The Diffusion of Chalcogen in $\text{CdS}_{1-x}\text{Se}_x$

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The diffusion coefficient of chalcogen in $\text{CdS}_{1-x}\text{Se}_x$ was measured for a specimen annealed under controlled chalcogen pressures using a reservoir containing molten S–Se mixtures. The diffusion coefficient D is independent of the composition x in the range $0 < x < 0.5$ and proportional to the square root of the sum of partial pressures of $\text{S}_2(\text{g})$ and $\text{Se}_2(\text{g})$. The estimated temperature dependence of D near the stoichiometric composition is $D = 2.2 \times 10^{-5} \exp(-4.2 \times 10^{-19} \text{ J/kT}) (\text{m}^2/\text{s})$ (1064 K $\sim$ 1281 K).

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I. Introduction

The impurity diffusion of Se in CdS under the saturation sulfur vapor pressure was studied by Woodbury and Hall⁽¹⁾ using radio isotope tracer. The interdiffusion coefficient in $\text{CdS}_{1-x}\text{Se}_x$ was measured by Handelman and Kaiser⁽²⁾ and by Taylor *et al.*⁽³⁾ by means of color change with an optical microscope and fluorescence measurement, respectively. According to Woodbury and Hall, the penetration curve has two stages, that is, a slow diffusion stage in the high tracer concentration part and a fast stage in the low concentration part. The diffusion coefficient is found to be proportional to the square root of S vapor pressure. But there has been no systematic investigation of the chalcogen diffusion in $\text{CdS}_{1-x}\text{Se}_x$. In the present paper, the diffusion coefficient has been studied on a sample annealed under the regulated chalcogen partial pressure using a reservoir containing molten S–Se mixtures.

II. Experimental

A specimen cleaved from a vapor grown CdS single crystal was annealed in a sealed quartz ampoule using a molten S–Se reservoir. This method was described in detail in a pre-

vious paper⁽⁴⁾. The sample was quenched in water after annealing for 20 ks–360 ks. It was sometimes sealed with Ar up to 70 kPa at room temperature in order to diminish the loss of sample through vaporization. The composition x in the sample ($\text{CdS}_{1-x}\text{Se}_x$) was measured by an electron probe X-ray micro-analyzer (EPMA). It was regulated by controlling the partial pressure ratio of $\text{S}_2(\text{g})$ and $\text{Se}_2(\text{g})$, ($P_{\text{S}_2}/P_{\text{Se}_2}$). The following assumption was used on regulating the atom ratio of metal to chalcogen by the sum of partial pressures of $\text{S}_2(\text{g})$ and $\text{Se}_2(\text{g})$ under a fixed partial pressure ratio.

(1) The vapor pressures, P_{S_2} and P_{Se_2} , over the specimen are proportional to the activities of S_2 and Se_2 in the molten S–Se mixture reservoir, respectively. Partial pressures do not change at the vapor temperature between 1050 K and 1300 K at a fixed composition and temperature of reservoir.

(2) Molten S–Se mixture is an ideal solution. As a reference condition for changing temperature and composition, the reservoir temperature $T_R = 723 \text{ K}$ and the atomic fraction of S in the reservoir $N_S = 0.650$ were adopted. The value of ($P_{\text{S}_2}/P_{\text{Se}_2}$) was 3.6 in this condition, as described in Fig. 10 in the previous report⁽⁴⁾. Then the following eq. (1) was derived:

$$(0.650/0.350)(P_{\text{S}_2 723}^\circ/P_{\text{Se}_2 723}^\circ) = \{N_S/(1-N_S)\}(P_{\text{S}_2 T_R}^\circ/P_{\text{Se}_2 T_R}^\circ), \quad (1)$$

where $P_{\text{S}_2 T_R}^\circ$ and $P_{\text{Se}_2 T_R}^\circ$ are the equilibrium pressures of pure S and Se at T_R , respectively. At first N_S and T_R were determined with eq. (1). In order to estimate P_{S_2} and P_{Se_2} , the

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following equations were used:

$$P_{S_2} = 0.26 N_S P_{S_2 T_R}^\circ, \quad (2)$$

$$P_{Se_2} = 7.3(1 - N_S) P_{Se_2 T_R}^\circ. \quad (3)$$

Here the constants were determined using the relation between (P_{S_2}/P_{Se_2}) and N_S shown in Fig. 10 in the previous report⁽⁴⁾, the equilibrium constant of the reaction between $S_2(g)$, $Se_2(g)$ and $SSe(g)$ ⁽⁵⁾, and the relation between chalcogen total pressure of the S-Se system and N_S reported by Devyatykh *et al.*⁽⁶⁾. This estimation is rough, but the validity will be checked experimentally by the constant surface composition of crystals.

III. Calculation Method of Diffusion Coefficient

Because the chemical potential at the surface of the sample is constant in the experimental condition of this study, the Fick's second law,

$$\partial c / \partial t = D \partial^2 x / \partial y^2, \quad (4)$$

is solved in the initial condition, $x=0$ at $y>0$ and $t=0$, and in the boundary condition, $x=x_0$ at $y=0$ and $t>0$, where D is the diffusion coefficient, x is the concentration at the depth y , x_0 is the surface concentration and t is the diffusion time. The solution is expressed by the following equation⁽⁷⁾:

$$x = x_0 \operatorname{erfc} \{y / (2\sqrt{Dt})\}, \quad (5)$$

and

$$\operatorname{erfc}(z) = 1 - \operatorname{erf}(z) = 1 - (2/\sqrt{\pi}) \int_0^z e^{-\eta^2} d\eta.$$

Equation (5) is derived on the assumption that D is independent of x , and is used to be independent of the concentration. If the experimental result satisfies eq. (5), D is known to be independent of the concentration.

The ordinate of a normal probability paper is graduated with the cumulative normal probability function,

$$F(z) = (1/\sqrt{2\pi}) \int_{-\infty}^z e^{-\tau^2/2} d\tau. \quad (6)$$

Replacing τ by $\sqrt{2}\eta$, the following equation is derived:

$$\operatorname{erf}(z/\sqrt{2}) = 2F(z) - 1. \quad (7)$$

Equation (5) gives the following expression:

$$\operatorname{erf} \{y/2\sqrt{Dt}\} = 1 - (x/x_0). \quad (8)$$

The following equation is derived from eqs. (7) and (8).

$$F(y/\sqrt{2Dt}) = 1 - (x/2x_0). \quad (9)$$

When $1 - (x/2x_0)$ is plotted against y on a normal probability paper, the plot gives a straight line and its slope is equal to $(2Dt)^{-1/2}$, if the experimental data satisfy eq. (5). As a first step the linearity was confirmed with the plot on a normal probability paper, and then the slope of the line was calculated using the numerical table between z and $F^{-1}(z)$ by the method of least squares. The diffusion coefficient was determined from the slope.

IV. Results and Discussion

In Fig. 1 is shown an example of the penetration curve at the sample temperature $T_s = 1273$ K, the reservoir temperature $T_R = 723$ K, the atomic fraction of S in reservoir $N_S = 0.650$ and the diffusion time $t = 86.4$ ks. The surface concentration x_0 was obtained to be $x_0 = 0.192$ by extrapolating the profile to the surface ($y=0$). In Fig. 2 is shown the relation between $F^{-1}\{1 - (x/2x_0)\}$ and the distance from the surface y . This plot gives a straight line. The value of D was obtained from the slope of the straight line to be 6.2×10^{-15} m²/s. The solid line in Fig. 1 is a calculated line with

Fig. 1 An example of penetration curve. [$T_s = 1273$ K, $T_R = 723$ K, $N_S = 0.650$, $t = 86.4$ ks (24 h)].

Fig. 2 Normal probability plot of the values in Fig. 1.

this value in eq. (5). The normal probability paper plots give straight lines in several runs in the conditions, $0 < x_0 < 0.5$, $T_s = 1273$ K, 1173 K or 1073 K and $T_R = 723$ K or 637 K, and so it is clarified that the diffusion coefficient is independent of composition in the range $0 < x < 0.5$. In the surface composition range $0.5 \leq x_0 < 1$, the vaporization rate of the sample is too large to prove the linearity of the plot.

The surface compositions of annealed samples at $T_s = 1273$ K and 1173 K are plotted against $(P_{S_2} + P_{Se_2})$ at constant (P_{S_2}/P_{Se_2}) in Fig. 3. Experimental values of x_0 are 0.21 ± 0.02 in the pressure range, $0.5 \text{ kPa} < (P_{S_2} + P_{Se_2}) < 50 \text{ kPa}$ (where $0.3 < N_s < 0.75$ and $563 \text{ K} < T_R < 773 \text{ K}$). It can be said that the estimation of the pressures using the molten S-Se reservoir is reasonable in a limited range because the composition of $\text{CdS}_{1-x}\text{Se}_x$ is regulated by $(P_{S_2}/P_{Se_2})^{(2)(4)}$. In the range $(P_{S_2} + P_{Se_2}) > 50 \text{ kPa}$, however, x_0 tends to decrease steeply, and the estimation of the pressures is not so good. The value of (P_{S_2}/P_{Se_2}) is considered to deviate from the estimated one to a higher one. The diffusion coefficient D is plotted

Fig. 3 Surface composition as a function of $(P_{S_2} + P_{Se_2})$ at $P_{S_2}/P_{Se_2} = 3.6$. The broken lines show the composition range $x_0 = 0.21 \pm 0.02$.

Fig. 4 Diffusion coefficient as a function of $(P_{S_2} + P_{Se_2})$ on the samples in Fig. 3. The solid lines are proportional to $(P_{S_2} + P_{Se_2})^{1/2}$.

against $(P_{S_2} + P_{Se_2})$ in Fig. 4 on the samples in Fig. 3. The data are nearly on the solid lines proportional to $(P_{S_2} + P_{Se_2})^{1/2}$. Thus D is known to be nearly proportional to $(P_{S_2} + P_{Se_2})^{1/2}$ at constant x and (P_{S_2}/P_{Se_2}) .

Subsequently D was measured changing T_s from 1064 K to 1281 K at $N_s = 0.650$ and $T_R = 723$ K (●) or 673 K (■). The surface composition of the samples are $x_0 = 0.20 \pm$

0.02. D is plotted against the reciprocal absolute samples temperature in Fig. 5. The upper solid line can represent the obtained data and is given by the following equation determined by the method of least squares on the values for $T_R = 723$ K:

$$D = 3.8 \times 10^{-9} \exp(-2.4 \times 10^{-19} \text{ J/kT}) \quad (\text{m}^2/\text{s}), \quad (10)$$

(1064 K ~ 1281 K)

where k is Boltzmann's constant.

The values represented by open symbols $\circ$ and $\square$ are calculated for the cases corresponding to the minimum of the total pressure using the relation $D \propto (P_{S_2} + P_{Se_2})^{1/2}$. This plot shows the temperature dependence of D near the stoichiometric composition. The lower solid line is given by the following equation:

$$D = 2.2 \times 10^{-5} \exp(-4.2 \times 10^{-19} \text{ J/kT}) \quad (\text{m}^2/\text{s}). \quad (11)$$

Fig. 5 Diffusion coefficient as a function of the reciprocal absolute sample temperature. $\bullet$: $T_R = 723$ K, $\blacksquare$: $T_R = 673$ K [$N_S = 0.650$]. Open symbols $\circ$ and $\square$ are the calculated values for the minimum of the total pressure.

The dissociation constant of $\text{CdS}_{1-x}\text{Se}_x$ is estimated by the following equation which is used in calculating the pressure corresponding to the minimum of the total pressure:

$$K_{\text{CdS}_{1-x}\text{Se}_x} = P_{\text{Cd}}^2 \times (P_{S_2} + P_{Se_2}) = a_{\text{CdS}}^2 K_{\text{CdS}} + a_{\text{CdSe}}^2 K_{\text{CdSe}}, \quad (12)$$

where K_{CdS} and K_{CdSe} are dissociation constants of the component compounds $\text{CdS}^{(8)}$ and $\text{CdSe}^{(9)}$, respectively, and a_{CdS} and a_{CdSe} are activities of CdS and CdSe in ternary compounds $\text{CdS}_{1-x}\text{Se}_x^{(4)}$, respectively.

The relation, $D \propto (P_{S_2} + P_{Se_2})^{1/2}$, is obtained for constant (P_{S_2}/P_{Se_2}) as shown in Fig. 4. The diffusion of chalcogen atoms under high chalcogen pressure is suggested to be due to neutral interstitial atoms for CdS and CdSe⁽¹⁰⁾. This suggestion is derived from the experimental results that the diffusion coefficient of chalcogen is proportional to the square root of chalcogen vapor pressure and that no change of diffusion coefficient is observed for any doping donor impurity (for example In). On the other hand, under a low chalcogen pressure, that is, under a high Cd vapor pressure, the diffusion of chalcogen is suggested to be due to chalcogen vacancies as well as neutral interstitial atoms.

The relation observed, $D \propto (P_{S_2} + P_{Se_2})^{1/2}$, can be interpreted well by assuming the diffusion mechanism of chalcogen as neutral interstitial atoms. Namely, Se neutral interstitial atoms diffuse into CdS from the surface, and replace S atoms at S sites. Then S neutral interstitial atoms diffuse out to the surface. These two diffusion processes are affected by P_{Se_2} and P_{S_2} , respectively.

V. Summary

The diffusion coefficient of chalcogen in $\text{CdS}_{1-x}\text{Se}_x$ is studied on annealed samples under the controlled chalcogen partial pressures by using a molten S-Se reservoir. The diffusion coefficient D is independent of composition x in the range $0 < x < 0.5$ at the sample temperature $T_s = 1173$ K and 1273 K. The temperature dependence of D near the stoichiometric composition is estimated in the temperature range between 1064 K and

1281 K. The diffusion of chalcogen atoms is deduced to be due to neutral interstitial atoms, from the relation $D \propto (P_{\text{S}_2} + P_{\text{Se}_2})^{1/2}$.

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