

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 40, No. 1, 1970

# PHYSICO-CHEMICAL PROPERTIES OF ZINC AND CADMIUM IN GALLIUM ARSENIDE

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The diffusion process of zinc and cadmium in gallium arsenide from gaseous phase has been investigated as the function of temperature and the arsenic vapor pressure by the radioactivation analysis.

The diffusion profile of zinc could not be described by a complementary error function and the diffusion coefficient of zinc was concentration-dependent. Over the range of zinc concentrations, the diffusion coefficient of zinc was found to decrease as the arsenic vapor pressure increases. The diffusion profile of cadmium followed a complementary error function and the diffusion coefficient was found to increase as the amounts of the added arsenic increase.

These results may be explained by assuming that zinc diffuses due to an arsenic divacancy and that cadmium diffuses through the gallium sublattice.

## Introduction

In recent years, several theories have been reported to explain the diffusion mechanism of zinc in gallium arsenide. Kendall and Jones<sup>1)</sup> assumed that the substitutional diffusion rate of zinc increased with increasing zinc concentrations by the charge compensation effects. Longini<sup>2)</sup> showed that at high zinc concentrations a small fraction of zinc should go into the donor interstitial positions and these should diffuse very rapidly, thereby being dominant in the over-all diffusion process. Weisberg and Blanc<sup>3)</sup> explained the zinc diffusion profiles by means of an interstitial-substitutional model and concluded that the fraction of interstitial zinc atoms varied with the total zinc concentrations. For the diffusion of cadmium, Goldstein<sup>4)</sup> and Kogan *et al.*<sup>5)</sup> showed that the diffusion mechanism of cadmium was the vacancy migration through the gallium sublattice.

These reports described above, however, have not taken into account the influence of the arsenic vapor pressure upon the diffusion coefficient. Since the non-stoichiometric defects in gallium arsenide vary with the arsenic vapor pressure, the diffusion through vacancies or interstitials should be influenced by the arsenic vapor pressure. Recently, Shih *et al.*<sup>6)</sup> have shown that the diffusion coefficients of zinc decrease as the arsenic vapor pressure increases and explained the results by means of the

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(Received April 1, 1970)

1) D. L. Kendall and M. S. Jones, AIEE-IRE Device Research Conference, Stanford (1961)

2) R. L. Longini, *Solid-State Electronics*, **5**, 127 (1962)

3) L. R. Weisberg and J. Blanc, *Phys. Rev.*, **131**, 1548 (1963)

4) B. Goldstein, *ibid.*, **118**, 1204 (1960)

5) L. M. Kogan, S. S. Meskin and A. Ya. Goikhman, *Soviet Physics-Solid State*, **6**, 882 (1964)

6) K. K. Shih, J. W. Allen and G. L. Pearson *J. Phys. Chem. Solids*, **29**, 379 (1968)

interstitial-substitutional model.

In this report are presented the experimental data on the diffusion profiles of zinc and cadmium in gallium arsenide and theoretical considerations for the diffusion mechanism of zinc and cadmium. The radioactivation analysis and the electrical conductivity method are utilized in this study.

## Experimentals

### Materials

Single crystals of gallium arsenide were obtained from Nippon Keikinzoku laboratory. All samples used in this experiment were cut parallel to {100} or {111} planes from the undoped or tellurium doped gallium arsenide. Each crystal has  $6.7 \times 10^{16}$  to  $5 \times 10^{17}$  excess electrons per  $\text{cm}^3$ . The dimensions of the samples used in the radioactivation analysis were about  $8 \times 8 \times 0.5$  mm. Zinc, cadmium and arsenic (99.9999%) were obtained from New Metals and Chemical Company.

### Experimental procedure

The lapped and polished samples, together with the weighed chips of zinc or cadmium and arsenic, were sealed into an evacuated quartz tube at pressure of about  $2 \times 10^{-5}$  mmHg. The ampoule volume and the weights of the zinc, cadmium and arsenic used in the experiments are listed in Table 1 for diffusions of zinc and Table 2 for diffusions of cadmium.

The diffusion was carried out in a furnace with constant temperature over the length of the quartz tube. The temperature was controlled by the P.I.D. system within  $\pm 0.1^\circ\text{C}$  during the diffusion. After diffusion, the quartz tube was immersed into water to prevent the condensation of vapor species on the surface of the samples. The sides and back faces of the samples were lapped to remove the

Table 1 The weights of As and Zn and the volume of the ampoule used for experiments

(a) Diffusion at  $850^\circ\text{C}$

Sample No.	$W_{\text{As}}$ , mg	$W_{\text{Zn}}$ , mg	Ampoule volume, ml
Zn-16		3.50	5.5
Zn-22	8.82	2.05	5.3
Zn-10	19.89	2.10	6.2
Zn-20	33.37	2.15	5.1

(b) Diffusion at  $900^\circ\text{C}$

Sample No.	$W_{\text{As}}$ , mg	$W_{\text{Zn}}$ , mg	Ampoule volume, ml
Zn-23		3.45	5.5
Zn-08	9.47	3.58	5.7
Zn-04	20.41	3.80	6.1
Zn-09	38.02	3.70	6.0

Table 2 The weights of Cd and As and the volume of the ampoule used for experiments

Sample No.	$W_{\text{Cd}}$ , mg	$W_{\text{As}}$ , mg	Ampoule volume, ml	Diffusion temperature, °C
Cd-22	15.67		6.2	800
Cd-35	13.89		6.4	1,000
Cd-15	13.47		6.7	1,100
Cd-16	7.15		6.6	1,000
Cd-18	13.42	1.53	6.1	1,000
Cd-23	10.11	6.70	4.7	1,000
Cd-28	10.03	13.47	4.7	1,000

diffusion layers.

#### Phase diagram and vapor pressure

**GaAs-Zn system:** Under the experimental conditions, the gaseous and liquid phases and the gallium arsenide in the closed tube are in equilibrium. Then, an equilibrium arsenic, gallium and zinc vapor pressure within the closed tube must be determined by the liquid composition at equilibrium. The liquidus isothermal sections of the phase diagram for GaAs-Zn system at 850°C, 900°C and 1,000°C are shown in Fig. 1 from the data of Panish<sup>7)</sup>. At 850°C and 900°C the vapor pressures of arsenic along the liquidus lines show an abrupt change in passing from the point B or F to C or G in Fig. 1<sup>6)</sup>. Since the liquidus line is continuous above 1,000°C, the vapor pressure of arsenic increases gradually as the amounts of added arsenic increase.

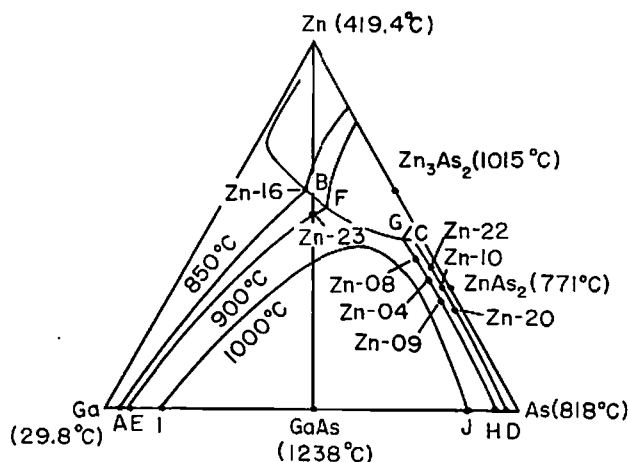


Fig. 1 Liquidus isothermal sections of the phase diagram for GaAs-Zn system at 850°C, 900°C and 1,000°C<sup>7)</sup>

7) M. B. Panish, *J. Phys. Chem. Solids*, **27**, 291 (1966)

Assuming that the vapor pressure of gallium is negligible, the number of moles of gallium in the liquid phase is equal to the number of moles of arsenic released from gallium arsenide. The total number of moles of arsenide in the liquid and vapor phase will be equal to the number of moles of arsenic added plus the number of moles of gallium in the liquid. Under these assumptions, the vapor pressure of arsenic is represented as follows<sup>6)</sup>:

$$P_{As_4} = \frac{RT}{4V} \left\{ \frac{W_{As}^a}{M_{As}} - \frac{W_{Zn}^a - W_{Zn}^v}{M_{Zn}} \left( \frac{X_{As} - X_{Ga}}{X_{Zn}} \right) \right\}, \quad (1)$$

where  $V$  is the ampoule volume,  $W_{As}^a$  and  $W_{Zn}^a$  are the weights of arsenic and zinc added to the ampoule,  $M_{As}$  and  $M_{Zn}$  are the atomic weights,  $X_{As}$ ,  $X_{Ga}$  and  $X_{Zn}$  are the atomic fractions in the liquid phase and  $W_{Zn}^v$  is the weight of zinc in the vapor phase.

The actual vapor pressure of arsenic in the vapor phase consists of tetramer, dimer and monomer of arsenic. But in eq. (1), only the tetramer is considered, since the dimer and monomer are negligible<sup>9)</sup>.

The vapor pressures of zinc and arsenic along the liquid lines have been obtained by Shih *et al.*<sup>9)</sup>. Then, the liquid composition and the partial vapor pressure can be estimated by the self-consistent method. It is necessary first to assume where the system lies on the phase diagram. The vapor pressure for this composition is calculated from the weights of zinc and arsenic and the ampoule volume by use of eq. (1), and the results are compared with the data of Shih *et al.*<sup>9)</sup>. The calculations are repeated for several points on the phase diagram until the two values of arsenic pressure coincide. The vapor pressures of zinc and arsenic for each sample are shown in Table 3 with the values of the corresponding liquid compositions, which are labeled in Fig. 1.

Table 3 Atomic fractions and the vapor pressures of  $As_4$  and Zn  
(a) Diffusion at 850°C

Sample No.	Atomic fraction			$P_{As_4}$ , atm	$P_{Zn}$ , atm
	$X_{Ga}$	$X_{As}$	$X_{Zn}$		
Zn-16	0.209	0.193	0.598	$6.5 \times 10^{-6}$	$3.2 \times 10^{-1}$
Zn-22	0.030	0.585	0.385	$3.7 \times 10^{-1}$	$1.2 \times 10^{-1}$
Zn-10	0.038	0.645	0.317	$8.1 \times 10^{-1}$	$6.0 \times 10^{-2}$
Zn-20	0.050	0.700	0.250	1.7	$5.0 \times 10^{-2}$

(b) Diffusion at 900°C

Sample No.	Atomic fraction			$P_{As_4}$ , atm	$P_{Zn}$ , atm
	$X_{Ga}$	$X_{As}$	$X_{Zn}$		
Zn-23	0.240	0.235	0.525	$1.2 \times 10^{-4}$	$4.2 \times 10^{-1}$
Zn-08	0.038	0.545	0.417	$3.7 \times 10^{-1}$	$1.3 \times 10^{-1}$
Zn-04	0.053	0.610	0.337	$8.0 \times 10^{-1}$	$1.1 \times 10^{-1}$
Zn-09	0.033	0.675	0.292	1.7	$8.5 \times 10^{-2}$

8) C. D. Thermond, *J. Phys. Chem. Solids*, **26**, 785 (1965)

9) K. K. Shih, J. W. Allen and G. L. Pearson, *ibid.*, **29**, 367 (1968)

**GaAs-Cd system :** In the Cd-As system there are two intermetallic compounds,  $\text{CdAs}_2$  and  $\text{Cd}_3\text{As}_2$ , which show the melting points of  $621^\circ\text{C}$  and  $721^\circ\text{C}$ , respectively<sup>10)</sup>. Since the phase diagram and the partial vapor pressure along the liquidus lines for the GaAs-Cd system are not known, the vapor pressures of cadmium and arsenic in the ampoule cannot be exactly determined. However, the liquidus line of  $1,000^\circ\text{C}$  for the GaAs-Cd system may be considered to be continuous like those of the GaAs-Zn system at  $1,000^\circ\text{C}$ .

#### *Radioactivation analysis of diffused zinc and cadmium in gallium arsenide*

The diffusion profiles of zinc and cadmium in gallium arsenide were determined by the radioactivation analysis based on the quantitative isotope dilution principle as proposed by Suzuki, Kudo<sup>11)–14)</sup>, Ruzicka and Stary<sup>15)16)</sup>.

The gallium arsenide wafers containing the diffused zinc or cadmium and the standard samples were simultaneously irradiated for 130~180 hr in the nuclear reactor JRR-2 at a neutron flux of  $3\sim4\times10^{13}$  n/cm<sup>2</sup>/sec. The temperature of the samples was increased to about  $200^\circ\text{C}$  by irradiations. After irradiations, each of the samples was successively etched at  $20^\circ\text{C}$  in the solution consisting of the equal volume of concentrated sulfuric acid, 30% solution of hydrogen peroxide and redistilled water. Thus, the sample solutions corresponding to the successive layers were obtained. The thickness of the etched layer was estimated from the weight loss of the sample. The amount of zinc or cadmium in those sample solutions was determined by the following procedure. The sample solution was transferred into an evaporating dish, in which a platinum plate was placed as a catalyst and an appropriate amount of zinc or cadmium carrier was added. The solution was concentrated by moderate heating until the hydrogen peroxide was completely decomposed. Then, in the case of zinc solution, 0.1 M citric acid was added and the solution was adjusted within  $\text{pH}=8\sim9$  with aqueous ammonia. In the case of cadmium, 0.1 M tartrate solution and 10 N sodium hydroxide solution were added. The solution was made 1 N with respect to sodium hydroxide. These solutions were shaken with substoichiometric amounts of dithizone solution in carbon tetrachloride for 10 min. The extraction was repeated. The organic layer was separated and radioactivity ( $a$ ) was measured. A known amount of zinc or cadmium standard ( $M_s$ ), irradiated simultaneously, was treated in exactly the same way as described above and the radioactivity of the organic phase ( $a_s$ ) was measured. The amount of zinc or cadmium ( $M_x$ ) to be determined was calculated by the following equation,

$$M_x = M_s \frac{a}{a_s} . \quad (2)$$

#### *Electrical conductivity method*

In parallel with the radioactivation analysis, the surface concentrations and the diffusion

10) M. Hansen, "Constitution of Binary Alloys", 2nd ed., p. 156, McGraw-Hill Book Co., New York (1958)

11) N. Suzuki and K. Kudo, *Anal. Chem. Acta*, **32**, 456 (1965)

12) K. Kudo and N. Suzuki, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **86**, 1059 (1965)

13) K. Kudo, *Radioisotopes*, **15**, 209 (1966)

14) K. Kudo, *ibid.*, **16**, 199 (1967)

15) J. Ruzicka and J. Stary, *Talanta*, **10**, 287 (1963)

16) A. Zemzn, J. Ruzicka and J. Stary, *ibid.*, **10**, 685 (1963)

coefficients of cadmium were determined by the electrical conductivity method, as proposed by Backenstoss<sup>17)</sup>.

Assuming that the diffusion profiles of cadmium follow the complementary error functions and cadmium in the diffusion layer is singly ionized, the surface concentrations and the diffusion coefficients of cadmium can be calculated if we know the average electrical conductivity of the diffusion layer, the depth of the p-n junction and the relation between the mobility and the carrier concentration in gallium arsenide<sup>5)</sup>.

The average electrical conductivity of the diffusion layer was determined by the following procedure. The samples were cut into the rectangular shape of  $3 \times 8 \times 0.5$  mm. After diffusion, the diffusion layer was removed from one of the large faces of the sample. The ohmic current contacts were made at the ends of the surface of the diffusion layer by non-electrolytic deposition of nickel and the potential contacts were prepared at the surface of the diffusion layer by fusing indium. The voltage drop between the potential contacts was measured at room temperature. The relation between the hole mobility and the hole concentration in gallium arsenide was assumed to be expressed as follows<sup>5)</sup>,

$$\mu = 10^7 P^{-0.27} . \quad (3)$$

## Experimental Results

### Diffusion of zinc

The diffusion profiles at 850°C and 900°C are shown in Figs. 2 and 3. The penetration depth of zinc decreases with the arsenic vapor pressure increases. A dashed line in Fig. 3 shows the complementary error function with  $D = 1.6 \times 10^{-9}$  cm<sup>2</sup>·sec<sup>-1</sup>,  $C_s = 1.8 \times 10^{20}$  cm<sup>-3</sup> and  $t = 1.44 \times 10^4$  sec, determined by fitting the curve to the data of Zn-08 near the surface. The complementary error function is expressed by the equation,

$$C(x) = C_s \{ 1 - \operatorname{erf} \frac{x}{2(Dt)^{1/2}} \} . \quad (4)$$

where  $C_s$  is the surface concentration in solid,  $C$  is the concentration at the distance  $x$  from the surface in cm,  $D$  is the diffusion coefficient in cm<sup>2</sup>·sec<sup>-1</sup> and  $t$  is the diffusion time in seconds. It is clear from Fig. 3 that the diffusion profiles of zinc cannot be described by the complementary error functions and that a concentration-dependent diffusion coefficient must be assumed. The diffusion coefficients were then obtained by the Boltzmann-Matano method<sup>18)</sup>. In order to eliminate the uncertain points of the data, the value of  $P = 100 (1 - C/2C_s)$  vs  $\lambda = x/t^{1/2}$  were plotted on the probability paper as shown in Fig. 4. In any case a straight line on the probability paper could not be obtained, indicating that the diffusion coefficients were concentration-dependent.

A slight increase in surface zinc concentrations with excess arsenic vapor (Figs. 2 and 3) quantitatively agrees with the solubility data of McCaldin<sup>19)</sup>. In Figs. 5 and 6, the calculated results for the

17) G. Backenstoss, *B. S. T. J.*, **37**, 699 (1958)

18) J. Crank, *Mathematics of Diffusion*, p. 148 Oxford University Press (1956)

19) J. O. McCaldin, *J. Appl. Phys.*, **34**, 1748 (1963)

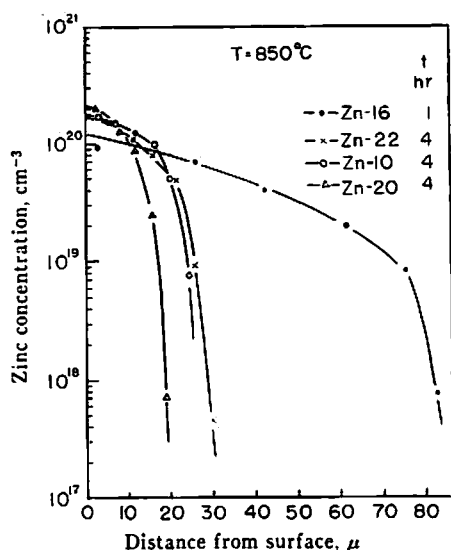


Fig. 2 Diffusion profiles of Zn in GaAs at 850°C

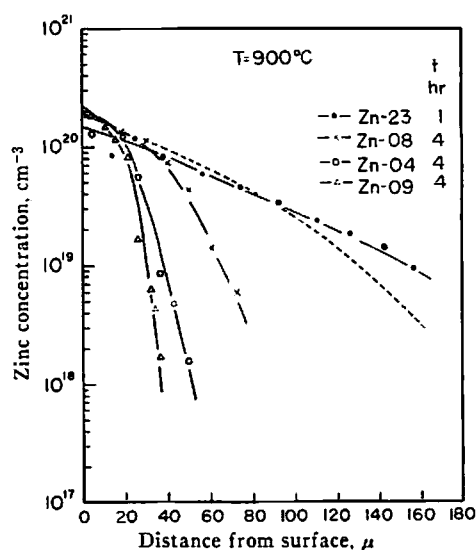
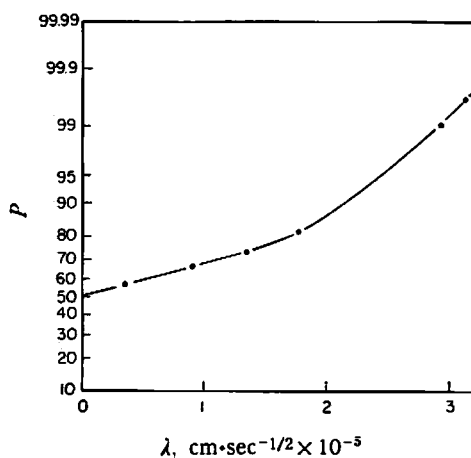


Fig. 3 Diffusion profiles of Zn in GaAs at 900°C. A dotted line is a complementary error function fitted the curve to the data of Zn-08 near the surface.

Fig. 4 Diffusion profile of Zn-09.  $P=100(1-C/2C_s)$  as a function of  $\lambda=x/t^{1/2}$ 

diffusion coefficients at 850°C and 900°C are plotted as a function of zinc concentrations. The diffusion coefficients decrease with increasing arsenic vapor pressure in the whole range of zinc concentrations and are concentration-dependent at high zinc concentrations, while concentration-independent at low zinc concentration. In comparison, the data of Rupprecht and LeMay at 850°C under 1.3 atm of arsenic vapor pressure and that of Shih *et al.* at 900°C under  $10^{-4}$  atm of arsenic vapor pressure are shown in Figs. 5 and 6 as dotted lines, respectively<sup>6)20)</sup>. In Fig. 7 the diffusion coefficients at low zinc concentrations are plotted as a function of arsenic vapor pressure. The diffusion coefficients decrease with increasing arsenic vapor pressure.

20) H. Rupprecht and C. Z. LeMay. *J. Appl. Phys.*, **35**, 1970 (1964)

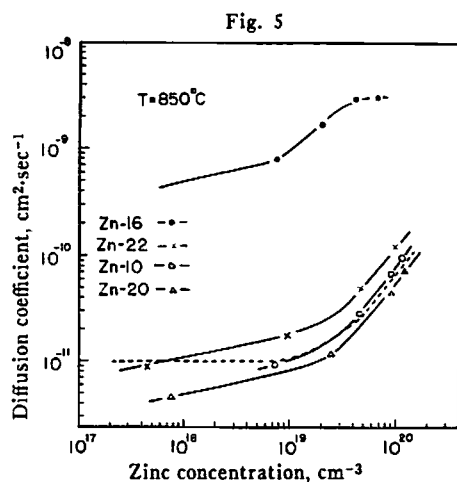
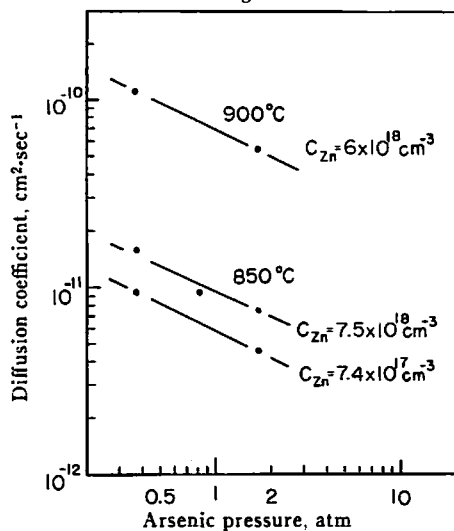


Fig. 7



#### Diffusion of cadmium

The diffusion profiles of cadmium at 800°C, 1,000°C and 1,100°C are shown in Fig. 8. The weight of the cadmium added in the ampoule is the amount which produces the cadmium vapor pressure of 2 atm, if it is all in vapor phase. Since the cadmium was diffused without excess arsenic, the system is assumed to attain the equilibrium near the GaAs-Cd pseudo-binary liquid phase composition. The vapor pressure of arsenic is estimated to be in order of the dissociation pressure of gallium arsenide, which is  $10^{-6}$ – $10^{-2}$  atm at 800°C–1,100°C<sup>8)</sup>.

The solid lines in Fig. 8 show the complementary error functions given by eq. (4). The diffusion coefficients were determined by fitting the data points to eq. (4) at each temperature.

The temperature dependence of the diffusion coefficient of cadmium, plotted in Fig. 9, is expressed

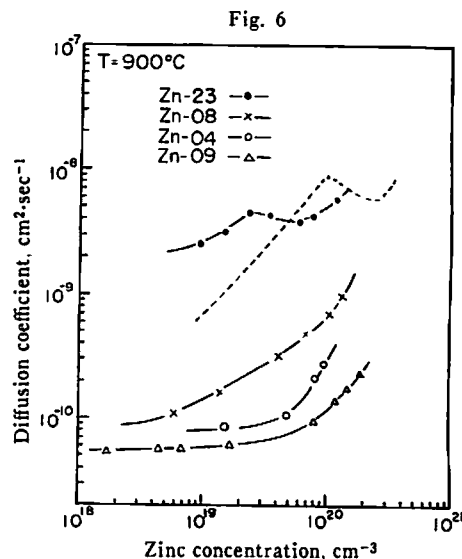


Fig. 5 Diffusion coefficient vs Zn concentration for Zn in GaAs at 850°C. A dotted line represents the data of Rupprecht and LeMay at 850°C under 1.3 atm of arsenic vapor pressure.

Fig. 6 Diffusion coefficient vs Zn concentration for Zn in GaAs at 900°C. A dotted line represents the data of Shih *et al.* at 900°C under  $10^{-4}$  atm of arsenic vapor pressure<sup>6)</sup>.

Fig. 7 Diffusion coefficient vs arsenic pressure for Zn in GaAs at 850°C and 900°C



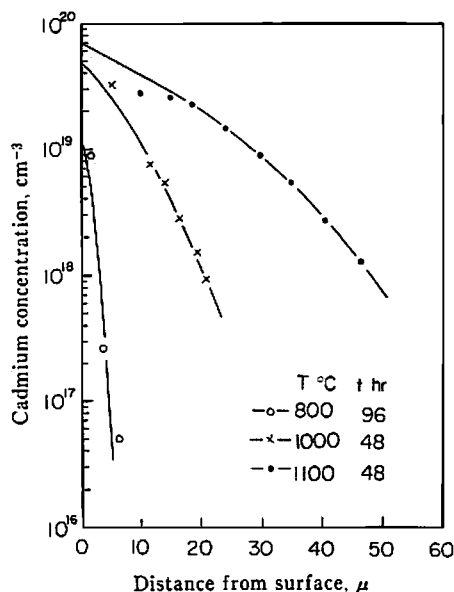


Fig. 8 Diffusion profiles of Cd in GaAs. Solid lines are the theoretical error function complement.

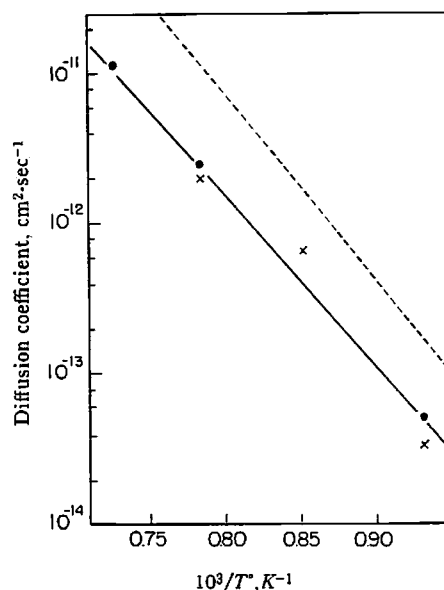


Fig. 9 Temperature dependence of the diffusion coefficient of Cd in GaAs. ● : radioactivation analysis  
× : electrical conductivity method  
The dotted line represents the data obtained by Goldstein<sup>4)</sup>.

by the equation,

$$D = D_0 \exp\left(\frac{-E}{kT}\right) \quad (5)$$

where  $D_0 = 1.3 \times 10^{-3} \text{ cm}^2 \cdot \text{sec}^{-1}$  and  $E = 2.2 \text{ eV}$ . The closed circles and the crosses in Fig. 9 show the diffusion coefficients obtained by the radioactivation analysis and the electrical conductivity method, respectively. In comparison, the data of Goldstein<sup>4)</sup> at the arsenic vapor pressure sufficient to prevent the dissociation of gallium arsenide are shown in Fig. 9 as a dotted line with  $D_0 = 5 \times 10^{-2} \text{ cm}^2 \cdot \text{sec}^{-1}$  and  $E = 2.43 \text{ eV}$ .

The dependence of the diffusion profile on the initial amounts of cadmium is shown in Fig. 10. These curves can be described well by the complementary error functions given by eq. (4), (solid lines in Fig. 10). The samples subjected to diffusion at 1,000°C for 48 hr without excess arsenic were measured. Both the surface concentration and the penetration depth of cadmium increase as the amounts of cadmium increase.

Fig. 11 shows the dependence of the diffusion profiles of cadmium on the amounts of the added arsenic at a diffusion temperature of 1,000°C. The solid lines show the complementary error functions given by eq. (4). The diffusion profiles of cadmium with excess arsenic are expressed by two overlapping complementary error functions. The diffusion profile for small amounts of the added arsenic Cd-18, which are quite rich in cadmium, is close to that of Cd-35 without excess arsenic, which seems to indicate that the vapor pressure of arsenic changes continuously as arsenic is added. For large amounts of the added arsenic, both the surface concentration and the penetration depth of

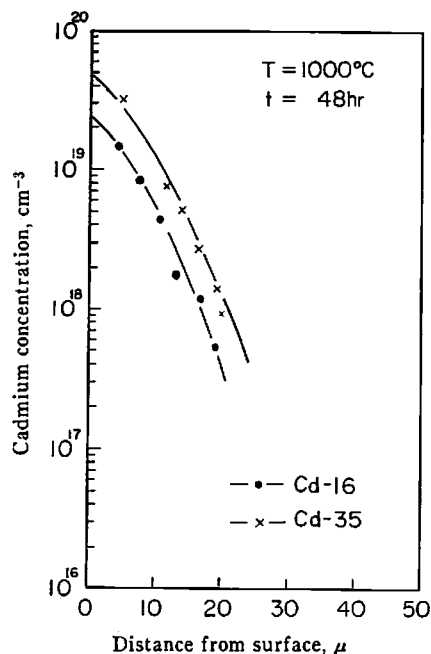


Fig. 10 Diffusion profiles of Cd in GaAs at 1,000°C. Solid lines are the theoretical error function complement.

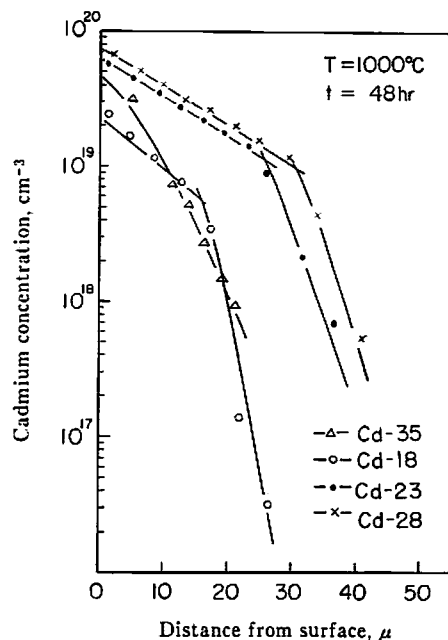


Fig. 11 Diffusion profiles of Cd in GaAs under arsenic pressure at 1000°C. Solid lines are the theoretical error function complement.

cadmium increase as the amounts of the added arsenic increase. In Fig. 12 the diffusion coefficients at 1,000°C obtained from both branches of the diffusion profiles shown in Fig. 11 are plotted as a function of the amounts of arsenic. It is noted that the effects of arsenic pressure on the diffusion coefficients of cadmium are different from that of zinc.

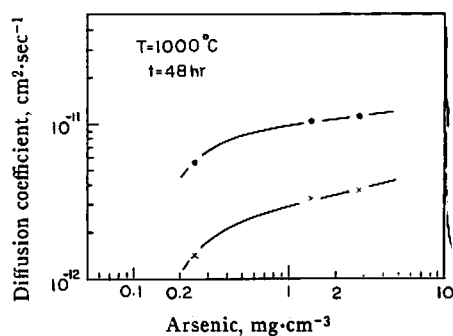


Fig. 12 Diffusion coefficients vs amounts of added arsenic for Cd in GaAs  
● : calculated from the fast diffusion profile  
× : calculated from the slow diffusion profile

## Discussions

### Diffusion mechanism of zinc

The work of Rupprecht and LeMay<sup>20)</sup> has shown that the diffusion coefficient of zinc in the pre-

sence of excess arsenic is smaller at the zinc concentrations above  $5 \times 10^{18} \text{ cm}^{-3}$  but larger below  $5 \times 10^{18} \text{ cm}^{-3}$ , as compared with the data in the absence of excess arsenic<sup>1)</sup>.

According to Rupprecht and LeMay's derivation, the effective diffusion coefficient for an interstitial-substitutional mechanism is given by

$$D_{\text{eff}} = K_1[V_{\text{Ga}}] + K_2[\text{Zn}_{\text{Ga}}]^2/[V_{\text{Ga}}], \quad (6)$$

where  $[V_{\text{Ga}}]$  and  $[\text{Zn}_{\text{Ga}}]$  are the concentrations of gallium vacancy and of zinc at gallium sublattice, respectively.  $K_1$  and  $K_2$  are the constants depending only on temperature. The first term of eq. (6) represents a substitutional diffusion, while the second term an interstitial diffusion. Applying the mass action law to an equilibrium equation between the gallium vacancy concentration and the arsenic pressure, one obtains

$$[V_{\text{Ga}}] = K_3 P_{\text{As}_4}^{1/4}, \quad (7)$$

where  $K_3$  is an equilibrium constant. From eqs. (6) and (7) Rupprecht concluded that the substitutional diffusion *via* gallium vacancy dominated at low zinc concentrations and the interstitial part was the dominant factor in the range of higher zinc concentrations, where the effective diffusion coefficient was concentration-dependent.

If Rupprecht and LeMay's model is valid, the diffusion coefficient of zinc at low zinc concentrations should increase as the arsenic vapor pressure increases. In our experiments, however, the effective diffusion coefficients decrease as the arsenic vapor pressure increases over the whole range of zinc concentrations as shown in Figs. 5 and 6.

Shih *et al.*<sup>9)</sup> have shown that the diffusion coefficient of zinc at constant zinc concentration was proportional to  $P_{\text{As}_4}^{-1/4}$  and explained the results by an interstitial diffusion model. However, the dependence of the diffusion coefficients on zinc concentrations cannot be understood by this model.

Seltzer<sup>21)</sup> has found that the effective diffusion coefficients of manganese in gallium arsenide decrease as the arsenic vapor pressure increases at low manganese concentrations. He assumed that the arsenic divacancy  $(V_{\text{As}}V_{\text{As}})^{++}$  was associated with the manganese atom at the gallium sublattice  $\text{Mn}_{\text{Ga}}$  to form a complex such as  $(V_{\text{As}}\text{Mn}_{\text{Ga}}V_{\text{As}})^+$  which plays an important role for the diffusion process in gallium arsenide.

Applying the Seltzer analysis to the zinc-gallium arsenide system, the effective diffusion coefficient of zinc in the intrinsic region is given by

$$D_{\text{eff}} = \frac{DK_4^2}{K_i K_5} P_{\text{As}_4}^{-1/2}, \quad (8)$$

and in the extrinsic region

$$D_{\text{eff}} = \frac{3DK_4^2}{K_i^2 K_5} [\text{Zn}]^2_{\text{total}} P_{\text{As}_4}^{-1/2}, \quad (9)$$

where  $K_4$  is an equilibrium constant between arsenic vacancy and arsenic vapor pressure,  $K_5$  between the arsenic divacancy and zinc at gallium sublattice,  $K_i$  the intrinsic constant and  $D$  a diffusion coefficient of  $(V_{\text{As}}\text{Zn}_{\text{Ga}}V_{\text{As}})^+$  assumed to be so much larger than that of  $\text{Zn}_{\text{Ga}}$ . From eqs. (8) and (9) it is clear that the effective diffusion coefficients should be expected to be inversely proportional to the square

21) M. S. Seltzer, *J. Phys. Chem. Solids*, **26**, 243 (1965)

root of the arsenic vapor pressure in the whole range of zinc concentrations. In our results the effective diffusion coefficients at low zinc concentrations seem to vary in such a way as shown in Fig. 7, although there remains an ambiguity due to the lack of the data in a wide range of the arsenic vapor pressure. The intrinsic carrier concentration in gallium arsenide is estimated to be about  $3\sim 4 \times 10^{18} \text{ cm}^{-3}$  at  $850^\circ\text{C}\sim 900^\circ\text{C}$  from the data of McCaldin<sup>19)</sup>.

In Seltzer's model it has been assumed that the thermal equilibrium is achieved everywhere in the sample between zinc at gallium sublattice and arsenic vacancy. However, the activation energy of vacancy diffusion of arsenic in gallium arsenide has been reported to be about  $3.0 \text{ eV}$ <sup>22)</sup>, which is the same order as that of zinc in gallium arsenide<sup>4)</sup>. The activation energy of zinc diffusion at low zinc concentrations is obtained about  $3.5\sim 4.5 \text{ eV}$  from the temperature dependence of the diffusion coefficients at a constant arsenic vapor pressure, though it may be somewhat over-estimated. This value is compared with the value of  $2.49 \text{ eV}$  reported by Goldstein<sup>4)</sup>.

Although there remains some doubt about whether the divacancy model assumed for the manganese diffusion may be applied to zinc diffusion in gallium arsenide, the experimental results in this study for both effects of arsenic vapor pressure and zinc concentration on the diffusion coefficients seem to suggest that the divacancy mechanism is operative for zinc diffusion as well as for the manganese diffusion in gallium arsenide. However, for the detailed discussions of the diffusion mechanism of zinc, it is necessary to take into account several charge states of zinc and vacancies, un-ionized or ionized.

#### Diffusion mechanism of cadmium

There are many differences in the experimental results between zinc and cadmium diffusions. It may be seen from the results that the diffusion profiles of cadmium can be described by the complementary error functions and that the diffusion coefficients are much less than those of zinc by a factor of about  $10^4$ . Although the vapor pressures of arsenic and cadmium in the ampoule cannot be exactly determined, it may be considered from the analogy of the phase diagram of the GaAs-Zn system that the vapor pressure of arsenic at  $1,000^\circ\text{C}$  increases continuously as the amounts of arsenic increase. From the results presented in Fig. 12, it is seen that the diffusion coefficients of cadmium in gallium arsenide increase as the amounts of arsenic increase.

Assuming that cadmium atoms diffuse by successive jumps through the gallium vacancies, the effective diffusion coefficient of cadmium is a linear function of the vacancy concentration. Using eq. (7), it is clear that the effective diffusion coefficients of cadmium should be proportional to the fourth root of the arsenic vapor pressure.

$$D_{\text{eff}} = K_6 D P_{\text{As}_4}^{1/4}, \quad (10)$$

where  $K_6$  is an equilibrium constant and  $D$  the substitutional diffusion coefficient of cadmium.

22) H. R. Potts and G. L. Pearson, *J. Appl. Phys.*, **37**, 2098 (1966)

### Conclusion

The comparisons of the diffusion properties between zinc and cadmium are summarized in Table 4. The same arsenic pressure dependence of the surface concentrations is found for zinc and cadmium. These facts indicate that both atoms enter into gallium sublattice. The other properties, such as diffusion profiles and the effects of excess arsenic on the diffusion coefficients, are very different from

Table 4 Comparison of diffusion properties between Zn and Cd diffusion in GaAs

		Zinc	Cadmium
Diffusion profile		Concentration dependent	Error function
Diffusion coefficient ( $\text{cm}^2\cdot\text{sec}^{-1}$ )		$10^{-10}$ (900°C)	$2 \times 10^{-12}$ (1,000°C)
Surface concentration ( $\text{cm}^{-2}$ )		$2 \times 10^{20}$ (900°C)	$5 \times 10^{19}$ (1,000°C)
Effect of arsenic vapor pressure	( $C_s$ )	increase	increase
	( $D$ )	decrease	increase
Diffusion mechanism		divacancy	Ga vacancy

each other. From the effect of excess arsenic on the diffusion coefficients, it is suggested that the diffusion due to the arsenic divacancy is responsible for zinc diffusion and that the diffusion through gallium vacancy is responsible for cadmium diffusion in gallium arsenide. If the same basic diffusion mechanism is operative for both atoms, the arsenic vapor pressure dependence of the diffusion coefficients should be identical for them.

### Acknowledgments

The author would like to express his sincere gratitude to Prof. J. Osugi for valuable discussions. He also thanks Dr. T. Imai, Dr. K. Kudo and Mr. Y. Sato for their continued encouragements and valuable discussions.

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