Chemical Self Diffusion in CdTe*

S. S. CHERN AND F. A. KRÖGER

*Department of Materials Science, University of Southern California,
Los Angeles, California 90007*

The diffusion constant determining the rate of the variation in the stoichiometric composition of CdTe for a change in cadmium pressure is measured for indium doped crystals. The results for doped as well as undoped crystals are expressed in terms of previously determined equiconcentration tracer diffusion constants using a detailed point defect model. Factors responsible for asymmetrical behavior are discussed.

Die Diffusionskonstante welche die Geschwindigkeit der Variation der Zusammensetzung von CdTe bei Änderung der Kadmium druck bestimmt wurde gemessen für CdTe dotiert mit Indium. Die Resultate für dotierte und undotierte Kristallen werden interpretiert auf dem Grunde eines detaillierten Fehlstellen-modelles. Mögliche Ursachen eines asymmetrischen Verhaltens werden diskutiert.

1. Introduction

If CdTe crystals are heated in an atmosphere with a well-defined cadmium pressure, in equilibrium a certain stoichiometric ratio is established which depends uniquely on cadmium pressure, temperature and—if applicable—doping concentration. Variation of the cadmium pressure leads to a variation of this ratio. The change involves diffusion of at least one of the components of the crystal. This type of chemical diffusion can be studied by measuring as a function of time any property dependent on stoichiometry. For CdTe such studies have been made by Zanio (1) and Rud and Sanin (2) using conductivity as the property monitored.

For undoped CdTe, $\tilde{D}_{Cd}$ could be represented by

$$\tilde{D} = 4 \exp(-1.15 \text{ eV}/kT) \text{ cm}^2 \text{ sec}^{-1} \quad (1)$$

Whelan and Shaw (3) reported for 700°C $\tilde{D} = 2 \times 10^{-4}$ cm^2 sec^{-1}, a value that is

$\simeq 40\times$ larger than indicated by (1). Rud et al. (2) found a smaller activation energy of 0.6 eV and a 900°C value of $\tilde{D}$ of 2×10^{-5} cm^2 sec^{-1} for copper-doped CdTe in which the conductivity $\sigma \propto p_{Cd}^{0.43}$. A similar study for CdS was carried out by Kumar and Kröger (4).

The migration of components involves the migration of point defects. For CdTe, just as for CdS, there are various complications:

(1) There are several mobile defects; the change in composition will be brought about mainly by the species with the largest mobility concentration product (S_D).

(2) S_D, if charged, migrates by ambipolar diffusion.

(3) The migrating species will in general be present in a concentration different from that of other, less mobile species, S_S. If the latter are present in larger concentrations and thus represent the greater fraction of the deviation from stoichiometry, secondary defect reactions transforming the mobile species S_D into the less mobile, major defect species S_S (for in-diffusion) or vice versa (for out-diffusion) will markedly affect the rate of chemical diffusion.

Kumar et al. (4) assumed the secondary reactions to be fast relative to the diffusion proper, so that defect equilibrium remains maintained at all penetration depths. They were able to relate on this basis the chemical diffusion in CdS to tracer diffusion constants. Recently Shaw (5) pointed out that the model used in this paper, with $[V_S^{\cdot}] > [Cd_i^{\cdot}]$ as deduced from $D^*_{Cd} = [Cd_i^{\cdot}] D_{Cd_i} > [Cd_i^{\cdot\cdot}] D_{Cd_i^{\cdot\cdot}}$, is not necessarily correct. From the latter inequality we can only deduce that $D_{Cd_i}/D_{Cd_i^{\cdot\cdot}} > [Cd_i^{\cdot\cdot}]/[Cd_i^{\cdot}]$. Thus if $D_{Cd_i} \gg D_{Cd_i^{\cdot\cdot}}$, we may still have $[Cd_i^{\cdot\cdot}] > [Cd_i^{\cdot}]$. Shaw further showed that the known $D^*_{Te} = D_{Te}[V_{Te}^{\cdot\cdot}]$ is not fast enough to maintain local equilibrium during chemical diffusion if the V_{Te} are generated at dislocations present in a reasonable concentration. However, local equilibrium may possibly be maintained by generation or annihilation of vacancies by the breaking up or growth of dislocation loops or vacancy clusters.

Zanio (1) and Rud et al. (2) reported the relaxation times of composition changes to be dependent on the direction of the changes, relaxation times found with increasing $p_{Cd}(\tau_+)$ being smaller than those found with decreasing $p_{Cd}(\tau_-)$. Normally ratios τ_-/τ_+ were in the range 1–1.5. In indium doped CdTe the ratio increased with increasing doping concentration, the largest values occurring if during the pressure change, the pressure passed the cadmium pressure where the incorporation mechanism of indium changes from one governed by $[In_{Cd}^{\cdot}] \approx [e']$ to $[In_{Cd}^{\cdot}] = [A_n'] +$ $2[A_n'']$, A_n indicating the native acceptors V_{Cd} and Te_i. Values of τ_-/τ_+ as large as 12 have been observed.

In some cases Rud et al. (2) observed a two-step relaxation consisting of an initial relaxation characterized by τ_{1-} followed after a certain time by a second relaxation characterized by τ_{2-}. The ratio's τ_{2-}/τ_{1-} are in the same range as reported for τ_-/τ_+. The occurrence of a second relaxation after a certain time suggests that nucleation is involved. This nucleation must be related to the secondary defect reactions referred to above. The way in which the secondary process affects the overall relaxation time τ is complicated by the fact that the final state reached after a pressure change is to a certain extent dependent on the rate of the secondary processes. Later in this paper we give an analysis of the relaxation process for the case that the secondary processes are governed by a relaxation time τ_r. The results are as follows.

For $\tau_r = \infty$ complete equilibrium is not reached; one observes an exponential relaxation due to the primary reaction only, the conductivity changing comparatively little (Fig. 1, $\sigma_0 \to \sigma'_\infty$, curve $c1$, $\tau = \tau_{c1}$).

For $\tau_r = 0$, equilibrium between the primary and secondary processes is maintained throughout. Now the relative conductivity change is larger (Fig. 1, $\sigma_0 \to \sigma_\infty$). The overall relaxation process is again exponential with a $\tau > \tau_{c1}$ (Fig. 1, τ_a).

For $0 < \tau_r < \infty$ the relaxation curve contains a factor $1 + k \exp(-t/\tau_r)$ in the exponent and
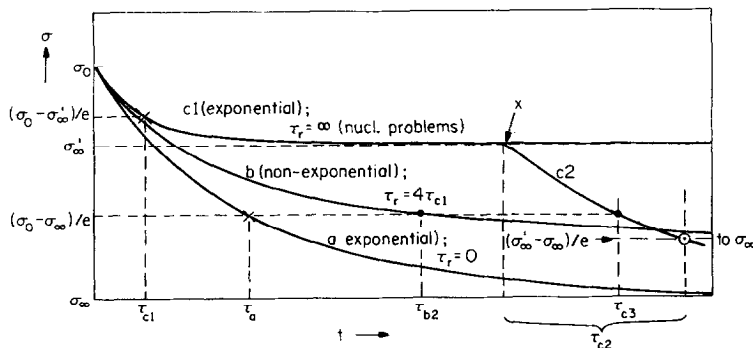

FIG. 1. Conductivity relaxation curves and the corresponding relaxation times, showing the effect of a secondary defect reaction with relaxation time τ_r. Curve b contains the factor $(1 + 2\exp{-t/\tau_r})$ in the exponent.

is no longer exponential (Fig. 1, curve b). All curves for τ_r finite have σ_∞ as the asymptotic value.

As long as we can recognize this asymptote, τ, defined as the time in which σ has changed from σ_0 to $\sigma_0 - (\sigma_0 - \sigma_\infty)/e$, even when the curve is not exponential, increases with increasing τ_r (Fig. 2, $\tau_a \rightarrow \tau_{c2} \rightarrow \tau_b$). When τ gets large, however, the curves flatten out and it is no longer possible to recognize the true asymptotic value. The tendency exists to under-estimate the expected conductivity reduction; this tends to decrease the experimentally determined τ to a false τ, τ_f (Fig. 2). With increase of τ_r, τ_f decreases and approaches τ_{c1}, the τ for $\tau_r = \infty$. A curve with $\tau_r = \infty$ can arise for two reasons. In the first place it may be that indeed the secondary process is extremely slow. It is also possible, however, that it occurs as a result of impaired nucleation of secondary products (e.g., vacancy clusters or dislocation loops). Once nucleation occurs, a second relaxation, characterized by the appropriate finite τ_r, sets in and the measured τ will have some value on the $\tau_a - \tau_b$ line of Fig. 2. Figure 1 shows such a two step relaxation in the curves $c1$, 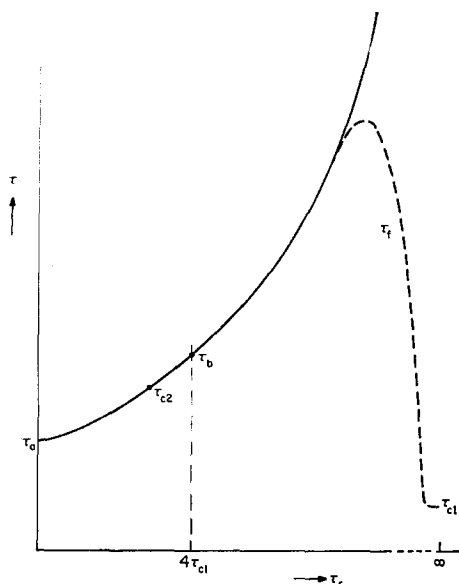$c2$, nucleation occurring at point x. One could formally characterize the curve pair $c1$, $c2$ by the relaxation time τ_{c3}, but this clearly makes little sense.

The largest τ's are to be expected for curves of type b with medium τ_r. For such medium τ_r, a difference between τ_r's at increasing and decreasing p_{Cd} (τ_{+r} and τ_{-r}) will lead to a difference between τ_+ and τ_- as observed.

In this paper we report on some further experiments in this area. A derivation of the ambipolar diffusion coefficient will be given for both pure and indium doped CdTe, and the relaxation effects are discussed on the basis of a previously established defect model (6).

2. Experimental

2.1. Relaxation Experiments on CdTe—2.7 × 10^{17} In cm^{-3}

Relaxation experiments in which the electrical conductivity of a sample was measured after step-wise positive and negative variations of p_{Cd} were carried out on a sample of CdTe doped with 2.7×10^{17} In cm^{-3} at 645° and 700°C, with p_{Cd} at the high p_{Cd}-side of the CdTe stability range. The rectangular sample with dimensions $0.6 \times 3 \times 7$ mm was cut from the same plate used earlier in tracer diffusion measurements (1). A four-probe method, with the probes arranged in a straight line, was used to measure conductivity. A constant current of 1 mA was applied through the current contacts at the end of the sample. The measured variable was the voltage across the central probes which were 3 mm apart. The experimental arrangement was similar to that used by Kumar et al. (4), in which the crystal and excess Cd are present in an evacuated quartz tube placed in a two-temperature furnace, with the crystal at the high, the Cd at the low-temperature end. In order to reduce the heat capacity of the cadmium reservoir, electrical leads were made to enter the tube at the high-temperature end. The cadmium pressure was varied by changing the temperature of the Cd reservoir, keeping the crystal temperature unchanged. This was done by changing the position of the tube relative to the furnace.

FIG. 2. τ as $f(\tau_r)$ as obtained from curves such as shown in Fig. 1.

The measured change of voltage is proportional to the resistivity ρ of the crystal which in turn is related to the change in the conductivity σ by

$$\frac{\rho_0}{\rho}\frac{\rho-\rho_\infty}{\rho_0-\rho_\infty}=\frac{\sigma-\sigma_\infty}{\sigma_0-\sigma_\infty}. \tag{2}$$

The subscripts 0 and ∞ refer to the initial and final values. For a flat sample with thickness d, the chemical diffusion coefficient $\tilde{D}$ is related to the relaxation time τ and the conductivity change $\Delta\sigma$ by (8):

$$\frac{\Delta\sigma}{\Delta\sigma_0}=\frac{\sigma-\sigma_\infty}{\sigma_0-\sigma_\infty}=\exp(-t/\tau)\quad\text{with}\quad \tau=\frac{d^2}{\pi^2\tilde{D}}. \tag{3}$$

The apparatus was designed to keep the response time of the temperature change of the cold end of the tube after a change in position to less than 30 seconds. The width of the temperature range in which experiments can be done is limited. Below 640°C the conductivity variations become too slow as a result of the decrease of $\tilde{D}$. Above 750°C we lose accuracy due to the increase in $\tilde{D}$ which brings τ close to the relaxation time of the pressure change.

2.2. Experimental Results

For positive Δp_{Cd}, all response curves had a purely exponential form. Values of $\tilde{D}$ deduced from the measured τ using Eq. (3) are shown
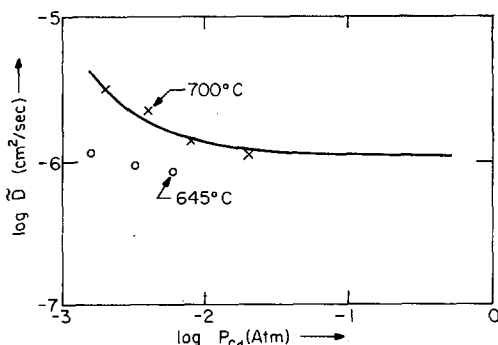

FIG. 3. Experimental values of the chemical diffusion constant, $\tilde{D}_{Cd}$ of CdTe—2.7 × 10^17 In cm^{-3} as a function of p_{Cd} measured at 700°C with $\Delta p_{Cd} > 0$, and a calculated curve, assuming maintenance of the secondary reaction equilibrium.

in Fig. 3. For negative Δp_{Cd} the relaxation times are slightly longer; at p_{Cd} of the boundary between the ranges $[In]=[e']$ and $[In]=\Sigma r[A_n^{r'}]$,

$$\tau_-/\tau_+ \approx 1.4 \pm 0.1.$$

3. Theoretical

3.1. Undoped CdTe

As we saw in the introduction, chemical diffusion changing the stoichiometry of a compound may involve ambipolar diffusion and secondary reactions by which fast moving minority defects are transformed into slow moving majority defects. In undoped CdS at high p_{Cd} the fast moving species is $Cd_i^{\cdot}$, the majority species $V_S^{\cdot\cdot}$, or $Cd_i^{\cdot\cdot}$ (5), and with maintenance of local defect equilibrium

$$\tilde{D} = \tfrac{3}{2}D_{Cd_i}[Cd_i^{\cdot}]/([Cd_i^{\cdot}]+[V_S^{\cdot}]+[Cd_i^{\cdot\cdot}])$$

$$= \tfrac{3}{2}D_{Cd}^{*}/([Cd_i^{\cdot}]+[V_S^{\cdot}]+[Cd_i^{\cdot\cdot}])$$

$$\approx \tfrac{3}{2}D_{Cd}^{*}/([V_S^{\cdot}]+[Cd_i^{\cdot\cdot}]) \tag{4}$$

The numerical factor $\tfrac{3}{2}$ accounts for the ambipolar character of the diffusion; the correlation coefficient for tracer diffusion by an interstitial mechanism was assumed to be one.

Since D_{Cd}^{*}, the Cd tracer diffusion coefficient is $\propto p_{Cd}^{2/3}$ while $[V_S^{\cdot}]$ and $[Cd_i^{\cdot\cdot}] \propto p_{Cd}^{1/3}$, one expects $\tilde{D} \propto p_{Cd}^{1/3}$. In undoped CdTe under similar conditions the fast moving species is $Cd_i^{\cdot\cdot}$, with this species probably the major positive species at $T > 800°C$, $V_{Te}^{\cdot\cdot}$ probably being the major species at $T < 800°C$ (6).

Secondary reactions involved in this case are the transfer of cadmium from an interstitial site to a lattice site, the Frenkel disorder reaction for Cd:

$$Cd_i^{\cdot\cdot} + V_{Cd}'' \rightleftarrows (Cd_iV_{Cd})^{\times} \rightleftarrows Cd_{Cd}^{\times} + V_{Cd,i}^{\times} \tag{5}$$
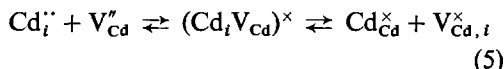
($V_{Cd,i}^{\times}$ being an unoccupied interstitial site open to Cd) and the reestablishment of equilibrium for Schottky disorder, upset as a result of reaction (5):

$$0 \rightarrow V_{Cd}'' + V_{Te}^{\cdot\cdot} + V_{Cd,i}^{\times} + V_{Te,i}^{\times}. \tag{6}$$
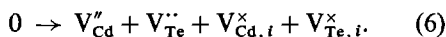
Both processes together result in the transformation of $Cd_i^{\cdot\cdot}$ into $V_{Te}^{\cdot\cdot}$ or vice versa, the

reactions going to the right for $\Delta p_{Cd} > 0$ to the left for $\Delta p_{Cd} < 0$:

$$Cd_i^{\cdot\cdot} \rightleftarrows Cd_{Cd}^x + V_{Te}^{\cdot\cdot} + 2V_{Cd,i}^x + V_{Te,i}^x. \quad (8)$$
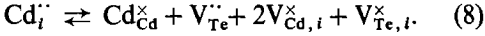
The Schottky reaction changes the volume of the crystal and therefore requires a volume source or sink. Note that ring diffusion which was found to contribute considerably to the tracer diffusion (7) does not contribute to the chemical diffusion.

The calculation of $\tilde{D}$ on the basis of the defect model, assuming ambipolar diffusion of $Cd_i^{\cdot\cdot}$ and e', and maintenance of equilibrium for the secondary defect reactions (5)–(8) proceeds along lines similar to those followed with CdS (3). Determining $\tilde{D}$ from the rate of change of the conductivity as given by (3), and remembering that $\sigma \propto$ the electron concentration c_e, provided by the donors Cd_i and V_{Te} with

$$c_e = 2(c_{Cd_i^{\cdot\cdot}} + c_{V_{Te}^{\cdot\cdot}}). \quad (10)$$

The particle current of electrons is related to $\tilde{D}$ by

$$J_e = -\tilde{D}\, dc_e/dx = -2\tilde{D}\, d(c_{Cd_i^{\cdot\cdot}} + c_{V_{Te}^{\cdot\cdot}})/dx. \quad (11)$$

Ambipolar diffusion of e' and $Cd_i^{\cdot\cdot}$ is described by

$$J_e = -D_e\, dc_e/dx + c_e\, D_e(q/kT)\, d\phi/dx \quad (12)$$

$$J_{Cd_i^{\cdot\cdot}} = -D_{Cd_i^{\cdot\cdot}}\, dc_{Cd_i^{\cdot\cdot}}/dx$$
$$\qquad - c_{Cd_i^{\cdot\cdot}}\, D_{Cd_i^{\cdot\cdot}}(2q/kT)\, d\phi/dx \quad (13)$$

with

$$J_e = 2J_{Cd_i^{\cdot\cdot}}. \quad (14)$$

Here ϕ is the inner electric potential, and D_e and D_{Cd_i} are the diffusion coefficients of e' and $Cd_i^{\cdot\cdot}$. Eliminating $d\phi/dx$ from (12) and (13) using (14), we find

$$J_e = 3D_{Cd_i^{\cdot\cdot}}\{[Cd_i^{\cdot\cdot}]/([Cd_i^{\cdot\cdot}] + [V_{Te}^{\cdot\cdot}])\}\, dc_e/dx \quad (15)$$

and, comparing (15) with (11)

$$\tilde{D} = 3D_{Cd_i^{\cdot\cdot}}[Cd_i^{\cdot\cdot}]/([Cd_i^{\cdot\cdot}] + [V_{Te}^{\cdot\cdot}])$$
$$\quad = 3D_{Cd}^*/([Cd_i^{\cdot\cdot}] + [V_{Te}^{\cdot\cdot}]), \quad (16)$$

taking again the correlation coefficient for normal interstitial diffusion equal to one. The difference in the numerical constants, 3/2 in

(4) and 3 in (16), results from the difference in charge of the diffusing species: $Cd_i^{\cdot}$ in CdS, $Cd_i^{\cdot\cdot}$ in CdTe.

D_{Cd}^*, $[Cd_i^{\cdot\cdot}]$ and $[V_{Te}^{\cdot\cdot}]$ are all $\propto p_{Cd}^{1/3}$, and therefore one expects $\tilde{D}_{Cd}$ to be independent of p_{Cd}—as actually observed (1). Using in Eq. (5)

$$D_{Cd}^* = 0.95 p_{Cd}^{1/3} \exp(-2.11 \text{ eV}/kT) \quad (17)$$

as reported by Chern et al. (7) and

$$[D_n^{\cdot\cdot}] = \tfrac{1}{2}[e']$$
$$\quad = 3.63 \times 10^{-3} p_{Cd}^{1/3} \exp(-0.62 \text{ eV}/kT) \quad (18)$$

as given in Ref. (6), we find

$$(\tilde{D}_{Cd})_{calc} = 7.89 \times 10^2 \exp(-1.49 \text{ eV}/kT). \quad (19)$$

Combination with (1) gives the ratio between the calculated and experimental values

$$\frac{\tilde{D}_{calc}}{\tilde{D}_{exp}} = r = 1.97 \times 10^2 \exp(-0.34 \text{ eV}/kT) \quad (20)$$

with $r = 2.15$ at 600°C, 3.4 at 700°C and 5 at 800°C. This relatively small discrepancy can be removed by assuming the secondary processes to be not infinitely fast. The fact that the discrepancy is largest at the highest temperature may seem to argue against this: we expect the largest activation energy for the slower process—the secondary reaction—and therefore would expect the discrepancy to become less at higher temperatures. If the secondary reaction would be the slowest process because it had the larger activation energy, the discrepancy would become less at higher temperatures. It is possible, however, that the secondary processes are slow primarily due to a small entropy, the activation energy being somewhat smaller than for the diffusion proper. Then the discrepancy would indeed increase at higher temperatures. Such a situation may indeed be present if the secondary process involves a volume source or sink for vacancies. It is also possible that the discrepancy is due to experimental errors in D_{Cd}^* or $\tilde{D}$. For a treatment involving a finite rate for the secondary process see Ref. (9).

3.2. CdTe—2.7×10^{17} In cm^{-3}

In indium doped crystals at medium cadmium pressures as used in our relaxation experiments, the fast moving species are V'_{Cd} and V''_{Cd}, other native species present being Te'_i, Te^x_i and Te'_i. The concentrations of the latter two are probably relatively small (6) and will be neglected. The local neutrality condition is

$$[In_{Cd}^{\cdot}] = [e'] + [V'_{Cd}] + [Te'_i] + 2[V''_{Cd}] \quad (21)$$

and the flow neutrality condition

$$J_{e'} + J_{V'_{Cd}} + 2J_{V''_{Cd}} = 0. \quad (22)$$

Writing expressions for the particle currents of V'_{Cd}, V''_{Cd} and e' similar to Eqs. (12) and (13), eliminating $d\phi/dx$ with the aid of (22), and comparing the expression for J_e with expression (11) defining $\tilde{D}$, we find

$$\tilde{D} = (1/c_e)(c_{V'_{Cd}} D_{V'_{Cd}} + 4c_{V''_{Cd}} D_{V''_{Cd}}) + (D_{V'_{Cd}} F' + D_{V''_{Cd}} F'') \quad (23)$$

with

$$F' = 1/(1 + B' + R), \qquad F'' = F' R,$$
$$B' = dc_{Te'_i}/dc_{V'_{Cd}}$$
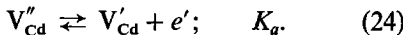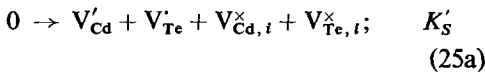
and

$$R = 2dc_{V''_{Cd}}/dc_{V'_{Cd}}$$

In order to evaluate B' and R we must consider the processes by which the concentrations of V''_{Cd}, V'_{Cd} and Te'_i vary.
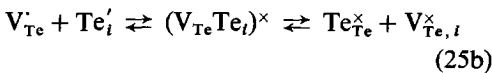
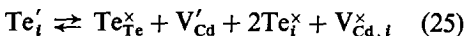Equilibrium between the fast moving species V'_{Cd} and V''_{Cd} is maintained by the ionization process

$$V''_{Cd} \rightleftarrows V'_{Cd} + e'; \qquad K_a. \quad (24)$$

That between V'_{Cd} and Te'_i involves the Schottky disorder reaction

$$0 \rightarrow V'_{Cd} + V^{\cdot}_{Te} + V^x_{Cd,i} + V^x_{Te,i}; \qquad K'_S \quad (25a)$$

and the Frenkel disorder reaction for Te

$$V^{\cdot}_{Te} + Te'_i \rightleftarrows (V_{Te}Te_i)^x \rightleftarrows Te^x_{Te} + V^x_{Te,i} \quad (25b)$$

which add up to

$$Te'_i \rightleftarrows Te^x_{Te} + V'_{Cd} + 2Te^x_i + V^x_{Cd,i} \quad (25)$$

$V^x_{Te,i}$ and $V^x_{Cd,i}$ are interstitial sites that can be occupied by Te and Cd, respectively. These reactions proceed to the right for $\Delta p_{Cd} > 0$, to the left in the opposite case. It may be assumed that local equilibrium for (24) is maintained. Then at all times

$$dc_{V''_{Cd}}/c_{V''_{Cd}} = dc_{V'_{Cd}}/c_{V'_{Cd}} + dc_{e'}/c_{e'}. \quad (26)$$

Reaction (25) on the other hand may be slow relative to the diffusion. If it is so slow that no transformation of V'_{Cd} into Te'_i takes place, there will still be transformation of V''_{Cd} into $V'_{Cd} + e'$ or vice versa during diffusion both because V'_{Cd} and V''_{Cd} have different diffusion constants and because of the non-linear character of (24). Let us call the rate of formation of V'_{Cd} and e' from V''_{Cd} under such conditions X. Then

$$\left. \begin{array}{l} dc_{V'_{Cd}}/dt = D_{V'_{Cd}} d^2 c_{V'_{Cd}}/dx^2 + X \\ dc_{e'}/dt = D_e d^2 c_e/dx^2 + X \\ dc_{V''_{Cd}}/dt = D_{V''} d^2 c_{V''_{Cd}}/dx^2 - X \end{array} \right\}. \quad (27)$$

If reaction (25) also occurs, this will lead to additional changes in the concentration of V''_{Cd}, V'_{Cd} and e' by the transformation of Te'_i into V'_{Cd} (reaction (25), rate Y) and of $Te'_i + e'$ into V''_{Cd} (combination of (25) and (24), rate Z).

With (25) occurring,

$$\left. \begin{array}{l} dc_{V'_{Cd}}/dt = D_{V'_{Cd}} d^2 c_{V'_{Cd}}/dx^2 + X + Y \\ dc_e/dt = D_e d^2 c_e/dx^2 + X - Z \\ dc_{V''_{Cd}}/dt = D_{V''_{Cd}} d^2 c_{V''_{Cd}}/dx^2 - X + Z \end{array} \right\} \quad (28)$$

Substituting (27) and (28) and taking the difference leads to

$$Y/c_{V'_{Cd}} = Z(1/c_e + 1/c_{V''_{Cd}}). \quad (29)$$

The amount of Te formed, $-\int (Y + Z)dt$, is a function of time. We can find an expression for it if we know how the reaction rates depend on concentration. This we do not, since we do not know the detailed reaction mechanism.

The transformation rates are proportional to the deviations of the concentrations of the various species from their equilibrium values. These deviations are increased by the diffusion process and reduced by the transformation, the latter always remaining smaller than the

former. When the diffusion proceeds, we expect the deviation and therewith the transformation rates to increase up to a maximum value close to the end of the diffusion process when the concentration gradients are reduced to zero. We shall introduce these maximum values of Y and Z, Y_{max} and Z_{max}, and assume that values at shorter times are related to it by

$$Y = f Y_{max}, \qquad Z = f Z_{max},$$

with

$$f = 1 - \exp(-t/\tau_r).$$

Here τ_r is the relaxation time of the transformation reactions. This approximation will be valid for most of the diffusion process, becoming invalid only close to the end of the diffusion which is not reached in our diffusion experiments.

Assuming $dc_{Te} \propto c_{Te}$ and $dc_{V'_{Cd}} \propto c_{V'_{Cd}}$, we can write at the point where Y and Z approach the values Y_{max} and Z_{max},

$$K' = c_{Te'_i}/c_{V'_{Cd}} = \frac{(dc_{Te'_i}/dt)_{max}}{(dc_{V'_{Cd}}/dt)_{max}}$$
$$= -(Y_{max} + Z_{max})/(D_{V'_{Cd}} d^2 c_{V'_{Cd}}/dx^2$$
$$+ X + Y_{max}). \qquad (31)$$

From (29) and (31) one gets

$$Z_{max} = Y_{max} c_e/(K_a + c_{V'_{Cd}}) \qquad (32)$$

$$Y_{max} = -K'(D_{V'_{Cd}} d^2 c_{V'_{Cd}}/dx^2$$
$$+ X)/\{K' + 1 + c_e/(K_a + c_{V'_{Cd}})\} \qquad (33)$$

leading to

$$B' \equiv dc_{Te'_i}/dc_{V'_{Cd}} =$$
$$\frac{\{1 + c_e/(K_a + c_{V'_{Cd}})\} K'\{1 - \exp(-t/\tau_r)\}}{\{1 + c_e/(K_a + c_{V'_{Cd}})\} + K' \exp(-t/\tau_r)}.$$
$$(34)$$

Differentiation of the local neutrality condition (21) gives

$$dc_{In} = 0 = dc_e + dc_{Te'_i} + dc_{V'_{Cd}} + 2dc_{V''_{Cd}}. \qquad (35)$$

Combination of (21), (26), (34) and (35) gives

$$R \equiv 2dc_{V''_{Cd}}/dc_{V'_{Cd}} =$$
$$\frac{2\{c_e - c_{V'_{Cd}}(1 + K')\}\{1 + c_e/(K_a + c_{V'_{Cd}})\}}{}$$
$$\frac{+ 2K' c_e\{1 + c_{V'_{Cd}}/(K_a + c_{V'_{Cd}})\} \exp -t/\tau_r}{(K_a + 2c_{V'_{Cd}})\{1 + c_e/(K_a}$$
$$+ c_{V'_{Cd}}) + K' \exp(-t/\tau_r)\}$$
$$(36)$$

with $K' = c_{Te'_i}/c_{V'_{Cd}}$. Equation (23) together with (34) and (36) gives the expression for $\tilde{D}$ in terms of $D_{V'_{Cd}}$ and $D_{V''_{Cd}}$, τ_r, equilibrium constants and the concentrations of various species.

For $[In] = 2.7 \times 10^{17}$ cm^{-3} and $T = 700°C$, $[In] \approx 5K_a$ while $K' \approx 1$ the expressions for F' and F'' holding at various p_{Cd} are as shown in Table I. Figure 3 shows experimental values of $\tilde{D}$ for CdTe—2.7 × 10^{17} cm^{-3} In as $f(p_{Cd})$ at 645 and 700°C, and values for 700°C calculated from (23) with the F's from Table I. There is excellent agreement if we take $\tau_r = 0$. A ratio $\tilde{D}_+/\tilde{D}_- = \tau_-/\tau_+$ slightly larger than one at medium p_{Cd} is explained by (23) with $\tau_{r+} < \tau_{r-}$. As seen in Table I, at high p_{Cd}, F' and F'' depend in the same way on τ_r. At low p_{Cd}, F' and F'' show a different dependence, but the terms in which they appear are negligibly small. Only at medium p_{Cd} does the ratio $\tau_{r+}/\tau_{r-} \neq 1$ noticeably affect $\tilde{D}$. At $T = 750°C$ and $K' > 1$, $\tilde{D}_+ = 1.5\tilde{D}_-$ is explained with $\tau_{r-} \approx \tau$ and $\tau_{r+} = \tau/10$ or $\tau_{r-}/\tau_{r+} = 10$. In order

TABLE I

APPROXIMATE FORMS OF EQUATION (23)

	Low p_{Cd}	Medium p_{Cd}	High p_{Cd}
Major native defect:	$[V'_{Cd}] = 5K_a/2$	$[V'_{Cd}] = [e'] = K_a$	$[e'] = 5K_a$
F':	$3\{1 + K' \exp(-t/\tau_r)\}$	$\dfrac{1\frac{1}{2} + \exp(-t/\tau_r)}{2 + \frac{1}{2}\exp(-t/\tau_r)}$	$\dfrac{6 + \exp(-t/\tau_r)}{72 + 5\exp(-t/\tau_r)}$
F'':	5	$\dfrac{-1 + \exp(-t/\tau_r)}{2 + \frac{1}{2}\exp(-t/\tau_r)}$	$\dfrac{10(6 + \exp(-t/\tau_r))}{72 + 5\exp(-t/\tau_r)}$

to avoid the uncertainties in the definition of τ for nonexponential curves discussed in the introduction, we have to construct the entire relaxation curve, taking τ to be equal to the time at which $\sigma = (\sigma_0 - \sigma_\infty)/e$.

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