Vacancies in $Hg_{1-x}Cd_xTe$[†]

August 16, 1999

H.F. Schaake, D. Chandra, F. Aqariden
DRS Infrared Technologies
PO Box 740188 Dallas, Texas 75374

J.T. Tregilgas
Raytheon Systems Company
Dallas, Texas 75365

ABSTRACT

Some measurements have been made recently of the carrier concentrations in vacancy-doped $Hg_{1-x}Cd_xTe$ with x=0.22, 0.29, 0.45 and 0.5. The anneals to establish the carrier concentrations were performed on both the mercury- and tellurium-rich sides of the phase field. Hole concentrations at measured 77K on the mercury side of the phase field for x=0 (measurement at 4K), 0.2, 0.22 and 0.29 are well described by the equation $3.13\text{x}10^{23}\exp(-(0.8+0.9*x)/kT)$. On the tellurium rich side, the hole concentrations varied as $7.00\text{x}10^{21}\exp(-(0.45+0.51*x)/kT)$, with a good fit to x=0.2,0.22,0.29 and 1. Published data on x=0.4 material is anomalous with this model, however. A measurement made on x=0.45 material tends to confirm the published data. It is proposed for small concentrations, the vacancy concentration in all $Hg_{1-x}Cd_xTe$ is proportional to (1-x), with the vacancy formation energy nearly independent of x. At higher temperatures, another mechanism results in a reduced measured concentration in comparison to a simple extrapolation of the low temperature results. Possible mechanisms are discussed.

1. Introduction

During the course of producing $Hg_{1-x}Cd_xTe$, the material is generally subjected to a variety of anneals under different Hg ambients. It has long been recognized that these anneals result in vacancies in the material whose concentration is reflective of the anneal and its ambient. The resulting defect structure of the material has significant impact on its use in focal plane arrays. Extensive work has been reported on material with x=0.2, and it can be said that this material is fairly well understood. The situation is less clear for other x values, however, making it difficult to predict defect properties of $Hg_{1-x}Cd_xTe$ into new spectral regions.

[†] This work was supported by IR & D funding from DRS Infrared Technologies and its predecessor, Raytheon Systems Company

Form SF298 Citation Data

Report Date *("DD MON YYYY")* 16081999	**Report Type** N/A	**Dates Covered (from... to)** *("DD MON YYYY")*

Title and Subtitle Vacancies in Hg1-xCdxTe	**Contract or Grant Number**
	Program Element Number
Authors	**Project Number**
	Task Number
	Work Unit Number
Performing Organization Name(s) and Address(es) DRS Infrared Technologies PO Box 740188 Dallas, Texas 75374	**Performing Organization Number(s)**
Sponsoring/Monitoring Agency Name(s) and Address(es)	**Monitoring Agency Acronym**
	Monitoring Agency Report Number(s)
Distribution/Availability Statement Approved for public release, distribution unlimited	
Supplementary Notes	
Abstract	
Subject Terms	
Document Classification unclassified	**Classification of SF298** unclassified
Classification of Abstract unclassified	**Limitation of Abstract** unlimited
Number of Pages 7	

In this work, measurements made at 77K on x=0.22, 0.29, 0.45 and 0.50 material annealed on both the mercury-rich and the tellurium-rich sides of the phase field are reported. The primary purpose of this effort has been to aid in the development of processes for diode fabrication, for which anneals near the phase limit are the most controllable. The composition of the reference phase at the phase limits is relatively independent of the x-value, being essentially pure mercury on the mercury-rich side of the existence region, and solid tellurium saturated with mercury on the tellurium-rich side of the existence region, at least below the eutectic temperature. This means that the mercury pressure is a function only of temperature. This in turn allows the annealed properties of $Hg_{1-x}Cd_xTe$ with different x values to be directly compared at the same temperature at these phase limits, with the only differences being in the $Hg_{1-x}Cd_xTe$ phases themselves. From these comparisons, relationships between $Hg_{1-x}Cd_xTe$ with different x values can be made. It is hoped that these relationships are predictive of materials with other x values, and that they shed light on the defect properties of the materials that may affect device performance.

2. Results

The experimental results are shown in Figure 1 for the mercury-rich anneals, and in Figure 2 for the tellurium-rich anneals.

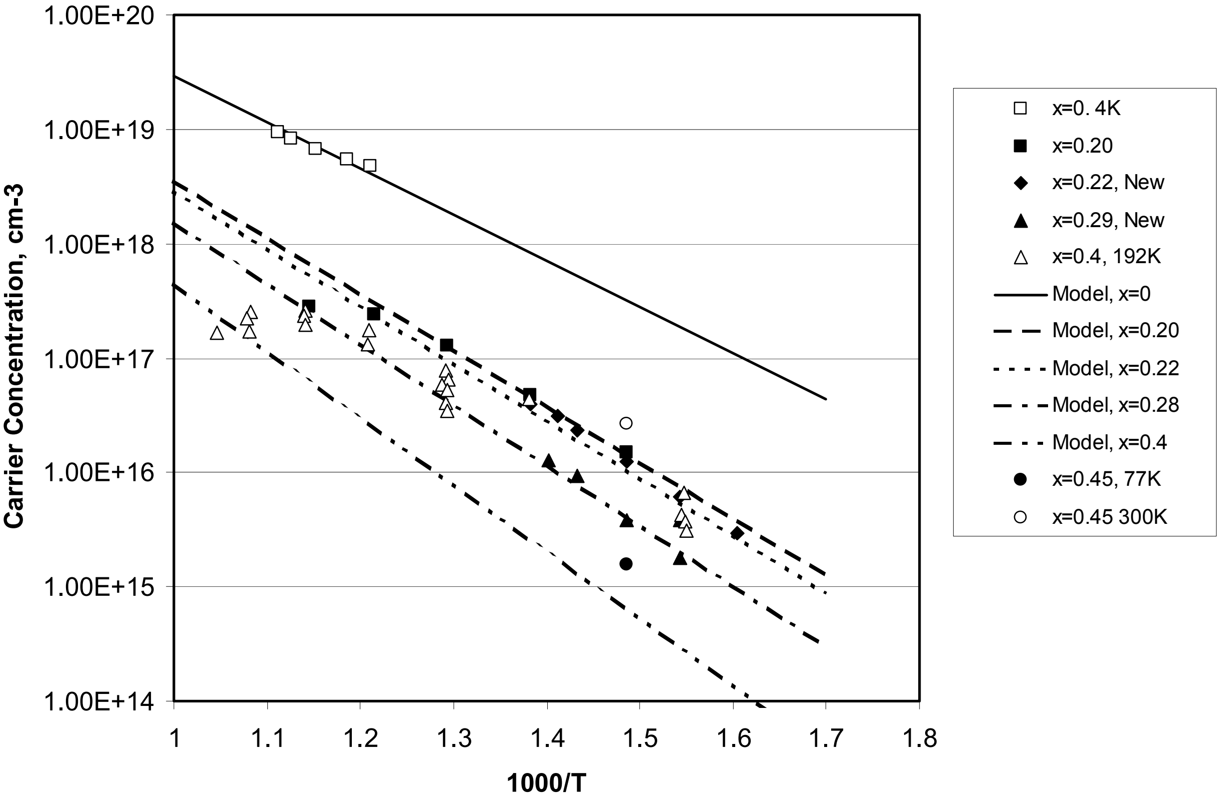

Figure 1. Carrier concentrations of $Hg_{1-x}Cd_xTe$ annealed on the mercury-rich side of the existence region for different x values. The data for x=0 is from reference 1, x=0.2 from 2, x=0.4 from 3 and 4. The data for x=0.22, x=0.29 and x=0.45 are new. The model is equation 1.

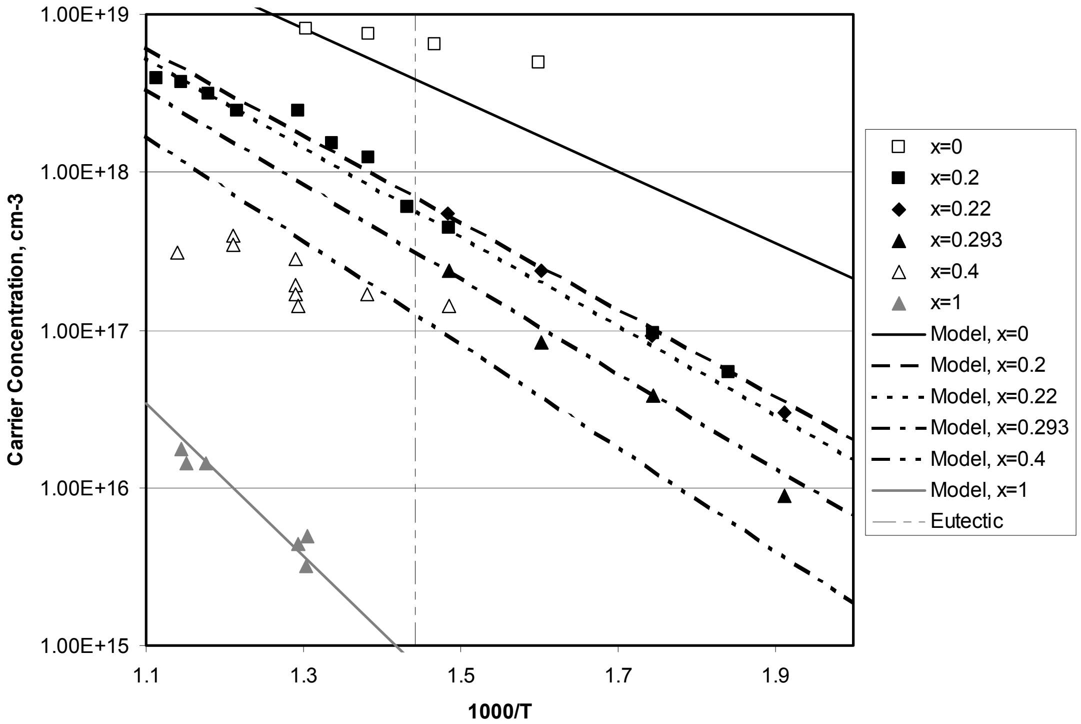

Figure 2. Carrier concentrations of $Hg_{1-x}Cd_xTe$ annealed on the tellurium-rich side of the existence region for different x values. The data for x=0 is from reference 1, x=0.2 from 2, x=0.4 from 3 and 4. The data for x=0.22, x=0.29 and x=0.45 are new. The model is equation 2.

3. Discussion

The results on the mercury-side of the phase field, Figure 1, can be fit to an equation (the Model lines in Figure 1):

$$p = 3.13x10^{23} \exp\left[-\frac{0.8+0.9x}{kT}\right] \tag{1}$$

This gives a fairly good fit to all data except for that of x=0.4. The results on the tellurium-side of the phase field, Figure 2, can be fit to the equation:

$$p = 7.00x10^{21} \exp\left[-\frac{0.45+0.51x}{kT}\right] \tag{2}$$

which gives a good fit to all data except x=0, and x=0.4.

The fit for these two equations is remarkably good, except for the x=0.4 data. This data is considerably different from that of lesser x-values, and shows significantly smaller activation energy. More important, for temperatures <400C (1000/T > 1.5) the measured carrier concentrations are greater for x=0.4 than for x=0.29, and comparable to those of x = 0.2. Since the vacancy concentration of x=0.29 cannot rationally be less than x=0.4, it would appear that the vacancies are not completely ionized at the measurement temperature of 77K for the x=0.29 data. For the x=0.2 data (measured at 77K) and the x=0.4 data (measured at 192K) the ionization is complete, at least for carrier concentrations less than ~1x10^{16}cm^{-3}. This interpretation is supported also by measurement of a sample of x=0.45 annealed at 400C on the mercury side of the phase field. As shown in Figure 1, the carrier concentration measured at room temperature (where, according to Hansen, Schmit and Casselman[5], $n_{i} < 10^{14}$cm^{-3}) is also greater than the x=0.29 data for the same anneal, and comparable to the carrier concentration of x=0.2 (at 77K). Thus, at suitably low vacancy concentrations, it appears that the vacancy concentration of $Hg_{1-x}Cd_xTe$ is nearly independent of x. In the following, we ignore the results at x=0, as the solid is a semimetal.

A simple model that incorporates the previous work of Vydyanath[3,6] and Su, et al.[7] is able to fit this data as shown in 3 and Figure 4. Assuming that the vacancies are doubly ionized throughout the annealing regime, and with p_i the intrinsic carrier concentration, the mass action equation is given by:

$$\frac{p_{Hg}[V''][h^*]^2}{p_i^2(1-x)} = K\exp\left(-\frac{E_{V''}}{kT}\right) \tag{3}$$

There are two limits of interest. First is when the vacancy concentration is very small, and the hole concentration is thus equal to the intrinsic carrier concentration:

for $h^\bullet = p_i$:

$$[V''] = \frac{K(1-x)\exp\left(-\frac{E_{V''}}{kT}\right)}{p_{Hg}} \tag{4}$$

The second regime is when the vacancy concentration is large, and the solid is extrinsic.

for $h^\bullet = 2[V'']$

$$[V''] = \frac{(K(1-x))^{1/3}\,p_i^{2/3}\exp\left(-\frac{E_{V''}}{3kT}\right)}{(4p_{Hg})^{1/3}} \tag{5}$$

These equations may be fit to the data. Essentially, there are only 2 parameters to fit, K and $E_{V''}$, the formation energy of a doubly-ionized vacancy in intrinsic HgCdTe. To fit the data, K and $E_{V''}$ were determined from x=0.2 data. On the mercury side of the phase field, equations 4 and 5 become, respectively:

$$[V''] = 2.81x10^{22}(1-x)\exp\left[-\frac{0.65}{kT}\right] \tag{6a}$$

$$[V''] = 1.92x10^{7}(1-x)^{1/3}\,p_i^{2/3}\exp\left(-\frac{0.22}{kT}\right) \tag{6b}$$

while on the mercury rich-side, they become:

$$[V''] = 2.50x10^{23}(1-x)\exp\left[-\frac{1.00}{kT}\right] \tag{7a}$$

$$[V''] = 3.97x10^7 (1-x)^{1/3} p_i^{2/3} \exp\left(-\frac{0.33}{kT}\right) \tag{7b}$$

Equations 6 and 7 are plotted in Figures 3 and 4, using the intrinsic carrier concentration predicted by Hansen, Schmit and Casselman[5]. For x=0.293, the carrier concentrations have been reduced by a factor of 2.5 for anneals on both sides of the phase field, under the assumption that the vacancies are only 40% ionized at 77K.

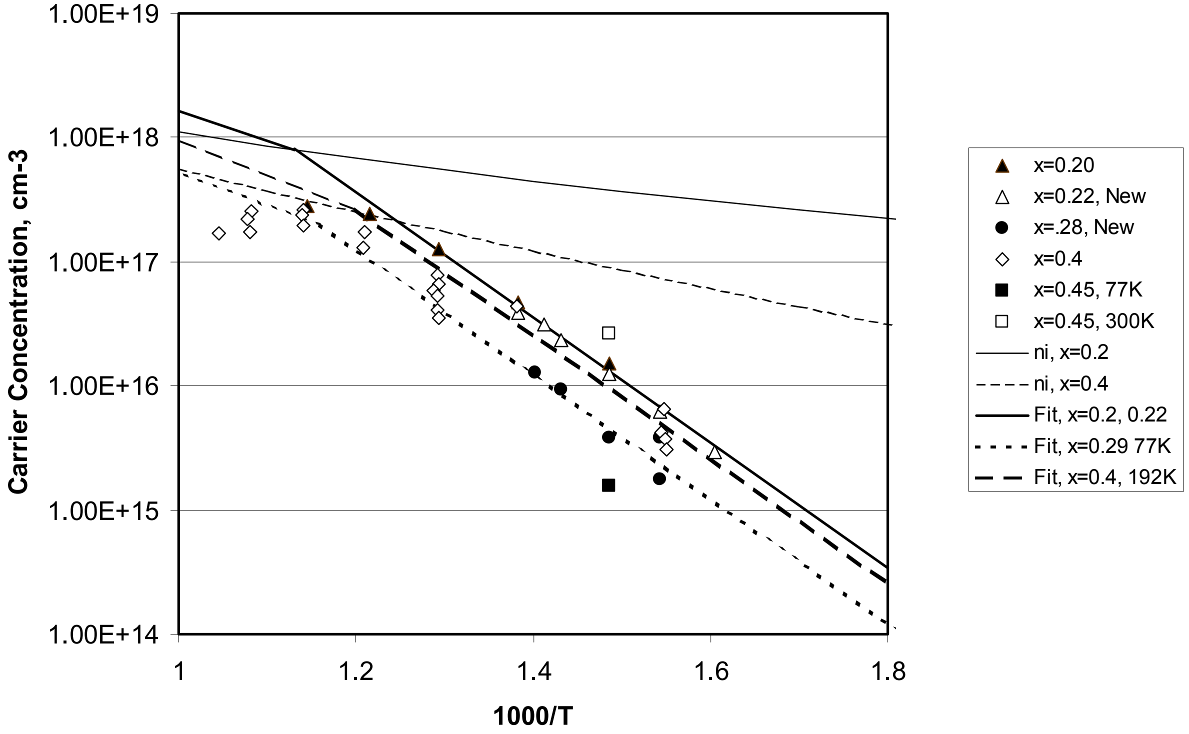

Figure 3. Carrier concentration data for anneals on the mercury-rich side of the phase field.

The fit is quite good, overall. At low concentrations, the material is intrinsic, and the vacancy concentration is inversely proportional to the mercury vapor pressure. At suitably high annealing temperatures the vacancy concentrations will become high enough that the material will become extrinsic. As pointed out by Vydyanath[3], when this happens, the vacancy concentration will become inversely proportional to the cube root of the mercury pressure, again assuming that the vacancy is doubly ionized. Under these circumstances, the activation energy becomes one-third of that of the activation energy at low concentrations. The extrinsic carrier concentrations predicted by Hansen, Schmit and Casselman[5] are shown in 3 and Figure 4 by the thin lines. It should be remembered that these values are extrapolations from data taken at room temperature and below, and may be in considerable error in the temperature regime covered in these figures. For carrier concentrations below n_i, equations 6a or 7a are applicable, while above, equations 6b or 7b are used. The only major discrepancy is in the high concentration region for x=0.2 on the tellurium side of the phase field (Figure 4). Increasing the intrinsic carrier concentration for this x-value by 40% from that predicted by Hansen, et al.[5] results in good agreement with experiment.

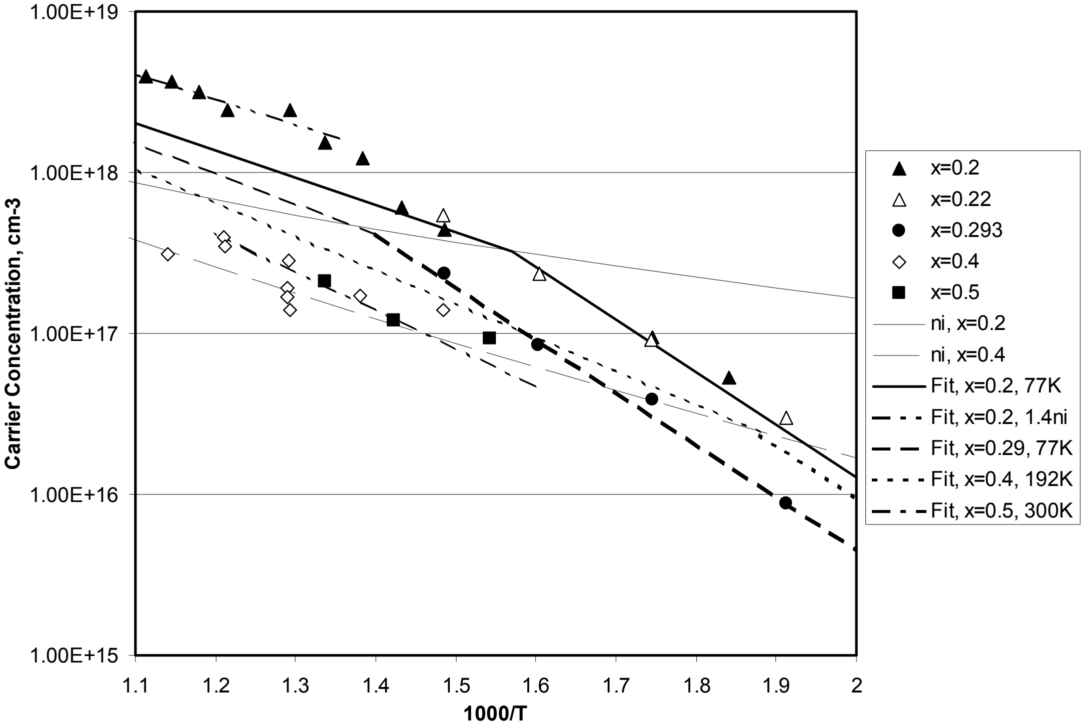

Figure 4. Carrier concentration data for anneals on the tellurium-rich side of the phase field.

There are several points worth emphasizing in this work:

1. Equations 6 and 7, in conjunction with the intrinsic carrier concentration predicted by the work of Hansen, et al.[5], describe the vacancy concentrations in $Hg_{1-x}Cd_xTe$ that result from annealing at the limits of the phase field. Extension to all mercury pressures in between is straightforward. A small correction is necessary to the intrinsic carrier concentrations for x=0.2 to gain agreement with experiment.
2. The model points to the vacancy formation energy being independent of x-value. Thus, at least at low concentrations, the vacancy concentration in different alloys annealed at the same temperature differs only by a fact of (1-x).
3. The data indicate that x=0.2 material becomes extrinsic on the tellurium side of the phase field. In previous work[2] it was postulated that the break in the activation energy which was observed on the tellurium rich side of the phase field was the result of the transition in the tellurium-rich reference phase on passing through the eutectic temperature. While a change in the reference field composition cannot be ruled out at this high temperature, where the liquid phase is beginning to amass a substantial amount of mercury, the modeling makes such a transition seem reasonable.

4. Vacancies are not completely ionized at 77K in the x=0.29 alloy. The carrier concentration is reduced by a factor of ~2.5 from the fully ionized state.

Additional work is needed, particularly with the x=0.29 alloy, and with some higher x values. Nevertheless, there is substantial agreement with the simple model described by equations 6 and 7, allowing the calculation of vacancy concentrations from a simple spreadsheet.

Acknowledgments

The authors gratefully acknowledge helpful conversations with Mike Kinch, Pok-Kai Liao, and Marcy Berding.

---

[1] A.J. Strauss and R.F. Brebrick, 513 (1985), J. Phys. Chem. Solids **31**, 2293 (1970).
[2] H.F. Schaake, J. Electron. Material. **14**, 513 (1985).
[3] H.R. Vydyanath, J.C. Donovan and D.A. Nelson, J. Electrochem. Soc., **128**, 2625 (1981).
[4] J.L. Schmit and E.L. Stelzer, J. Electron. Mater. **7**, 65 (1978).
[5] G.L. Hansen, J.L. Schmit, and T.N. Casselman, J. Appl. Phys. **53**, 7099 (1982).
[6] H.R. Vydyanath, J. Electrochem. Soc. **128**, 2609, 1981.
[7] C.-H. Su, P.-K. Liao and R.F. Brebrick, J. Electron. Mater. **12**, 771 (1983).