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Mass flux of ZnSe by physical vapor transport

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Abstract

Mass fluxes of ZnSe by physical vapor transport (PVT) were measured in the temperature range of 1050 to 1160°C using an in-situ dynamic technique. The starting materials were either baked out or distilled under vacuum to obtain near-congruently subliming compositions. Using an optical absorption technique Zn and Se₂ were found to be the dominant vapor species. Partial pressures of Zn and Se₂ over the starting materials at temperatures between 960 and 1140°C were obtained by measuring the optical densities of the vapor phase at the wavelengths of 2138, 3405, 3508, 3613, and 3792 Å. The amount and composition of the residual gas inside the experimental ampoules were measured after the run using a total pressure gauge. For the first time, the experimentally determined partial pressures of Zn and Se₂ and the amount and composition of the residual gas were used in a one-dimensional diffusion limited analysis of the mass transport rates for a PVT system. Reasonable agreement between the experimental and theoretical results was observed.

1. Introduction

Zinc selenide (ZnSe) has been studied extensively in the last several years because of its potential for advanced opto-electronic applications [1]. Crystallization of ZnSe by vapor transport (including both physical vapor transport (PVT) and chemical vapor transport (CVT) is a preferred choice due to its high melting temperature (1526°C) [2]. Without a prior contaminant by a transport agent as in CVT growth, PVT growth also offers other advantages such as the purification effect and high solid–vapor interfacial mor-

phological stability [3] during growth. Bulk ZnSe crystals have been successfully grown using this technique by a number of investigators [4,5].

Experimental and theoretical investigations of the mass flux in a PVT system are essential in optimization of the experimental parameters for crystal growth. It is known both experimentally and theoretically that the mass flux in PVT systems of II–VI compound depends strongly on the composition of the vapor phase [6,7] which is in turn extremely sensitive to the composition of the source material [8] and the degassing properties of the container. Even a slight deviation of the source material from its congruent subliming composition may substantially reduce the mass flux of the system [7]. For these reasons, a consistent heat treatment of source materials prior to the seal-off of the experimental ampoule is cru-

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cial in order to ensure a reproducible composition near the congruent subliming condition, and the partial pressure data over the source material are highly desirable for the determination of results of the heat treatment and for a meaningful comparison between the experimental and theoretical mass flux data. Systematic studies have been reported in the past [9] as well as recently [10,11] on the residual gas formation in sealed silica ampoules. Volatile impurities such as H_2 , H_2O , CO , CO_2 , N_2 , O_2 may desorb from silica ampoules at high temperatures [12] and form a significant amount of gas in a PVT system, thereby reducing the mass flux. This effect depends on the brand of silica tubing, and on the outgassing and the processing condition of the ampoule [9,11].

In this investigation, mass flux of ZnSe was measured, for the first time, using an in-situ dynamic technique. Also for the first time, the experimentally determined partial pressures of the transport elements and the amount and composition of the residual gas were incorporated in a theoretical analysis for a PVT system.

2. Theory

2.1. Diffusive transport without the presence of a residual gas

A one-dimensional diffusion limited transport model developed by Faktor and Garrett [6] was used to calculate the mass flux in a ZnSe PVT system. The model has been used previously by one of the authors to analyze the CdS PVT system [13] and its assumptions and results for a binary system were summarized there. It is confirmed experimentally (see Section 3.3) that Zn and Se_2 are the predominant vapor species in the entire temperature range of our interest. Further analysis showed that $Se(g)$, the species with the highest vapor pressure among other thermodynamically allowable selenium species, accounts for less than 0.5% of the selenium in the vapor at 1100°C.

Using the Gibbs energy of formation for the vapor phase, which is, within experimental error,

independent of the deviation from stoichiometry, determined experimentally (see Section 3.3), we have

$$\log P_{Zn} P_{Se_2}^{1/2} = -17818/T + 9.1888, \quad (1)$$

where P is in atm and T in K. A quantity $\alpha(L)$, defined as $P_{Zn}(L)/P_{Se_2}(L)$, measuring the stoichiometry of the vapor over the source material, was used together with Eq. (1) to calculate $P_{Zn}(L)$ and $P_{Se_2}(L)$ at the source temperature, $T(L)$. Then $P_{Zn}(0)$ and $P_{Se_2}(0)$, the partial pressures at the deposition region, were solved using $P_T \equiv P_{Zn}(0) + P_{Se_2}(0) = P_{Zn}(L) + P_{Se_2}(L)$ and Eq. (1) at the deposition temperature, $T(0)$. The mass flux was calculated by setting $x = 0$ in the following equation [6],

$$J = \frac{2}{3} \frac{DP_T}{RT_a(L-x)} \ln \frac{P_{Zn}(x) - \frac{2}{3}P_T}{P_{Zn}(L) - \frac{2}{3}P_T}, \quad (2)$$

where D is the binary diffusion coefficient, R the gas constant, and T_a the average temperature. The calculation of the binary diffusion coefficient was outlined in Ref. [13].

2.2. Diffusive transport in the presence of a residual gas

The residual gas in our experimental ampoule was treated as a single component and its molecular parameters were calculated as weighted averages of those of individual species according to the composition of the vapor. The diffusion limited mass flux equations for a ternary system with one stagnant component (Z) were established by Gilliland [14]:

$$\frac{J_{Zn}}{D_{Zn-Z}} + \frac{J_{Se_2}}{D_{Se_2-Z}} = \frac{P_T}{RT_a(L-x)} \ln \frac{P_Z(x)}{P_Z(L)}, \quad (3)$$

$$\begin{aligned} & \frac{J_{Zn} + J_{Se_2}}{D_{Zn-Se_2}} \\ &= \frac{P_T}{RT_a(L-x)} \ln \left\{ \left[a \left(1 + J_{Zn}/J_{Se_2} \right) P_{Se_2}(x) \right. \right. \\ & \quad \left. \left. - \left(1 + J_{Se_2}/J_{Zn} \right) P_{Zn}(x) + b \right] \right. \\ & \quad \times \left[a \left(1 + J_{Zn}/J_{Se_2} \right) P_{Se_2}(L) \right. \\ & \quad \left. \left. - \left(1 + J_{Se_2}/J_{Zn} \right) P_{Zn}(L) + b \right]^{-1} \right\}, \quad (4) \end{aligned}$$

where

$$a = \frac{D_{\text{Zn-Se}_2}^{-1} - D_{\text{Zn-Z}}^{-1}}{D_{\text{Zn-Se}_2}^{-1} - D_{\text{Se}_2-\text{Z}}^{-1}}, \quad b = \frac{D_{\text{Zn-Z}}^{-1} - D_{\text{Se}_2-\text{Z}}^{-1}}{D_{\text{Zn-Se}_2}^{-1} - D_{\text{Se}_2-\text{Z}}^{-1}} P_T. \quad (5)$$

In view of the fact that the vapor was not saturated with either element due to the heat treatment performed on the source material, it is justified to assume that the deposited material does not contain any liquid phase. This leads to the relation $J_{\text{Zn}} = 2J_{\text{Se}_2}$ for a nearly stoichiometric and most likely narrow homogeneity range of ZnSe.

For the given values of $T(L)$ and $\alpha(L)$, $P_{\text{Zn}}(L)$ and $P_{\text{Se}_2}(L)$ were calculated from Eq. (1). Then $P_{\text{Zn}}(0)$, $P_{\text{Se}_2}(0)$, $P_Z(0)$, and the mass flux $J \equiv J_{\text{Zn}}$ were solved from Eqs. (3) and (4) with $x = 0$, Eq. (1) at a given $T(0)$, and $P_T \equiv P_{\text{Zn}}(0) + P_{\text{Se}_2}(0) + P_Z(0) = P_{\text{Zn}}(L) + P_{\text{Se}_2}(L) + P_Z(L)$ with an input value of $P_Z(L)$. Finally, the average residual vapor pressure can be calculated as

$$\bar{P}_Z = \frac{1}{L} \int_0^L P_Z(x) dx, \quad (6)$$

where $P_Z(x)$ can be obtained by rearranging Eq. (3).

3. Experimental procedure

3.1. Heat treatment of source materials

Because vapor partial pressures depend strongly on the deviation from stoichiometry of the coexisting solid, it is practically impossible to reproducibly synthesize the compound with desired values of partial pressures. One method to adjust the stoichiometry of the starting material is to bake out the material at the processing temperature under dynamic vacuum (method A). The change in stoichiometry stops when the material sublimates congruently. The other method is to distill the material by subliming it from one end of the ampoule to the other under dynamic vacuum and an auxiliary heater can be used to confine the deposition to a designated region (method B).

Commercially available ZnSe was obtained from both Cleveland Crystals, Inc. (purity 99.995% or 99.999%) and Eagle Picher Research Laboratory (high purity grade). Both heat-treatment methods were applied after these starting materials were ground into powder. In method A, the bake-out was performed for about 10 min at 1080°C. This temperature was also used in method B at the subliming end. At the end of the distillation all of the starting ZnSe was transported in most of the runs.

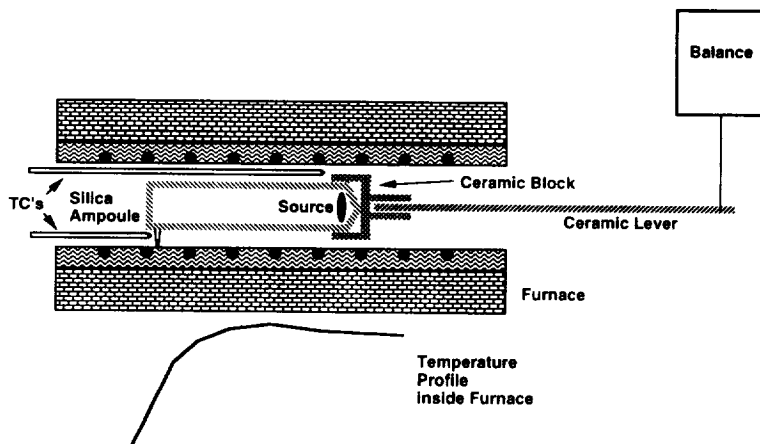


Fig. 1. Schematic drawing of the experiment set-up for the in-situ dynamic measurement of mass flux in ZnSe PVT system.

3.2. Apparatus and description of transport experiment

The experiment ampoules were made of 15×18 mm silica tubing and were about 12 cm in length. The cleaned and outgassed ampoule was loaded with 2–3 g of heat-treated ZnSe and sealed at a pressure of 5×10^{-7} Torr or less. A three-zone furnace was employed to perform the transport experiments. A schematic drawing of the experimental set-up with a typical temperature profile along the centerline of the furnace is given in Fig. 1. Two legs attached to the left end of the ampoule served as a fulcrum. The right end of the ampoule was, via a ceramic block, connected to a ceramic lever which extended out of the furnace and rested on a wire suspended from a Mettler AE 100 electronic balance. The temperatures, T_s at the source and T_d at the deposited material, were measured by two thermocouples placed at the both ends of the ampoule and, together with the balance readings, were recorded by a computer.

During the experiment the balance readings were recorded at 15 or 30 min intervals. The readings were then converted to the mass transported during the run using the dimensions of the ampoule/lever assembly. These mass data were plotted versus time and the mass flux was obtained from the slope of the curve. For most of the runs a few different temperature settings were used in order to determine the dependence of the mass flux on the source temperature.

3.3. Partial pressure measurements

The partial pressures of the constituent elements coexisting with ZnSe solid were measured using an optical absorption technique [15]. In the temperature range 960–1140°C the predominant vapor species were identified to be Zn and Se_2 . The partial pressure of Zn, P_{Zn} , was obtained by measuring the optical density at the 2138 Å peak of Zn whereas that of Se_2 , P_{Se_2} , was obtained by measuring the optical densities at the 3405, 3508, 3613, and 3792 Å vibronic peaks of Se_2 . Two optical cells containing starting materials from Cleveland Crystals were used to measure both

P_{Zn} and P_{Se_2} and the Gibbs energy for the reaction $\text{ZnSe(s)} \rightarrow \text{Zn(g)} + \frac{1}{2}\text{Se}_2\text{(g)}$ was determined to be

$$\Delta G_f^0 \text{ (cal/mole)} = RT \ln P_{\text{Zn}} P_{\text{Se}_2}^{1/2} \\ = -81520 + 42.04T. \quad (7)$$

The measured values of $\alpha = P_{\text{Zn}}/P_{\text{Se}_2}$ range from ~ 2.9 between 1350 and 1410 K to ~ 7 at ~ 1250 K. Samples from two transport experimental ampoules were reloaded into the optical cells, and the partial pressures were also measured and the corresponding α -values used as references in the theoretical calculation. Since the reloading procedure could cause a preferential loss of the excess species due to the condensation on the ampoule wall during cool-down of the transport experiment, the α -values measured could be closer to 2 than those in the original ampoule. The details of the partial pressure measurement will be published elsewhere.

3.4. Residual vapor pressure measurement

The amount of the residual gas in the transport experiment ampoules was measured using a total pressure gauge (barocel). The technique and the apparatus used were described in Ref. [11]. An L-shaped tip was fabricated on the side of several experiment ampoules. After the transport experiment the ampoule was placed in the measuring chamber and was slid so that the tip was struck by an obstacle and broken. The original pressure of residual gas in the ampoule was calculated based on the chamber-to-ampoule volume ratio. The composition of the residual gas was determined by selectively freezing out the gas components using a cold finger which was cooled to predetermined temperatures with appropriate cold bath mixtures [11].

4. Results and discussion

4.1. Theoretical calculations

4.1.1. Without the presence of a residual gas

Fig. 2 shows the results calculated from Eq. (2) for the mass flux for $T(L) = 1080^\circ\text{C}$ as a function

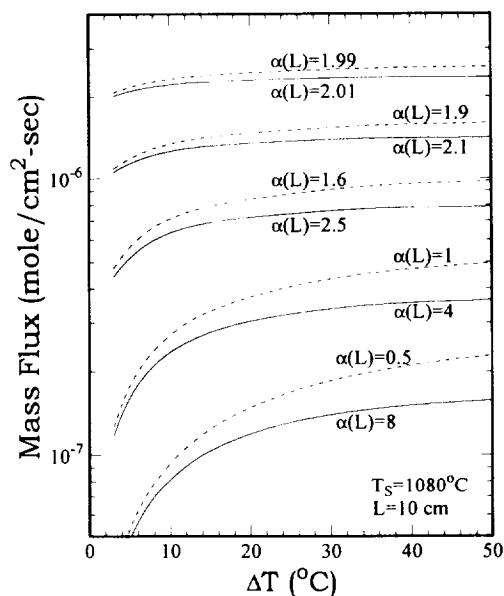


Fig. 2. Calculated mass fluxes of ZnSe as a function of ΔT for source temperature at 1080°C and different $\alpha(L)$ values. Solid lines are for $\alpha(L) > 2$ and dashed lines are for $\alpha(L) < 2$.

of $\Delta T \equiv T(L) - T(0)$ for various values of $\alpha(L)$. Table 1 lists the molecular parameters used for computing the binary diffusion coefficients. As the source material approaches congruent sublimation, or $\alpha(L) = 2.0$, the mass flux increases rapidly. Fig. 2 also shows that the mass flux reaches an upper limit at $\Delta T \approx 30^\circ\text{C}$ for rather non-congruently subliming vapor and this ΔT reduces when $\alpha(L)$ is closer to 2.0. This is because the ΔT -dependence of the mass flux is mainly

Table 1
Molecular parameters used for computing binary diffusion coefficients

| Species | σ (Å) | ϵ/k (K) | Ref. |
|---------------------|--------------------|-------------------|------|
| Zn(g) | 4.70 | 522 | [16] |
| Se ₂ (g) | 3.576 ^a | 1130 ^b | |
| CO(g) | 3.690 | 91.7 | [17] |
| CO ₂ (g) | 3.941 | 195.2 | [17] |
| N ₂ (g) | 3.798 | 71.4 | [17] |
| H ₂ (g) | 2.827 | 59.7 | [17] |

^a Estimated from the molar volume at the melting point [17,18].

^b Estimated from the normal boiling temperature [17,19].

due to that of the diffusion of the minority species whose partial pressure at $T(0)$ becomes very low at a certain ΔT -value. A further increase in ΔT does not produce much change in the partial pressure and therefore cannot effectively increase the transport rate. In principle, a source material with an α -value either higher than 8 or lower than 0.5 could result transport rates which are 2 or more orders of magnitude lower than the highest values shown in Fig. 2. The calculated mass fluxes for T_s between 900 and 1200°C for a fixed value of $\alpha(L)$ remain almost constant with very slight increase with increasing T_s . This can be attributed to a weak increase in the minority partial pressure (more so for larger values of $|\alpha(L) - 2|$) and a decrease in the diffusion coefficient with increasing total pressure. However, this should not to be confused with the reality where the mass flux is likely to increase with T_s because the amount of excess element is fixed within an ampoule and $\alpha(L)$ is approaching 2 with increasing T_s .

4.1.2. In the presence of a residual gas

Fig. 3 shows the mass fluxes calculated by the procedure described in Section 2.2 as a function of the total residual gas pressure for several values of $\alpha(L)$ and other specified conditions. The composition of the residual gas was chosen to be 25% each for CO and N₂ and 50% CO₂. The curves in Fig. 3 indicate that the residual gas starts to measurably reduce the mass flux when its total pressure approaches $P_{\text{Zn}} - 2P_{\text{Se}_2}$. Beyond this region, the residual gas becomes more important and the $\alpha(L)$ -dependence of the mass flux becomes weak. The temperature dependence of the mass flux becomes relatively strong in the presence of residual gas. For instance, the flux for $\alpha(L) = 2.7$ and $P_{\text{Z}}(L) = 0.01$ atm increases by almost 70 times when T_s changes from 900 to 1200°C.

4.2. Experimental results

A series of transport experiments was performed using the in-situ dynamic technique described in Section 3.2 and the results of the mass

flux are plotted in Fig. 4 versus the reciprocal of the source temperature. Each mass flux value was derived from a well defined straight line generally consisting of 40 or more data points on the mass versus time plot and was normalized to $L = 10$ cm. With a few exceptions, the ΔT -values used range from 13 to 20°C. The source materials from Cleveland Crystals used in ampoules ZST-2, 4, and 5 display in general somewhat lower fluxes with stronger temperature dependence than those of source materials from Eagle Picher, which were used in all other ampoules. The methods of heat treatment did not show any apparent effect on the mass transport rate observed.

The residual gas pressure was measured for four ampoules after the transport experiment. The total residual pressure measured ranges from 0.0011 to 0.0041 atm at room temperature and four different species were found – H_2 , CO , N_2 , and CO_2 . The majority species is CO_2 which accounts for 28–43% of the total. CO and N_2 , being indistinguishable by the measuring method,

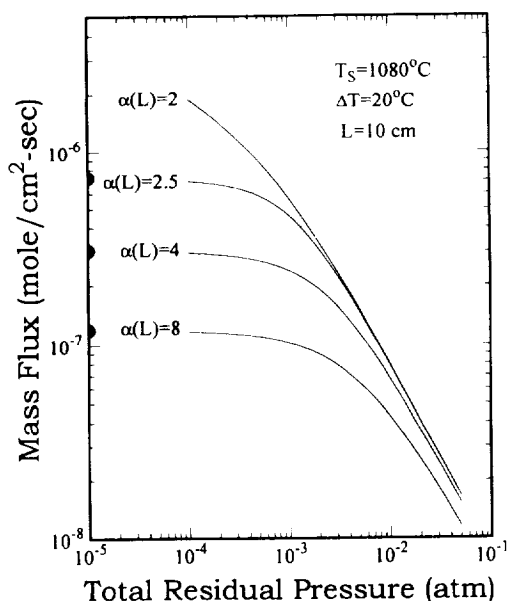


Fig. 3. Calculated mass fluxes of ZnSe as a function of $P_R(L)$ for source temperature at 1080°C and different $\alpha(L)$ values. The solid dots on the left axis are those under the same conditions but with a zero residual pressure.

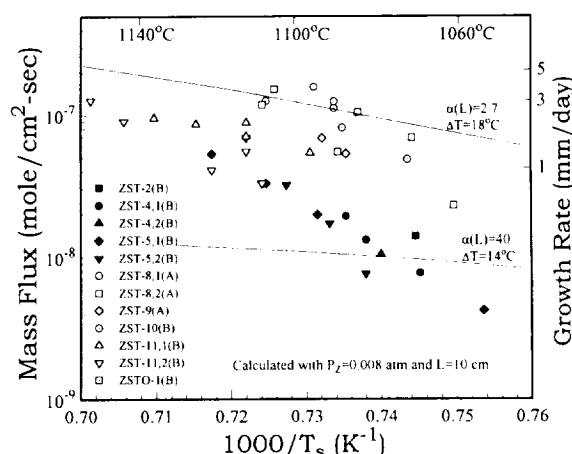


Fig. 4. Mass fluxes of ZnSe as a function of reciprocal source temperature. Solid symbols: source materials from Cleveland Crystals, open symbols: source materials from Eagle Picher. The letters in parentheses in the legend indicate the method of heat treatment. Two solid lines are calculated with specified conditions. The composition of the residual gas used in the calculations is 36% CO_2 , 26% each for CO and N_2 , and 12% H_2 .

together contribute 35–64%. H_2 accounts for the remaining 8–22% of the residual vapor.

A theoretical curve, calculated with $\Delta T = 18^\circ C$, $\bar{P}_Z = 0.008$ atm, and $\alpha(L) = 2.7$ – the lowest value obtained from the equilibrium partial pressures measured over two starting materials, is also plotted in Fig. 4. The pressure and composition of the residual gas used in the calculation are the average of those measured from four experiment ampoules. For the same amount and composition of the residual gas, another curve is calculated with $\Delta T = 14^\circ C$ and $\alpha(L) = 40$ which is based on the partial pressures measured over one sample undergone the transport experiment. Most of our experimental data fall between these two theoretical curves and some agree well with the first curve which represents the highest mass flux values achievable in respect of the source materials used and the experimental conditions. The stronger temperature dependence of the mass flux measured from some ampoules could be caused by a progressive improvement towards the congruent subliming condition of the source materials with increasing source temperature.

5. Summary

The general agreement observed between the experimental and theoretical results of the mass flux in ZnSe PVT system is satisfactory. It is also significant in that the comparison incorporates the experimentally determined information of partial pressures of the transport elements and of the residual vapor. However, the $\alpha(L)$ -value could vary during a sufficiently long experiment if it differs from 2.0 and, therefore, so could the transport rate. Since this was in general not observed during our transport experiments even for runs as long as 140 h at fixed temperatures, a simultaneous in-situ measurement of the transport rates and the partial pressures over the source material has been designed and is in progress to shed light on the thermodynamics of this PVT system. The mass flux results obtained in this work have served as guidance for the PVT bulk crystal growth experiment. For instance, the mass flux was converted to the linear growth rate and is shown on the right scale in Fig. 4. As results, several large, high quality single crystals of ZnSe were grown from the source materials which had undergone the same heat treatment. The results on crystal growth and characterization are to be published separately.

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