Native defect equilibrium in semi-insulating CdTe(Cl)

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Abstract

CdTe single crystals doped with Cl were grown by normal freezing from a Te-rich solution. The results of charge carrier transport measurements were used to investigate the semi-insulating properties of CdTe(Cl) samples. Using the results of the theoretical calculation of the total energy, it was shown that Cd vacancies V_{Cd} are the dominant defects on the Te-rich side of the phase diagram. The deep acceptor level, probably connected to the second ionized state of divalent V_{Cd}, was determined to be $E_{a2} \approx 0.65$ eV. The probabilities of the occurrence of free vacancies, vacancies bound into acceptor complexes $(V_{Cd}Cl_{Te})$ and neutral complexes $(V_{Cd}2Cl_{Te})$ theoretically determined for various possible distances in the zincblende structure were used to explain the semi-insulating properties.

1. Introduction

The use of wide bandgap II–VI semiconductors in opto-electronic applications is often limited by self-compensation (SC), [1, 2]. Some materials (*e.g.* ZnS and ZnSe) remain n type and some remain p type (*e.g.* ZnTe) independent of doping with foreign acceptors or donors. An exception is CdTe, with which it is possible to prepare both n type and p type materials. In this case, the semi-compensation effect is widely utilized in the preparation of semi-insulating (SI) p-CdTe crystals by doping shallow donors, such as In_{Cd} and Cl_{Te}. The SI properties are important in the preparation of CdTe(In) on the Te-rich side of the phase boundary [3]. Donor impurities In_{Cd} and Cl_{Te} are fully effective as n-type dopants only when the CdTe is equilibrated on the Cd-saturated phase boundary [4, 5].

The basic idea of SI material follows from the three-level model [6]. In material that contains an excess of shallow donors (N_D) over shallow acceptors (N_A) $(N_D > N_A)$, the deep acceptor level at about $E_g/2$, to which the Fermi level E_F is pinned, must be present with a concentration $N_t \geqslant (N_D - N_A)$.

In accordance with different estimates in SI p-CdTe(Cl), the total concentration of Cl_{Te} $[Cl_{Te}]_{tot} = 10^{17}\text{--}10^{18}$ cm^{-3} [7, 8] and the concentration of deep levels does not exceed $10^{13}\text{--}10^{15}$ cm^{-3} [8]. This fact demonstrates very strong compensation, *i.e.* $N_D \approx N_A$.

It is difficult to explain why at different levels of Cl doping foreign residual shallow acceptors (*e.g.* Cu) are present at the same concentration as Cl_{Te}, and why the

concentration of deep levels (*e.g.* Ge, Si) is correlated with the residual shallow acceptors. Therefore, the main candidates for shallow and deep acceptors are intrinsic native defects. This paper tries to explain quantitatively the process of SC in close connection to the method of preparation of SI p-CdTe.

2. Experimental details

The vertical Bridgmann method was used to grow CdTe single crystals by normal freezing from a Te-rich solution [7]. CdTe single crystals contain Cl in a total concentration $[Cl_{Te}]_{tot} \approx 10^{17}$ cm^{-3}.

After the completion of growth, the CdTe crystal, which contains some Te precipitates, was equilibrated at 450 °C for several days. These conditions are equivalent to annealing on the Te-rich side of the phase boundary where, for a vapour pressure of Cd, we have $p_{Cd} = 2.47 \times 10^7 \exp(-2.45 \text{ eV } k_0 T)$ atm. We first shall collect the results of the experimental measurements on our SI p-CdTe samples and combine these with the results of other authors to reach some conclusions, which are a basis for verification of the SC model predicted in the next section.

It was determined by the time-of-flight technique [9] that our samples contain "shallow" acceptors lying 0.10–0.15 eV above the valence band, and shallow donors (Cl_{Te}) in approximately the same concentration, *i.e.* about 5×10^{16} cm^{-3}. We understand "shallow" acceptors to mean acceptors lying below E_F, which is localized in the midgap. The acceptor level is most

probably created by a complex $(V_{Cd}Cl_{Te})$ whose existence was recently confirmed from photoluminescence measurements [4, 10] and whose position above the valence band was found to be $E_{ac} = 0.120$ eV. The activation energy of the Cl_{Te} shallow donors corresponds to a hydrogenic donor-level depth $E_d = 0.014$ eV [11]. Opinions differ on the position of the first ionized state of a divalent acceptor V_{Cd}. For example, from luminescence measurements it was determined that $E_{a1} = 0.069$ eV [12]. We shall suppose that it is completely ionized. The deep acceptor level $E_{a2} \gtrsim 0.6$ eV above the valence band, which appears in samples equilibrated on the Te-rich side, is often connected with the second ionized state of V_{Cd} [8, 13, 14]. An exact determination of the position of this level is very sensitive to the method of analysis of the experimental data (*e.g.* from $1/eR_H = f(1/T)$).

We have measured the Hall coefficient and conductivity in the temperature range 250–450 K [15]. New simultaneous analyses of $R_H(T)$ and $\sigma(T)$ were performed with the help of theoretically determined mobilities and Hall factors of both electrons and heavy holes. From the electric neutrality condition we obtained the value $E_{a2} = 0.65$ eV above the valence band. The same value for the deep level was determined for our samples by d.c. measurements of space charge limited currents (SCLC) [16]. The Fermi level $E_F = -E_g + E_{a2} + 0.72 k_0 T$ is pinned to E_{a2}. The electric neutrality condition is

$$(1 + f_2)[V_{Cd}] = [Cl_{Te}] - [V_{Cd}Cl_{Te}] \qquad (1)$$

where $f_2 = \{1 + g_{2a} \exp[(-E_g + E_{a2} - E_F)/k_0 T]\}^{-1}$ and $g_{2a} = 2/3$. The total concentrations of Cl_{Te} and V_{Cd} are

$$[Cl_{Te}]_{tot} = [Cl_{Te}] + [V_{Cd}Cl_{Te}] + 2[V_{Cd}2Cl_{Te}] \qquad (2a)$$

$$[V_{Cd}]_{tot} = [V_{Cd}] + [V_{Cd}Cl_{Te}] + [V_{Cd}2Cl_{Te}] \qquad (2b)$$

where

$$[V_{Cd}Cl_{Te}] = \sum_i [(V_{Cd}Cl_{Te})_i]$$

$$[V_{Cd}2Cl_{Te}] = \sum_i [(V_{Cd}2Cl_{Te})_i]$$

and index i is the order of nearest neighbours. The square brackets indicate the concentration. For the binding energy of the complex $(V_{Cd}Cl_{Te})_1$ we have $H_C^1 = 2(E_{ac}^1 - E_{a2}) = 2(0.12 - 0.65)$ eV$= -1.06$ eV. This value is in a good agreement with the Coulomb binding energy for the first nearest neighbours $H_C^1 = -2e^2/(\varepsilon_0 r_1) = -1.08$ eV for $\varepsilon_0 = 9.7$ and $r_1 = a3^{1/2}/4 = 2.8 \times 10^{-8}$ cm, when $a = 6.48 \times 10^{-8}$ cm is the lattice constant.

3. Theory and discussion

3.1. Defect equilibrium

We shall consider the intrinsic defects that can accommodate excess Te: Cd vacancy V_{Cd}, Te anti-site Te_{Cd} and Te interstitial Te_I which can as acceptors affect the process of compensation during Cl doping. The defects, in principle, can be created by thermic generation or as a result of the compensation of shallow donors.

Berding *et al.* [17] have calculated the formation energy of native point defects in CdTe using the full potential linearized muffin tin orbital (FP-LMTO) method. Free atom initial and final states were used as references. It is convenient for the analysis of defects in our case to consider pure solid CdTe(s) and Cd in the vapour Cd(g) as references for the defects. Using the values from Table 1 in ref. 17, we obtain

$$E_{V_{Cd}} + CdTe \leftrightarrow V_{Cd}Te + Cd(g) \qquad E_{V_{Cd}} = 4.72 \text{ eV} \quad (3)$$

$$E_{Te_{Cd}} + 2CdTe \leftrightarrow Te_{Cd}Te + 2Cd(g) \qquad E_{Te_{Cd}} = 7.28 \text{ eV} \quad (4)$$

$$E_{Te_I} + CdTe \leftrightarrow Te_I + Cd(g) \qquad E_{Te_I} = 6.21 \text{ eV} \quad (5)$$

If we calculate the values of the equilibrium constants of reactions (3)–(5), *i.e.* $K_{V_{Cd}} = C_0^{-1}[V_{Cd}]p_{Cd}$, $K_{Te_{Cd}} = C_0^{-1}[Te_{Cd}]p_{Cd}^2$, $K_{Te_I} = C_0^{-1}[Te_I]p_{Cd}$, where $C_0 = 1.47 \times 10^{22}$ cm^{-3}, by a method analogous to the method described in ref. 18 for HgTe, for the Te-rich side we obtain $[V_{Cd}] \approx 10^8$ cm^{-3}, $[Te_{Cd}]/[V_{Cd}] \approx 10^{-4}$ and $[Te_I]/[V_{Cd}] \approx 10^{-11}$ at 450°C and $p_{Cd} \approx 2 \times 10^{-10}$ atm, and $[V_{Cd}] \approx 10^{13}$ cm^{-3}, $[Te_{Cd}]/[V_{Cd}] \approx 10^{-4}$ and $[Te_I]/[V_{Cd}] \approx 10^{-8}$ at 700°C and $p_{Cd} \approx 5 \times 10^{-6}$ atm.

We can see that on the Te-rich side the Cd vacancy is the dominant native point defect. The same situation is of course valid for defects generated during the process of SC.

In principle, for the Te-rich side we can take CdTe(s) and Te(s) or Te(l) as references in reactions (3)–(5). Then for the Te-rich side, the energies of creation of V_{Cd} (about 2.15 eV), Te_{Cd} (about 2.14 eV) and Te_I (about 3.44 eV) are directly obvious.

3.2. Self-compensation

To explain the mechanism of SC it is necessary to know which portion of the vacancies created by SC remains free (deep acceptor), and which portion is bound in complexes $(V_{Cd}Cl_{Te})$ separated by various possible distances in the sphalerite structure or in neutral complexes $(V_{Cd}2Cl_{Te})$.

The concentrations $[V_{Cd}2Cl_{Te}]$, $[V_{Cd}Cl_{Te}]$ and $[V_{Cd}]$ are calculated by the partition function formalism

$$Z = \sum_i \exp(-E_i/k_0 T) \qquad (6)$$

TABLE 1. The configuration parameters, the activation energy of the complexes $(V_{Cd}Cl_{Te})_i$ and the probabilities of different configurations

i	$\dfrac{r_1}{r_i}$	$E_{ac}{}^i$ (eV)	D_i	$g1_i$	$g2_i$	$\dfrac{[(V_{Cd}Cl_{Te})_i]}{[V_{Cd}]_{tot}}$	$\dfrac{[(V_{Cd}2Cl_{Te})_i]}{[V_{Cd}]_{tot}}$
1	1	0.120	1.694	4	6	0.590	0.403
2	0.5222	0.373	1.345	12	12	5.2×10^{-4}	2.1×10^{-3}
3	0.3974	0.439	1.306	12	12	6.2×10^{-5}	1.1×10^{-3}
4	0.3333	0.473	1.244	16	12	2.8×10^{-5}	3.8×10^{-4}
5	0.2928	0.495	1.221	24	24	2.1×10^{-5}	5.1×10^{-4}

$[V_{Cd}{}^{2-}]/[V_{Cd}]_{tot} = 8.86 \times 10^{-4}$.

The energy E_i is here given by the Coulomb interaction of two atoms $Cl_{Te}{}^+$ and a vacancy $V_{Cd}{}^{2-}$ located in the mean volume $1/[V_{Cd}]_{tot} = 2/[Cl_{Te}]_{tot} = 2 \times 10^{-17}$ cm^3, corresponding to a fully compensated regime.

By including the most probable events in the calculation, the three dominant configurations are as follows:

(1) Both atoms $Cl_{Te}{}^+$ are distant from $V_{Cd}{}^{2-}$ — the case of a single vacancy $V_{Cd}{}^{2-}$. The partition function contribution is then given by (E_i is neglected here)

$$Z1 = \frac{32}{[Cl_{Te}]^2 a^6} = Z \frac{[V_{Cd}{}^{2-}]}{[V_{Cd}]_{tot}} \tag{7}$$

(2) One atom $Cl_{Te}{}^+$ is located near $V_{Cd}{}^{2-}$ — the case of the complex $(V_{Cd}Cl_{Te})^-$. Here we have

$$Z2 = \frac{8}{[Cl_{Te}] a^3} \sum_i g1_i \exp\left[-\frac{H_c^1}{k_0 T}\left(\frac{r_1}{r_i}\right) \right]$$

$$= Z \sum_i \frac{[(V_{Cd}Cl_{Te})_i]}{[V_{Cd}]_{tot}} \tag{8}$$

(3) Both atoms Cl^+ are near $V_{Cd}{}^{2-}$ — the case of the complex $(V_{Cd}2Cl_{Te})$. Here we have

$$Z3 = \sum_i g2_i \exp\left[-\frac{H_c^1}{k_0 T} D_i \right] = Z \sum_i \frac{[(V_{Cd}2Cl_{Te})_i]}{[V_{Cd}]_{tot}} \tag{9}$$

where Z is the total partition function $Z = Z1 + Z2 + Z3$, $r_i = (a/4)(8i - 5)^{1/2}$ is the radius of the nearest neighbour spheres and

$$D_i = \frac{r_1}{r(Cl_1)} + \frac{r_1}{r(Cl_2)} - \frac{r_1}{2r(Cl_1, Cl_2)} \tag{10}$$

describes different configurations of the pair $Cl_{Te}{}^+$ around $V_{Cd}{}^{2-}$. Also, $r(Cl)$ and $r(Cl_1, Cl_2)$ are Cl–V_{Cd} and Cl–Cl distances, respectively, and $g1_i$ and $g2_i$ are the factors of degeneracy. The coefficients used and the activation energies of the complexes $(V_{Cd}Cl_{Te})_i$

given by

$$E_{ac}{}^i = E_{a2} + \frac{1}{2} H_C^1 \left(\frac{r_1}{r_i}\right)$$

are shown in Table 1. The results for temperature $T = 450\,^\circ C$ are given on the right-hand side of Table 1. As can be seen, the close-packed complexes $(V_{Cd}Cl_{Te})$ and $(V_{Cd}2Cl_{Te})$ are dominant (59% and 40%) in CdTe(Cl), while the single V_{Cd} has a small concentration (0.089%). These theoretical values obtained on the basis of the proposed model of SC are in good agreement with experimental data.

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References

1 G. Mandel, Phys. Rev., 134 (1964) A1070.
2 F. F. Morehead and G. Mandel, Phys. Rev., 137 (1965) A924.
3 F. W. Wald and R. O. Bell, Nat. Phys. Sci., 237 (1972) 13.
4 S. Seto, A. Tanaka, Y. Masa and M. Kawaskima, J. Cryst. Growth, 117 (1992) 271.
5 N. V. Agrinskaya and V. V. Shashkova, Sov. Phys. Semicond., 24 (1990) 437.
6 A. J. Strauss, Rev. Phys. Appl., 12 (1977) 167.
7 P. Höschl, P. Polívka, V. Prosser, M. Vaněček, Rev. Phys. Appl., 12 (1977) 229.
8 N. V. Agrinskaya and O. A. Matveev, Sov. Phys. Semicond., 21 (1987) 333.
9 P. Höschl, P. Polívka, F. Nava and R. Minder, Czech. J. Phys. B, 26 (1978) 812.
10 D. M. Hoffmann, P. Omling, H. B. Grimmeiss, B. K. Meyer, K. W. Benz and D. Sinerius, Phys. Rev. B, 45 (1992) 6247.
11 K. Zanio, Cadmium telluride, in R. K. Willardson and A. C. Beer (eds.), Semiconductors and Semimetals, Vol. 13, Academic Press, New York, 1978, p. 129.

12 N. V. Agrinskaya, O. A. Matveev, A. V. Nikitin and V. A. Sladkova, *Fiz. Tekh. Polup.*, *21* (1987) 666.

13 F. A. Kröger, *Rev. Phys. Appl.*, *12* (1977) 205.

14 N. V. Agrinskaya and O. Matveev, *Nucl. Instrum. Methods A*, *283* (1989) 263.

15 P. Höschl, P. Moravec, V. Prosser, R. Kužel, R. Grill, J. Franc,

E. Belas and Yu. M. Ivanov, *J. Cryst. Growth*, *101* (1990) 822.

16 A Zoul and E. Klier, *Czech. J. Phys. B*, *27* (1977) 789.

17 M. A. Berding, M. van Schilfgaarde, A. T. Paxton and A. Sher, *J. Vac. Sci. Technol. A*, *8* (1990) 1103.

18 A. Sher, M. A. Berding, M. van Schilfgaarde and A. Chen, *Semicond. Sci. Technol. C*, *59* (1991) 6.