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Vapor-phase stoichiometry and heat treatment of CdTe starting material for physical vapor transport

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Abstract

Six batches of CdTe, having total amounts of material from 99 to 203 g and gross mole fraction of Te, X_{Te} , 0.499954–0.500138, were synthesized from pure Cd and Te elements. The vapor-phase stoichiometry of the as-synthesized CdTe batches was determined from the partial pressure of Te_2 , P_{Te_2} , using an optical absorption technique. The measured vapor compositions at 870°C were Te-rich for all of the batches with partial pressure ratios of Cd to Te_2 , P_{Cd}/P_{Te_2} , ranging from 0.00742 to 1.92. After the heat treatment of baking under dynamic vacuum at 870°C for 8 min, the vapor-phase compositions moved toward that of the congruent sublimation, i.e. $P_{Cd}/P_{Te_2} = 2.0$, with the measured P_{Cd}/P_{Te_2} varying from 1.84 to 3.47. The partial pressure measurements on one of the heat-treated samples also showed that the sample remained close to the congruent sublimation condition over the temperature range 800–880°C. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The partial pressures of the species II and VI₂ in equilibrium with the II–VI semiconducting compounds, at a fixed temperature, can vary over orders of magnitude as the composition of the compound varying over the narrow homogeneity

range from Group II saturation to Group VI saturation [1–3]. As a result, the transport rate of the vapor species in the physical vapor transport (PVT) process can also vary from a maximum transport rate corresponding to the condition of congruent sublimation for the solid phase to transport rates which are orders of magnitude lower when the solid composition deviates significantly from congruent sublimation. A precise control on the stoichiometry of the starting compound from the weighing of the constituent elements is practically impossible. Nevertheless, with certain heat-treatment methods the partial pressures over the starting compound material can be reasonably reproduced for the

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congruent sublimation condition. One of the methods to adjust the stoichiometry of the starting material is to bake out the material at the processing temperature under a dynamic vacuum condition. However, the effectiveness of the heat treatment on the vapor-phase composition was never reported nor confirmed. The direct way to determine vapor-phase stoichiometry is by measurement of the partial pressures coexisting with the sample. Using an optical absorption technique, Brebrick and co-workers have reported partial pressure data over the systems of HgTe [4, 5], HgSe [6], CdTe [3, 7], ZnTe [2], ZnSe [8, 9], PbTe [10, 11], SnTe [12, 13], PbSnTe [13], HgCdTe [14–16] and HgZnTe [17]. In this paper, using the same optical absorption technique, we report the effectiveness of the heat treatment by measuring the partial pressures of Te_2 , P_{Te_2} , over a series of as-synthesized CdTe samples as well as P_{Te_2} over these samples after they have been heat treated under dynamic vacuum.

2. Experimental procedure

2.1. Homogenization of CdTe

The ampoules were made from either 27×25 (27 mm OD, 25 mm ID), 23×20 or 22×20 mm fused silica tubings supplied by Heraeus Amersil, Inc. The ampoules were cleaned and outgassed at 1045°C under vacuum for over 16 h and, except for batch # 13, were then graphitized inside by flowing a mixture of 10% methane-Ar gas at 1045°C for 5–10 min. The starting elements were quadruple

zone refined (QZR), six–nine grade, 7 mm diameter Cd rods and QZR, six–nine grade Te bars from Johnson Matthey, Inc. The Cd bars were cut into approximately 1.5 cm segments and the Te bars were cut into chunks with typical linear dimensions of 2–4 mm. The elements were weighed to an accuracy of 0.1 mg. The ampoules were sealed under vacuum after the elements had been loaded with the Cd rods surrounded by the Te chunks. The amounts of Cd and Te in each ampoule as well as the corresponding gross Te mole fraction are listed in Table 1. The sealed ampoules were heated inside a furnace with an isothermal heat-pipe liner from room temperature to the homogenization temperatures, T_{H} , in several hours and maintained at T_{H} for certain hours before cool down. On batch # 6 the furnace was heated from room temperature to 500°C in 1 h and maintained at 500°C for 22 h before being heated to 925°C in 2 h. The homogenization temperature, T_{H} , and the time at T_{H} are also listed in Table 1. During heat-up the homogenization reaction takes place at the CdTe–Te eutectic temperature of 447.2°C [18]. The readings of the thermocouple attached to the ampoule jumped from 450°C to over 500°C (600°C on batch # 11) within 1 min because of the heat from the exothermic eutectic reaction.

2.2. Heat treatment and partial pressure measurements

After the homogenization process, the ampoule for each batch was opened and the reacted sponge-like CdTe was crushed, ground and mixed with mortar and pestle into particles of diameter less

Table 1
Amounts of Cd and Te, the corresponding Te content, the homogenization temperature, T_{H} , and the homogenization duration for each batch

Batch number	Cd (g)	Te (g)	$X_{\text{Te}} - \frac{1}{2}$	T_{H} ($^\circ\text{C}$)	T_{H} (h)
6	61.1715	69.4311	-4.6×10^{-5}	925	63
7	71.1613	80.7791	-1.7×10^{-5}	925	16
9	64.3485	73.0792	9.8×10^{-5}	955	64
10	77.0927	87.5088	-2.6×10^{-5}	1015	39
11	95.1116	107.9900	3.8×10^{-5}	985	40
13	46.5623	52.8885	13.8×10^{-5}	940	21

than 0.5 mm. The T-shape cells for the optical absorption measurement were made of fused silica with path lengths varying from 18 to 30 mm. The cells were cleaned and outgassed at 1000–1030°C for over 16 h before loading the samples. One set of the optical cells was loaded with the as-synthesized material from various batches and sealed under vacuum. The other cells were loaded with the as-synthesized materials followed by a heat-treatment process to adjust the stoichiometry prior to seal off. The heat treatment of these cells was performed by baking out the loaded cell at the processed temperature under dynamic vacuum. Table 2 lists the cell number (corresponding to the CdTe batch), the amounts of CdTe loaded, the bake-out temperature and the bake-out duration for each optical cell. The amounts of CdTe as well as the bake-out temperatures were selected to match the parameters usually employed in our laboratory for the crystal growth of CdTe by physical vapor transport. The loss of the material during the baking process under vacuum was reasonable. After baking at 870°C for 8 min the loss of a typical 18 g charge of CdTe was 1.8 g, i.e. about 10%.

The basic principles for the partial pressure measurements and the experimental procedure have been described in detail in Refs. [2–17]. In brief, the sample beam of a double-beam monochromator travelled along the top of a constant temperature T-shaped cell and passed through the optical windows. During measurements, the

sample, located at the bottom of the vertical leg of the T-shaped cell, was held at one of a set of temperatures lower than the optical path temperature. The optical absorbance was measured between 190 and 800 nm and the partial pressures of individual vapor species were calculated using the data determined from the calibration runs with pure elements in the cells. As mentioned in the Introduction, the predominant vapor species in equilibrium with condensed CdTe are Cd and Te₂. All other thermodynamically possible Te monomer or polymers have partial pressures at least two orders of magnitude lower than that of Te₂ under the processing temperature and condition. Therefore, only the Te dimer will be considered in the measurements of stoichiometry. For all the cells the measurements indicated that the samples were either Te-rich or near congruent sublimation. Under these conditions the 238.7 nm atomic Cd absorption peak was not strong enough to give accurate measurements of P_{Cd} . The partial pressures of Te₂ were taken as the average of several values calculated from the Beer's law constants established in the calibration runs of pure Te for the wavelengths between 363.4 to 537.2 nm [16]. For each cell the partial pressure of Te₂ was measured while the sample was held at 870°C and the optical cell was at 900°C. The base line was established with the sample at 400°C. Each cell was held at an 870°C sample temperature for at least 24 h prior to the measurements.

Table 2

Amounts of CdTe loaded, heat-treatment conditions, the measured partial pressure of Te₂, P_{Te_2} , and the calculated pressure ratio, P_{Cd}/P_{Te_2} , at 870°C for as-synthesized and heat treated batches

Cell	Amount of CdTe (g)	Heat-treatment temperature (°C)	Heat-treatment duration (min)	P_{Te_2} (atm) at 870°C	P_{Cd}/P_{Te_2} at 870°C
6	15.0	—	—	4.06×10^{-3}	1.92
7	15.0	—	—	1.65×10^{-1}	0.00742
7A	13.0	870	8	3.44×10^{-3}	2.47
9	12.4	—	—	8.90×10^{-2}	0.0187
10	14.9	—	—	4.95×10^{-3}	1.43
10A	20.3	870	8	2.74×10^{-3}	3.47
11	6.9	—	—	1.51×10^{-2}	0.268
11A	20.0	860	8	2.96×10^{-3}	3.11
13A	17.9	800	8	4.18×10^{-3}	1.84

3. Results

The measured partial pressure of Te_2 at 870°C for each optical cell is given in the 5th column of Table 2. The given values were usually the average of two measurements obtained after the cells were at temperature for 24 and 48 h. The corresponding partial pressures of Cd can be obtained from the stoichiometric invariant, ΔG_f , the Gibbs energy of formation of CdTe from the vapor phase [19]:

$$\begin{aligned} \Delta G_f &= RT \ln(P_{\text{Cd}} P_{\text{Te}_2}^{1/2}) \\ &= -68\,640 + 44.94T \text{ (cal/mol)}. \end{aligned} \quad (1)$$

The stoichiometry of the vapor phase at 870°C , defined as $P_{\text{Cd}}/P_{\text{Te}_2}$, was then calculated for each cell using the measured P_{Te_2} and the calculated P_{Cd} and is given in the last column of Table 2.

The vapor-phase stoichiometry at temperatures other than 870°C was also measured for cell 10A and is plotted in Fig. 1. The first series of measured P_{Te_2} is shown as open circles and was started at about 825°C ($1000/T = 0.91$). Several measurements were taken when the sample temperature

was increasing to above 880°C before the sample was cooled to 795°C . The second series of measurements is shown as solid squares and agreed well with the results of the first series. The time between each run is also given in the figure. The solid line shown is the P_{Te_2} for the congruent sublimation condition, i.e. $P_{\text{Cd}}/P_{\text{Te}_2} = 2.0$.

4. Discussion

The measured partial pressures of Te_2 over various as-synthesized CdTe batches, having total amounts of material from 99 to 203 g and gross Te mole fraction, X_{Te} , from 0.499954 to 0.500138, show that the vapor compositions at 870°C were always Te-rich. The P_{Te_2} in equilibrium with four CdTe samples of known condensed-phase compositions have previously been measured over the temperature range $635\text{--}1025^\circ\text{C}$ [7]. The measured P_{Te_2} at 870°C and the corresponding Te contents for these four samples were scaled from Figs. 2 and 4 of Ref. [7], respectively, and are tabulated in Table 3. By comparing the measured P_{Te_2} of our

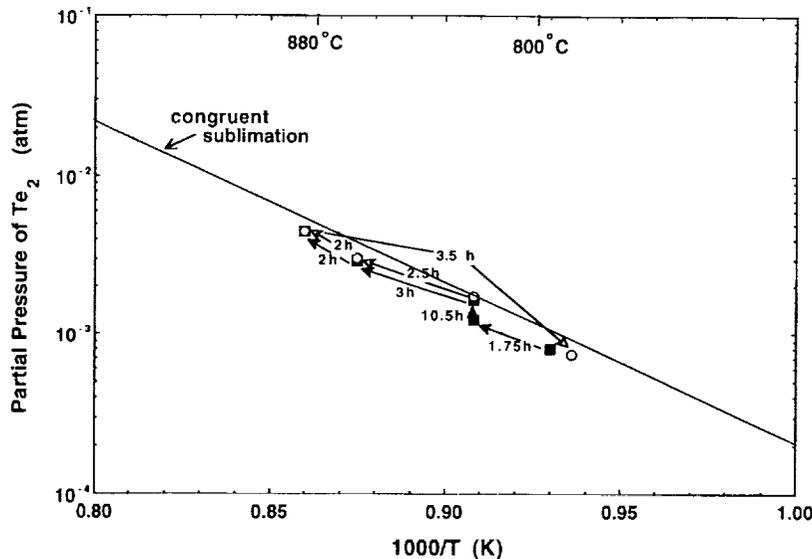


Fig. 1. The measured P_{Te_2} as a function of $1000/T$ for cell 10 A. The first series of measured P_{Te_2} is shown as open circles and was started at about 825°C ($1000/T = 0.91$). Several measurements were taken when the sample temperature was increasing to above 880°C before the sample was cooled to 795°C . The second series of measurements is shown as solid squares. The time between each run is also given.

Table 3
Te mole fraction, X_{Te} and measured P_{Te_2} at 870°C for CdTe samples from Ref. [7]

Samples	$X_{Te} - \frac{1}{2}$	P_{Te_2} (atm)
CT-93E	4.4×10^{-5}	0.135
CT-92A	2.2×10^{-5}	0.105
CT92-C	1.4×10^{-5}	0.0595
CT92-D	1.2×10^{-5}	0.0306
Congruent sublimation ^a	0.3×10^{-5}	0.00396

^aRef. [20].

as-synthesized samples with those in Table 3, it can be concluded that (a) the samples in cell #6 and #10 were near the congruent sublimation composition at 870°C (from a defect chemistry analysis, [20], this congruent sublimation composition is $(X_{Te} - \frac{1}{2}) = 0.3 \times 10^{-5}$); (b) having $P_{Te_2} = 0.165$ atm at 870°C the sample in cell #7 was almost Te-saturated with $(X_{Te} - \frac{1}{2})$ greater than 4.4×10^{-5} (note: the equilibrium P_{Te_2} for Te-saturated condition at 870°C is 0.18 atm [7]); (c) the sample in cell #9, with the measured $P_{Te_2} = 0.089$ atm at 870°C, has composition $(X_{Te} - \frac{1}{2})$ in the range 1.4 – 2.2×10^{-5} ; (d) the CdTe in cell #10 and #11 have $(X_{Te} - \frac{1}{2})$ values below 1.2×10^{-5} and above that for congruent sublimation, i.e. $(X_{Te} - \frac{1}{2}) = 0.3 \times 10^{-5}$, with the value for cell #10 lower than that for cell #11. A possible cause for the Te-rich nature of the as-synthesized CdTe samples is that during the grinding of the synthesized material, occasionally, a small smear of unreacted Cd element was found and was taken out.

Table 2 clearly shows that after the heat treatment under dynamic vacuum, the vapor-phase compositions moved toward that of congruent sublimation with the measured P_{Cd}/P_{Te_2} varying from 1.84 to 3.47. The error associated with the measured P_{Te_2} is estimated to be 15%. With the same error assumed for the ΔG_f given in Eq. (1), the experimentally measured P_{Cd}/P_{Te_2} for a congruently subliming CdTe sample would be in the range 1.38–2.93. The rate-controlling step for the heat treatment should be the solid-state diffusion inside each CdTe particle. The composition of the sample in each cell changed from its original value as outlined in the last paragraph to a value close to

that of congruent sublimation during the 8 min bake out even when the starting composition was near the Te-saturated condition such as the case of cell #7. The change in composition stopped when the sample reached the congruent sublimation condition because the sample started to lose Cd and Te at the same rate through the sublimation process. The required baking time can be estimated from the CdTe interdiffusion coefficient reported by Brown et al. [21] which gave $D_{CdTe} = 3.4 \times 10^{-5}$ cm²/s at 870°C. The estimated diffusion length $(Dt)^{1/2}$ for 8 min annealing time is 0.128 cm, which is about 5 times the radius of the ground particle. Also, although the heat treatment was performed at 870°C the heat-treated sample remains close to the congruent sublimation condition in the temperature range 800–880°C as indicated in Fig. 1. This was also evident from the defect chemistry analysis in Ref. [20]; the congruent sublimation composition almost follows a constant X_{Te} curve for temperatures below 900°C.

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