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DEFECT ANALYSIS OF $(Hg_{0.6}Cd_{0.4})_{1-y}Te_y$

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The values of p-n and P_{Hg} for metal-saturated $Hg_{0.60}Cd_{0.40}Te$ are fit by a simple model of a non-degenerate semiconductor containing doubly-ionized native donors and acceptors, and foreign donors in the 1-4 x $10^{15}cm^{-3}$ range. The parameters obtained are consistent with present values for the room temperature energy gap and intrinsic carrier concentration as well as with the high degree of compensation necessary to account for the calculated ionized impurity scattering. The parameters are

$$\log_{10} n_i = -1118/T + 13.76 + 1.5 \log T$$

$$\log P_{Hg}(\mathrm{int}) = -4850/T + 7.926$$

$$\log k_s^{\frac{1}{2}} = -4032/T + 21.52$$

Key words: defect chemistry, partial pressures, 40 mole% CdTe, HgTe-CdTe solid solutions.

Introduction

Schmit and Stelzer (1) have recently reported values for the net hole concentration, p-n, for both metal-saturated and Te-saturated $(Hg_{0.60}Cd_{0.40})_{1-y}Te_y(c)$. This material

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is one of a continuous range of solid solutions with the zinc-blende structure that forms between the compounds HgTe and CdTe. The narrow homogeneity ranges of the binary compounds is reflected in the behavior of the solid solutions in that y is restricted to values close to ½. The particular composition studied is a semiconductor with a band-gap of 0.44-0.50eV and an intrinsic carrier concentration in the $10^{14}cm^{-3}$ range at room temperature (2). It is the purpose here to show that, under certain plausible assumptions, it is possible to find a simple defect model such that the experimental data can, in general, be adequately fit. Using this solution the electronic carrier concentrations can be extrapolated to higher temperatures and to materials with varying impurity concentration. In this analysis we use values for the partial pressure of Hg, P_{Hg}, which have been recently determined for both the metal-saturated and Te-saturated solid solution from measurements of the optical density of the coexisting vapor (3).

Defect Model

The following assumptions are made. a) The vapor phase is ideal so that the chemical potential of Hg is given by

$$\mu_{Hg} = RT\ln P_{Hg} + \mu^{o}_{Hg}(T) \qquad (1)$$

where P_{Hg} is the partial pressure of Hg in atm and $\mu^{o}_{Hg}(T)$ is the chemical potential of Hg(g) at 1 atm and temperature, T. The assumption of ideality is not strictly valid at the high pressures of 10-30 atm encountered but the ensuing error is negligible (4). b) The ternary solid solution is a non-degenerate semiconductor so that the product of the electron and hole concentrations is given by

$$np = n_i^2\,(T) \qquad (2)$$

where the intrinsic carrier concentrations, n_i, is a function of T only. c) The electronic carriers originate from electrically active impurity atoms and from the ionization of donor and acceptor levels arising from the presence of native atomic point defects. The latter are assumed to be completely, z-fold ionized with z = 1 or 2. For concreteness the native defects are taken as vacancies in the Hg-Cd, metal sublattice, V_M, acting as acceptors and vacancies in the

Te-sublattice, V_N, acting as donors. (The alternative assumption of metal interstitials acting as the z-fold ionized donors leaves the equations unchanged in form at the low defect concentrations encountered here.) The equation for electrical neutrality is then

$$p-n = z\{[V_M^{-z}] - [V_N^{+z}]\} - [D^+] \tag{3}$$

where $[D^+]$ is the net-concentration of singly-ionized impurity donors. d) The vacancies are distributed at random on the sites of each sublattice and increase the Gibbs free energy of the crystal a fixed amount per vacancy of a given type. Moreover the vacancy concentrations are assumed small enough in comparison to the concentration of sites in each sublattice that the positions of the electronic energy levels and the total site concentrations are independent of the vacancy concentration. Then it can be shown that (5,6,7) the following equations hold:

$$[V_M^{-z}]\ [V_N^{+z}] = k_s(T) \tag{4}$$

where k_s is the Schottky constant for ionized vacancies and

$$\ln P_{Hg} = \ln P_{Hg}(\text{int}) - z \sinh^{-1}\left(\frac{p-n}{2n_i}\right) - \sinh^{-1}\left(\frac{p-n+D^+}{2zk_s^{1/2}}\right) \tag{5}$$

where $P_{Hg}(\text{int})$ is the partial pressure over the pure, intrinsic crystal. Both equations (4) and (5) are of the same form as those describing a binary, semiconductor compound containing Hg as one element and have been derived using statistical thermodynamic arguments (5,6). For the ternary solid solution, $(Hg_{1-x}Cd_x)_{1-y}Te_y(c)$, the intrinsic material parameters, $P_{Hg}(\text{int})$, n_i, and k_s, are unspecified functions of x. Equation (5) embodies the remarkably simple result that for a given x that the net hole concentration, p-n, is a function of P_{Hg} and T only (assuming no large pressure changes of hundreds of atm). This result follows from the fact that the chemical potentials of the thermodynamic components, HgTe and CdTe, are independent of y for ranges of y close to ½ to a good approximation (7). When z = 1 and for a binary solid e.g. x = 0 or 1, an explicit equation can be obtained for p-n (8) which has been shown (9) to be equivalent to Eq. (5).

e) The temperature dependence of the intrinsic material parameters is given by

$$\log_{10} n_i = W/T + A + 1.5 \log T \tag{6}$$

$$\log P_{Hg}(\text{int}) = V/T + B \tag{7}$$

$$\tfrac{1}{2} \log k_s = C/T + D \tag{8}$$

where the values of W, A, V, B, C, and D are to be determined from a best fit of Eq. (5) to the observed values of p-n.

In addition to the above, the following specific assumptions are also made. (1) The native defects are always doubly-ionized; i.e. z = 2. This is in keeping with the information on the native defects in CdTe and HgTe. (10,11) (2) The Schottky constant at 500°C is large and about 4×10^{32} cm^{-6}. The analysis (12) of the low temperature mobility indicates significant ionized impurity scattering for samples metal-saturated at 500°C and 375°C. Assuming singly-ionized impurities, the concentration of compensating foreign donors was calculated to be about $10^{17} cm^{-3}$. Here we assume the ionized impurity scattering is due to doubly-ionized vacancies. This reduces the concentration of compensating donor centers to about 5×10^{16} cm^{-3} and gives a Schottky constant in the 10^{32} - 10^{33} range. (3) The crystals used by Schmit and Stelzer contain foreign impurities with a net ionized donor concentration in the 1 - 4×10^{15} cm^{-3} range. Then consistent with the experimental values for p-n, shown by the points in Fig. 1, it is desired that the theory predict nearly temperature independent, negative values of p-n for metal-saturation at 250 and 300°C. Moreover, the calculated values of p-n should overlap the spread of experimental points as closely as possible for values of $[D^+]$ in the 0 - 4×10^{15} cm^{-3} range. (4) Only the Te-saturated point of p-n = 1.4×10^{17} cm^{-3} at 400°C is taken. The values of p-n at higher temperatures are assumed to be too low due to inadequate quenching, even though the quench used should have been very rapid. The values of p-n show almost no increase with increasing temperature and at 600°C overlap the values obtained for metal-saturation. In contrast, the value of P_{Hg} for Te-saturation increases monotonically with increasing temperature and at 600°C is twenty times lower than that for metal saturation. This behavior of p-n and P_{Hg} is inconsistent with any simple defect model. Moreover,

quench effects have been observed with Te-saturated HgTe at 550°C (10). Therefore it is assumed that quenching problems underlie the discrepancy between the partial pressure data and the data for p-n and the latter are discarded.
(5) The values of p-n for metal saturation at 650 and 700°C show a decrease from that at 600°C even though P_{Hg} is continuing to rise. Inclusion of these points in the analysis would require an antistructure donor defect (Te on metal sites) which is predominant only at 600°C and above. The value of p-n at 650 and 700°C would be even smaller for Te-saturation than for metal-saturation. Lacking any data for Te-saturation at these high temperatures, it is not believed that such a complicated model is warranted at present and the metal-saturation points at 650 and 700°C are excluded from the analysis. (6) The parameters determining n_i through Eq. (6) should give a value in the 10^{14} cm^{-3} range for n_i at 25° and in particular W should give an energy gap of 0.44 eV, where

$$E_g(eV) = 3.972(10^{-4})W \tag{9}$$

Any temperature dependence of the energy gap above room temperature is neglected. (7) Consistent with the partial pressure measurements, P_{Hg} for metal-saturation is equal to the vapor pressure of Hg below 352°C and is given by (11)

$$\log_{10}P_{Hg}(atm) = -3080/T + 4.8910 \tag{10}$$

Analysis and Results

A trial-and-error search routine was used to find those values of the material parameters appearing in Eqns. (6) - (8) that would give a minimum squared fractional difference between observed values of p-n and those calculated from Eq. (5) with z = 2 for the experimental values of T and P_{Hg}. As indicated in items 4 and 5 of the last section, certain experimental points were excluded from the fit. In addition, values of p-n = -1×10^{15} for metal-saturation at 300 and 250°C were included. In a given set of calculations the parameters C and D of Eq. (8) were related to give a fixed value for the Schottky constant at 500°C in order to meet the constraints given in item 2 above, the search was limited to values of W within ± 10% of a fixed value, and the parameters V and B of Eq. (7) were related so that

P_{Hg}(int) would equal P^o_{Hg} at a specified temperature (where a pure crystal would be intrinsic).

The range of parameters tried consisted of: a) values of 10^{32}, 4×10^{32}, 10^{33}, and 3.6×10^{33} for the Schottky constant at 500°C. b) values of W that were allowed to vary to find an optimum fit over 10% of three fixed values corresponding to room temperature energy gaps of 0.40, 0.44, and 0.50 eV. c) Values of 0, 10^{15} and 4×10^{15} cm^{-3} for the concentration of singly ionized foreign donors and d) Temperatures between 270 and 350°C for the equality of P_{Hg}(int) and P^o_{Hg}. The overall most satisfactory fit was given by

$$\log_{10} n_i = -1118/T + 13.76 + 1.5 \log T \tag{11}$$

$$\log P_{Hg}(\text{int};\text{atm}) = -4850/T + 7.926 \tag{12}$$

$$\log k_s^{1/2} = -4032/T + 21.52 \tag{13}$$

These equations give room temperature values for the energy gap and intrinsic carrier concentration of, respectively, 0.44eV and 5×10^{13} cm^{-3}. The square root of the Schottky constant is 2×10^{16} cm^{-3} at 500°C and the pure, metal-saturated crystal is intrinsic at 310°C. It should be noted that the parameters in Eqs. (6-8) are highly correlated and changes in one can be to some extent offset by changes in another with no significant change in the fit to the experimental values of p-n. However, our optimization trials always led to values for W and A that corresponded to values for n_i at 25°C of 10^{14} cm^{-3} or less.

Theoretical curves are shown in Fig. 1 for various concentrations of simply-ionized foreign donors. It is to be noted that at 250 and 300°C, p-n is essentially independent of temperature, as desired, and is nearly equal to the foreign donor concentration. For metal-saturation at 375°C the calculated values of p-n are a little low and are 3.62×10^{15} for $[D^+] = 10^{15}$ and 4.29×10^{15} for the pure crystal (not shown). At higher temperatures, and for Te-saturation at all temperatures, the values of p-n for the pure crystal are essentially equal to those for $[D^+]$ as high as 8×10^{15} cm^{-3}. Table 1 gives the values of P_{Hg} as a function of temperature up to the solidus temperature of 744 ±2°C (determined from discontinuities in the slope of log optical density vs $10^3/T$ for various wavelengths and in agreement with other measurements (13)) as well as the calculated values of p-n for $[D^+] = 0$.

Calculated curves of constant net hole concentration for $[D^+] = 0$ are shown in a plot of P_{Hg} vs $10^3/T$ in Fig. 3. Also shown are the vapor pressure of Hg and the parabola-like, three-phase curve for $Hg_{0.60}Cd_{0.4}Te$. The experimental values of P_{Hg} defining the three-phase curve are shown as closed circles (3). The solid solution with x = 0.40 is a stable phase only for values of P_{Hg} and $10^3/T$ on or within the three-phase curve. Curves of constant p-n are extended outside this field of stability to show their structure. The Figure does not quite extend to temperatures of 310°C and below where the pure metal-saturated crystal is n-type.

Although the theoretical curves for metal-saturation below 300°C represent an extrapolation from where the most reliable experimental data lie, and so are less reliable than at higher temperatures, they give the lowest carrier concentrations. Therefore they are shown in Fig. 2 for a pure crystal and for three net, singly-ionized acceptor concentrations. It is to be noted that the sign of p-n changes twice for both $D^+ = -10^{+14}$ and -2×10^{14} cm^3. Since the calculated values of p-n are least dependent on metal-saturation temperature near 275°C, this would appear to be the optimum temperature for obtaining n-type material in the $10^{13} - 10^{14}$ cm^{-3} range.

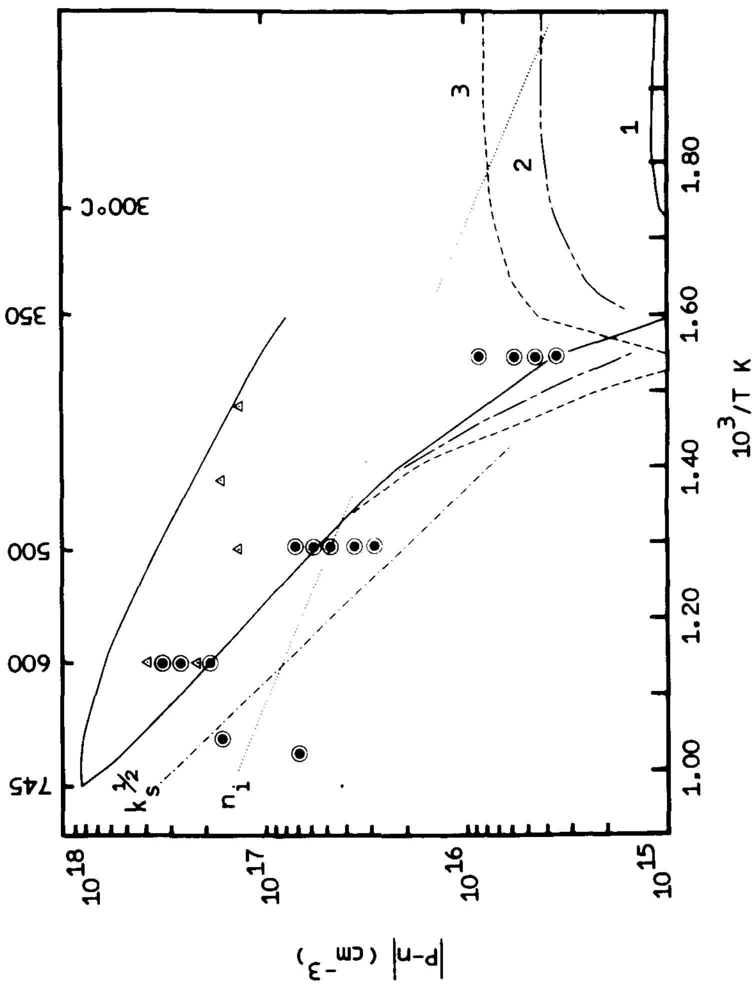
745
600
500
350
300°C
10^{18}
10^{17}
10^{16}
10^{15}
$|p-n|$ (cm^{-3})
1.00
1.20
1.40
1.60
1.80
$10^3/T$ K
$k_s^{1/2}$
n_i
1
2
3

Table I

Temperature in °C, mercury pressure in atm, and calculated value of p-n in cm^{-3} for the pure metal-saturated crystal and, for the last six temperatures, for the tellurium-saturated crystal.

T	200	250	300	350	441	500	560
$100 \times P_{Hg}$	2.4	10.1	32.9	88.7	330	660	1280
$10^{-15} \times (p-n)$	-0.092	-0.22	-0.13	1.55	22.3	58.8	121

T	600	642.4	711.4	728.4	745
$100 \times P_{Hg}$	1700	2290	2990	2910	2690
$10^{-15} \times (p-n)$	191	289	558	671	816

T	350	400	500	600	682.5	730.8
$100 \times P_{Hg}$	0.13	0.60	8.2	82	584	1900
$10^{-15} \times (p-n)$	77.3	140	347	634	799	821

Figure 1. Calculated values of the net hole-concentration, p-n, for Te-saturated (upper branch of loop) and for metal-saturated (lower branch) $Hg_{0.60}Cd_{0.40}Te$. Curves are shown for net concentrations of singly-ionized foreign donors of (1) 10^{15}, (2) 4×10^{15}, and (3) $8 \times 10^{15} cm^{-3}$. For $10^3/T$ values greater than about 1.60, p-n is negative for the metal-saturated crystal. The intrinsic carrier concentration and square root of the Schottky constant are shown as the labeled straight lines. Experimental points are from Ref. 1.

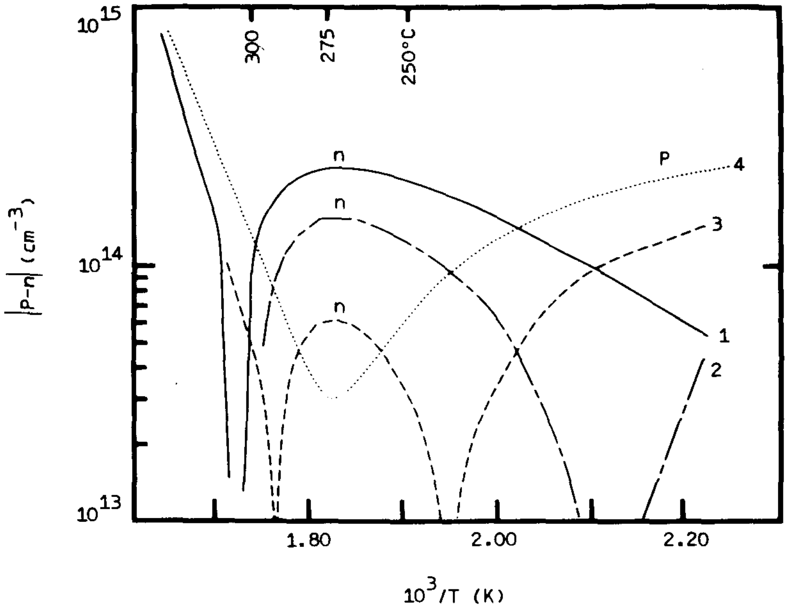

Figure 2. Calculated values of p-n for metal-saturation at low temperatures and with various net concentrations of singly ionized foreign acceptors. (1) zero, (2) 10^{14}, (3) 2 x 10^{14}, and (4) 3 x 10^{14}cm^{-3}.

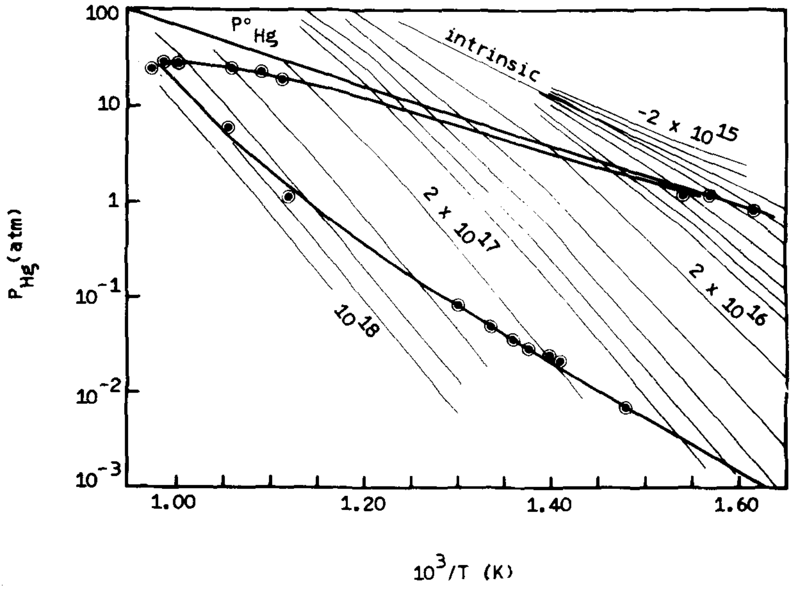

Figure 3. Curves of constant p-n on a plot of P_{Hg} on a log scale vs $10^3/T$. The vapor pressure of Hg is shown as the labeled straight line. The value of P_{Hg} along the three-phase curve and the experimental points defining this curve are shown as the parabola-like curve with its apex at upper left and as closed circles, respectively.

Summary

The experimental values of p-n for metal-saturated $Hg_{0.60}Cd_{0.40}Te$ have been closely fit using a simple model of a non-degenerate semiconductor containing doubly-ionized native donors and acceptors and foreign donor concentrations in the $1 - 4 \times 10^{15}$ cm^{-3} range. The intrinsic carrier concentration used gives room temperature values for the energy gap and intrinsic carrier concentration of, respectively, 0.44 eV and 5×10^{13}eV, both close to present best values. The Schottky constant for the ionized, native centers leads to a high degree of self-compensation and is consistent with the strong ionized impurity scattering invoked to fit the low temperature mobility of samples metal-saturated at 375 and 500°C. Moreover, the values of p-n for metal-saturation at 375°C and above are only slightly changed for singly-ionized foreign donor concentrations up to 4×10^{15} cm^{-3}, consistent with the experimental results. All the above would seem to strengthen our assumption that the values of p-n for Te-saturation are too low because of inadequate quenching. The energy required to create a doubly-ionized metal vacancy and a similar Te-vacancy is 3.2eV from Eq. (13). However, it is emphasized that this value cannot be considered as reliable as that of the Schottky constant itself.

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