Fast Penetration of Sn into Ag by Diffusion Induced Recrystallization

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At interconnection between a Ag-base conductor alloy and a Sn-base solder alloy, fast penetration of Sn into the conductor alloy occurs due to diffusion induced recrystallization (DIR) during solid-state heating under usual energization conditions. Like formation of binary Ag–Sn compounds, the penetration of Sn deteriorates the electrical conductivity at the interconnection. In order to examine the penetration rate of Sn into the conductor alloy, the kinetics of DIR in the Ag(Sn) system was experimentally observed in the present study. The experiment was carried out using Sn/Ag/Sn diffusion couples prepared by a diffusion bonding technique. The diffusion couples were isothermally annealed at temperatures of $T = 433\text{–}473\text{ K}$ for various times up to $t = 1100\text{ h}$ in an oil bath with silicone oil. Due to annealing, a region alloyed with Sn is formed in Ag due to DIR at $T = 453$ and $473\text{ K}$. At $T = 433\text{ K}$, however, the DIR region could not be recognized clearly. The concentration of Sn in the DIR region is about half of the solubility of Sn in Ag. The mean thickness $l$ of the DIR region reaches to 4 μm for $t = 1100\text{ h}$ at $T = 453\text{ K}$ and 5 μm for $t = 890\text{ h}$ at $T = 473\text{ K}$. The experimental results were theoretically analyzed using mathematical models. The analysis indicates that the growth of the DIR region is controlled by the interface reaction at the moving boundary of the DIR region within the experimental annealing times. At longer annealing times, however, the interface reaction is no longer the bottleneck for migration of the moving boundary and the grain boundary diffusion across the DIR region governs the growth of the DIR region.

(Received November 7, 2005; Accepted January 18, 2006; Published March 15, 2006)

Keywords: conductor, solder, intermetallic compounds, grain boundary diffusion, interface reaction

1. Introduction

Due to high electrical conductivity, Cu-base conductor alloys are widely used in electronic industry. When the Cu-base conductor alloy is interconnected with a Sn-base solder alloy, Cu–Sn compounds are produced at the interface between the conductor and solder alloys during soldering. Such compounds soakingly grow owing to heating at solid-state temperatures under usual energization conditions. The Cu–Sn compounds are very brittle and possess high electrical resistivities, and thus their growth gradually deteriorates the electrical and mechanical properties of the interconnection. In order to suppress the production of the Cu–Sn compounds, the Cu-base conductor alloy is usually plated with a Ni layer. Furthermore, the Ni layer is plated with a Au layer for improvement of the corrosion resistance. If the Au/Ni/Cu multilayer conductor alloy is interconnected with the Sn-base solder alloy, Au–Sn compounds are formed during soldering, and then grow during solid-state heating. The Au–Sn compounds as well as the Cu–Sn compounds are brittle and possess high electrical resistivities. Consequently, the growth of the Au–Sn compounds also causes the gradual deterioration of the electrical and mechanical properties of the interconnection.

In order to examine the growth behavior of compounds at the interconnection, the reactive diffusion between Sn and various conductor metals at solid-state temperatures was experimentally observed in previous studies. As to the Au–Sn system, the experiment was carried out using Sn/Au/Sn diffusion couples prepared by a diffusion bonding technique. The diffusion couples were isothermally annealed at temperatures of $T = 393\text{–}473\text{ K}$ for various periods in an oil bath with silicone oil, where $T$ is the annealing temperature. Due to annealing, compound layers composed of the $\delta$ (AuSn), $\epsilon$ (AuSn$_2$), and $\eta$ (AuSn$_3$) phases are formed at the Au/Sn interface in the diffusion couple. The observation indicates that the total thickness of the compound layers is expressed as a power function of the annealing time, and the exponent of the power function is $0.48, 0.42$ and $0.36$ at $T = 393$, $433$ and $473\text{ K}$, respectively. Such a temperature dependency of the exponent implies that the grain boundary diffusion contributes to the rate-controlling process of the reactive diffusion and grain growth takes place in the compound layers at certain rates at higher annealing temperatures. As the annealing temperature decreases, the contribution of the grain boundary diffusion becomes conspicuous, but the grain growth slows down.

This type of rate-controlling process was recognized also for the reactive diffusion in the Ag–Sn system. In this system, Sn/Ag/Sn diffusion couples were prepared by a diffusion bonding technique, and then isothermally annealed at temperatures between $T = 433$ and $473\text{ K}$. Owing to annealing, compound layers consisting of the $\delta$ (Ag$_2$Sn) and $\zeta$ phases are produced at the Ag/Sn interface in the diffusion couple. Furthermore, penetration of Sn into the Ag phase occurs from the $\zeta$/Ag interface due to diffusion induced recrystallization (DIR) during annealing. DIR is the phenomenon that new fine grains with discontinuously different solute concentrations are formed behind moving grain boundaries owing to recrystallization combined with diffusion of solute atoms along the moving boundaries. The kinetics of DIR was experimentally observed for various binary A(B) systems in previous studies. Here, the notation A(B) indicates that a solute B diffuses into a pure metal A or a binary A–B alloy of the A-rich phase according to convention. Penetration of a solute into a solvent usually takes place much faster for DIR than for volume diffusion.

Silver-base alloys are used as excellent conductor materials with adequate corrosion resistance in electronic industry. If the Ag-base conductor alloy is interconnected with the Sn-base solder alloy and the penetration of Sn into the conductor alloy occurs owing to DIR during solid-state heating under
usual energization conditions, the electrical conductivity at the interconnection will be deteriorated not only by the formation of the $\epsilon$ (Ag$_3$Sn) and $\zeta$ phases but also by the penetration of Sn in the conductor alloy. Such duplicate deterioration remarkably shortens the lifetime of the interconnection. Nevertheless, reliable information is not available for the penetration rate of Sn by DIR in the Ag-base conductor alloy so far. In the present study, the kinetics of DIR in the Ag(Sn) system was experimentally examined using Sn/Ag/Sn diffusion couples prepared by the diffusion bonding technique. The diffusion couples were isothermally annealed at $T = 433-473$ K in a manner similar to previous studies. The penetration depth of Sn in the Ag phase was observed metallographically. The experimental results were theoretically analyzed using mathematical models in order to evaluate the kinetic features.

2. Experimental

Diffusion couples consisting of Ag and Sn were prepared by a technique similar to a previous study. Polycrystalline pure Ag plates with a size of $10 \times 4 \times 2$ mm$^3$ were cut by spark erosion from a commercial 1 kg rectangular bar of pure Ag with purity of 99.99% and then cold rolled to a thickness of 0.1 mm. Sheet specimens with a dimension of $20 \times 7 \times 0.1$ mm$^3$ were cut from the cold rolled specimens and then separately annealed in evacuated silica capsules at 1173 K for 2 h, followed by air cooling without breaking the capsules. The annealed sheet specimens were chemically polished in an etchant composed of 10 vol% of nitric acid and 90 vol% of methanol.

Polycrystalline pure Sn plates with a size of $12 \times 5 \times 2$ mm$^3$ were prepared by cold rolling and spark erosion from a commercial 1 kg rectangular ingot of pure Sn with purity of 99.997%. The cold-rolled Sn plates were separately annealed in evacuated silica capsules at 473 K for 2 h, followed by air cooling without breaking the capsules. The annealed sheet specimens were chemically polished in an etchant consisting of 20 vol% of nitric acid, 20 vol% of hydrochloric acid and 60 vol% of distilled water.

The two surfaces with an area of $20 \times 7 \times 0.1$ mm$^3$ were cut from the cold rolled specimens mechanically polished on 1500 emery paper until a depth of 100$\mu$m and then finished using diamond with a diameter of 3$\mu$m.

After chemical polishing, a Ag sheet specimen was immediately sandwiched between two freshly prepared Sn plate specimens in methanol. The Sn/Ag/Sn couples were entirely dried and then heat treated for diffusion bonding in an oil bath with silicone oil for 72 h at $T = 453, 453$ and 473 K. The diffusion couples were annealed at the same temperatures for various periods up to 1028 h. The summation of the heat-treating and annealing times is hereafter merely called the annealing time. Cross-sections of the annealed diffusion couples were mechanically polished using diamond with diameters of 15, 3 and 1$\mu$m, and then finished utilizing an OP-S liquid by Struers Ltd. Concentration profiles of Ag and Sn were determined on the cross-section along the direction normal to the interface by electron probe microanalysis (EPMA).

3. Results and Discussion

3.1 Composition of DIR region

A typical concentration profile determined by EPMA is shown as open circles in Fig. 1. This figure indicates the result for the Sn/Ag/Sn diffusion couple annealed at $T = 453$ K for $t = 1100$ h ($3.96 \times 10^4$ s). Here, $t$ is the annealing time. In Fig. 1, the abscissa shows the distance $x$ along the direction normal to the interface, and the ordinate indicates the mol fraction $y$ of Sn. As can be seen, two compound layers are discerned in the concentration profile. They are the $\epsilon$ (Ag$_3$Sn) and $\zeta$ phases. According to a recent phase diagram in the binary Ag–Sn system, the $\epsilon$ and $\zeta$ phases are the only stable intermetallic compounds. Furthermore, a region alloyed with Sn is recognized in the Ag phase adjacent to the $\zeta$/Ag interface. This region is formed due to DIR, and hence hereafter called the DIR region. In the DIR region, the composition $y$ is almost constant on the side of the $\zeta$/Ag interface. The composition on this side of the DIR region is denoted by $y^*$ as shown in Fig. 1. On the contrary, the composition $y$ slightly decreases on the opposite side in the DIR region, and discontinuously changes across the moving boundary between the DIR region and the untransformed matrix. In Fig. 1, the compositions of the Ag and $\zeta$ phases for the Ag + $\zeta$ tie-line are shown as an open triangle and an open square, respectively, at the $\zeta$/Ag interface, and those of the $\zeta$ and $\epsilon$ phases for the $\zeta + \epsilon$ tie-line are indicated as an open square and an open rhombus, respectively, at the $\epsilon$/Ag interface. The open triangle corresponds to the solubility $y^*$ of Sn in the Ag phase. According to the result in Fig. 1, however, $y^*$ is smaller than $y^*$. The value of $y^*$ was determined by EPMA for various diffusion couples with different annealing times at each temperature. The determination indicates that $y^*$ is almost constant independent of the annealing time. Hence, the mean value of $y^*$ was evaluated at each annealing temperature. The results at $T = 453$ and 473 K are shown as open circles with error bars in Fig. 2. At
Fig. 2 The mol fraction \( y \) of Sn in the DIR region versus the annealing temperature \( T \) shown as open circles with error bars. The solubility \( y \) of Sn in Ag\(^{28}\) and the composition \( y^d \) evaluated by the MDF model\(^{19}\) are indicated as a solid line and a dotted curve, respectively.

\[
G_m = (1 - y)G_A + yG_B + RT[(1 - y) \ln(1 - y) + y \ln y] + E_G_m
\]  

Here, \( G_B \) is the molar Gibbs energy of pure element B for the same crystal structure as the \( \alpha \) phase. \( E_G_m \) is an excess Gibbs energy, and \( R \) is the gas constant. According to a subregular solution model,\(^{29}\) \( E_G_m \) is described by

\[
E_G_m = y(1 - y)\left[0L + \frac{1}{2}L(1 - 2y) + \frac{3}{2}L(1 - 2y^2)\right] 
\]

for the chemical potentials of elements A and B, respectively. Inserting eqs. (4a) and (4b) into eq. (1), \( y^d \) is calculated for a given value of \( y^c \).

In the case of DIR in the Ag(Sn) system, Sn atoms are transported to the DIR region from the \( \zeta \) phase across the \( \zeta / \text{Ag} \) interface. Hence, the composition \( y^c \approx 0.0935 \) may correspond to \( y^c \) in eq. (1). The value \( y^d = 0.0935 \) is shown as a horizontal solid line in Fig. 2. The interaction parameters for the Ag phase in the binary Ag–Sn system are reported by Chevalier\(^{30}\) as follows: \( 0L = -11196.6 + 18.50995T, 1L = -24806.9 \) and \( 2L = 0J/mol \). Using these parameters, \( y^d \) was calculated as a function of \( T \) for \( y^c = 0.0935 \) from eqs. (1), (4a), and (4b). The result is indicated as a dotted curve in Fig. 2. The calculation gives values of \( y^d = 0.0880-0.0879 \) at \( T = 433 - 473K \), respectively. Thus, \( y^d \) is insensitive to \( T \). This qualitatively explains the constancy of \( y^d \). However, \( y^d \) is slightly smaller than \( y^c \) but much greater than \( y^s \). Therefore, the MDF model merely partially accounts for the nonequilibrium value of \( y^d \) for DIR in the Ag(Sn) system. As mentioned earlier, the MDF model was proposed for DIR in the A(B) system where A is an element with a very low vapor pressure like Cu but B is a volatile element like Zn. Consequently, the nonequilibrium composition for DIR in the Cu(Zn) system could be explained successfully by the MDF model.\(^{19,25}\) On the other hand, Sn is not volatile under the present annealing conditions, and transported to the Ag phase from the \( \zeta \) phase across the \( \zeta / \text{Ag} \) interface by solid-state diffusion. In such a case, a different mathematical model may be needed to explain the nonequilibrium composition in the DIR region quantitatively.

### 3.2 Growth behavior of DIR region

The \( \varepsilon \) and \( \zeta \) compound layers are discriminable from the Sn and Ag phases in each diffusion couple by optical microscopy as reported in a previous study.\(^{14}\) However, it is difficult to distinguish the \( \varepsilon \) and \( \zeta \) compounds each other. Hence, the total thickness \( w \) of the compound layers was
determined for each diffusion couple in a previous study.\textsuperscript{14)} The results at $T = 453$ and 473 K are represented as open triangles and rhombuses, respectively, in Fig. 3. Hereafter, the layer consisting of the $\varepsilon$ (Ag$_{39}$Sn$_{61}$) and $\zeta$ compound layers are also indicated as open triangles and rhombuses at $T = 453$ and 473 K.\textsuperscript{14)} respectively.

The results at $T = 453$ and 473 K are represented as open triangles and rhombuses, respectively, in Fig. 3. Hereafter, the layer consisting of the $\varepsilon$ and $\zeta$ compounds is merely called the intermetallic layer. In this figure, the ordinate on the right-hand side shows the logarithm of the total thickness $w$ of the intermetallic layer, and the abscissa indicates the logarithm of the annealing time $t$. The total thickness $w$ is mathematically expressed as a power function of the annealing time $t$ as follows:\textsuperscript{14)}

$$w = k(t/t_0)^n$$ \hfill (5)

Here, $t_0$ is unit time, 1 s. It is adopted to make the ratio $t/t_0$ dimensionless. The proportionality coefficient $k$ and the exponent $n$ in eq. (5) were determined to be $k = 5.36 \times 10^{-8}$ m and $n = 0.384$ at $T = 453$ K, and $k = 1.17 \times 10^{-7}$ m and $n = 0.364$ at $T = 473$ K from the plotted points in Fig. 3 by the least-squares method in a previous study.\textsuperscript{14)} Using these values, the total thickness $w$ was calculated as a function of the annealing time $t$ from eq. (5). The results are shown as dashed straight lines in Fig. 3.

On the other hand, the DIR region is not clearly discriminated from the Ag phase by optical microscopy and scanning electron microscopy. Therefore, the mean thickness $l$ of the DIR region was determined from the concentration profile like Fig. 1. The results at $T = 453$ and 473 K are shown as open squares and circles, respectively, in Fig. 3. At $T = 433$ K, however, the thickness $l$ is smaller than 2 $\mu$m even at the longest annealing time as mentioned in Section 3.1. Thus, at $T = 433$ K, the thickness $l$ could not be determined reliably by EPMA. Also at $T = 453$ and 473 K, $l$ is smaller than 2 $\mu$m at shorter annealing times. Consequently, only the results at longer annealing times are indicated in Fig. 3. In this figure, the ordinate on the left-hand side shows the logarithm of $l$. As can be seen, the thickness $l$ monotonically increases with increasing annealing time $t$ at each temperature. At a constant value of $t$, $l$ is greater at $T = 473$ K than at $T = 453$ K.

The penetration distance $d$ of Sn in the Ag phase due to volume diffusion is roughly estimated by

$$d = 2\sqrt{Dt},$$ \hfill (6)

where $D$ is the diffusion coefficient of the volume diffusion. The temperature dependence of $D$ is usually described by the following equation.

$$D = D_0 \exp(-Q/RT),$$ \hfill (7)

Here, $D_0$ and $Q$ are the pre-exponential factor and the activation enthalpy, respectively. Values of $D_0 = 2.5 \times 10^{-5}$ m$^2$/s and $Q = 164$ kJ/mol are reported for the tracer diffusion of Sn in Ag.\textsuperscript{31)} Using these parameters, $d$ was calculated from eqs. (6) and (7). The calculation provides $d = 7.0$ nm for $t = 3.96 \times 10^6$ s (1100 h) at $T = 453$ K and $d = 6.3$ nm for $t = 3.20 \times 10^6$ s (890 h) at $T = 473$ K. Comparing these values of $d$ with the corresponding ones of $l$ in Fig. 3, we may find that the thickness of the DIR region is more than 500 times greater than the penetration distance of the volume diffusion at the longest annealing times. As mentioned earlier, the annealing time dependence of the total thickness $w$ is described by eq. (5). As to the experimental values of the thickness $l$ in Fig. 3, however, the open circles are rather scattered at $T = 473$ K and the open squares are obtained for only two annealing times at $T = 453$ K. Therefore, the annealing time dependence of the thickness $l$ cannot be determined directly from the open circles and squares. Consequently, the experimental values of $l$ have been theoretically analyzed using a new extended (NE) model proposed in a previous study.\textsuperscript{21)} The NE model is applicable to DIR in the A(B) system where both elements A and B possess very low vapor pressures. This model will be explained briefly below.

When one mol of the DIR region with composition $y^e$ is produced from $(y^a - y^0)/(1 - y^0)$ mol of element B and $(1 - y^e)/(1 - y^0)$ mol of the $\alpha$ phase with composition $y^0$, a penetration zone of element B will be formed by volume diffusion in the untransformed matrix of the $\alpha$ phase ahead of the moving boundary of the DIR region. Under such conditions, the effective driving force $\Delta^e G$ acting on the moving boundary is expressed by the following equation according to the NE model:\textsuperscript{21)}

$$\Delta^e G = \{1 - y^e\} \left\{ \frac{RT}{V_m} \left[ \ln \frac{1 - y^{\text{atf}}}{1 - y^e} + \frac{\gamma^0}{1 - y^0} \ln \frac{y^{\text{atf}}}{y^e} \right] - \eta \left( \frac{(\gamma^{\text{atf}} - \gamma^0)^2}{1 - y^0} \right) \right\}$$ \hfill (8)

Here, $y^{\text{atf}}$ is the composition of the penetration zone at the interatomic distance $\lambda$ from the moving boundary, $Y$ is the biaxial elastic modulus of the untransformed matrix along the plane parallel to the moving boundary, and $\eta$ and $V_m$ are the misfit parameter and the molar volume, respectively. If the $\alpha$ phase is elastically isotropic, $Y$ is described by

$$Y = \frac{E}{1 - \nu},$$ \hfill (9)

where $E$ and $\nu$ are the Young’s modulus and the Poisson’s ratio, respectively. The migration rate $r$ of the moving
boundary is related to the effective driving force \( \Delta \phi G \) by the following equation.

\[
r = \frac{dl}{dt} = M \Delta \phi G
\]

(10)

Here, \( M \) is the mobility of the moving boundary. Since \( \Delta \phi G \) has the dimension of force per unit area or energy per unit volume, \( M \) takes a unit of \( m^2/Js \) on condition that \( l, t \) and \( \Delta \phi G \) are measured in m, s and J/m$^2$, respectively. Equation (10) indicates that the growth rate \( dl/dt \) of the DIR region is equal to \( r \) and \( r \) is proportional to \( \Delta \phi G \). Let \( \psi \) be the composition in the penetration zone at the interface between the untransformed matrix and the moving boundary. This interface is called the front interface. The composition \( \psi \) in eq. (8) is approximately described as a function of \( \psi \), \( \psi_0 \), \( r \) and \( \lambda \) by the following equation:\(^{21)}

\[
\psi = \psi_0 + (\psi - \psi_0) \exp(-r \lambda / D)
\]

(11)

Here, \( D \) is the diffusion coefficient for volume diffusion of element B in the penetration zone. Considering the local equilibrium between the moving boundary and the penetration zone at the front interface, \( \psi \) is evaluated by the parallel-tangent construction (PTC) method.\(^{32)}\) When the concentration gradient of element B across the moving boundary is negligible, the following equation is obtained by the PTC method.

\[
\ln \frac{\psi}{1-\psi} + \frac{2Y_{m}m^2}{RT} (\psi - \psi_0) = \ln \frac{\psi_e}{1-\psi_e}
\]

(12)

If \( \psi \) is the initial composition of the DIR region at the beginning of the reaction and \( s \) is the diameter of the columnar grain in the DIR region, \( \psi_e \) is a function of \( l, s, r, \delta \) and \( D \) for a given value of \( \psi \) as follows.

\[
\psi_e = \frac{\psi_0 s r + \psi_2 s \delta D}{s r + 2 s \delta D}
\]

(13)

Here, \( D \) is the diffusion coefficient for grain boundary diffusion of element B, and \( \delta \) is the thickness of the grain boundary.

The temperature dependence of \( D \) is described by the following equation of the same formula as eq. (7).

\[
D = D_0^b \exp(-Q^b/RT)
\]

(14)

Here, \( D_0^b \) and \( Q^b \) are the pre-exponential factor and the activation enthalpy, respectively. Values of \( \delta D_0^b = 6.0 \times 10^{-10} \) m$^3$/s and \( Q^b = 59.87 \) kJ/mol are determined by Kaygorodov et al.\(^{33)}\) for the grain boundary diffusion of Sn in Ag. Furthermore, the following parameters are reported: \( E = 10.05 \) GPa and \( \nu = 0.367 \)\(^{30)}\) and \( V_m = 10.27 \times 10^{-6} \) m$^3$/mol and \( \eta = 0.10733 \)\(^{34)}\) Using these parameters as well as values of \( \lambda = 0.3 \) nm, \( \phi = 0 \) and \( \gamma = 0.05 \), the thickness \( l_{i} \) was calculated at each experimental annealing time \( t_i \) from eqs. (7)–(14). In this calculation, the mobility \( M \) in eq. (10) is the only unknown parameter. Unfortunately, however, information of \( M \) is not available for DIR in the Ag(Sn) system. Thus, \( M \) was chosen as the fitting parameter to minimize the function \( f \) defined by the following equation.

\[
f = \sum_{i=1}^{p} (l_i - l_i^*)^2
\]

(15)

Here, \( l_i^* \) is the experimental value of \( l \) at \( t = t_i \), and \( p = 2 \) and \( 3 \) at \( T = 453 \) and \( 473 \) K, respectively. From the open squares and circles in Fig. 3, \( M = 5.81 \times 10^{-20} \) and \( 8.86 \times 10^{-20} \) m$^4$/Js are obtained at \( T = 453 \) and \( 473 \) K, respectively. Using these values of \( M, l \) was calculated as a function of \( t \) from eqs. (7)–(14). The results are shown as solid curves in Fig. 3. At first glance, however, the open circle at the shortest annealing time of \( 6.84 \times 10^5 \) s (190 h) seems to deviate considerably from the solid curve at \( T = 473 \) K. As mentioned earlier, the minimumization for the summation of the differences between \( l_i \) and \( l_i^* \) was carried out using the function \( f \) defined by eq. (15). On the other hand, the ordinate in Fig. 3 indicates the logarithm of \( l \). Thus, the deviation from the solid curve is visually exaggerated for a small absolute value of \( l \) at the shortest annealing time in Fig. 3. According to the results in this figure, the calculation satisfactorily reproduces the experimental values of \( l \). Consequently, it is concluded that the kinetics of DIR in the Ag(Sn) system is quantitatively explained by the NE model.

As shown in Fig. 3, the absolute value is smaller for \( l \) of the DIR region than for \( w \) of the intermetallic layer at the experimental annealing times. As the annealing time increases, however, the thickness increases more remarkably for \( l \) than for \( w \). In order to evaluate the growth rate of the DIR region at a wide range of annealing time, the calculation with eqs. (7)–(14) was carried out also at annealing times much longer than \( t = 10^5 \) s. The results are shown as solid curves in Fig. 4. In this figure, the ordinate and the abscissa indicate the logarithms of \( l \) and \( t \), respectively. Furthermore, the open squares and circles in Fig. 3 are also represented in Fig. 4. If the annealing time dependence of the thickness \( l \) is described by the following equation of the same formula as eq. (5), the exponent takes a value of \( m = 1 \) at an early stage of the reaction.\(^{21)}\)
\[ l = k(t/t_0)^m \]  

The value \( m = 1 \) means that \( l \) is proportional to \( t \) and thus the growth of the DIR region is controlled by the interface reaction at the moving boundary. As can be seen in Fig. 4, the experimental points at \( T = 453 \) and 473 K are mostly located at the early stage. This type of rate-controlling process was observed also for reactive diffusion in a bronze method.\(^{35,36} \) On the other hand, the exponent \( m \) gradually decreases with increasing annealing time and then reaches to 0.37 at a late stage of the reaction at both \( T = 453 \) and 473 K. This indicates that the interface reaction is no longer the bottleneck for the growth of the DIR region and the grain boundary diffusion across the DIR region governs the rate-controlling process at the late stage. The extrapolation is indicated as dashed and dotted lines with \( m = 1 \) and 0.37, respectively, for the solid curves in Fig. 4. Unlike the intermetallic layer, the thickness of the DIR region is not simply described as a power function of the annealing time with a constant value of the exponent. The observation for DIR in the Ni(Cu) system was actually carried out for intermediate stages at \( T = 453 \) and 1023 K.\(^{23} \) The annealing time dependence of the rate-controlling process for DIR is extensively discussed in a previous study.\(^{21} \)

### 3.3 Mobility

As already mentioned in Section 3.2, information of the mobility \( M \) is not available for DIR in the Ag(Sn) system. As a consequence, \( M \) was selected as the fitting parameter in the calculation of the solid curves in Fig. 3. The values of \( M \) determined at \( T = 453 \) and 473 K are plotted as open circles in Fig. 5. In this figure, the ordinate shows the logarithm of \( M \) and the abscissa indicates the reciprocal of \( T \). The temperature dependence of \( M \) may be described by the following equation of the same formula as eqs. (7) and (14).

\[ M = M_0 \exp(-Q_M/RT) \]  

The pre-exponential factor and the activation enthalpy in eq. (17) were determined to be \( M_0 = 1.23 \times 10^{-15} \text{ m}^2/\text{Js} \) and \( Q_M = 37.5 \text{kJ/mol} \), respectively, by interconnecting the open circles in Fig. 5 with a solid line. In this figure, the corresponding results for DIR in the Ni(Cu) system in a previous study\(^{21} \) are represented as open triangles with a dotted line of \( M_0 = 1.03 \times 10^{-15} \text{ m}^2/\text{Js} \) and \( Q_M = 290 \text{kJ/mol} \). Furthermore, the results for diffusion induced grain-boundary migration (DIGM) in the Cu(Zn) system are also shown as various open symbols with a dashed line of \( M_0 = 1.24 \times 10^{-15} \text{ m}^2/\text{Js} \) and \( Q_M = 177 \text{kJ/mol} \). DIGM is the phenomenon that a region with different composition is left behind a moving boundary owing to grain boundary migration combined with the diffusion of solute atoms along the moving boundary. Extrapolating the dashed and dotted lines to temperatures of \( T = 453 \) and 473 K, we may find that \( M \) is greater for DIR in the Ag(Sn) system than for DIGM in the Cu(Zn) system but smaller for DIR in the Ni(Cu) system than for DIGM in the Cu(Zn) system. The melting temperature \( T_m \) is 1235, 1358 and 1728 K for Ag, Cu and Ni, respectively.\(^{28,40} \) Normalizing the annealing temperature \( T \) by the melting temperature \( T_m \), the open symbols in Fig. 5 are plotted in a different manner in Fig. 6. In this figure, the ordinate shows the logarithm of \( M \) and the abscissa indicates the ratio \( T_m/T \). As can be seen in Fig. 6, the open symbols for DIR in the Ni(Cu) system and DIGM in the Cu(Zn) system lie rather well on one master line. This means that the mobility \( M \) is described as the same function of the normalized temperature \( T/T_m \) for these reactions. On the other hand, the open circles are located on the upper side of the master line in Fig. 6. This indicates that the growth of the DIR region at the early stage occurs particularly fast in the Ag(Sn) system. Consequently, like the formation of the \( \varepsilon \) (Ag\(_2\)Sn) and \( \zeta \) phases, the fast penetration of Sn by DIR in the Ag-base conductor alloy plays an important role in deterioration of the electrical conductivity at the interconnection during solid-state heating under usual energization conditions.

![Fig. 5](image1.png)  
**Fig. 5** The mobility \( M \) for the moving boundary of the DIR region versus the reciprocal of the annealing temperature \( T \) shown as open circles. The corresponding results for DIR in the Ni(Cu) system and DIGM in the Cu(Zn) system are also indicated as various open symbols.

![Fig. 6](image2.png)  
**Fig. 6** The values of \( M \) in Fig. 5 are plotted against the ratio \( T_m/T \), where \( T_m \) is the melting temperature of the solvent.
4. Conclusions

The kinetics of diffusion induced recrystallization (DIR) in the Ag(Sn) system was experimentally examined at solid-state temperatures using Sn/Ag/Sn diffusion couples. The diffusion couples were prepared by the diffusion bonding technique and then isothermally annealed at temperatures between \( T = 433 \) and 473 K for various periods in the oil bath with silicone oil. During annealing, the e (Ag3Sn) and \( \zeta \) compound layers are produced at the Sn/Ag interface in the diffusion couple. Furthermore, a region alloyed with Sn is produced in the Ag phase adjacent to the \( \zeta \)/Ag interface due to DIR. The mol fraction of Sn in the DIR region on the side of the \( \zeta \)/Ag interface takes a constant value of 0.05 independent of the annealing time \( t \) and the annealing temperature \( T \). This value is smaller than the solubility of Sn in the Ag phase with 0.0935. The mean thickness \( l \) of the DIR region reaches to 4 \( \mu \)m for \( t = 3.96 \times 10^6 \) s (1100 h) at \( T = 453 \) K and 5 \( \mu \)m for \( t = 3.20 \times 10^6 \) s (890h) at \( T = 473 \) K. However, at \( T = 433 \) K, the DIR region could not be recognized clearly even at the longest annealing time of \( t = 3.63 \times 10^6 \) s (1008h). The experimental values of \( l \) were theoretically analyzed using the new extended-model proposed in a previous study.\(^{21}\) In the analysis, the mobility \( M \) for the moving boundary of the DIR region is evaluated to be \( 5.81 \times 10^{-20} \) and \( 8.86 \times 10^{-20} \) m\(^2\)/Js at \( T = 453 \) and 473 K, respectively. The analysis indicates that \( l \) is almost proportional to \( t \) at the experimental annealing times. This means that the growth of the DIR region is controlled by the interface reaction at the moving boundary. At longer annealing times, however, the growth rate of the DIR region gradually decelerates with increasing annealing time. If \( l \) is described as a power function of \( t \), the exponent becomes 0.37 at a late stage of the reaction at both \( T = 453 \) and 473 K. Such a value of the exponent indicates that the interface reaction is no longer the rate-controlling process and the grain boundary diffusion across the DIR region governs the growth of the DIR region.

Acknowledgements

The authors are grateful to Mr. K. Suzuki with Graduate School at Tokyo Institute of Technology, Japan for assistance at early stages of the present study. The study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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