V}_{\text{Te}}^{\bullet\bullet}$, $\text{V}_{\text{Cd}}^{\bullet\bullet}$, $\text{V}_{\text{Cd}}^{\bullet}$, $\text{Te}_i^{\bullet}$, $\text{Te}_i^{\times}$.

In the following section we shall try to determine to what extent the proposed defect structure can be trusted and what aspects are open to doubt. This will be done by reviewing the evidence on which the analysis was based. A second point that deserves consideration concerns the techniques used to make CdTe of high resistivity as used as γ detectors and as windows for high energy CO_2 lasers. This will be done in section 3.

2. The defect structure of CdTe and diffusion coefficients of individual defects as determined from self-diffusion data and high-temperature hall data. — Established with a reasonable degree of certainty are the following points :

2.1 Hall effect measurements on undoped CdTe single crystals at high temperatures where the crystals are in equilibrium with a vapor of known cadmium pressure [2, 3] show that the crystals are n-type with $c_e \propto p_{\text{Cd}}^{1/3}$. The conductivity of such crystals at high temperature shows a similar dependence [4-6] : $\sigma_e \propto p_{\text{Cd}}^{1/3}$. This indicates that we are dealing with doubly ionized native donors which may be either $\text{Cd}_i^{\bullet\bullet}$ or $\text{V}_{\text{Te}}^{\bullet\bullet}$.

2.2 Cd tracer diffusion measurements on undoped CdTe at high p_{Cd} show a dependence for the tracer diffusion coefficient $D_{\text{Cd}}^* \propto p_{\text{Cd}}^{1/n}$ with $n \approx 5$ [1].

$$D_{\text{Cd}}^* = \sum_j f_j D_j [j],$$

f_j being the correlation coefficient for diffusion of the tracer by the species j , D_j being the diffusion coefficient of j , and $[j]$ its concentration expressed as a site fraction. The dependence found is weaker than expected for $\text{Cd}_i^{\bullet\bullet}$ and can be accounted for by the presence of this species only if there are contributions to D_{Cd}^* by species with a concentration varying $\propto p_{\text{Cd}}^{-1/n}$ as well as one by a species, the concentration of which is independent of p_{Cd} . Additional evidence for the presence of the latter will be presented later. The observation of D_{Cd}^* increasing with p_{Cd} is in agreement with a preliminary result by de Nobel [7], but is in disagreement with statements by Whelan and Shaw [8] and Borsenberger and Stevenson [9] who both report D_{Cd}^* to be independent of p_{Cd} . The results of the former authors scatter too much to reveal the weak dependence mentioned above. Inspection of the data points by Borsenberger and Stevenson shows, however, that their results allow a weak p_{Cd} dependence. Therefore, we believe that the conclusion reached above is correct.

2.3 Te tracer self-diffusion measurements on undoped CdTe at high p_{Cd} are in line with a contribution to $D_{\text{Te}}^* \propto p_{\text{Cd}}^{1/3}$ on top of a contribution $\propto p_{\text{Cd}}^{-1}$ (see 2.4), thus supporting the presence of $\text{V}_{\text{Te}}^{\bullet\bullet}$ as a tellurium transporting species at high p_{Cd} .

2.4 Te tracer self-diffusion in pure CdTe at low p_{Cd} is proportional to p_{Cd}^{-1} , indicating uncharged $\text{Te}_i^{\times}$ as the tellurium transporting species under these conditions [9, 10]. Since $\text{Te}_i^{\times}$ is neutral, its concentration should not be affected by doping. This has not been confirmed for CdTe, but it has been confirmed for the diffusion of sulphur tracer by $\text{S}_i^{\times}$ in CdS at low p_{Cd} [11].

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2.5 The dependence of the Cd vacancy concentration on p_{Cd} and $[\text{In}_{\text{Cd}}]$ in CdTe : In at medium to high p_{Cd} where $[\text{In}_{\text{Cd}}] \approx [e']$ depends on the charge of the vacancy :

$$[A'_n] \propto [\text{In}]^{-1} p_{\text{Cd}}^{-1}$$

$$[A''_n] \propto [\text{In}]^{-2} p_{\text{Cd}}^{-1}.$$

At low p_{Cd} , the concentrations of A'_n and A''_n have values fitting the neutrality condition

$$[\text{In}_{\text{Cd}}] \approx [A'_n] + 2[A''_n] + [e'].$$

Here also $[A'_n]$ and $[A''_n]$ depend in a different way on p_{Cd} . In general, therefore, the ratio between the concentrations of A''_n and A'_n vary with p_{Cd} as well as $[\text{In}_{\text{Cd}}]$. Analysis of the shape of Cd self-diffusion isotherms for CdTe with different amounts of indium shows that at the point where $[e'] = [h']$, $[A'_n]/[A''_n] = 8$ at 700 °C, 5 at 800 °C and 2.8 at 900 °C, independent of the ratio in which V_{Cd} and Te_i contribute to A'_n and A''_n . This fixes the isotherms for A'_n and A''_n but leaves the ratio $r' = [V'_{\text{Cd}}]/[\text{Te}_i]$ and $r'' = [V''_{\text{Cd}}]/[\text{Te}_i]$ undetermined. Note that since V'_{Cd} and Te_i and V''_{Cd} and Te_i depend pairwise in the same manner on p_{Cd} and $[\text{In}]$, r' and r'' are constants dependent on temperature only.

2.6 Cd tracer self-diffusion measurements of donor-doped CdTe show a complicated behavior : at high p_{Cd} , D_{Cd}^* as $f([\text{donor}])$ shows a decrease at low donor concentrations followed by an increase at high donor concentrations (Fig. 1). At low p_{Cd} , D_{Cd}^* increases with

FIG. 1. — D_{Cd}^* as a function of $[\text{In}]$ at 700 °C at $p_{\text{Cd}} = 1$ atm and $p_{\text{Cd}} = 0.006$ atm.

increasing donor concentration at all donor concentrations, but less than proportional. The initial decrease at high p_{Cd} is due to the suppression of Cd_i^{2+} in the presence of In_{Cd} . From

it follows that $[\text{Cd}_i^{2+}] \propto p_{\text{Cd}}/[e']^2$. Therefore, an increase of $[e'] \approx [\text{In}_{\text{Cd}}]$ gives a decrease in $[\text{Cd}_i^{2+}]$. The increa-

se at high p_{Cd} at higher $[\text{In}_{\text{Cd}}]$ is due to the increase in the concentrations of V'_{Cd} and V'_{Cd} :

$$[V'_{\text{Cd}}] \propto [e']^n/p_{\text{Cd}} \propto [\text{In}_{\text{Cd}}]^n/p_{\text{Cd}}.$$

At low p_{Cd} where $[\text{In}_{\text{Cd}}] \approx [V'_{\text{Cd}}] + [\text{Te}_i] + 2[V''_{\text{Cd}}]$, D_{Cd}^* increases right from the start because here $[\text{Cd}_i^{2+}]$ is so small that an initial decrease cannot be observed.

2.7 As we saw earlier, the dependence of D_{Cd}^* on p_{Cd} in CdTe : In has to be explained through

$$D_{\text{Cd}}^* = \sum_j D_{\text{Cd},j}^* = \sum_j f_j D_j[j],$$

j being the species V'_{Cd} , V''_{Cd} and possibly $(\text{In}_{\text{Cd}} V_{\text{Cd}})'$. We know already from 2.5 the values of $[A'_n]$ and $[A''_n]$ at each p_{Cd} and T . In isotherms, the contributions of the various species to D_{Cd}^* are given by

$$D_{V'_{\text{Cd}}}^* = \{ r' f_{V'_{\text{Cd}}} D_{V'_{\text{Cd}}}/(1 + r') \} [A'_n]$$

$$D_{V''_{\text{Cd}}}^* = \{ r'' f_{V''_{\text{Cd}}} D_{V''_{\text{Cd}}}/(1 + r'') \} [A''_n]$$

with the f factors constant, and the D 's and r' and r'' functions of temperature only. So far the D 's as well as r' and r'' are unknown. Here we come to the more doubtful parts of the analysis.

Points Open to Question. — 1. Determination of the parameters r' and r'' is possible if the electronic energy levels of the various species are known. The positions of several local levels are known, but their assignment to particular species is uncertain. Table I summarizes the positions of various donor and acceptor levels and the species they are believed to be due to. There is no general agreement on these assignments. The assignments we have believed to be correct and which were used in the analysis are underlined in table I.

With these level assignments one finds $r' \approx 1$ and $r'' \approx \infty$, i. e., V'_{Cd} and Te_i contribute almost equally to A'_n , whereas $A''_n \approx V''_{\text{Cd}}$. Using these values of r it was tried to find values of $D_{\text{Cd},j}^*$ fitting the data in such a manner that each $D_{\text{Cd},j}^*$ depends exponentially on inverse temperature. It is found that this is possible only if there is a contribution D_j that depends exponentially on T^{-1} but is independent of $[\text{In}]$ and p_{Cd} . The latter conclusion was already arrived at in 2.1). The requirement that individual $D_{\text{Cd}}^* = f_j D_j[j]$ should depend exponentially on T^{-1} is somewhat too restrictive. For although it is correct for D_j , it is correct for $[j]$ only if j is either a minority species or if $[j]$ is constant as is the case for V'_{Cd} if $[V'_{\text{Cd}}] = [\text{In}_{\text{Cd}}]$. It is not correct if various species j are equally close to dominance, e. g., $[V'_{\text{Cd}}] \approx [\text{Te}_i] \approx \frac{1}{2}[\text{In}_{\text{Cd}}]$, with the ratio $r' = [V'_{\text{Cd}}]/[\text{Te}_i]$ varying with temperature. However, even in this case the error is only small. Therefore, the error introduced in the analysis by the requirement of linearity cannot be appreciable.

TABLE I

Donor Levels	Ref.	Assignment	Ref.	Acceptor Levels	Ref.	Assignment	Ref.
$E_c-0.01$ eV	[1, 2]	$\text{Cd}_i^x, \text{V}_{\text{Te}}^x$		$E_c-0.05$ eV	[16, 27]	$(V_{\text{Cd}}^x \text{Cl}_{\text{Te}})$	[16]
$E_c-0.025$ eV	[19, 20, 27]			$E_c-0.06$ eV	[6-10]	Te_i''	
$E_c-0.035$ eV	[3]	V_{Te}^x		$E_c-(0.09-0.12)$ eV	[15]	A_n''	(*)
$E_c-(0.13-0.14)$ eV	[2, 4, 25, 29]	Cd_i^x		$E_c-0.42$ eV	[21]		
$E_c-0.20$ eV	[25]	Cd_i^x	[25]	$E_c-(0.6-0.7)$ eV	[1, 5, 9, 11, 12, 21]	$V_{\text{Cd}}'' (V_{\text{Cd}} X)$	[21]
$E_c-0.31$ eV	[25]			$E_c-0.7 \equiv E_v+0.9$ eV	[22]	A_n''	[22]
$E_c-0.44$ eV	[25]			$E_v+0.74$ eV	[26]	Ge ?	[26]
$E_v+0.55$ eV	[5]			$E_v+0.6$ eV $= E_c-1$ eV	[19, 21, 25, 31]		
				$E_v+(0.54-0.56)$ eV	[25, 28, 30]		
				$E_v+0.46$ eV	[21, 25]	V_{Te}	[21]
				$E_v+0.44$ eV	[28]		
				$E_v+(0.3-0.35)$ eV	[9, 11, 25, 27, 28, 29]	$\text{Ag}'_{\text{Cd}}\text{Cu}'_{\text{Cd}}\text{Au}'_{\text{Cd}}$	[9]
				$E_v+0.4$ eV	[22, 30]	A_n''	[22]
				$E_v+0.18, 0.25$ eV	[30]		
				$E_v+0.16, 0.19, 0.28$ eV	[25]	Ge ?	
				$E_v+(0.14-0.15)$ eV	[1, 11, 13, 27, 29]	Te_i' or $(\text{In}_{\text{Cd}} V_{\text{Cd}})'$	[14]
				$E_v+0.12$ eV	[19, 20]		
				$E_v+(0.05-0.06)$ eV	[3, 9, 11, 24, 29]	V'_{Cd}	[8, 9, 11]
				$E_v+(0.034-0.036)$ eV	[23, 24]	Li'_{Cd}	[23]
				$E_v+0.028$ eV	[23]	Na'_{Cd}	[23]
Unclassified Levels							
$E_c-0.55$ eV	[17]						
$E_v+0.30$ eV	[17]						
$E_v+0.13$ eV	[17]						
(*) Center concentration $\propto [\text{Cl}]^2$, which fits Te_i'' : $[\text{Te}_i''] \propto [\text{Cl}]^2 p_{\text{Cd}}$ when $[\text{Cl}_{\text{Te}}] \approx [V'_{\text{Cd}}]$. It does not fit the center proposed in ref. [16], for $[(V_{\text{Cd}}^x \text{Cl}_{\text{Te}})x] \propto [\text{Cl}]^4 p_{\text{Cd}}$.							

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A contribution to D_{Cd}^* that is independent of p_{Cd} may be explained by species V_{Cd}'' , V_{Cd}' or Cd_i^{**} formed by Schottky or Frenkel disorder. However, these would be charged and therefore their concentration would be modified by doping with indium, leading to a dependence on $[In]$ which is contrary to what was observed. The only possibility left is a contribution by an uncharged associate, $(Cd_i V_{Cd})^x$. This can be seen as the transition state of the simplest ring mechanism of diffusion: interchange of two neighboring Cd atoms.

2. In ref. [3] a division of D_n^{**} into V_{Te}^{**} and Cd_i^{**} was made on the basis of the consideration that the negative dependence of c_e on temperature observed in undoped CdTe after cooling can only be explained if Cd_i^{**} precipitates during cooling and that V_{Te}^{**} does not, and if the former species is dominant at high T , the latter at low T . We are not completely certain that this conclusion is correct. It seems possible that this negative T dependence can arise from the fact that the intrinsic carrier concentration $K_i^{1/2}$ has a stronger temperature dependence than the constant $K_{Cd}^{1/3}$ governing the establishment of a deviation from stoichiometry. The results obtained for the contributions of the various diffusion mechanisms to the Cd tracer diffusion coefficients of undoped CdTe and CdTe: $3.6 \times 10^{18} \text{ In cm}^{-3}$ at 700 °C are shown in figure 2.

FIG. 2. — D_{Cd}^* of undoped CdTe and CdTe: $3.6 \times 10^{18} \text{ In cm}^{-3}$ at 700 °C and contributions to it by various diffusion mechanisms $D_{Cd,j}^* = f_j D_j [j]$.

The temperature dependence of such contributions for Cd tracer diffusion and Te tracer diffusion in undoped CdTe are shown in figure 3. With the values of r' , r'' , and $[Te^x]/[Te_i']$ based on assumed level positions and $[A_n']$ and $[A_n'']$ as given above corresponding to the

FIG. 3. — Temperature dependence of contributions by various defects to $D_{Cd,j}^*$ and $D_{Te,j}^*$ in undoped CdTe at $p_{Cd} = 1 \text{ atm}$.

parameters for the constants of defect formation as presented in table III of ref. [3], we can calculate the concentrations of all species as $f(p_{Cd}, T, [In])$. Combination with the individual contributions to D_{Cd}^* and D_{Te}^* as presented in table I of ref. [1] then allows us to determine expressions for defect diffusion coefficients $D_j(T)$.

Such results were presented in table II of ref. [1]. However, it was pointed out to us that several of the parameters as given in this table are in error. Corrected values are presented in table II.

TABLE II
Parameters for the diffusion constants
of individual defects

$$D_j = D_j^0 \exp(-H_j^e/kT)$$

Defect j	$D_j^0 (\text{cm}^2 \text{ s}^{-1})$	$H_j (\text{eV})$
Cd_i^{**}	$29.4 \times \frac{1}{1.35} (*)$	1.23 ± 0.02
V_{Te}^{**}	$30 \times \frac{1}{1.25}$	1.91 ± 0.04
V_{Cd}'	380	1.65
V_{Cd}''	$2.24 \times 10^4 \times \frac{1}{1.7}$	2.09 ± 0.07
Te_i^x	$0.66 \times \frac{1}{1.6}$	0.77 ± 0.07

(*) This notation for the error limit on D_j^0 means that D_j^0 lies between $1.35 D_j^0$ and $D_j^0/1.35$.

If any of the assumptions recognized as doubtful would be changed, this would change the defect formation constants of table III, ref. [3], which in turn would cause a change in the contributions by various defects to D_{Cd}^* and in the expressions for D_j as given above.

One necessary change we are aware of at this stage concerns the expression for K_i as used in the analysis. The expression given in table III of ref. [3] gives a value of K_i at 900 °C which is slightly too large and leads for pure CdTe to $[e']_{900} \propto p_{\text{Cd}}^{1/n}$ with $n \gg 3$. Use of $K_i = 1.48 \times 10^{-14} T^3 \exp(-1.32 \text{ eV}/kT)$ atom $\text{fr.}^2 \approx 3.76 \times 10^{-4} \exp(-1.60 \text{ eV}/kT)$ atom fr.^2 as found by Smith [2] is to be preferred.

3. Preparation of high resistance material. — As found by de Nobel [7] reasonably pure material shows n-type conductivity after annealing at 700-900 °C at high p_{Cd} , and p-type conductivity after annealing at low p_{Cd} with a fairly sharp transition at some intermediate p_{Cd} . At this transition point the material is usually inhomogeneous, some sections being n-type, other sections being p-type. We recently found the same behavior for material doped with $5 \times 10^{16} \text{ cm}^{-3}$ Cl, donors, presumably compensated by an equal concentration of acceptor impurities [12]. It is also possible that most of the chlorine had precipitated removing the corresponding native defects and/or acceptor impurities (self-purification [13]).

The explanation put forward by de Nobel was that in undoped or compensated material, almost no levels are present in the center of the gap at which the Fermi level can be fixed. The slightest change of p_{Cd} or temperature causes the substance to change from n-type with a high to p-type with a low Fermi level. To get a material with its Fermi level stable at a mid-gap position, it is necessary to introduce species with levels near center gap. High resistance material obtained by donor doping combined with annealing below a critical cadmium pressure was believed to arise in this manner: the donor doping creates electrons at high p_{Cd} but ionic defects such as V'_{Cd} and V''_{Cd} at low p_{Cd} . If V''_{Cd} has a level close to mid-gap as assumed, V'_{Cd} will

act as an effective electron trap, and V''_{Cd} as an effective hole trap, thus causing a wide region of p_{Cd} and T where the Fermi level is close to mid-gap. Yet, even in undoped CdTe V'_{Cd} and V''_{Cd} are formed as a result of atomic disorder and deviation from stoichiometry. If precipitation of these species during cooling can be prevented, it should be possible to make even undoped CdTe of high resistance.

It is possible that the need for donor doping is due primarily to the need for avoiding acceptor doping, the latter reducing the concentrations of V'_{Cd} and V''_{Cd} . Positively charged defects such as Cd_i^+ , V_{Te}^+ , Cd_i^{++} and V_{Te}^{++} , the concentration of which are increased by acceptor doping, are ineffective as electron or hole traps because their levels are too close to the conduction band.

In various papers it is claimed that high resistance material can be made from undoped CdTe, the most recent one being that by Triboulet *et al.* [14]. However, this material was not really pure. It contained a donor (Al) at a concentration of the order 10^{15} - 10^{16} cm^{-3} . In addition, it contained carbon at a concentration of 10^{18} cm^{-3} . Even if the concentration of Al would be too low to be effective through the formation of V_{Cd} , one should still consider a possible role of C. Observation of high resistance in material containing another type of four valent atom, Ge, [15, 16] with an energy level at $E_v + 0.74 \text{ eV}$ suggests that C may well be active. In deciding the mechanism by which high resistance is achieved it should be realized that the mechanism of stabilizing the Fermi level at mid-gap, though always involving deep levels, need not always involve the levels of V_{Cd} . As in GaAs which is made semi-insulating by transition elements [17, 19], in particular chromium [20-22], the levels involved may be due to the dopant itself. We ourselves have made CdTe- $10^{17} \text{ Cr cm}^{-3}$ which had a hole concentration of $2 \times 10^{12} \text{ cm}^{-3}$ [23]. The energy level responsible for the high resistance of the Ge doped material may be a Ge-level, with stabilization of the Fermi level at that level by self-compensation of Ge_{Cd} donors by Ge_{Te} acceptors. It is likely that a systematic study involving other dopants will turn up other species able to make CdTe of high resistivity.

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