Measurement of Partial Pressures over CdSe and CdTe by an Optical Absorption Method*

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Partial pressures of the constituent elements over CdSe(s) and CdTe(s) have been measured by using optical cells consisting of an optical path chamber and a sample chamber. Dissociation constants were $\log K_{\text{CdSe}} = \log P_{\text{Cd}}^2 \times P_{\text{Se}_2} (\text{atm}^3) = -33416/T + 20.43$ (707~936°C) and $\log K_{\text{CdTe}} = \log P_{\text{Cd}}^2 \times P_{\text{Te}_2} (\text{atm}^3) = -29979/T + 19.62$ (763~908°C). Using another type of optical cell having a reservoir chamber, control of partial pressure over the sample (CdSe(s) or CdTe(s)) was attempted by regulating saturated pressure of one of the constituent elements at the reservoir temperature, T_R . When P_{i,T_R} (i : Cd, Se₂, Te₂), the partial pressure at the reservoir, is larger than P_i^* , the partial pressure corresponding to the total pressure minimum at a given temperature, partial pressure control is effective with such a reservoir. However, when P_{i,T_R} is smaller than P_i^* , partial pressure control by a reservoir is not effective, and the condition of the total pressure minimum dominates in the system.

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I. Introduction

A small deviation from stoichiometric composition often yields a large variation in characteristic properties of compounds. For binary compounds the deviation from stoichiometry is effectively controlled by annealing the sample in the partial pressure of the constituent element regulated by the reservoir temperature⁽¹⁾. The prior method⁽²⁾, which is a vapor growth technique with the reservoir containing one component, is often used to grow a crystal with the composition corresponding to the component partial pressure directly. However, the knowledge of the application limits of this reservoir technique is essential in controlling the composition of the prepared specimen.

In this work, the partial pressure of the constituent element, Cd(g), Se₂(g) or Te₂(g) in the vapor phase over the binary compound, CdSe or CdTe, was measured by an optical absorption method on regulating the temperature of the reservoir.

II. Experimental

A schematic drawing of the apparatus is shown in Fig. 1. The D₂-lamp is used as a light source. Light from the lamp is chopped, and absorbed by the vapor in an optical cell in the electric furnace in the shape of capital letter T. After passing a spectrophotometer it is detected by using a lock-in amplifier. Optical absorption by Cd, Se and Te in the vapor phase over CdSe and CdTe is measured in the wavelength region between 200 nm and 600 nm. CdSe and CdTe crystals used in this study were synthesized from elements, Cd, Se and Te of nominal purity 6-nines in a carbon coated silica ampule. Schematic drawings of optical silica cells used in this study is shown in Fig. 2. Optical path chamber is 22 mm in outer diameter and L mm

Fig. 1 Schematic drawing of the apparatus for measuring vapor pressure.

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Fig. 2 Optical cells.

in length, where L is 5.0, 50.0, 96.2 or 150.0 mm, and has optical flat parallel end windows. "A" type cell has optical path chamber and sample chamber which holds CdSe or CdTe crystal at 30 cm below the optical path chamber. "B" type cell has a sample chamber which is 20 cm below the optical path chamber and also a reservoir chamber which holds Cd, Se or Te at 25 cm below the sample position.

The magnitude of the optical absorption is given by the optical density, D_λ , defined by the following equation:

$$D_\lambda = -\log(I_\lambda/I_{0\lambda}), \quad (1)$$

where λ is the wavelength, I_λ and $I_{0\lambda}$ are the light intensity after and before absorption due to the vapor phase in the optical path chamber. Optical path temperature T_O and sample temperature T_S were measured with Pt-Pt·13% Rh thermocouples and reservoir temperature T_R , with a chromel-alumel thermocouple within an accuracy of $\pm 3^\circ\text{C}$. I_λ was measured after holding 1 or 2 h at the fixed temperature.

III. Results

The relations between D_i and P_i (i : Cd, Se₂, Te₂) are needed for the calibration on measuring the partial pressures of constituent elements over the compounds. The optical density at a number of wavelengths at $T_O = 960^\circ\text{C}$ is plotted in Figs. 3~5 on a logarithmic scale against the reciprocal absolute temperature of component, Cd, Se or Te, held in the sample chamber of "A" type cell. Cd vapor has two prominent

Fig. 3 Optical density of Cd(g) at two wavelengths for a 50.0 mm optical path at 960°C plotted on a logarithmic scale against the reciprocal absolute temperature of a pure Cd(s or l) sample. The broken line gives the vapor pressure of Cd(s or l) as read with the right hand ordinate.

Fig. 4 Optical density of Se₂(g) at a number of wavelengths for a 50.0 mm optical path at 960°C plotted on a logarithmic scale against the reciprocal absolute temperature of a pure Se(l) sample. The broken line gives the vapor pressure of Se(l) as read with the right hand ordinate.

absorption peaks at 228.8 and 326.1 nm. Se vapor and Te vapor have broad absorption bands at 300~400 and 380~500 nm respectively as reported by Brebrick *et al.*⁽³⁾⁽⁵⁾⁽⁶⁾ Absorption band maxima are at 340.5 and 418.7 nm respectively. According to Brebrick

Fig. 5 Optical density of $\text{Te}_2(\text{g})$ at a number of wavelengths for a 5.0 mm optical path at 960°C plotted on a logarithmic scale against the reciprocal absolute temperature of a pure $\text{Te}(\text{l})$ sample. The broken line gives the vapor pressure of $\text{Te}(\text{l})$ as read with the right hand ordinate.

et al. these absorption bands are regarded as being due to $\text{Se}_2(\text{g})$ and $\text{Te}_2(\text{g})$. Furthermore, it is known from the previous reports^{(7)~(9)} that the Se vapor and Te vapor are mainly composed of $\text{Se}_2(\text{g})$ and $\text{Te}_2(\text{g})$ (more than 98%) respectively in the vapor pressure and the temperature (960°C) used in this study. Therefore the vapor pressures of Se and Te are simply symbolized by P_{Se_2} and P_{Te_2} respectively. The optical densities at 228.8 and 326.1 nm are also shown in Figs. 4 and 5. Published data⁽¹⁰⁾ of the equilibrium vapor pressures as a function of temperature of the elements, Cd, Se and Te, are also shown in Figs. 3~5. Particularly in the case of Cd shown in Fig. 3, D_λ is not parallel with the vapor pressure. The reason for the lack of parallelism may be an insufficient resolution of the spectrometer to resolve a sharp absorption peak of monoatomic molecule like Cd(g). But the relation between D_λ and temperature is observed with good reproducibility, so the calibration is made on the basis of these figures.

Observed optical density due to the vapor phase over CdSe or CdTe is caused by two

Fig. 6 Dissociation constant for CdSe(s) plotted on a logarithmic scale against the reciprocal absolute temperature.

vapor species. As the optical density due to Cd(g) was negligible at 340.5 and 418.7 nm, where the absorption by $\text{Se}_2(\text{g})$ and $\text{Te}_2(\text{g})$ were measured, the data at these wavelengths shown in Figs. 4 and 5 were used to determine P_{Se_2} and P_{Te_2} . The contribution of $\text{Se}_2(\text{g})$ or $\text{Te}_2(\text{g})$ to the optical densities at 228.8 and 326.1 nm, where the absorption by Cd(g) was measured, was read using the data shown in Fig. 4 or 5. The partial optical density of Cd(g) at each of these wavelengths was taken as difference between the observed density and the contribution of $\text{Se}_2(\text{g})$ or $\text{Te}_2(\text{g})$. The value of P_{Cd} corresponding to each of these partial optical densities was then read using the data shown in Fig. 3.

P_{Cd} and P_{Se_2} or P_{Te_2} over CdSe or CdTe have been measured with "A" type cells and these values give dissociation constant. K_{CdSe} and K_{CdTe} are plotted on a logarithmic scale against the reciprocal absolute temperature in Figs. 6 and 7 respectively. The data of Wösten⁽¹¹⁾ and Flögel⁽¹²⁾ obtained by using transportation method are also shown in Fig. 6. The result of this study is close to the recent data of Flögel.

Fig. 7 Dissociation constant for CdTe(s) plotted on a logarithmic scale against the reciprocal absolute temperature.

The data obtained by Brebrick⁽¹³⁾ using the optical absorption method are also shown in Fig. 7. The data of this study and of Brebrick correspond to each other and no detectable deviation between them is recognized. The solid lines in Figs. 6 and 7 are given by the following equations determined by the method of least squares:

$$\begin{aligned} \log K_{\text{CdSe}} &= \log P_{\text{Cd}}^2 \times P_{\text{Se}_2} \text{ (atm}^3\text{)} \\ &= -33416/T + 20.43 \text{ (707} \sim \text{936}^\circ\text{C)}, \end{aligned} \quad (2)$$

and

$$\begin{aligned} \log K_{\text{CdTe}} &= \log P_{\text{Cd}}^2 \times P_{\text{Te}_2} \text{ (atm}^3\text{)} \\ &= -29979/T + 19.62 \text{ (763} \sim \text{908}^\circ\text{C)}. \end{aligned} \quad (3)$$

Subsequently the vapor pressure over CdSe or CdTe was measured on using "B" type cell under controlled vapor pressure with a reservoir. P_{Cd} and P_{Se_2} over CdSe are plotted against P_{CdTR} , Cd pressure due to Cd reservoir, in Fig. 8 for constant T_s , 889°C, and different Cd reservoir temperatures. The length of error bars of experimental values was estimated on the basis of scatter of points in Figs. 3 and 4.

Fig. 8 Partial pressures of Cd(g) and Se₂(g) over CdSe(s) at 889°C plotted against apparent partial pressure of Cd(g) given by a pure Cd(s or l) reservoir temperature. □, P_{Cd}^* and ■, $P_{\text{Se}_2}^*$ correspond to the total pressure minimum.

Symbols □ and ■ indicate P_{Cd}^* and $P_{\text{Se}_2}^*$ respectively, which are the vapor pressures corresponding to those at the total pressure minimum, ($P_{\text{Cd}} = 2P_{\text{Se}_2}$ at the minimum of the total pressure, $P_{\text{tot}} = P_{\text{Cd}} + P_{\text{Se}_2}$) and are plotted at the abscissa of P_{CdTR} where $P_{\text{Cd}}^* = P_{\text{CdTR}}$. The chain line shows the relation between P_{Cd} and P_{CdTR} on the assumption that P_{CdTR} controls the vapor phase over CdSe, $P_{\text{Cd}} = P_{\text{CdTR}}$. The broken line shows the relation between $P_{\text{Se}_2} = K_{\text{CdSe}}/P_{\text{Cd}}^2$ and P_{CdTR} on the assumption, $P_{\text{Cd}} = P_{\text{CdTR}}$. Similar expression is used in Figs. 9~11. In the region, $P_{\text{CdTR}} < P_{\text{Cd}}^*$, P_{Cd} and P_{Se_2} over CdSe are nearly equal to P_{Cd}^* and $P_{\text{Se}_2}^*$ respectively with no dependence on P_{CdTR} . In the other region, $P_{\text{CdTR}} > P_{\text{Cd}}^*$, P_{Cd} is nearly equal to P_{CdTR} and P_{Se_2} varies along the broken line proportional to P_{CdTR}^{-2} . Similar trend is observed in other experiments with Cd reservoir in the temperature range, $816^\circ\text{C} \leq T_s \leq 955^\circ\text{C}$. The result for Se reservoir at $T_s = 950^\circ\text{C}$ is shown in Fig. 9, where the chain line shows the relation on the assumption, $P_{\text{Se}_2} = P_{\text{Se}_2\text{TR}}$, and the broken line shows the value of P_{Cd} calculated

Fig. 9 Partial pressures of Cd(g) and Se₂(g) over CdSe(s) at 905°C plotted against apparent partial pressure of Se₂(g) given by a pure Se(l) reservoir temperature. □, P_{Cd}^* and ■, $P_{Se_2}^*$ correspond to the total pressure minimum.

with K_{CdSe} and P_{Se_2TR} . In the region, $P_{Se_2TR} < P_{Se_2}^*$, P_{Cd} and P_{Se_2} are nearly equal to P_{Cd}^* and $P_{Se_2}^*$, respectively, with no dependence on P_{Se_2TR} . In the region, $P_{Se_2TR} > P_{Se_2}^*$, P_{Se_2} is nearly equal to P_{Se_2TR} and P_{Cd} varies along the broken line proportional to $P_{Se_2TR}^{-1/2}$. The deviation of P_{Cd} and P_{Se_2} from P_{Cd}^* and $P_{Se_2}^*$ in the region, $P_{Se_2TR} < P_{Se_2}^*$, as shown in Fig. 9 is due to the residual excess Se in CdSe, because P_{Se_2TR} was varied from high value to low in this run. Similar trend is observed in other experiments with Se reservoir in the temperature range, $860^\circ\text{C} \leq T_s \leq 929^\circ\text{C}$.

The results of similar measurements with CdTe sample are shown in Figs. 10 and 11. Measurements were performed with Cd and Te reservoirs in the temperature ranges, $734^\circ\text{C} \leq T_s \leq 910^\circ\text{C}$ and $738^\circ\text{C} \leq T_s \leq 903^\circ\text{C}$, respectively. The relation between P_{Cd} or P_{Te_2} over CdTe and P_{CdTR} or P_{Te_2TR} is similar to that obtained for CdSe.

Thus it is confirmed that partial pressure control by a reservoir is not effective in the region, $P_{iTR} < P_i^*$, but is effective in the region, $P_{iTR} > P_i^*$ (i : molecular species, Cd, Se₂ or Te₂).

When the optical cell was taken out from the furnace, deposition of sample was usually observed between the sample chamber and the reservoir chamber due to vapor transportation caused by the temperature difference. The reason why the partial pressure over CdSe or

Fig. 10 Partial pressures of Cd(g) and Te₂(g) over CdTe(s) at 857°C plotted against apparent partial pressure of Cd(g) given by a pure Cd(s or l) reservoir temperature. □, P_{Cd}^* and ■, $P_{Te_2}^*$ correspond to the total pressure minimum.

Fig. 11 Partial pressures of Cd(g) and Te₂(g) over CdTe(s) at 903°C plotted against apparent partial pressure of Te₂(g) given by a pure Te(l) reservoir temperature. □, P_{Cd}^* and ■, $P_{Te_2}^*$ correspond to the total pressure minimum.

CdTe correspond to the total pressure minimum in the region, $P_{iTR} < P_i^*$, is understood as follows. In this experimental region, the partial pressures due to the sample composition dominate the system, and excess component preferentially escapes from the sample through vapor transportation. When the initial sample composition is not the one corresponding to

the total pressure minimum, the sample composition finally tends to become the one corresponding to the total pressure minimum.

IV. Summary

When partial pressure control by a reservoir is attempted for **II-VI** compound, CdSe or CdTe, in the region where component partial pressure due to a reservoir is lower than that corresponding to the total pressure minimum, partial pressure corresponding to the total pressure minimum arises in the system, that is to say, the system cannot be controlled by the apparent partial pressure regulated by reservoir temperature and partial pressure control on using a reservoir is not effective. Possible occurrence of such a situation has been pointed out in the study of the crystal growth of **II-VI** compound, ZnSe⁽¹⁴⁾ and in the study of **IV-VI** compound, PbSe⁽¹⁵⁾, containing component elements of relatively high equilibrium vapor pressure. In the present study the conditions of the occurrence of the total pressure minimum is experimentally verified from the measurements of partial pressure. It is made clear that the replenishment with replacement of reservoir elements is essential in order to get information in the whole stability range for binary compounds, especially for the compounds consisting of the component elements of relatively high equilibrium vapor pressure.

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