

ELECTRICAL MEASUREMENT OF ZnSb AND CdSb PHASES IN THE DIFFUSION ZONE AT HIGH PRESSURE

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The electrical resistances of both Zn-Sb and Cd-Sb couples were measured over the range of 180–260°C and 8–25 kb and for up to 17 hr. The technique in the present study was devised to check the behavior of the layer growth of both ZnSb and CdSb phases formed in the diffusion zone. The resistance increase nearly obeyed the parabolic law, indicating that its change was almost in proportion to the layer width. The data obtained were fitted to an analytical equation, $R-R_0 = k_2 t^{1/2}$. The resistance-time curves were divided into two parts which consisted of the initial and the latter stage. By assuming that the resistance is rigorously proportional to the width and the slight deviation from the equation in the initial stage is attributed to the cause involved in the growth kinetics, the factors responsible for the net resistance are discussed. The resistance per unit layer width, K , depended on temperature and pressure; the higher the temperature and the lower the pressure, the larger the value of K . The variations in K between the initial and the latter stage were interpreted by considering that the crystallinity of the phase relevant to the resistivity changed with time.

Introduction

Up to the present, the isothermal layer growths of the intermediate phase in binary systems have been numerously investigated, and it has generally been found that the width of the diffusion layers obeys a simple parabolic law¹⁻⁵⁾. The kinetics of the layer growth in various systems has been studied by measuring the mean value of the layer width formed in the diffusion zone. Recently the author et al.^{6,7)} have reported that ZnSb and CdSb phases are formed in the Zn-Sb and the Cd-Sb couples, and that they grow in parabolic form. In those cases, the uncertainties of $\pm 15\%$ were unavoidably included in determining the width. As the causes for this considerable errors we can enumerate the non-uniform growth, the individuality in the specimen, and the temperature variation. Thus, a question arises whether the parabolic law is obeyed perfectly. The precise judgment on this problem seems to remain as an important subject to be solved.

(Received October 3, 1978)

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

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In the present study the electrical resistance was pursued successively at high pressure instead of the usual microscopic measurement of the layer width. It is interesting to correlate the measured resistance to the layer width since the resistance change with time offers the possibility to reply to the problem mentioned above. For the purpose of the present research, the Zn-Sb and the Cd-Sb systems are chosen for the following reasons: i) both ZnSb and CdSb phases are formed at relatively low temperature; ii) the phases have a definite composition and no solid solution is formed on either side of the diffusion zone; iii) the phases are well-known typical semiconductors and their resistivities are higher by a few orders of magnitude than those of their constituent metals. In addition, pressure keeps the interface in good contact and omits the complicated welding procedure.

The resistance is explicitly expressed in terms of the layer width, the contact cross-sectional area and the resistivity in which the microstructural properties, such as the crystallinity, the density of dislocation, and the vacancy concentration, must be also taken into account. Among them the width is obviously a major factor contributing to the resistance. The other factors responsible for the resistance increase will be also discussed. This work was undertaken to provide more detailed information with respect to the layer growth.

Experimentals

Zinc metal (99.999%) was supplied by Mitsuwa Pure Chemicals, Ltd. and both cadmium (99.999%) and antimony (99.999%) were supplied by Osaka Asahi Metal Co., Ltd. The disks having 3 mm-diameter and 1.5 mm in length were made of these ingots. After heat-treatment and polishing, the diffusion couple was inserted in a teflon capsule without thermal welding. The diffusion annealing was performed by using a compact cubic anvil apparatus⁸⁾ in the temperature range of 190–260°C and at pressures of 8 and 15 kb in the Zn-Sb system, and in the range of 180–230°C and at 10, 18 and 25 kb in the Cd-Sb system. Fig. 1 shows the assembly of the pressure apparatus and an electric circuit. Fig. 2 shows a schematic diagram of the sample cell which was designed for the resistance measurement. The sample cell was constructed by the 14mm-pyrophyllite cube, the

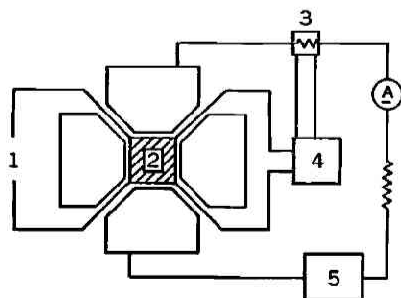


Fig. 1 Assembly of the compact cubic anvil apparatus, the sample cell and an electric circuit

- 1 : chromel-alumel thermocouple
- 2 : sample cell (pressure transmitting pyrophyllite cube)
- 3 : standard resistor (1.00001×10^{-3} ohm)
- 4 : potentiometer
- 5 : DC constant current power supply

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

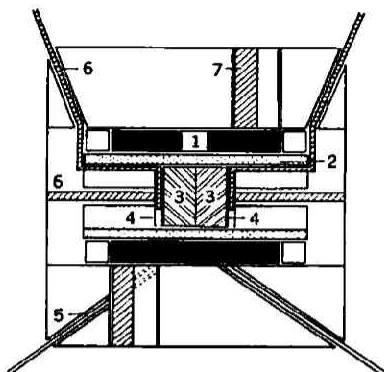


Fig. 2 Schematic diagram of the sample cell

- 1 : glassy carbon heater
- 2 : tefflon tube
- 3 : specimen
- 4 : platinum foil
- 5 : chromel-alumel thermocouple
- 6 : copper wire
- 7 : copper rod

glassy carbon heater, the tefflon tube, the copper lead wire, and the specimen. Copper lead wire (1 mm ϕ) and the potential lead (0.3 mm ϕ) were attached to the platinum foil (30 μ) in order to prevent the direct contact between copper and the specimen. The potential lead and the chromel-alumel thermocouple were set through the pyrophyllite gaskets between the anvils. To heat the specimen the anvil was connected through copper rod (2.3 mm ϕ) with the 6 mm-diameter heater containing the tefflon capsule.

The resistance between both ends of the couple was measured by means of the four probe method as described below. After the generation of pressure, temperature was elevated in a minute and then controlled within $\pm 3^\circ\text{C}$. The couple was annealed at that condition for a fixed time, and then it was quenched in about 30 seconds by cutting off the electric current. This comparatively slow quenching rate from high temperature is necessary to remove the resistance associated with the quenched-in vacancies. The cell comes to equilibrium at room temperature (22 $^\circ\text{C}$) in a few minutes after quenching, and then the measurement was carried out at room temperature. In order to keep the specimen at 22 $^\circ\text{C}$, a fixed current (0.100 \pm 0.001 A) was passed through a closed circuit by using a DC constant-current power supply (Metronix model 691A). The standard resistor (1.00001 $\times 10^{-3}$ ohm) was employed to determine the absolute current. The potential drop between both ends of the couple for the forward and the reverse current was measured with DC potentiometer (Shimadzu Type-PD) in which the potential difference of 10 $^{-6}$ V was detectable. The exchange of the current direction resulted in no significant difference in the potential drop, and so the effect of the thermal emf of the couple was negligible. The balance of the bridge was observed by using an electronic galvanometer with the sensitivity of 0.3 $\times 10^{-6}$ V (TōA Model AD-7). The accuracy of the measurement was 3 $\times 10^{-6}$ ohm.

In the experiments using only one specimen among Zn, Cd and Sb disks, the fluctuations of the resistance were within 2 $\times 10^{-5}$ ohm even though the operations of quenching and heating were repeated. On the other hand, the resistance changes with time in both couples were in the order of magnitude of 10 $^{-4}$ ohm. Based on this large difference in the resistance and the fact that no diffusion zone was observed between the platinum foil and the specimen below 260 $^\circ\text{C}$, it was confirmed that the resistance change accompanying with the layer growth was surely pursued. After each run, the

couple was polished parallel to the direction of diffusion. Then the layer width was determined with a microscope.

Results

Profile of the Annealing Curve

The several terms used here are defined before analysis ;

R = measured resistance between both ends of the couple

ΔR = resistance change of the couple during the measured time

R_0 = initial resistance of the couple before annealing

R_{ZnSb} and R_{CdSb} = net resistance of ZnSb and CdSb phases formed in the diffusion zone

W_{ZnSb} and W_{CdSb} = layer width of ZnSb and CdSb phases

The initial resistance R_0 was about 1×10^{-4} ohm for both systems. The resistance of Zn, Cd and Sb specimens with the shape of disk were calculated to be 1.3, 1.6, and 8.2×10^{-5} ohm, respectively, from the resistivity and the dimension. The resistances of the couple before annealing were estimated to be 9.5×10^{-5} ohm for the Zn-Sb couple and 9.8×10^{-5} ohm for the Cd-Sb couple. Thus, the agreement with R_0 was good. In Fig. 3(a) and (b) the resistance R vs the time were plotted under

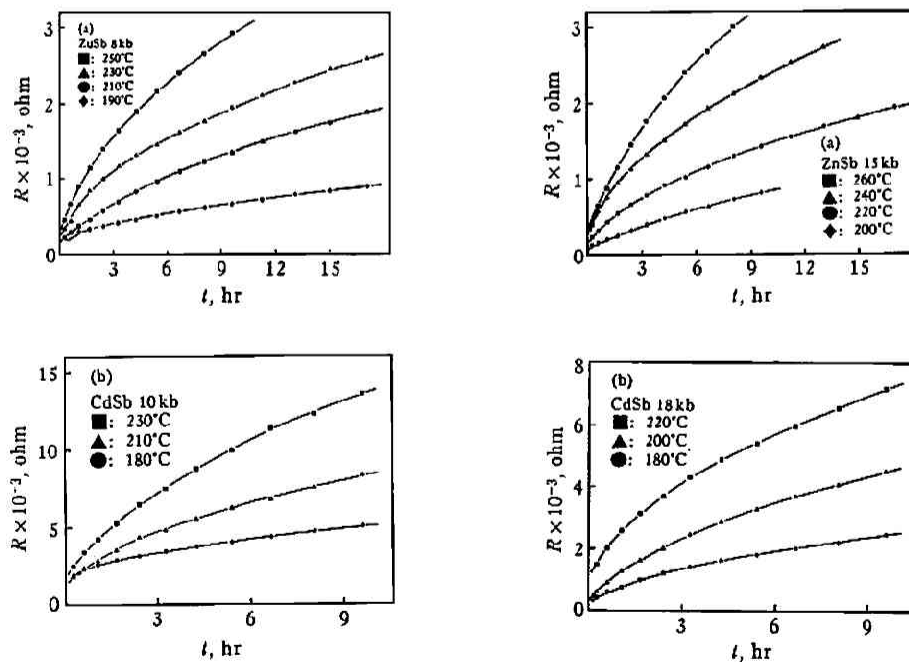


Fig. 3 Plots of the resistance vs the time
 (a): Zn-Sb system at 8 and 15 kb
 (b): Cd-Sb system at 10 and 18 kb

various conditions. Since W_{ZnSb} and W_{CdSb} were less than 30μ , the ratio of W_{ZnSb} and W_{CdSb} to the length of the couple was as follows :

$$\frac{W_{ZnSb}}{W_{Zn} + W_{Sb}}, \quad \frac{W_{CdSb}}{W_{Cd} + W_{Sb}} < 1 \times 10^{-2},$$

where W_{Zn} , W_{Cd} and W_{Sb} represent the length of Zn, Cd and Sb specimens, respectively. When the length of each specimen decreases by 1% because of the phase formation, the resistance is estimated to decrease by 1×10^{-6} ohm. This contribution to the measured resistance can be completely neglected because the resistance change ΔR is the range of 10^{-4} – 10^{-3} ohm as seen in Fig. 3. Therefore, the net resistance (R_{ZnSb} and R_{CdSb}) is given by subtracting R_c from R with no correction. The plots of resistance against the time exhibited approximately the same parabolic increase irrespective of temperature, pressure, and the system. The behavior of the change depended on temperature and pressure; the higher the temperature and the lower the pressure, the larger the value of R . From several runs it was found that at a fixed temperature and pressure the variations in the absolute value of R were as much as $\pm 15\%$. The curves in Fig. 3 were nearly equivalent to those of the parabolic layer growth as reported elsewhere^{6,7}.

Analysis of the Annealing Curve

The simple parabolic law is expressed as

$$W = k_1 t^{1/2}, \quad (1)$$

where W is the layer width, k_1 the rate constant and t the time. The author presented in the precedent papers^{6,7} that this law was almost obeyed in both Zn–Sb and Cd–Sb systems, though there was contained a considerable error of $\pm 15\%$ in the measurement of the width. Furthermore, Eq. (1) has been confirmed to be valid for other systems¹⁻⁵) within some uncertainties. The relation connecting the net resistance ($R - R_c$) with the layer width W will be given as follows :

$$R - R_c = K(T, P)W, \quad (2)$$

where K is the proportional constant and represents the resistance per unit length of the layer. By substituting Eq. (1) into Eq. (2), the resistance change with time should be described as

$$R - R_c = k_2 t^{1/2}, \quad (3)$$

where the rate constant k_2 is given by $k_1 K$. Fig. 4 shows the relation between R and the squared root time $t^{1/2}$. As obviously seen from these plots, the data points seem to lie on the respective straight lines each at the initial stage and the latter one, though the change at the initial stage should be considered to be the smooth curve. Both stages were separated at 1–2 hours and a point of intersection shown by the dotted line was denoted as the bending time for convenience. Higher temperature shortened the bending time. At the latter stage Eq. (3) was satisfied perfectly for the increment of the resistance with time and no deviation from the parabolic law was observed. In the present study the smooth curve in Fig. 4 was appropriately treated as the straight line so that the parabolic law was obeyed, but at the initial stage a slight deviation from Eq. (3) was observed as discussed later. The rate constant k_2 was separately considered because two stages exhibited the different behavior. The values of k_2 were obtained from Eq. (3) by using the value of R_c in Eq. (4).

Electrical Measurement of ZnSb and CdSb Phases in the Diffusion Zone at High Pressure

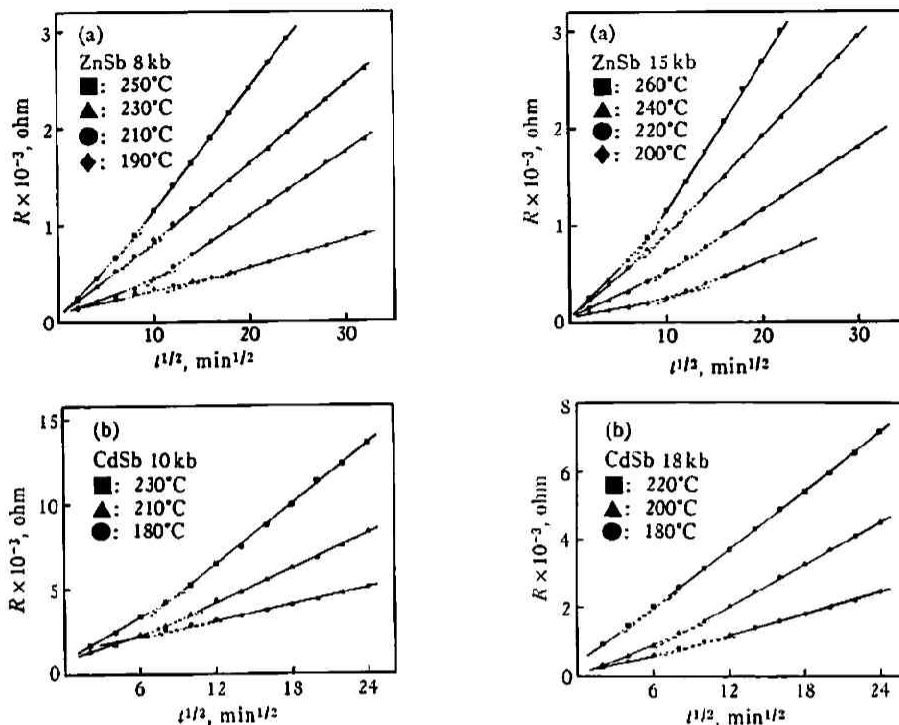


Fig. 4 Relationship between the resistance and the squared root time
 (a): Zn-Sb system at 8 and 15 kb (b): Cd-Sb system at 10 and 18 kb

Table 1 The values of k_1 , k_2 and K

Pressure, kb	Temperature, °C	$k_1 \times 10^5$ cm/sec ^{1/2}	$k_2(i) \times 10^5$ ohm/sec ^{1/2}	$k_2(l) \times 10^5$ ohm/sec ^{1/2}	$K(i)$ ohm/cm	$K(l)$ ohm/cm	
CdSb	10	180	1.1	2.0 ₄	2.1 ₁	1.8	1.9
	10	210	1.5	3.5 ₈	4.4 ₈	2.4	3.0
		230	2.0	5.7 ₃	7.6 ₈	2.9	3.8
	18	180	0.9	1.1 ₇	1.3 ₇	1.3	1.5
		200	1.2	2.0 ₃	2.6 ₉	1.7	2.2
		220	1.6	3.5 ₃	3.7 ₄	2.2	2.3
25	200	1.0	1.2 ₇	1.3 ₉	1.3	1.4	
	230	1.5	2.6 ₅	3.1 ₄	1.8	2.1	
ZnSb	8	190	0.6	0.27	0.37	0.45	0.62
		210	1.0	0.47	0.81	0.47	0.81
		230	1.2	1.0 ₀	1.0 ₅	0.83	0.88
		250	1.6	1.3 ₈	1.6 ₃	0.86	1.0
	15	200	0.7	0.27	0.48	0.39	0.69
		220	1.1	0.60	0.82	0.55	0.75
15	240	1.4	1.0 ₈	1.3 ₀	0.77	0.93	
	260	1.8	1.4 ₀	1.9 ₇	0.78	1.1	

(i): initial stage (l): latter stage

$$R_0 = \frac{R_1 t_2^{1/2} - R_2 t_1^{1/2}}{t_2^{1/2} - t_1^{1/2}}, \quad (4)$$

where R_1 and R_2 are the measured resistances at time t_1 and t_2 , respectively. The averaged values of R_0 obtained at each time interval corresponded to those extrapolated from each stage to $t=0$ in Fig. 4, but R_2 at the latter stage was the hypothetical value. The values of K were evaluated by k_2/k_1 , where k_1 determined from Eq. (1) agreed well with those previously obtained^{6,7)}. The values of K are listed together with k_1 and k_2 in Table 1, where the initial and the latter stage are represented by the symbols (i) and (l), respectively. K had the different value at each stage because of the variation of k_2 with time, and undoubtedly became larger at higher temperature and lower pressure.

Discussion

Rate Constant k_2 and K

The uncertainties of $\pm 15\%$ in the layer width are mainly caused by the non-uniform growth, and it seems that the layer formed at an early stage grows without changing the shape extensively, as far as no crack is formed. Since the contact area at the interface is practically held constant at an arbitrary place, the resistance will be proportional to the width and the resistivity of the layer which can be calculated by multiplying K by the area (0.06 cm^2). It should be considered here what kind of factors are responsible for the resistivity because the values of k_2 and K at both stages are different as seen in Table 1. We can enumerate the following factors.

- i) crystallinity of the phases formed in the diffusion zone
 - ii) defects, such as vacancies and dislocations
 - iii) quenched-in resistance
- i) The resistivity will change whenever the crystallinity differs with time. The information on the crystallinity of ZnSb phase synthesized in the Zn-Sb system was obtained by examining the stability of ZnSb to NaOH solution; the reaction of the powder mixture of Zn/Sb=2 took place completely at 20 kb and 200–250°C and for 2–4 hours. After the removal of the unreacted excess Zn with 1–2 N NaOH, the atomic ratio of Zn/Sb was determined to be about 0.85 by the gravimetric and the fluorescence X-ray analysis. The deficient quantity of Zn from the stoichiometrical value was 15%, and that at the shorter reaction time this quantity became larger. This result indicates that NaOH solution removes not only excess Zn, but also Zn of the part having the imperfect structure in ZnSb phase. Thus, the crystallinity depends on the time up to 2–4 hours and the structure is not perfect.
- ii) In the diffusion reaction there exists usually the net flux of the vacancies toward the region of the faster atomic species because of the unequal diffusivities. It has been also demonstrated by other several authors^{9,10)} that the Kirkendall effect is accompanied with the climb of edge dislocations and the structural changes associated with the dislocations occur in the diffusion zone. Although the distribution of the density of the dislocations must change with time, the net number would change

9) V.Y. Doo and R.W. Balluffi, *Acta Met.*, 6, 428 (1958)

10) J. Schlipf, *ibid.*, 21, 435 (1973)

little during the annealing. It is, therefore, unlikely that the dislocation is effective for the resistivity. In the present systems the void formation has been observed at Zn-ZnSb and Cd-CdSb interface because the vacancies flow toward the Zn and the Cd side, respectively. These voids formed by the change in the vacancy distribution will act as increasing the resistivity. The interface was, however, sufficiently kept in good contact under pressure and the flux of atom was not hindered by the voids so much. Accordingly, the void is not a major factor which contributes to the resistivity.

iii) In the experiments of quenching using metals such as Au, Pt and Al, Emrick¹¹⁾ and other workers^{12, 13)} have established that the resistance increase is attributed to the quenched-in vacancies and the ratio of the increase to the resistance of the specimen is about 10^{-3} when the initial quenching rate becomes larger than 10^3 °C/sec. In the present study the vacancies existing excess as compared with the equilibrium concentration at room temperature would migrate to sinks and may be fairly annealed out during quenching because the initial quenching rate is the order of magnitude of 10^2 °C/sec. This effect will be, furthermore, reduced by the repeated quenching and annealing. Thus, it is estimated that the quenched-in resistance is less than 1×10^{-7} ohm and so is not detectable at all with the present experimental accuracy.

From the above consideration, the factors responsible for the resistivity change are regarded to be primarily the crystallinity and secondarily the Kirkendall voids. As seen in Table 1, increasing temperature tends to increase K and contrarily increasing pressure tends to decrease K . Although there is no evidence indicating clearly that at the different temperature the matrix in the diffusion zone differs a little in the crystallinity, it is conceivable that ZnSb and CdSb phases have higher crystallinity at higher temperature. If this is the case and the fact that the voids do not change so much even though temperature becomes higher is taken into account, the temperature change of K is deduced to be caused mainly by the change in the crystallinity. This point of view is indirectly supported by the fact that the bending time becomes shorter at higher temperature, if the bending time can be considered to correspond to the time required to attain the definite state in the crystallinity. As to the variation of K with pressure, there are some factors, such as the interface composition and the density other than the crystallinity and the voids. The void formation was reduced by increasing pressure in accordance with the result reported in Cu-Ni system¹⁴⁾. Increasing pressure tends to decrease the concentration of the diffusing species and to increase the density. It is unknown whether these matrix changes influence the resistivity. In addition, the pressure dependency on the crystallinity is also unknown, so that the situation becomes more complicated. Thus, it is difficult to explain the pressure change of K because some factors may simultaneously participate in the resistivity, though the decrease of the voids tends to decrease in the resistivity.

11) R.M. Emrick and P.B. McArdle, *Phys. Rev.*, **188**, 1156 (1969)

12) T. Kino and J.S. Koehler, *ibid.*, **162**, 632 (1967)

13) M. Charles and J. Hillairet, *Phys. Rev. B*, **11**, 4808 (1975)

14) R.S. Barnes and D.J. Mazey, *Acta Met.*, **6**, 1 (1958)

Growth Kinetics

As seen in Fig. 4, the behavior of the resistance change with time was reasonably analyzed by considering that k_2 was time dependent and the growth kinetics concerned with $1/2$ in Eq. (3) was apparently time independent. At the initial stage, however, a little deviation from Eq. (3) was surely observed, and so instead of Eq. (3) the data were also examined by the general formula as Eq. (5).

$$R - R_0 = k_3 t^n \quad (5)$$

where n is regarded as the quantity to reflect the growth kinetics and may be called as the reaction index. The values of n obtained from the plots of $\log(R - R_0)$ vs $\log t$ by means of the least-square-fit were within the range of 0.4-0.5. Here, it is important to indicate that Eq. (1) for the layer growth should be obeyed rigorously in the present systems as discussed below. When both interfacial reaction and nucleation processes rapidly occur and the rate determining step is the diffusion through the layer, Eq. (1) is derived by assuming that the flux of atom is proportional to the instantaneous growth rate dW/dt and is inversely proportional to the width W . This assumption is satisfied if the phase interface reaches the local equilibrium which means that the vacancy concentration and the thermodynamic variables such as the chemical potential are fixed at early stage. Eq.(1) has been experimentally validated when the diffusion coefficient, the interface composition, the concentration gradient and the crystallographic structure remain fixed with time. The author has already confirmed^{6,7)} that the diffusion reaction in the Zn-Sb and Cd-Sb systems are controlled by the vacancy mechanism, and that the interface composition becomes constant within 15 minutes and then shows no time dependency. According to the metallographical observation with the microscope, no new phase appears in both systems. Thus, the steady state is accomplished at early stage and no change in the reaction mechanism occurs. Hence, it should be noticed that the growth kinetics and k_1 in Eq.(1) are substantially time independent for the layer growth. Consequently, the deviation from $n=1/2$ must be due to essentially the resistance method. The deviation may be induced by the change in the properties such as the crystallinity and the voids sensitive to the present method because the value of n should reflect only the growth kinetics and not depend the properties of the phases.

Acknowledgement

The author wishes to thank Professor J. Osugi for his kind guidance and helpful advice throughout this work.

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