Formation Energy of the Sulfur Vacancy in ZnS Crystals

by

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Abstract

The sulfur vacancies in ZnS crystals are introduced by firing in zinc vapor or liquid and then the 2.3eV optical absorption band appears. The relative concentration of the sulfur vacancies is estimated by the optical absorption coefficient of the 2.3eV band. The activation energies for the introduction of the vacancy are obtained from the dependence of relative concentration of sulfur vacancies upon firing temperatures, which are 2.8eV for zinc liquid and 0.4eV for zinc vapor. These values are qualitatively discussed and the formation energy in zinc vapor is tentatively estimated to be about 1.6eV.

1. Introduction

With firing ZnS in zinc vapor or liquid an optical absorption band appears with a peak at 2.3eV, which is proposed to be due to the F^+center,[1-4] that is, a sulfur vacancy with a trapped electron, This defect is one of the simplest intrinsic defects and it is very important to clarify the formation process of the center for understanding the behavior of the lattice defects in the II–VI compounds. However, the formation energy of the sulfur vacancy in ZnS has not been known.

The 2.3eV band produced by firing zinc vapor or liquid is enhanced by uv excitation. Matsuura et al.[4] have suggested that the enhancement of the 2.3eV band by uv excitation is caused by the conversion of F^{2+} centers to F^+centers and that the absorption coefficient of the 2.3eV band after uv excitation is proportional to the concentration of the sulfur vacancies.

The reactions for the vacancy formation by firing in zinc liquid of vapor may be expressed by the following equations,

$$ZnS_{(s)} + \delta Zn_{(l)} \longrightarrow Zn_{(1+\delta)}S_{(s)} + \delta V_s \quad \text{(liquid)} \quad (1)$$
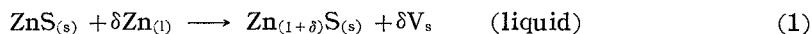
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$$ZnS_{(s)} + \delta Zn_{(g)} \longrightarrow Zn_{(1+\delta)}S_{(s)} + \delta V_s \quad \text{(vapor)} \tag{2}$$
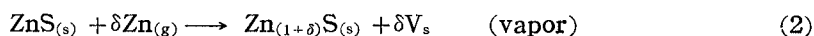
with $\delta \ll 1$,
where (s), (l) and (g) represent solid, liquid and gas phase respectively and V_s the sulfur vacancies.

Application of the law of mass action to these reactions leads to,

$$K_L = \frac{[\{Zn_{(1+\delta)}S\}_{(s)}][\delta V_s]}{[ZnS_{(s)}][\delta Zn_{(l)}]} \tag{3}$$

$$K_G = \frac{[\{Zn_{(1+\delta)}S\}_{(s)}][\delta V_s]}{[ZnS_{(s)}][\delta Zn_{(g)}]} \tag{4}$$

where K_L and K_G are the equilibrium constant and the bracket represents the activity of the substance indicated in the bracket. These activities are expressed approximately as follows,

$$[V_s] = \gamma n, \quad [\delta Zn_{(g)}] = \frac{P_{Zn}}{P_{Zn}^0}, \quad [ZnS_{(s)}] \cong [\{Zn_{(1+\delta)}S\}_{(s)}] \cong [\delta Zn_{(l)}] \cong 1,$$

where γ represents the activity coefficient, n the concentration of vacancies, P_{Zn}^0 the saturated vapor pressure of pure zinc, and P_{Zn} the pressure of the zinc vapor during firing.
Thus, eqs. (3) and (4) are reduced to

$$K_L = n_L \tag{5}$$

$$K_G = \frac{\gamma \cdot P_{Zn}^0}{P_{Zn}} n_G \tag{6}$$

The equilibrium constant K_L and K_G also are expressed as follows,

$$K_L = \exp\left(-\frac{\Delta G_L}{kT}\right) \tag{7}$$

$$K_G = \exp\left(-\frac{\Delta G_G}{kT}\right), \tag{8}$$

where ΔG_G represents the change of the Gibbs free energy in these reactions of eqs. (1) and (2) respectively. Using eqs. (5), (6), (7) and (8), the concentration of vacancies is expressed as follows,

$$n_L = A_L \exp\left(\frac{\Delta S_L}{k}\right) \exp\left(-\frac{\Delta H_L}{kT}\right) \tag{9}$$

$$n_G = A_G P_{Zn} \exp\left(\frac{\Delta S_G}{k}\right) \exp\left(-\frac{\Delta H_G}{kT}\right) \tag{10}$$

with $A_L = \gamma$, $A_G = \dfrac{\gamma}{P_{Zn}^0}$,

where ΔS_L and ΔS_G represent the entropies of these reactions, ΔH_L and ΔH_G the enthalpies.   According to simple thermodynamical consideration,

$$\Delta H_G - \Delta H_L = - H_{\ell}' , \tag{11}$$

where H_{ℓ}' is the heat of vaporization of zinc metal under the vapor pressure of pure zinc metal at a heating temperature.

In this paper, ZnS specimens are fired in zinc vapor or liquid at temperature of 1100-1250°C and the relative concentrations of the sulfur vacancies produced by the heat treatments are estimated by the optical absorption coefficient at 2.3eV photon energy.   Using eqs. (9) and (10), the formation energy of the sulfur vacancy is discussed.

2. Experimental

Undoped zinc sulfide crystals (Grade HP) obtained from Eagle-Picher Co.[*] were used in this work. The specimens were polished mechanically, and this typical size was $6 \times 3 \times 1 \text{mm}^3$.   Zn heat-treatment in zinc vapor or liquid was carried out in the quartz tube. After baking for a few hours at 1100°C, the zinc metal and the specimens were charged.   These tubes were sealed in vaccum (1×10^{-6} Torr) and heated at the range from 1100°C to 1250°C for about 25 minutes, and then quenched in the water.

The temperature distribution of the electric furnace used in firing is shown in Fig. 1. On firing the specimens in zinc liquid, the specimens were immersed in the melted zinc metal. The specimens, then, were put out of the melt and quenched. On firing in zinc vapor, the specimens were kept apart from zinc metal source during firing. The pressure of zinc vapor was controlled by the lowest temperature in quartz tube during firing. In this work, the pressure of zinc vapor was adjusted at 3.5 atm.
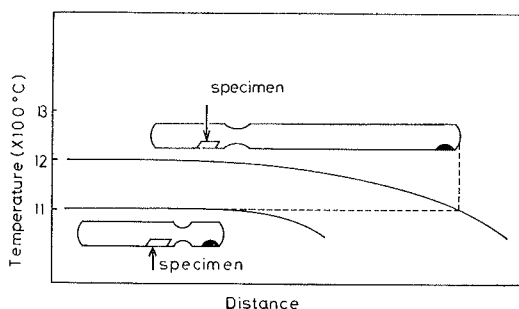
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Fig. 1. The distribution of temperature in the furnace.

Optical absorption spectra were measured by a double beam monochromator from 350 to 2500 nm before and after the excitation with uv light from an Hg-lamp with appropriate glass filters. The concentration of vacancies was estimated by the optical absorption coefficient at 540nm after uv excitation. Since the oscillator strength of the 2.3 eV absorption band has not been known, the relative concentration of the sulfur vacancy can be obtained by the above method.

3. Results and Discussion

Fig. 2 shows the optical absorption spectra of specimens fired in zinc vapor at 1200°C for 20 minutes.   Fig. 3 shows the difference spectra between the absorption coefficients before and after uv excitation in the specimens fired in zinc vapor or liquid.   As shown in Figs. 2 and 3, the zinc-liquid treatments produce optical
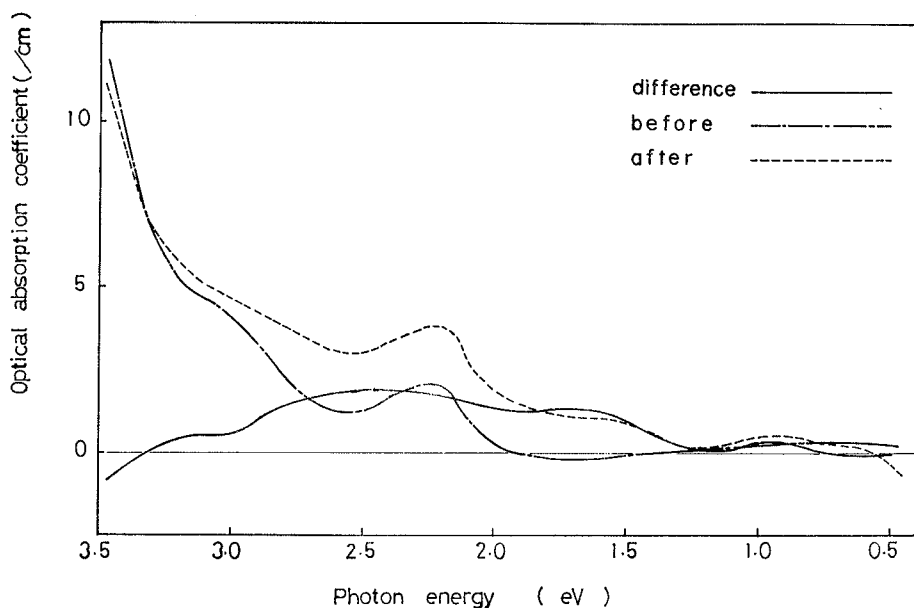

Fig. 2. The optical absorption coefficients in the specimens fired in a 3.5 atm zinc vapor at 1200°C for 20 min measured at 77 K. A chain line, a broken line and a solid line represent the absorption spectra before and after uv excitation and the difference curves between them, respectively.

absorption bands with peaks at 3.5, 3.2, 2.9 and 2.3 eV, and the vapor treatments produce an optical absorption band with a peak at 1.75eV in addition to them. These behaviors are consistent with the results reported by Matsuura *et al.*[4]

Figs. 4 and 5 show the optical absorption coefficient of the 2.3 eV band after uv excitation as a function of firing times at various temperatures of firing in zinc vapor and liquid, respectively. It seems clearly that in both cases, the optical absorption coefficients of the 2.3eV band are increased with increasing the firing time and finally, attain to a certain saturated value for each firing temperature.
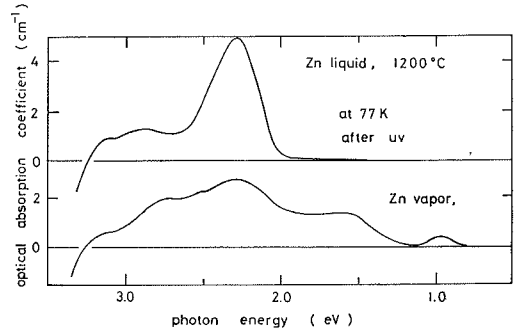

Fig. 3. The photosensitive optical absorption coefficients in the specimens fired in zinc liquid at 1200°C for 5 min and in a 3.5 atm zinc vapor at 1200°C for 10min.
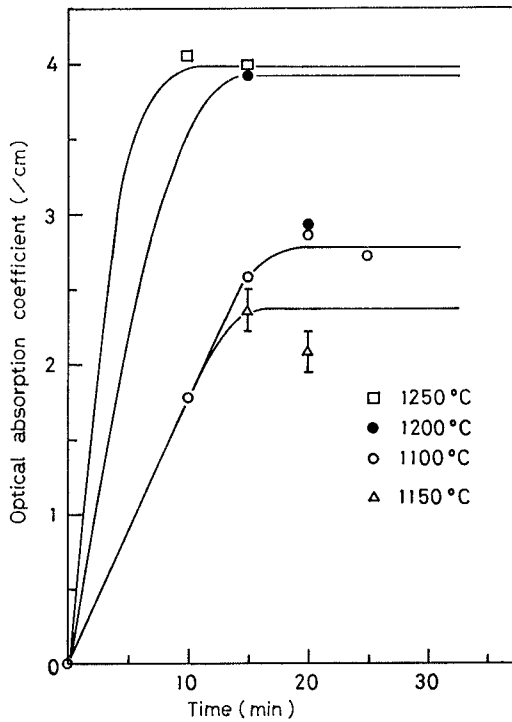

Fig. 4. The 2.3eV band absorption coefficients as a function of heating time in a 3.5 atm zinc vapor at 1100, 1150, 1200 and 1250°C.
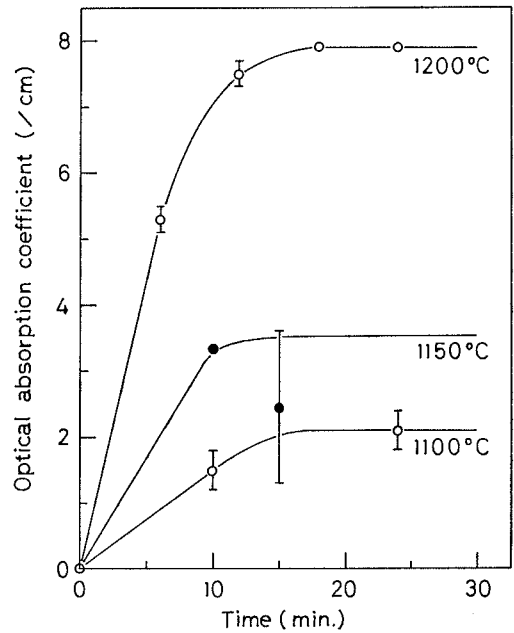
Fig. 5. The 2.3eV band absorption coefficients as a function of heating time in zinc liquid at 1100, 1150 and 1200°C.

The relations between the saturated value of the 2.3eV absorption coefficient α and firing temperature T are shown in Fig. 6. From these results, the activation energy for the introduction of the F^+ centers is estimated to be about 2.8eV for the firing in zinc liquid and about 0.4eV in zinc vapor.
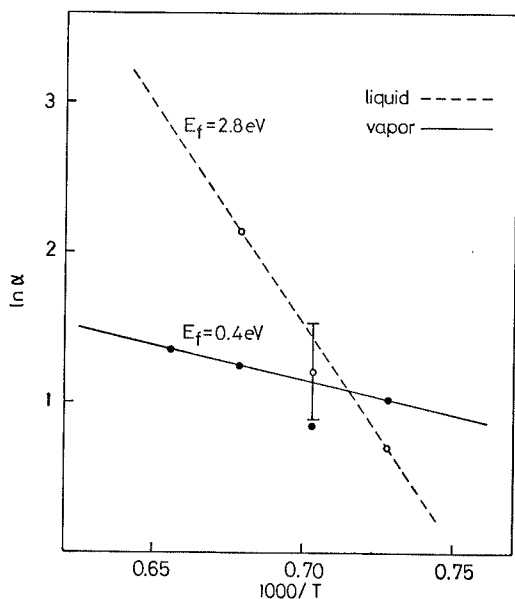

Fig 6. 2.3eV band absorption coefficients as a function of heating temperature.

As the concentration of the F^+ centers is assumed to be equal to that of the sulfur vacancies introduced by firing, the activation energies obtained from the results shown in Fig. 6. may be the enthalpies of the reactions expressed by eqs. (1) and (2). If it is the case, the enthalpies of the reactions in zinc liquid and zinc vapor are estimated to be 2.8eV and 0.4eV respectively. Since the change of volume on the firing is negligibly small, the enthalpy is nearly equal to the formation energy of the vacancy.

As shown by eq.(11), the enthalpy in zinc liquid is different from one in zinc vapor by H_f'. Here, if H_f' is assumed to be equal to the heat of vaporization H_f at the boiling point of zinc metal, H_f' is about 1.2eV.[13] However, the difference in the enthalpies obtained from the experimental results is 2.4 eV and is larger than H_f by a factor of two. Moreover, the formation energy in firing in zinc vapor is much smaller than the vacancy formation energies reported previously in other II – VI compounds as shown in the Table 1. These facts may make one suppose that the quenching rate in the additive coloration in zinc vapor was not fast enough to preclude the annealing of the vacancies into complex centers, since the thermal conductivity of zinc vapor is lower

Formation Energy

	Ef(eV)	defect
ZnS$_{(\ell)}$[12]	2.8	F^+
ZnS$_{(g)}$[12]	0.4	F^+
CdSe[5]	1.9 ± 0.2	V_{Se}^{2+} , Cd_{Int}^{2+}
CdTe[6]	1.7	V_{Te}^{2+} , Cd_{Int}^{2+}
ZnSe[7]	1.6 ± 0.2	Zn excess defect
CdTe[8]	1.65 ± 0.15	Cd excess defect
CdS[9]	2.5	Cd-Frenkel pair
CdSe[10]	2.10	interstitial
ZnTe[11]	3.95	V_{Zn}^{2+}

Table 1. The formation energies of defects in II-VI compounds.

than one of zinc liquid. These effects reduce the apparent formation energy.   The appearance of the 1.75eV absorption band by firing in zinc vapor may be due to such associations.   Therefore, it may be more reasonable to suppose that the value of the activation energy determined from the additive coloration in zinc vapor is a lower limit of the formation energy of sulfur vacancies in firing in zinc vapor and this energy should rather be estimated from the results of the additive coloration experiment in zinc liquid.

Consequently, the formation energy is tentatively estimated to be about 1.6eV by subtracting the heat of vaporization of zinc metal from the activation energy deduced from the firing experiments in zinc liquid.

As seen in Fig. 6, the concentration of the F^+ centers in the specimens firing in zinc vapor seems lower than one in the specimens fired in zinc liquid at high temperature, while higher at low temperature.   These may be due to the fact that the entropy and enthalpy of the reaction in zinc vapor are smaller than those in zinc liquid.

Some alternative explanations, of course, can not be ruled out, and it may be important to ensure rapid cooling of the specimens after firing in zinc vapor for further investigations.

References

(1) J. Schneider, L. Leutwein, and A. Räuber ; Solid State Commun. 5 (1967) 738.

(2) J. Schneider and A. Räuber ; Solid State Commun. 5 (1967) 779.

(3) K.P. Lott ; phys. stat. sol. (a) 9 (1972) K43.

(4) K. Matsuura, I.Tsurumi, and F. Takeda ; phys. stat. sol. (a) 28 (1975) 379.

(5) F.T.J. Smith ; Solid State Commun. 8 (1970) 263.

(6) F.T.J. Smith ; Proc. AIME Conf. on Defects in Electronic Materials, Boston, 1969, to be published in Met. Trans., March 1970 ; through Solid State Commun. 8 (1970) 263.

(7) F.T.J. Smith ; Solid State Commun. 7 (1969) 1757.

(8) R.C. Whelanand D.Shaw ; phys. stat. sol. 29 (1968) 145.

(9) R. Boyn, O. Goede, and S. Kuschnerus ; phys. stat. sol. 12 (1965) 57.

(10) W.D. Callister Jr., C.F. Varotto and D.A. Stevenson ; phys. stat. sol. 38 (1970) K45.

(11) D.G. Thomas and E.A. Sadowski ; J. Phys. Chem. Solids 25 (1964) 395.

(12) the present work.

(13) *Butsuri josuhyo* (Physical constant tables), ed. S. Iida (Asakura, Tokyo, 1969) p.86 [in Japanese].