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LAYER GROWTH OF ZnSb PHASE IN THE Zn-Sb DIFFUSION COUPLE AT HIGH PRESSURE

BY MASATAKE KATAYAMA, KIMIHIKO HARA AND JIRO OSUGI

The kinetics of growth of the ZnSb phase layer in the Zn-Sb system has been investigated with the diffusion couples annealed in the temperature range of 240 to 320°C, under pressures up to 30 kb and for time up to 17 hr. Among all the intermetallic compounds present in the Zn-Sb equilibrium phase diagram, only ZnSb was the product detected in the diffusion zone. Concentrations of zinc in the ZnSb layer were 20–35 at%, which deviated extensively from the equilibrium concentration. Zinc was by far the faster moving species and the pronounced Kirkendall effect was observed. Since the parabolic rate law was obeyed and the Kirkendall markers moved toward the zinc side, it was concluded that volume diffusion controlled the layer growth and occurred by vacancy mechanism.

It has been found that pressure affects not only the growth of the ZnSb phase, but also the interface composition; the increase of 8 kb in the applied pressure reduces the rate constant by about 7% and the increase of pressure from 14 to 22 kb decreases by about 7% the concentration of zinc in the ZnSb layer. The apparent activation energies and the activation volumes are 12.1–14.3 kcal/mol in the range of 240–320°C and 0.9–1.2 cm^3/mol in the range of 14–30 kb, respectively. The diffusion coefficients of zinc calculated by using Kidson's method were 10^{-9}–10^{-10} cm^2/sec and they were 5–10 times as large as those obtained in the Zn-As system.

Introduction

Recently the analysis of the diffusion-reaction using diffusion couples has been facilitated by the development of the electron probe microanalyzer and the researches on the interdiffusion of various metallic systems have been carried out. There is, however, no report with respect to the solid-state bonding in the Zn-Sb system. It is interesting to investigate the growth kinetics of a typical semiconductor, ZnSb. It has been established that in the Zn-Sb system there exist three intermetallic compounds: ZnSb, Zn_4Sb_3, and Zn_3Sb_2[1,2]. Although Zn_4Sb_3 and Zn_3Sb_2 have many polymorphisms and their crystal structures are not always determined, ZnSb has one crystallographic form[3]. As seen from the phase diagram of the Zn-Sb system, the compounds have small solubility limit in

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* $T/K = 273.2 + (t/°C)$, 1 bar $= 10^5$ Pa, 1 $\mu = 10^{-6}$ m, 1 kcal $= 4.184$ kJ

[1] M. Hansen and K. Anderko, "Constitution of Binary Alloys", p. 1182, McGraw-Hill, New York (1959)

[2] V. Tydlitat, *Czech. J. Phys.*, 9, 638 (1959)

[3] K. E. Almin, *Acta Chem. Scand.*, 2, 400 (1948)

comparison with other metallic systems. There are such numerous precedents that some of the intermediate phases which can be seen in the equilibrium phase diagram are not detectable at all[4-8]. Taking these evidences into account, it is anticipated that the solid solution between zinc and antimony will not be formed, but one of the three intermetallic compounds, at least, will be formed.

In diffusion couples the reaction process is in need of the long-range mass transfer through the diffusion zone and in most cases both the process of nucleation and that of interfacial reaction at the phase boundaries have been out of discussion. According to many studies of the growth rate of diffusion layers, the width of the layers changes parabolically with time[9], though some systems are found to deviate from the parabolic rate law[10,11].

Up to the present, the effect of pressure on the formation of the intermetallic phases has been examined by several researchers. The effect of uniaxial pressure by means of a hot-pressing technique and the hydrostatic pressure by the argon gas medium are summarized as follows: the growth rate of intermetallic phases decreases with pressure in some systems: Ni-Al and Cu-Zn[12-14] and increases in other systems: U-Al, U-Ni, and U-Cu[15-17]. To our knowledge, no work on the effect of quasi-hydrostatic pressure on the growth rate has been performed. The purpose of this work is to investigate the effect of quasi-hydrostatic pressure on the growth of the layer and on the interface composition. It is hoped that the comparison of the present results with other measured behaviors of growth kinetics will give some insights into the mechanism responsible for the diffusion in the Zn-Sb system.

Experimental

Materials and Procedure

Zinc metal (99.999%) and antimony metal (99.999%) with the shape of a rod were supplied by Mitsuwa Pure Chemicals, Ltd. and Osaka Asahi Metal Co., Ltd., respectively. Tungsten powder (99.9%) was obtained from Wako Pure Chemical Industries, Ltd. Emission spectrochemical analysis indicated that the impurities contained in the Zn metal were Cu, Cd, Fe, Pb and Mg and those in the Sb metal were Cu and As.

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4) L. S. Castleman and L. L. Seigle, *Trans. Met. Soc. AIME*, **209**, 1173 (1957)
5) N. L. Peterson and R. E. Ogilvie, *ibid.*, **218**, 439 (1960)
6) L. S. Birks and R. E. Seebold, *J. Nuc. Mat.*, **3**, 249, 260 (1961)
7) G. V. Kidson and G. D. Miller, *ibid.*, **12**, 61 (1964)
8) K. Hirano and Y. Ipposhi, *Nippon Kinzoku Gakkaishi* (*J. Japan Inst. Metals*), **32**, 815 (1968)
9) M. Onishi, Y. Wakamatu, K. Fukumoto and M. Sagara, *ibid.*, **36**, 150 (1972)
10) D. J. Blickwede, *J. Metals*, **5**, 807 (1953)
11) D. H. Rowland, *Trans. ASM*, **40**, 983 (1948)
12) S. Storchheim, J. L. Zambrow and H. H. Hausner, *J. Metals*, **6**, 269 (1954)
13) L. S. Castleman and L. L. Seigle, *Trans. Met. Soc. AIME*, **212**, 589 (1958)
14) H. A. Froot and L. S. Castleman, *ibid.*, **227**, 838 (1963)
15) A. D. Le Claire and I. J. Bear, *J. Nucl. Energy*, **2**, 229 (1956)
16) Y. Adda, M. Beyeler, A. Kirianenko and B. Pernot, *Mem. Sci. Rev. Met.*, **57**, 423 (1960)
17) L. S. Castleman, *J. Nucl. Mater.*, **3**, 1 (1961)

The disks having 3 mm diameter and roughly 1.5 mm thickness were made of the Zn and Sb rods by a lathe rods. For the purpose of obtaining large grain sizes, these Zn and Sb disks were annealed in vacuum for 30 hr at 280 and 380°C, respectively. The grain sizes obtained were about 0.5 mm for both specimens. The surfaces of the disks were ground metallographically parallel through emery paper (2000) and then on a whetstone. The specimens were rinsed in water and then in ethanol.

A diffusion couple made of both disks was inserted in a teflon capsule in order to serve for compression. The teflon capsule was cramped with screws so as to have a tight contact. These treatments were made in ethanol. Then the samples were put into a silica tube evacuated by a diffusion pump ($<10^{-4}$ mmHg) and preannealed at 160°C for 1 hr in an electric furnace in order to weld thermally. A very thin layer in the diffusion zone, less than 2 μ wide, was formed during the welding treatment and it is quite negligible in comparison with the layer width formed during the diffusion annealing. Tungsten powder (about 3 $\mu\phi$) was used as a maker for the measurement of the Kirkendall effect.

The runs were carried out by using a compact cubic anvil apparatus described in the previous paper[18]. The assembly of the pressure transmitting pyrophyllite cube was already reported in detail[19]. The samples were compressed in the range of 14 to 30 kb. The diffusion annealing was performed in the temperature range of 240–320°C which was controlled within ±3°C and up to for 17 hr. After each run, the sample was quenched by cutting off the electric current and then taken out.

Analysis

The specimen was buried in polyester resin. It was sectioned and ground parallel to the direction of diffusion by emery papers and the metal polish. Finally it was polished on the DP-cloth by the diamond paste. Concentration-penetration curves were determined by using an electron probe microanalyzer (EPMA: Shimadzu EMX). An accelerating voltage of 25 kV was employed and the intensities of Zn$K\alpha$ and Sb$L\alpha$ were measured. The concentrations of Zn and Sb in the diffusion zone were determined from the calibration curve for the quantitative analysis. The calibration curve, representing the relation between the ratio of the observed relative intensity of the characteristic X-ray and that of the concentration in wt%, was obtained by calculating the correction factors for atomic number, fluorescence and absorption. Microscopic observation was made metallographically and the width of the layer was measured at five arbitrary positions.

Results and Discussions

Identification of reaction product

The orthorhombic ZnSb was synthesized at 500°C for 3 hr from the mixture of equal at% be-

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[18] J. Osugi, K. Shimizu, K. Inoue and K. Yasunami, *This Journal*, **34**, 1 (1964)

[19] M. Katayama, K. Hara and J. Osugi, *Nippon Kagaku Kaishi* (*J. Chem. Soc. Japan*), 953 (1975)

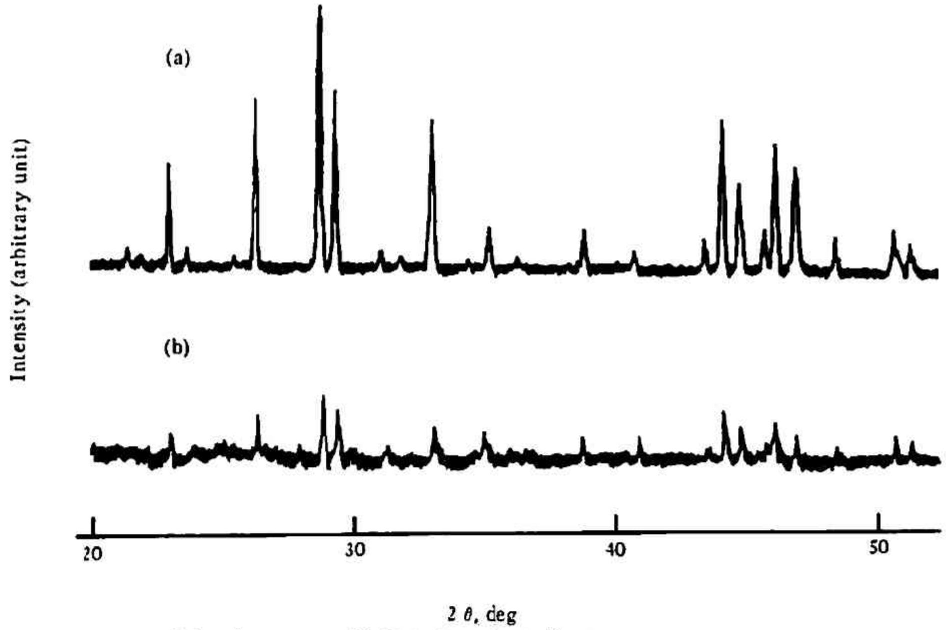

Fig. 1 X-ray diffraction pattern (CuKα) of (a) the ZnSb phase synthesized from the mixture of equal at% between Zn and Sb powder, and (b) the product formed in the Zn-Sb diffusion couple annealed at 22 kb, 280°C and for 26 hr

tween Zn and Sb powder in an evacuated silica tube. Fig. 1 (a) shows an X-ray diffraction pattern of ZnSb which agrees with the data reported by Almin³⁾. Fig. 1 (b) shows that of the product formed at 22 kb and 280°C and for 26 hr in the diffusion zone. This product seems to be crystalline. The pattern of the product is in agreement with that of the orthorhombic ZnSb, though the intensities of the peaks are relatively weak. Only ZnSb was formed above 240°C and the existence of Zn_4Sb_3 and Zn_3Sb_2 could not be confirmed by either EPMA or metallographic observation.

According to Kennedy *et al.*²⁰⁾, the melting points of Zn and Sb at the pressure of 14-30 kb are approximately within 470-540°C and 620-610°C, respectively. On the other hand, ZnSb melts at 546°C at atmospheric pressure as seen in the equilibrium phase diagram²⁾. Consequently, both reactants and the product are all in the solid-state under the present experimental conditions.

Kirkendall effect

Photo. 1 shows a representative microphotograph of the diffusion zone in the Zn-Sb couple annealed at 14 kb and 280°C and for 1024 min. Fig. 2 shows the scanning profiles obtained from the line analysis of EPMA for the diffusion zone of photo. 1. Tungsten markers, placed at the initial Zn-Sb boundary, were always found at the Zn-ZnSb interface after annealing. There is, moreover, no appreciable solid solution in both Zn and Sb sides. This result can be adequately explained by con-

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20) G. C. Kennedy and R. C. Newton, "Solids under Pressure", p. 163, ed. by W. Paul and D. M. Warschauer, McGraw-Hill, New York (1963)

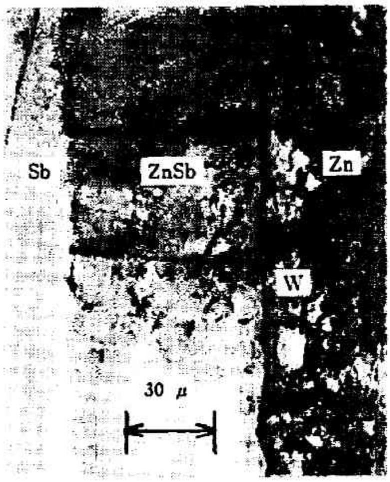

Photo. 1 Representative microphotograph of the diffusion zone in the Zn-Sb couple annealed at 14 kb, 280°C and for 1024 min (×300)

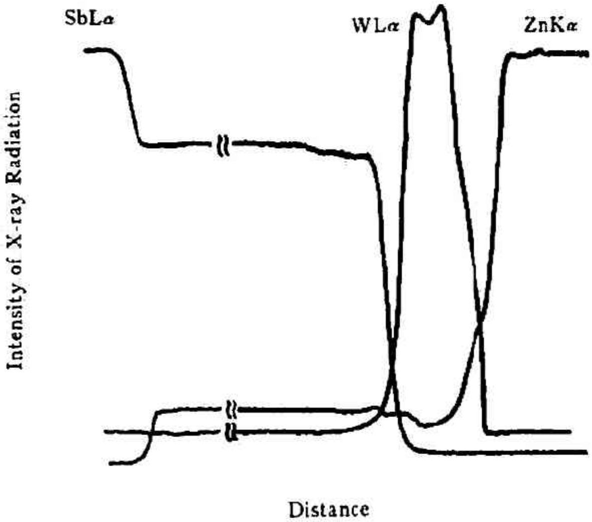

Fig. 2 Scanning profiles of EPMA for the diffusion layer of photo. 1, Accelerating voltage: 25 kV, Sample current: 3×10^{-8}A, Sample speed: 24 μ/min

sidering that Zn atoms at all times diffuse by far faster than Sb at the interface of the marker. Numerous papers have reported that in the binary metallic system each metal interdiffuses and that the self-diffusion coefficient of one component is usually comparable with the other[21-23]. There is, however, a remarkable difference in the diffusivity between Zn and Sb in the present study. In the Fe-Zn system, a similar phenomenon has been observed by Onishi *et al*[9]. Such a pronounced Kirkendall effect suggests that Zn atom diffuses through ZnSb phase by the vacancy mechanism. The preferential flow of Zn atoms will be accompanied by an equal flow of vacancies in the opposite direction.

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21) Y. Funamizu and K. Watanabe, *Trans. JIM*, **12**, 147 (1971)

22) T. Ustad and H. Sφrum, *phys. stat. sol.* (*a*), **20**, 285 (1973)

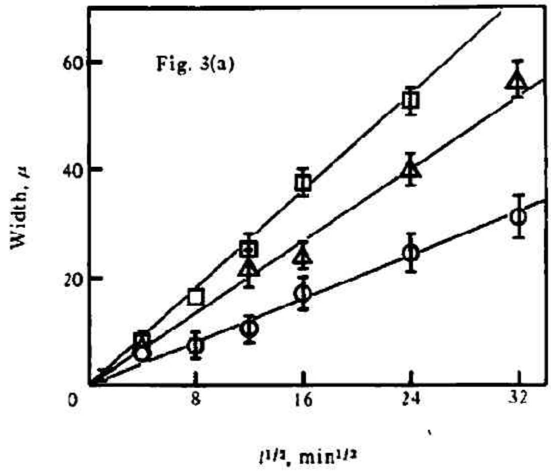
23) P. J. M. van der Straten, G. F. Bastin, F. J. J. van Loo and G. D. Rieck, *Z. Metallkde.*, **67**, 152 (1976)

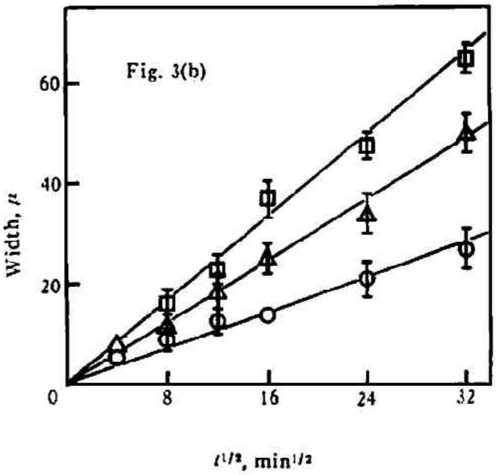
The vacancies necessary for this preferential flow can be generated from the lattice defects, such as grain boundaries and dislocations, and cannot be formed by the gas surrounding the couple in this case. If the above interpretation is the case and the supersaturation of vacancies at the interface is high enough, then some of the vacancies will unite and form voids. These voids at the interface of Zn side were proved to exist really after a long time diffusion as seen in photo. 1.

In this system the diffusion couple was easily separable at the interface between Zn and ZnSb phases. The phenomenon of the separation would be due to the following two effects: one is the accumulation of the excess vacancies and the other the shear stress in releasing pressure. The predominant cause for this phenomenon will be the excess vacancies, considering the fact that the diffusion run for more than 10 hr indeed makes the separation more easier.

Layer growth of ZnSb phase

A number of studies of the growth of the intermediate diffusion layers indicate that the width of





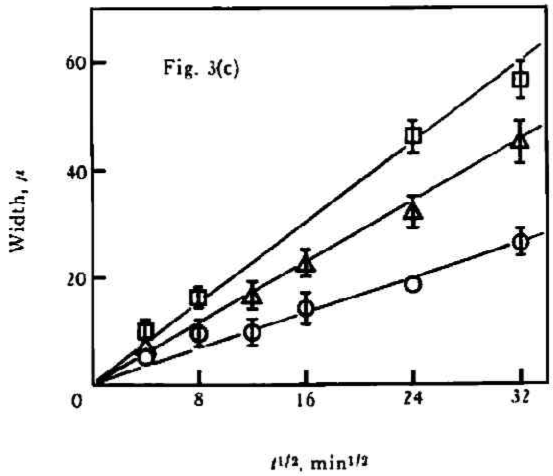


Fig. 3 Width of the ZnSb phase layers *vs* square root of diffusion time
(a) 14 kb, (b) 22 kb, (c) 30 kb
○: 240°C, △: 280°C, □: 320°C

the layer changes parabolically with time.

$$W=kt^{1/2}, \qquad (1)$$

where W is the width of the layer, t the time of diffusion-reaction. and k the rate constant. Eq. (1) is applicable if the interface composition is independent of time and the movement of the interface is diffusion controlled. Fig. 3 shows the linear relationship between the width and the square root of time for various experimental conditions. The layer width can be accurately decided within 1 μ with the microscope. The error of the experimental points would be caused by nonuniform growth. It turned out that the parabolic rate law was obeyed for this system at the quasi-hydrostatic pressure. Pressure evidently retards the rate of the growth. It is also interesting that pressure alters the composition of the interface as mentioned below but has no influence on the type of the growth.

The interface composition must be determined by the extrapolation towards the phase boundary because the steep gradient of the concentration exists in the vicinity of the phase boundary and the concentration at the interface cannot be exactly obtained within 2 μ of the phase boundary. The concentration of Zn expressed by at% are listed in Table 1. $C_{Zn,\,ZnSb}$ and $C_{ZnSb,\,Sb}$ represent the concentration of Zn at the interface between Zn and ZnSb phases and that between ZnSb and Sb phases, respectively. As seen in Table 1. the concentration of Zn extensively deviates from the equilibrium composition. Consideration of stoichiometry and X-ray examination suggest that the crystalline ZnSb coexists with amorphous Sb in the layer. Such a deviation has been often found that the concentration of the element having higher diffusivity is higher in the diffusion zone than that under the equilibrium condition[24,25]. Contrary to the finding, this opposite deviation in the Zn-Sb system would be caused by insufficient supply of Zn in an earlier stage because the state of the constant interface concentration is always attained after 15 min in the present study.

At the constant pressure the concentration at the interface is held invariably with time and is also independent of temperature. It is, therefore, significant to estimate the apparent activation ener-

Table 1 Interface composition in Zn at%

		$C_{Zn,\,ZnSb}$	$C_{ZnSb,\,Sb}$
14 kb	240°C	33.8~35.2	27.1~28.7
	280	33.5 35.5	26.7 28.1
	320	34.4 35.0	28.1 28.6
22 kb	240°C	26.8~28.2	20.7~21.6
	280	26.4 26.8	20.2 20.6
	320	25.2 25.4	20.0 20.6
30 kb	240°C	26.2~26.5	20.6~21.3
	280	26.7 27.4	20.0 20.7
	320	27.0 27.5	20.9 21.4

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24) J. R. Eifert. D. A. Chatfield, G. W. Powell and J. W. Spretnak, *Trans. Met. Soc. AIME*, **242**, 66 (1968)
25) T. Nishizawa and A. Chiba, *Nippon Kinzoku Gakkaishi* (*J. Japan Inst. Metals*). 34, 629 (1970)

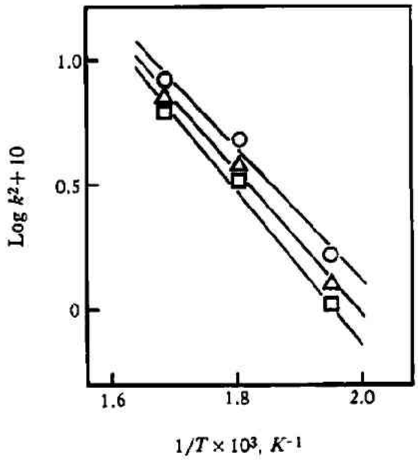

Fig. 4 Plots of log k^2 against $1/T$
○ : 14 kb, △ : 22 kb,
□ : 30 kb

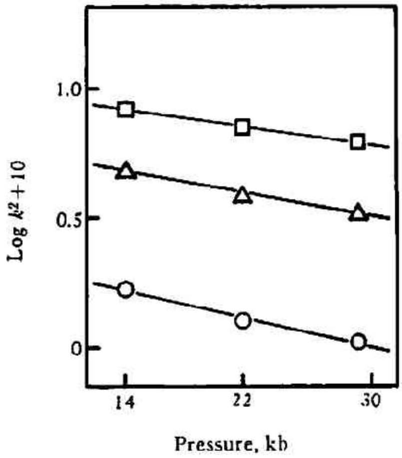

Fig. 5 Plots of log k^2 against pressure
○ : 240°C, △ : 280°C,
□ : 320°C

Table 2 Apparent activation energies and activation volumes

	E_a(kcal/mol)		$\Delta V^{\ne}$(cm^3/mol)
14 kb	12.1	240°C	1.2
22	13.3	280	1.1
30	14.3	320	0.9

gy E_a for the growth of the layers. The Arrhenius plots are presented in Fig. 4. The apparent activation volume $\Delta V^{\ne}$ can be estimated by the following equation,

$$(\partial \ln k^2/\partial P)_T = -\Delta V^{\ne}/RT. \tag{2}$$

The relation between log k^2 and pressure is shown in Fig. 5, where k^2 is the squared rate constant obtained from the slope in Fig. 3. The values of E_a and $\Delta V^{\ne}$ calculated thus are listed in Table 2.

Chemical diffusion coefficient

In this system the concentrations of each component remain fixed at the interface and the concentration gradient is also constant in the ZnSb layer. According to the well-known Matano-Boltzmann analysis[26], the concentration can be expressed as a function of a single parameter $\lambda = x/t^{1/2}$, where x is the distance and λ means the value of coordinates in which the origin is the Matano interface. Fig. 6 shows the relation between the concentration of Sb and λ. By applying Fick's law to the interface and considering the material balance at the phase interface[27], Kidson[28] presented the

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26) C. Matano, *Japan J. Phys.*, **8**, 109 (1933)

27) W. Jost, "Diffusion in Solids, Liquids and Gasses", p. 69, Academic Press, New York (1960)

28) G. V. Kidson, *J. Nucl. Mat.*, **3**, 21 (1961)

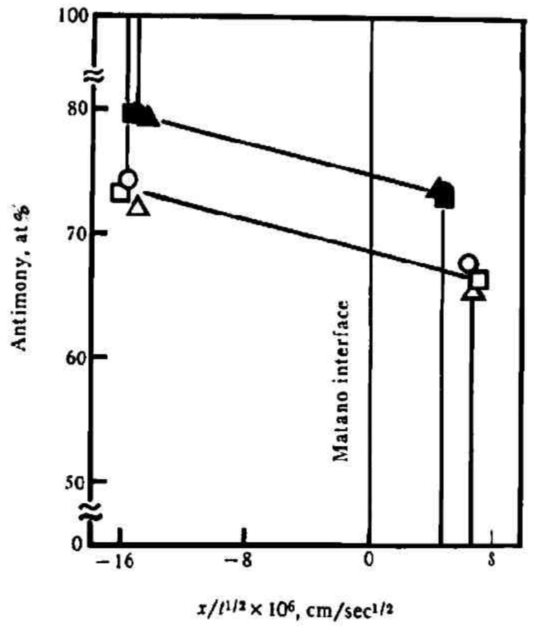

Fig. 6 Antimony concentration *vs* $x/t^{1/2}$ for the Zn-Sb diffusion couples annealed at 280°C, 14 kb and 22 kb
at 14 kb
○: 64 min, △: 576 min, □: 1024 min
at 22 kb
●: 144 min, ▲: 576 min, ■: 1024 min

following equation ;

$$W_j=2t^{1/2}\left[\left\{\frac{(DK)_{j+1,j}-(DK)_{j,j+1}}{C_{j,j+1}-C_{j+1,j}}\right\}-\left\{\frac{(DK)_{j,j-1}-(DK)_{j-1,j}}{C_{j-1,j}-C_{j,j-1}}\right\}\right], \tag{3}$$

where W_j is the width of the jth phase, C is the concentration, K is $dc/d\lambda$ $(=t^{1/2}dc/dx)$ and the suffix $(j, j+1)$ represents the interface between jth and $(j+1)$th phase in the jth phase. Consequently, we can calculate the diffusion coefficient D_{ZnSb} by means of Eq. (4), assuming that D_{ZnSb} is constant in the ZnSb layer and regarding $K_{\mathrm{Sb,ZnSb}}$ and $K_{\mathrm{Zn,ZnSb}}$ as zero.

$$D_{\mathrm{ZnSb}}=\frac{W^2 C_{\mathrm{ZnSb,Zn}}(C_{\mathrm{Sb,ZnSb}}-C_{\mathrm{ZnSb,Sb}})}{2t(C_{\mathrm{ZnSb,Sb}}-C_{\mathrm{ZnSb,Zn}})(C_{\mathrm{Sb,ZnSb}}-C_{\mathrm{ZnSb,Sb}}-C_{\mathrm{ZnSb,Zn}})}. \tag{4}$$

The averaged values of the diffusion coefficients obtained for each time are summarized with k^2 in Table 3. Eq. (4) shows that the diffusion coefficient D_{ZnSb} is proportional to the squared rate constant k^2. As can be seen in Table 3, the ratio of D_{ZnSb} to k^2 remains constant within the limits of the error at fixed pressure. The values of the ratio, however, decrease with increasing pressure ; that is, they change from 1.4 at 14 kb to 1.1 at 30 kb irrespective of temperature. This seems to be caused essentially by the change in the interface composition in Eq. (4).

It has been demonstrated that hydrostatic pressure decreases the rate of self-diffusion and increases the activation energy[29,30]. The increase of 8 kb in applied pressure increases the activation energy by about 1 kcal/mol. This value may correspond to the additional work required to create one mol of vacancies[13]. Nachtrieb *et al.*[29] have pointed out that the activation volume should be

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29) N. H. Nachtrieb, J. A. Weil, E. Catalano and A. W. Lawson, *J. Chem. Phys.*, **20**, 1189 (1952)

30) T. Liu and H. G. Drickamer, *ibid.*, **22**, 312 (1954)

Table 3 Squared rate constant k^2 and diffusion coefficient D_{ZnSb}

		k^2 (cm^2/sec)	*av.* D_{ZnSb} (cm^2/sec)
14 kb	240°C	1.7×10^{-10}	2.4×10^{-10}
	280	4.8	6.9
	320	8.3	13.0
22 kb	240°C	1.3×10^{-10}	1.7×10^{-10}
	280	3.8	5.0
	320	7.1	11.0
30 kb	240°C	1.1×10^{-10}	1.2×10^{-10}
	280	3.3	3.6
	320	6.3	8.5

positive for the self-diffusion due to the vacancy mechanism. The situation is, however, much more complicated as far as the chemical diffusion in the two-component system is concerned. We must consider, furthermore, the effect of pressure on the phase equilibrium. In the Zn-Sb system, pressure substantially influences on the interface compositions; namely, the increase in pressure from 14 to 22 kb leads to the change of about 7% as shown in Table 1. Since the matrix around the diffusing species alters with pressure, it may be difficult to discuss the values of activation volume explicitly. Onishi *et al.*[9] reported that the activation energies for the one-sided diffusion of Zn in the Fe-Zn system were 12.5–21.2 kcal/mol in the range of 360–412°C. For the self-diffusion of Zn, the activation energies and volumes are 19.6–25.0 kcal/mol and 2.68–3.62 cm^3/mol, respectively[30]. The values of the activation parameter listed in Table 2 coincide well with those obtained in the Zn-As system[19], but are relatively smaller than those reported in the Fe-Zn system. On the other hand, these values are extremely small as compared with those for the self-diffusion, though the direct comparison might not be made because in the present case the chemical diffusion through the ZnSb and amorphous Sb phase layers is concerned. The preferential flow of the vacancies across the interface will disturb the equilibrium conditions, and so the system is not completely equilibrium. If the excess vacancies exist inherently in the non-equilibrium state, the activation parameters will be reduced by a part of the amount necessary for the formation of vacancies, as compared with such a case of the self-diffusion in equilibrium vacancy concentration. Although the comparatively small activation parameters in this system seem to come from the excess vacancies, it is difficult to interpret explicitly this problem since the factors controlling the growth of the layer are not well-known.

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