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

Ching-Hua Su\textsuperscript{a,*}, Yi-Gao Sha\textsuperscript{a,1}, S.L. Lehoczky\textsuperscript{a}, Hao-Chieh Liu\textsuperscript{b}, Rei Fang\textsuperscript{b}, R.F. Brebrick\textsuperscript{b}

\textsuperscript{a}Space Sciences Laboratory, NASA/ Marshall Space Flight Center, Huntsville, AL 35812, USA
\textsuperscript{b}Materials Science and Metallurgy Program, Marquette University, Milwaukee, WI 53233, USA

Received 19 April 1997; accepted 18 August 1997
Scope of the Journal

Experimental and theoretical contributions are invited in the following fields: Theory of nucleation and growth, molecular kinetics and transport phenomena, crystallization in viscous media such as polymers and glasses. Crystal growth of metals, minerals, semiconductors, magnets, inorganic and organic biology. Substrates in bulk or as thin films. Apparatus instrumentation and techniques for crystal growth, and purification methods. Characterization of single crystals by physical and chemical methods.

Abstracted/indexed in:
American Industry Abstracts; Chemical Abstracts; Current Contents; Physical, Chemical and Engineering Sciences. EI Compendex Plus; Engineering Index; INSPEC; Metals Abstracts.

Subscription Information 1998
Volumes 182–194 of Journal of Crystal Growth (ISSN 0022-0248) are scheduled for publication (frequency semimonthly). Prices are available from the publishers upon request. Subscriptions are accepted on a prepaid basis only. Issues are sent by SAL (Surface Air Lifted) mail wherever this service is available. Airmail rates are available upon request. Please address all inquiries regarding orders and subscriptions to: Elsevier Science, B.V., Order Fulfillment Department P.O. Box 211, 1000 AE Amsterdam, The Netherlands Tel: +31 20 445 5642, Fax: +31 20 445 5598

The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper) North-Holland, an imprint of Elsevier Science

PRINTED IN THE NETHERLANDS
Vapor-phase stoichiometry and heat treatment of CdTe starting material for physical vapor transport

Ching-Hua Su, Yi-Gao Sha, S.L. Lehoczky, Hao-Chieh Liu, Rei Fang, R.F. Brebrick

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 Te₂, P_{Te₂}, 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 Te₂, P_{Cd}/P_{Te₂}, 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_{Te₂} = 2.0, with the measured P_{Cd}/P_{Te₂} 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.

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

Received 19 April 1997; accepted 18 August 1997

© 1998 Elsevier Science B.V. All rights reserved.
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 x 25 (27 mm OD, 25 mm ID), 23 x 20 or 22 x 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>
<thead>
<tr>
<th>Batch number</th>
<th>Cd (g)</th>
<th>Te (g)</th>
<th>$X_{Te} - \frac{1}{2}$</th>
<th>$T_h$ (°C)</th>
<th>$T_h$ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>61.1715</td>
<td>69.4311</td>
<td>$-4.6 \times 10^{-5}$</td>
<td>925</td>
<td>63</td>
</tr>
<tr>
<td>7</td>
<td>71.1613</td>
<td>80.7791</td>
<td>$-1.7 \times 10^{-5}$</td>
<td>925</td>
<td>16</td>
</tr>
<tr>
<td>9</td>
<td>64.3485</td>
<td>73.0792</td>
<td>$9.8 \times 10^{-5}$</td>
<td>955</td>
<td>64</td>
</tr>
<tr>
<td>10</td>
<td>77.0927</td>
<td>87.5088</td>
<td>$-2.6 \times 10^{-5}$</td>
<td>1015</td>
<td>39</td>
</tr>
<tr>
<td>11</td>
<td>95.1116</td>
<td>107.9900</td>
<td>$3.8 \times 10^{-5}$</td>
<td>985</td>
<td>40</td>
</tr>
<tr>
<td>13</td>
<td>46.5623</td>
<td>52.8885</td>
<td>$13.8 \times 10^{-5}$</td>
<td>940</td>
<td>21</td>
</tr>
</tbody>
</table>
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 \( P_{\text{Cd}} \). 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>
<thead>
<tr>
<th>Cell</th>
<th>Amount of CdTe (g)</th>
<th>Heat-treatment temperature (°C)</th>
<th>Heat-treatment duration (min)</th>
<th>( P_{\text{Te}_2} ) (atm) at 870°C</th>
<th>( P_{\text{Cd}}/P_{\text{Te}_2} ) at 870°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>15.0</td>
<td>–</td>
<td>–</td>
<td>4.06 × 10⁻³</td>
<td>1.92</td>
</tr>
<tr>
<td>7</td>
<td>15.0</td>
<td>–</td>
<td>–</td>
<td>1.65 × 10⁻¹</td>
<td>0.00742</td>
</tr>
<tr>
<td>7A</td>
<td>13.0</td>
<td>870</td>
<td>8</td>
<td>3.44 × 10⁻³</td>
<td>2.47</td>
</tr>
<tr>
<td>9</td>
<td>12.4</td>
<td>–</td>
<td>–</td>
<td>8.90 × 10⁻²</td>
<td>0.0187</td>
</tr>
<tr>
<td>10</td>
<td>14.9</td>
<td>–</td>
<td>–</td>
<td>4.95 × 10⁻³</td>
<td>1.43</td>
</tr>
<tr>
<td>10A</td>
<td>20.3</td>
<td>870</td>
<td>8</td>
<td>2.74 × 10⁻³</td>
<td>3.47</td>
</tr>
<tr>
<td>11</td>
<td>6.9</td>
<td>–</td>
<td>–</td>
<td>1.51 × 10⁻²</td>
<td>0.268</td>
</tr>
<tr>
<td>11A</td>
<td>20.0</td>
<td>860</td>
<td>8</td>
<td>2.96 × 10⁻³</td>
<td>3.11</td>
</tr>
<tr>
<td>13A</td>
<td>17.9</td>
<td>800</td>
<td>8</td>
<td>4.18 × 10⁻³</td>
<td>1.84</td>
</tr>
</tbody>
</table>
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$_r$, the Gibbs energy of formation of CdTe from the vapor phase [19]:

\[
\Delta G_r = RT \ln(P_{Cd}P_{Te}^{1/2})
\]

\[
= -68,640 + 44.94T \text{ (cal/mol).} \quad (1)
\]

The stoichiometry of the vapor phase at 870°C, defined as $P_{Te}/P_{Cd}$, was then calculated for each cell using the measured $P_{Te}$ 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 $P_{Te}$ 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 $P_{Te}/P_{Cd}$ for the congruent sublimation condition, i.e. $P_{Cd}/P_{Te} = 2.0$.

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 $P_{Te}$ in equilibrium with four CdTe samples of known condensed-phase compositions have previously been measured over the temperature range 635–1025°C [7]. The measured $P_{Te}$ 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 $P_{Te}$ of our
Table 3
Te mole fraction, $X_T$, and measured $P_{Te}$ at 870°C for CdTe samples from Ref. [7]

<table>
<thead>
<tr>
<th>Samples</th>
<th>$X_T - \frac{1}{2}$</th>
<th>$P_{Te}$ (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT-93E</td>
<td>$4.4 \times 10^{-5}$</td>
<td>0.135</td>
</tr>
<tr>
<td>CT-92A</td>
<td>$2.2 \times 10^{-5}$</td>
<td>0.105</td>
</tr>
<tr>
<td>CT92-C</td>
<td>$1.4 \times 10^{-5}$</td>
<td>0.0995</td>
</tr>
<tr>
<td>CT92-D</td>
<td>$1.2 \times 10^{-5}$</td>
<td>0.0306</td>
</tr>
<tr>
<td>Congruent sublimation*</td>
<td>$0.3 \times 10^{-5}$</td>
<td>0.00396</td>
</tr>
</tbody>
</table>

*Ref. [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 $(X_T - \frac{1}{2}) = 0.3 \times 10^{-5}$); (b) having $P_{Te} = 0.165$ atm at 870°C the sample in cell #7 was almost Te-saturated with $(X_T - \frac{1}{2})$ greater than $4.4 \times 10^{-5}$ (note: the equilibrium $P_{Te}$ for Te-saturated condition at 870°C is 0.18 atm [7]); (c) the sample in cell #9, with the measured $P_{Te} = 0.089$ atm at 870°C, has composition $(X_T - \frac{1}{2})$ in the range 1.4-2.2 $\times 10^{-5}$; (d) the CdTe in cell #10 and #11 have $(X_T - \frac{1}{2})$ values below 1.2 $\times 10^{-5}$ and above that for congruent sublimation, i.e. $(X_T - \frac{1}{2}) = 0.3 \times 10^{-5}$, 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 $P_{Cd}/P_{Te}$ varying from 1.84 to 3.47. The error associated with the measured $P_{Te}$ is estimated to be 15%. With the same error assumed for the $\Delta G_f$ given in Eq. (1), the experimentally measured $P_{Cd}/P_{Te}$ 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 $D_{CdTe} = 3.4 \times 10^{-5}$ cm$^2$/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 $X_T$ curve for temperatures below 900°C.

Acknowledgements

The work was supported by the Microgravity Research Division of the National Aeronautics and Space Administration.

References

Journal of Crystal Growth

Instructions to Authors (short version)

Submission of papers
Manuscripts (one original + two copies), should be sent to a member of the Editorial Board or preferably to an appropriate subject Associate Editor. News or announcements should be submitted through the Principal Editor; a duplicate should be sent directly to Elsevier Science B.V., address given below.

Original material. Submission of a manuscript implies it is not being simultaneously considered for publication elsewhere and that the authors have obtained the necessary authority for publication.

Types of contributions
Original research papers, Letters to the Editors and Priority communications are welcome. They should contain an Abstract (of up to 200 words) and a Conclusion section, which particularly in the case of theoretical papers translates the results into terms readily accessible to most readers.

As a guideline: experimental papers should not be longer than 16 double-spaced typed pages, and 8 figures + tables; for theoretical papers a maximum of 20 pages and 10 figures + tables is suggested.

Letters and Priority communications should not be longer than 5 double-spaced typed pages, and 3 figures + tables. They will be given priority in both the refereeing and production processes. The faster production schedule may preclude sending proofs of Letters and Priority communications to authors.

Manuscript preparation
Contributions may be written in English, French or German. They should have an abstract in English. The paper copies of the text should be prepared with double line spacing and wide margins, on numbered sheets.

Structure. Please adhere to the following order of presentation: Article title, Author(s), Affiliation(s), Abstract, PACS codes and keywords, Main text, Acknowledgements, Appendices, References, Figure captions, Tables.

Corresponding author. The name, complete postal address, telephone and fax numbers and the e-mail address of the corresponding author should be given on the first page of the manuscript.

Classification codes/keywords. Please supply one to four classification codes (PACS and/or MSC) and up to six keywords of your own choice that describe the content of your article in more detail.

References. References to other work should be consecutively numbered in the text using square brackets and listed by number in the Reference list. Please refer to the more detailed instructions for examples.

Illustrations
Illustrations should also be submitted in triplicate: one master set and two sets of copies. The line drawings in the master set should be original laser printer or plotter output or drawn in black India ink, with careful lettering, large enough (3–5 mm) to remain legible after reduction for printing. The photographs should be originals, with somewhat more contrast than is required in the printed version. They should be unmounted unless part of a composite figure. Any scale markers should be inserted on the photograph itself, not drawn below it.

Colour plates. Figures may be published in colour, if this is judged essential by the Editor. The Publisher and the author will each bear part of the extra costs involved. Further information is available from the Publisher.

After acceptance
Important. When page proofs of the accepted manuscripts are made and sent out to authors, this is in order to check that no undetected errors have arisen in the typesetting (or file conversion) process. At the proof stage only printer's errors may be corrected. No changes in, or additions to, the edited manuscript will be accepted.

Notification. The authors will receive the final answer of acceptance or rejection from the Office of the Principal Editor and will be invited to supply an electronic version of the accepted text, if this is not already available.

Copyright transfer. In the course of the production process you will be asked to transfer the copyright of the article to the Publisher. This transfer will ensure the widest possible dissemination of information.

Electronic manuscripts
The Publisher welcomes the receipt of an electronic version of your accepted manuscript. If there is not already a copy of this (on diskette) with the journal editor at the time the manuscript is being refereed, you will be asked to send a file with the text of the accepted manuscript directly to the Publisher by e-mail or on diskette (allowing formats 3.5" or 5.25" MS-DOS, or 3.5" Macintosh) to the address given below. (When e-mailing a non-ASCII word-processor file, you should encode it, e.g. with UUENCODE or BinHex, so as to retain all formatting codes.) The name and version of the word-processing program and the type of operating system should always be indicated. Please note that no deviations from the version accepted by the Editor of the journal are permissible without the prior and explicit approval by the Editor. Such changes should be clearly indicated on an accompanying printout of the file.

Author benefits
No page charges. Publishing in Journal of Crystal Growth is free.

Free offprints. The corresponding author will receive 50 offprints free of charge. An offprint order form will be supplied by the Publisher for ordering any additional paid offprints.

Discount. Contributors to Elsevier Science journals are entitled to a 30% discount on all Elsevier Science books.

Further information (after acceptance)

| Elsevier Science B.V., J. Crystal Growth |
| --- | |
| Issue Management | |
| Physics and Materials Science | |
| P.O. Box 2759, 1000 CT Amsterdam | |
| The Netherlands | |
| Fax: + 31 20 485 2319/ + 31 20 485 2704 | |
| E-mail: a.koch@elsevier.nl | |

North-Holland, an imprint of Elsevier Science