

Kinetics of Solid-State Reactive Diffusion between Au and Al

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In the wire bonding technique, a thin Au wire is interconnected with an Al layer on a Si chip. During energization heating at solid-state temperatures, however, brittle Au-Al compounds with high electrical resistivities are formed at the interconnection by the reactive diffusion between Au and Al. In order to examine the growth behavior of the Au-Al compounds, the kinetics of the reactive diffusion was experimentally observed using sandwich Al/Au/Al diffusion couples. The diffusion couple was prepared by a diffusion bonding technique and then isothermally annealed at temperatures of 623–723 K for various times up to 103 h. Under such annealing conditions, the diffusion couple is practically considered semi-infinite. Owing to annealing, compound layers consisting of AuAl₂, AuAl and Au₈Al₃ are produced at the initial Au/Al interface in the diffusion couple. The volume fraction in the compound layers is larger for Au₈Al₃ than for AuAl and AuAl₂ in the early stages but becomes smaller for Au₈Al₃ than for AuAl and AuAl₂ in the late stages. However, there are no systematic dependencies of the volume fraction on the annealing time and temperature. The total thickness of the compound layers is proportional to a power function of the annealing time. The exponent of the power function is smaller than 0.5 at 673–723 K. The exponent smaller than 0.5 means that the interdiffusion across the compound layers governs the layer growth and boundary diffusion predominantly contributes to the interdiffusion. On the other hand, at 623 K, the exponent is equal to unity for annealing times shorter than 8 h but smaller than 0.5 for those longer than 8 h. The exponent of unity indicates that the layer growth is controlled by the interface reaction at the migrating interface. Thus, at $T = 623$ K, the transition of the rate-controlling process occurs at a critical annealing time of 8 h. [doi:10.2320/matertrans.M2010433]

(Received December 24, 2010; Accepted January 20, 2011; Published March 2, 2011)

Keywords: reactive diffusion, intermetallic compounds, interface reaction, gold-aluminum system

1. Introduction

The wire bonding technique is widely used in the semiconductor industry. In this technique, a thin Au wire is usually interconnected with an Al layer on the Si chip. During heating under energization conditions at solid-state temperatures, however, Au-Al compounds are formed at the interconnection due to the reactive diffusion between Au and Al. The Au-Al compounds are brittle and possess high electrical resistivities. Thus, the formation of the Au-Al compounds deteriorates the electrical and mechanical properties of the interconnection.

The solid-state reactive diffusion between Au and Al has been experimentally studied by many investigators.^{1–13} According to a phase diagram in the binary Au-Al system,¹⁴ six compounds appear as stable phases at temperatures lower than 773 K. They are Au₄Al, Au₅Al₂, α -Au₂Al, β -Au₂Al, AuAl and AuAl₂. In a recent supplement of the phase diagram,¹⁵ however, Au₅Al₂ is replaced by Au₈Al₃. Thus, the stoichiometry Au₈Al₃ is adopted in the present article. An experiment of the reactive diffusion was conducted by Chang *et al.*⁸) using diffusion couples composed of a Au wire and a thin Al layer. In this experiment, the diffusion couple was isothermally annealed at 448 K for various times up to 1008 h. During annealing, Au₂Al, Au₈Al₃ and Au₄Al are formed at the initial Au/Al interface in the diffusion couple. However, AuAl and AuAl₂ were not clearly observed. Although the total volume of these compounds monotonically increases with increasing annealing time, the volume fraction of each compound varies depending on the annealing time in a complicated manner. Similar results were reported also by Noolu *et al.*¹⁰) and Breach and Wulff.¹¹) Since the

initial thickness of the Al layer in the diffusion couple is small,⁸) however, soft impingement of diffusion may occur in the Au layer after a certain annealing time and will influence the growth behavior of the compound. Furthermore, in the late stages, the Al layer is completely consumed by the growth of the compound. Consequently, such a finite diffusion couple may not be suitable for the reactive diffusion experiment. Nevertheless, this type of diffusion couple has been preferably used in most of the experiments.

The kinetics of the reactive diffusion was experimentally observed by Philofsky⁶) using semi-infinite Au/Al diffusion couples. Here, the semi-infinite diffusion couple means that the penetration distance of diffusion is much smaller than the thickness for each terminal specimen of the diffusion couple. In this experiment, the diffusion couple was isothermally annealed at temperatures of 473–733 K for various periods up to 97 h. According to the observation, all the stable compounds are formed as layers at the Au/Al interface in the diffusion couple, and the total thickness of the compound layers increases in proportion to the square root of the annealing time. Such a relationship is called the parabolic relationship. This relationship usually indicates that the growth of the compound layers is controlled by volume diffusion. Although the thickness was measured for four and five annealing times at 473 K and 673 K, respectively, it was determined for only two annealing times at 523 K, 573 K, 623 K and 733 K. The annealing time dependence of the thickness may be rather credibly estimated from the four or five experimental points. However, the two experimental points cannot guarantee that the parabolic relationship surely holds between the thickness and the annealing time. Thus, the temperature dependence of the growth rate of the compounds could not be reliably evaluated in a wide temperature range.

In order to examine the growth behavior of the Au-Al compounds, the kinetics of the solid-state reactive diffusion

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between Au and Al was experimentally observed in the present study. In the experiment, sandwich Al/Au/Al diffusion couples were prepared by a diffusion bonding technique and then isothermally annealed at temperatures of 623–723 K for various times up to 103 h. Under such annealing conditions, the diffusion couple is practically considered semi-infinite. The microstructure of the annealed diffusion couple was observed in a metallographical manner. The rate-controlling process was discussed on the basis of the observation.

2. Experimental

Polycrystalline pure Al plate specimens with a dimension of 14 mm × 5 mm × 2 mm were cut from a commercial pure Al sheet with a thickness of 2 mm and purity of 99.99%. Two parallel surfaces with an area of 14 mm × 5 mm of each Al plate specimen were mechanically polished on 600–1000 emery papers. One of the polished surfaces was again mechanically polished on 1500–4000 emery papers and then finished using diamond with a diameter of 1 μm. Polycrystalline pure Au sheet specimens with a dimension of 20 mm × 7 mm × 0.1 mm were cut from a commercial pure Au sheet with a thickness of 0.1 mm and purity of 99.99%. Each Au sheet specimen was degreased in acetone with an ultrasonic cleaner and then immediately sandwiched between two freshly prepared Al plate specimens in methanol by the technique reported in a previous study.¹⁶⁾ Each sandwich couple was completely dried and then isothermally heat treated for diffusion bonding in an evacuated silica tube at temperatures of 623 K, 673 K and 723 K for times of 5 h, 1 h and 1 h, respectively, followed by air cooling. The diffusion couples were separately encapsulated in evacuated silica capsules and then isothermally annealed at temperatures of 623 K, 673 K and 723 K for various periods up to 102 h, followed by water quenching without breaking the capsules. Hereafter, the summation of the heat-treating and annealing times is merely called the annealing time t , and the annealing temperature is denoted by T . Cross-sections of the annealed diffusion couple were mechanically polished using 1500–4000 emery papers and diamond with a size of 1 μm and then finished with an OP-S liquid manufactured by Struers Ltd. The microstructure of the cross-section was observed with a differential interference contrast optical microscope (DICOM). Concentration profiles of Au and Al on the cross-section were measured by electron probe microanalysis (EMPA).

3. Results and Discussion

3.1 Microstructure

Typical DICOM photographs of cross-section for the annealed diffusion couple are shown in Fig. 1. Figure 1(a) indicates the photograph of the freshly finished cross-section for the diffusion couple with $T = 723$ K and $t = 24$ h (8.64×10^4 s). In this figure, the top and bottom regions are the Au and Al specimens, respectively. As can be seen, three layers with different contrasts are formed at the initial Au/Al interface. The contrast of the intermediate layer is considerably different from that of the lower layer but rather close

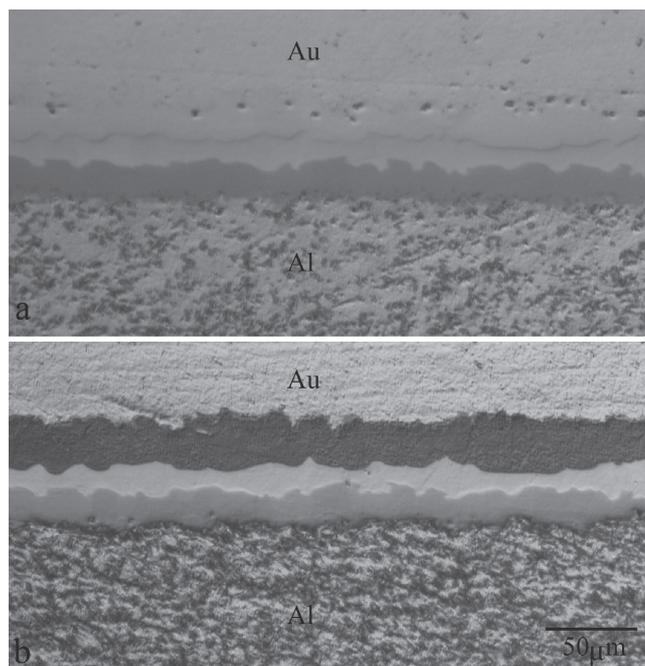


Fig. 1 DICOM photographs of cross-section for the diffusion couple with $T = 723$ K and $t = 24$ h (8.64×10^4 s): (a) fresh finishing, and (b) exposure to an ambient atmosphere for 4 days.

to that of the upper layer. The cross-section in Fig. 1(a) was exposed to an ambient atmosphere for 4 days and then observed in a similar manner. The resultant microstructure is shown in Fig. 1(b). Due to the exposure, the contrast of the upper layer becomes much darker than that of the intermediate layer. Consequently, the three layers are clearly distinguished one another in Fig. 1(b). Such a dark contrast of the upper layer may be attributed to the oxidation during the exposure. In order to identify each layer, concentration profiles of Au and Al along the direction normal to the initial Au/Al interface were measured by EPMA on the freshly finished cross-section like Fig. 1(a). A result of the diffusion couple with $T = 673$ K and $t = 89$ h (3.20×10^5 s) is indicated in Fig. 2. In this figure, the ordinate and the abscissa show the mol fraction y_i of component i and the distance x , respectively, and open circles and squares indicate the results of Au and Al, respectively. As can be seen in Fig. 2, the layers are Au_8Al_3 , AuAl and AuAl_2 from the Au side to the Al side. According to a recent phase diagram in the binary Au–Al system,¹⁵⁾ six compounds appear as stable phases at $T = 623$ –723 K. They are Au_4Al , Au_8Al_3 , α - Au_2Al , β - Au_2Al , AuAl and AuAl_2 . However, Au_4Al and Au_2Al were not clearly recognized even for the diffusion couple annealed at the highest temperature of $T = 723$ K for the longest time of $t = 101$ h (3.64×10^5 s). The compound layers consisting of Au_8Al_3 , AuAl and AuAl_2 were observed in all the annealed diffusion couples. Hereafter, the compound layers are merely called the intermetallic layer.

3.2 Growth behavior of intermetallic layer

From the DICOM photographs of cross-section like Fig. 1(b), the total thickness l of the intermetallic layer was evaluated by the equation

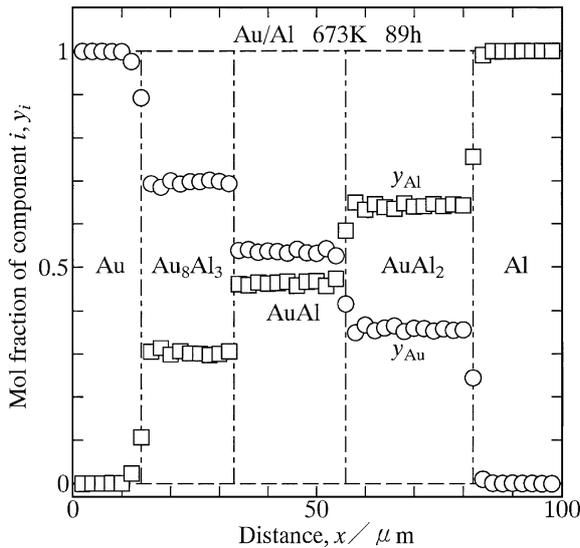


Fig. 2 Concentration profiles of Au and Al across the compound layers in the diffusion couple with $T = 673$ K and $t = 89$ h (3.20×10^5 s).

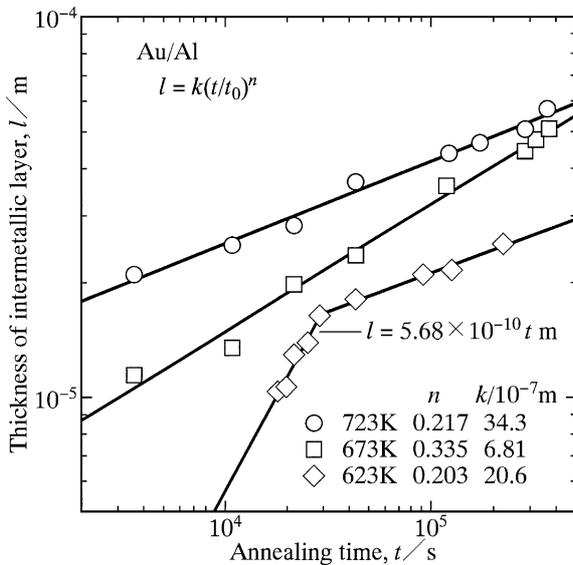


Fig. 3 The total thickness l of the intermetallic layer versus the annealing time t at $T = 623$ K, 673 K and 723 K shown as open rhombuses, squares and circles, respectively. Straight lines indicate the calculations from eq. (2).

$$l = \frac{A}{w}, \quad (1)$$

where w and A are the length parallel to the initial Au/Al interface and the total area of the intermetallic layer, respectively, on the cross-section. The results of $T = 623$ K, 673 K and 723 K are shown as open rhombuses, squares and circles, respectively, in Fig. 3. In this figure, the ordinate and the abscissa indicate the logarithms of l and t , respectively. As can be seen, the thickness l monotonically increases with increasing annealing time t . Furthermore, the plotted points at each annealing temperature are located well on a straight line. This means that l is mathematically expressed as a power function of t by the following equation.

$$l = k \left(\frac{t}{t_0} \right)^n \quad (2)$$

Here, t_0 is unit time, 1 s. It is adopted to make the argument t/t_0 of the power function dimensionless. The proportionality coefficient k has the same dimension as the thickness l , but the exponent n is dimensionless. From the open symbols in Fig. 3, k and n were estimated by the least-squares method as shown with solid lines. At $T = 673$ – 723 K, n is smaller than 0.5. On the other hand, at $T = 623$ K, n is equal to unity for $t < 8.08$ h (2.91×10^4 s) but smaller than 0.5 for $t > 8.08$ h. Thus, at $T = 623$ K, n discontinuously varies depending on t at $t_c = 8.08$ h, where t_c is the critical annealing time. This discontinuous variation of n is attributed to the transition of the rate-controlling process for the growth of the intermetallic layer. The relationship between the rate-controlling process and the exponent n will be discussed in detail later on.

According to a recent phase diagram in the binary Au–Al system,¹⁵⁾ the solubility of Al in Au is around 10 at% and that of Au in Al is negligible at $T = 623$ – 723 K. Thus, the interdiffusion coefficient of the Al-rich solid phase is very close to the tracer diffusion coefficient of Au in Al, and that of the Au-rich solid phase is not so different from the tracer diffusion coefficient of Al in Au.¹⁷⁾ In such a case, the penetration distance d of diffusion is roughly estimated by the following equation.¹⁷⁾

$$d = 2\sqrt{Dt} \quad (3)$$

Here, D is the tracer diffusion coefficient. The temperature dependence of D is expressed as

$$D = D_0 \exp\left(-\frac{Q}{RT}\right), \quad (4)$$

where D_0 is the pre-exponential factor, Q is the activation enthalpy, and R is the gas constant. The following parameters are reported in a literature:¹⁸⁾ $D_0 = 2.2 \times 10^{-4}$ m²/s and $Q = 134$ kJ/mol for Au in Al; and $D_0 = 1.07 \times 10^{-5}$ m²/s and $Q = 177$ kJ/mol for Au in Au. However, no reliable information is available for the corresponding parameters of Al in Au. Thus, as to Al in Au, the values of D_0 and Q for Au in Au were used to evaluate D . For the longest time of $t = 101$ h (3.64×10^5 s) at the highest temperature of $T = 723$ K, the evaluation provides the penetration distances $d_{\text{Au}}^{\text{Al}} = 52$ μm and $d_{\text{Al}}^{\text{Au}} = 1.6$ μm for Au in Al and Al in Au, respectively, but the thicknesses of the Al and Au specimens in the diffusion couple are $l_{\text{Al}} = 2$ mm and $l_{\text{Au}} = 52$ μm , respectively. Hence, $d_{\text{Au}}^{\text{Al}}$ and $d_{\text{Al}}^{\text{Au}}$ are much smaller than l_{Al} and l_{Au} , respectively. This means that the Al/Au/Al diffusion couple is surely considered semi-infinite under the annealing conditions in the present study.

As mentioned in Section 1, the kinetics of the reactive diffusion between Au and Al was experimentally observed by Philofsky⁶⁾ using semi-infinite Au/Al diffusion couples. In this experiment, the diffusion couple was prepared by a butt-welding technique and then isothermally annealed at temperatures of $T = 473$ – 733 K for various times up to $t = 97$ h (3.49×10^5 s). After annealing, all the stable compounds were observed as layers at the Au/Al interface in the diffusion couple. The dependencies of l on t at $T = 623$ K,

673 K and 733 K reported by Philofsky⁶⁾ are represented as open squares with dashed lines in Fig. 4(a), (b) and (c), respectively. Like Fig. 3, the ordinate and the abscissa in Fig. 4 indicate the logarithms of l and t , respectively. At $T = 673$ K in Fig. 4(b), the dashed line was obtained from the five open squares by the least-squares method. However, at $T = 623$ K and 733 K in Fig. 4(a) and (c), respectively, the two open squares are merely connected with each other by a dashed line. On the other hand, the results of $T = 623$ K, 673 K and 723 K in Fig. 3 are shown again as open circles with solid lines in Fig. 4(a), (b) and (c), respectively. In Fig. 4(c), T is higher by 10 K for the dashed line than for the solid line, and l is larger for the former line than for the latter line. Thus, it is anticipated that the larger value of l is attributed to the higher value of T . Even at the equivalent temperatures in Fig. 4(a) and (b), however, l is greater for the dashed line than for the solid line. This means that the overall growth rate of the intermetallic layer is greater in the study by Philofsky⁶⁾ than in the present study. The diffusion couple was prepared by the butt-welding technique in the former study but by the diffusion bonding technique in the latter study. Thus, the preparation method of the diffusion couple is dissimilar in the two studies. In the diffusion bonding technique, the bonding was conducted at the same temperature as the isothermal annealing, and the annealing time t corresponds to the summation of the bonding and annealing times. Hence, t indicates the net annealing time. On the other hand, the heating conditions of the butt-welding technique were not explicitly explained by Philofsky.⁶⁾ Hence, no information is available for the influence of the butt-welding on the growth of the intermetallic layer. If the intermetallic layer is formed during the butt-welding and t merely indicates the annealing time excluding the butt-welding time, l is overestimated for a given value of t or t is underestimated for that of l . In such a case, the dashed line is located on the upper side of the solid line.

The reactive diffusion between Au and an Al-base alloy containing 1 mass% of Si and 0.5 mass% Cu was experimentally observed by Breach and Wulff¹³⁾ using Au/(Al-Si-Cu) diffusion couples. Here, the thickness is 1 μm for the Al-Si-Cu alloy but sufficiently large for Au. In their experiment, the diffusion couple was isothermally annealed at 448 K for various times up to 497 h (1.79×10^6 s). Owing to annealing, Au_8Al_3 and Au_4Al layers are produced at the interface in the diffusion couple. Unlike the experiment by Philofsky,⁶⁾ however, Au_2Al , AuAl and AuAl_2 were not clearly recognized. Breach and Wulff reported that the parabolic relationship held between the total thickness l of the Au_8Al_3 and Au_4Al layers and the annealing time t in the range of $t = 3.42 \times 10^3$ – 4.14×10^4 s. Their result for the dependence of l on t in this range is represented as open circles in Fig. 5. In this figure, like Figs. 3 and 4, the ordinate and the abscissa show the logarithms of l and t , respectively. As can be seen, l is proportional to a power function of t . From eqs. (3) and (4), the penetration distance of Au in Al is evaluated to be 0.093 μm at $T = 448$ K for $t = 4.14 \times 10^4$ s. Although the Al-Si-Cu alloy is finally consumed by the growth of the compound layers, the thickness l_{Al} of the alloy at each annealing time was not reported by Breach and Wulff.¹³⁾ If l_{Al} is much larger than 0.1 μm at $t = 4.14 \times 10^4$ s, however, the

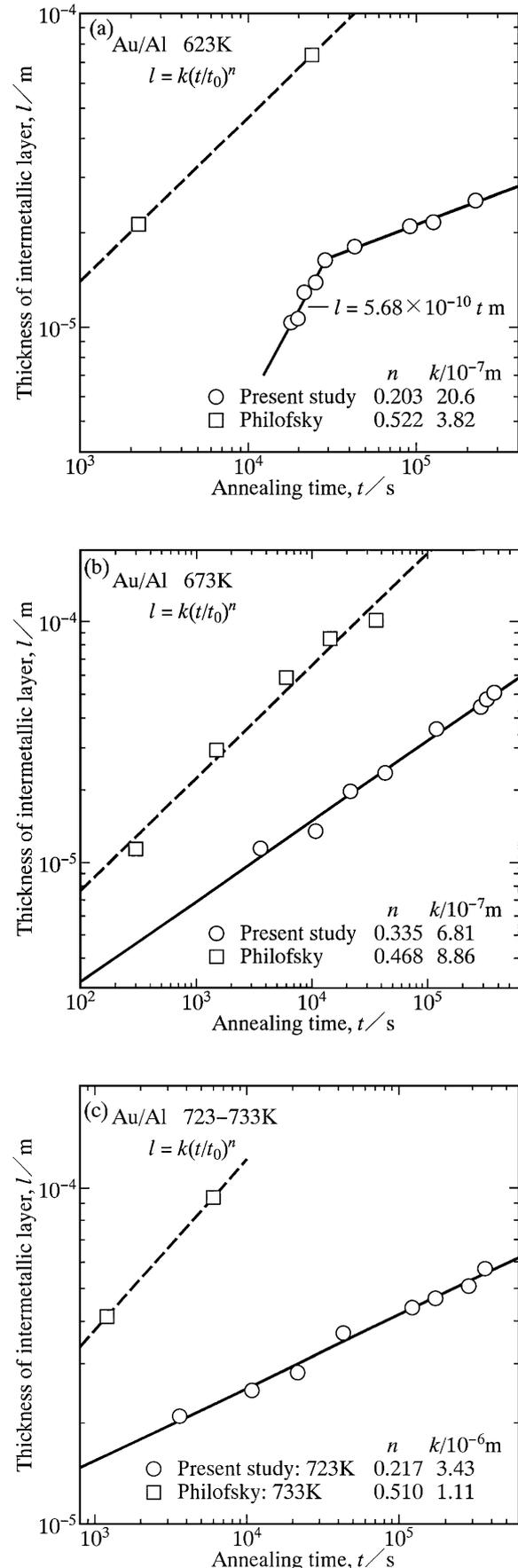


Fig. 4 The results in Fig. 3 are shown as open circles with solid lines for (a) $T = 623$ K, (b) $T = 673$ K and (c) $T = 723$ K. The corresponding results of $T = 623$ – 733 K by Philofsky⁶⁾ are also indicated as open squares with dashed lines.

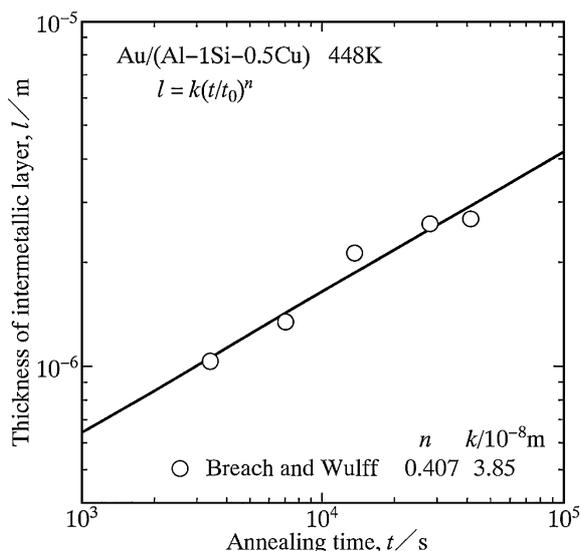


Fig. 5 The total thickness l of the intermetallic layer versus the annealing time t at $T = 448$ K shown as open circles by Breach and Wulff.¹³ A straight line indicates the calculation from eq. (2).

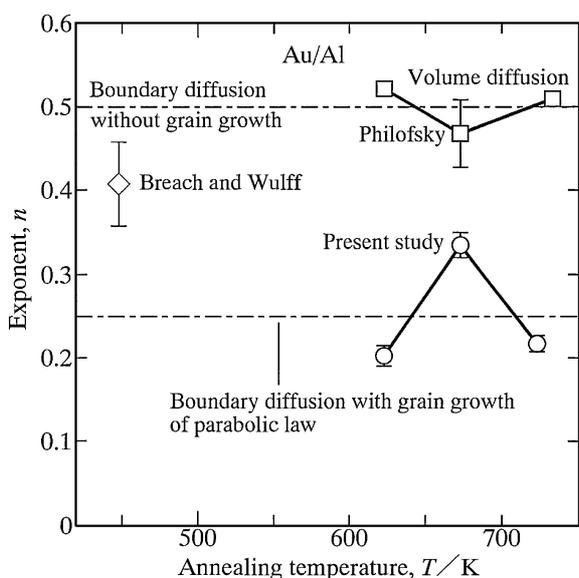


Fig. 6 The exponent n versus the annealing temperature T shown as open circles with error bars. The experimental result by Philofsky⁶ is used for estimation of open squares with errors bars.

Au/(Al-Si-Cu) diffusion couple is considered semi-infinite within the experimental annealing times in Fig. 5. A solid line in this figure indicates the calculation from eq. (2) by the least-squares method. According to this solid line, the exponent n of the power function is smaller than 0.5.

The exponent n is plotted against the annealing temperature T in Fig. 6. In this figure, open circles and squares with error bars show the results of the solid and dashed lines, respectively, in Fig. 4, and an open rhombus with an error bar indicates that of the solid line in Fig. 5. At $T = 623$ K in Fig. 4(a), however, $n = 1$ for $t < t_c = 8.08$ h (2.91×10^4 s), but $n = 0.203$ for $t > t_c$. The physical meaning of $n = 1$ will be discussed later on, and hence only the value $n = 0.203$ is indicated for $T = 623$ K in Fig. 6. On the other hand,

at $T = 623$ K and 733 K in Fig. 4(a) and (c), respectively, the dashed line merely connects the two open squares with each other and thus cannot provide the standard error of n . Consequently, for the open squares in Fig. 6, n is less reliable at $T = 623$ K and 733 K than at $T = 673$ K. When the growth of the intermetallic layer is controlled by the interdiffusion across the intermetallic layer and the interdiffusion is governed by volume diffusion, n is equal to 0.5. The value $n = 0.5$ is realized also for the layer growth controlled by boundary diffusion unless grain growth occurs in the intermetallic layer.¹⁹ If grain growth takes place in the intermetallic layer, however, n becomes smaller than 0.5 for the boundary diffusion rate-controlling process. Furthermore, n is equivalent to 0.25, if the grain growth obeys the parabolic law.²⁰ Here, the parabolic law means that the mean grain size of the intermetallic layer increases in proportion to the square root of the annealing time. As to the open circles in Fig. 6, n is rather close to 0.25, and there is no systematic dependence of n on T . Thus, we may conclude that the layer growth is predominantly controlled by the boundary diffusion across the intermetallic layer and the grain growth takes place almost according to the parabolic law. In order to test the validity of this conclusion, the metallographical observation of the polycrystalline grain in the intermetallic layer was tried by a chemical etching technique with various etchants. Although the oxidation of Au_8Al_3 occurs during the exposure of the cross-section to an ambient atmosphere for 4 days as shown in Fig. 1(b), the Au-Al compounds are highly corrosion resistant against the chemical etching. As a consequence, the polycrystalline grain was not clearly observed on the DICOM photograph of the chemically etched cross-section, and thus the grain growth of the intermetallic layer could not be confirmed in a metallographical manner. On the other hand, n is close to 0.5 for the open squares in Fig. 6. In this case, however, there are two possibilities of the rate-controlling process as mentioned above. Nevertheless, the open circles deduce that the boundary diffusion considerably contributes to the rate-controlling process of the layer growth at $T = 623$ – 723 K. This implies that the grain growth is sluggish for the open squares. As mentioned earlier, the open squares and diffusion-bonding techniques, respectively. Though the heating conditions were not explicitly explained for the butt-welding technique,⁶ the difference of n between the open circles and squares in Fig. 6 indicates that the grain growth behavior of the intermetallic layer is dissimilar in the diffusion couples prepared by the diffusion-bonding and butt-welding techniques. As mentioned earlier, Breach and Wulff¹³ reported that $n = 0.5$ at $T = 448$ K. However, the open rhombus in Fig. 6 shows that n is close to 0.4 at $T = 448$ K. Considering the open rhombus and circles, we may anticipate that the exponent n gradually increases from 0.25 to 0.4 with decreasing annealing temperature T from 723 K to 448 K. Consequently, it is concluded that the layer growth is predominantly controlled by boundary diffusion and the grain growth becomes rather sluggish at lower temperatures.

As shown in Fig. 2, the intermetallic layer is composed of Au_8Al_3 , AuAl and AuAl_2 . The volume fraction f_i of

compound i in the intermetallic layer is estimated by the following equation.

$$f_i = \frac{A_i}{A} \quad (5)$$

Here, A_i is the area of compound i on the cross-section, and $i = 1, 2$ and 3 for Au_8Al_3 , AuAl and AuAl_2 , respectively. The results of $T = 623$ K, 673 K and 723 K obtained from eq. (5) are shown in Fig. 7(a), (b) and (c), respectively. In this figure, the ordinate and the abscissa indicate f_i and the logarithm of t , respectively, and open circles, squares and rhombuses represent f_1 , f_2 and f_3 , respectively. Although the open symbols are rather scattered, f_1 is greater than f_2 and f_3 in the early stages but becomes smaller than f_2 and f_3 in the late stages. Hence, as t increases, f_1 decreases, but f_2 and f_3 increase. This means that Au_8Al_3 is predominantly formed in the early stages and then replaced by AuAl and AuAl_2 in the late stages. However, there are no systematic dependencies of f_1 , f_2 and f_3 on t and T .

The results of f_1 , f_2 and f_3 at $T = 673$ K reported by Philofsky⁶⁾ are shown in Fig. 8 with the same symbols as Fig. 7. Furthermore, in Fig. 8, open triangles and inverse-triangles indicate f_4 of Au_2Al and f_5 of Au_4Al , respectively, by Philofsky.⁶⁾ Since the chemical compositions of α - Au_2Al and β - Au_2Al are close to each other,¹⁵⁾ α - Au_2Al and β - Au_2Al were not distinguished by Philofsky.⁶⁾ As can be seen, f_1 is greater than f_2 – f_5 . As t increases, f_1 and f_3 decrease, but f_2 , f_4 and f_5 increase. However, f_2 and f_5 are negligible within the experimental annealing times. Thus, the layer growth behavior of each compound is dissimilar in Figs. 7(b) and 8. As mentioned earlier, the results in Figs. 7 and 8 are obtained for the diffusion couples prepared by the diffusion-bonding and butt-welding techniques, respectively. At $T = 623$ – 723 K, the boundary diffusion plays an important role in the diffusion rate-controlling process of the layer growth. If the grain growth occurs in the compound layer, the volume fraction of the grain boundary in the compound layer monotonically decreases with increasing annealing time. Such decrease in the volume fraction diminishes the effective diffusion coefficient of the compound layer and hence decelerates the layer growth. This deceleration makes the exponent n smaller than 0.5 .^{19,20)} As previously mentioned, however, the grain growth behavior of each compound is not similar to each other between the two types of diffusion couples. This means that the effective diffusion coefficient of each compound is dissimilar in Figs. 7 and 8. Hence, the difference of the layer growth behavior may be attributed to the dissimilarity in the grain growth behavior.

In spite of such a difference of the growth behavior, f_1 is greater than f_2 – f_3 for $t < 10$ h (3.6×10^4 s) at $T = 623$ – 723 K in Figs. 7 and 8. The predominant formation of Au_8Al_3 in the early stages was explained by Pretorius *et al.*²¹⁾ using a thermodynamic model. As shown in Fig. 1(b), the oxidation resistivity in an ambient atmosphere is much smaller for Au_8Al_3 than for AuAl and AuAl_2 . As a consequence, the predominant formation of Au_8Al_3 may deteriorate the oxidation resistance of the interconnection. This deterioration also influences the mechanical and electrical properties of the interconnection.

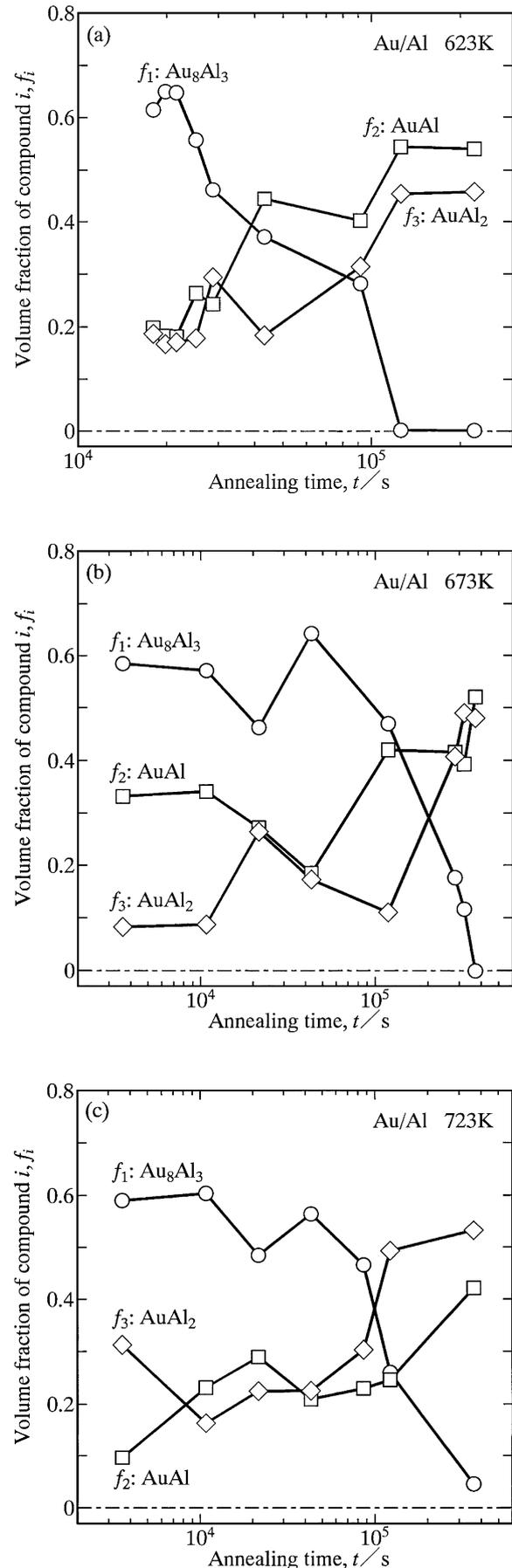


Fig. 7 The volume fraction f_i versus the annealing time t shown as open circles, squares and rhombuses for Au_8Al_3 , AuAl and AuAl_2 , respectively, at (a) $T = 623$ K, (b) $T = 673$ K and (c) $T = 723$ K.

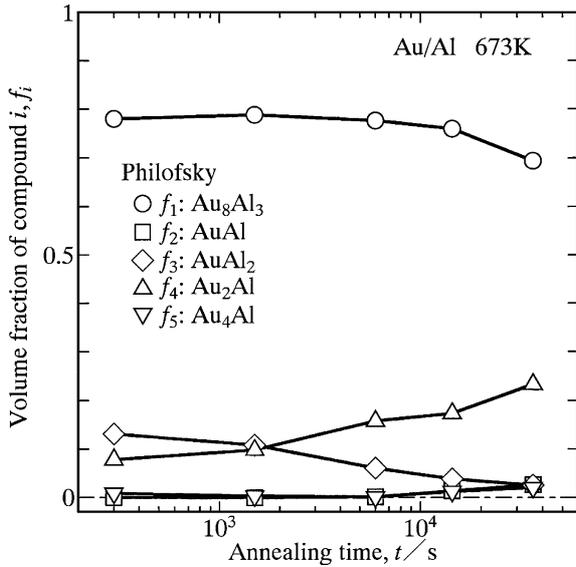


Fig. 8 The volume fraction f_i versus the annealing time t shown as open circles, squares, rhombuses, triangles and inverse-triangles for Au_8Al_3 , AuAl , AuAl_2 , Au_2Al and Au_4Al , respectively, at $T = 673$ K by Philofsky.⁶⁾

3.3 Transition of rate-controlling process

As indicated in Fig. 3, the exponent n is equal to unity for $t < 8.08$ h (2.91×10^4 s) but smaller than 0.5 for $t > 8.08$ h at $T = 623$ K. Hence, at the lowest annealing temperature, n discontinuously changes depending on t at $t_c = 8.08$ h. Here, t_c is the critical annealing time. This discontinuous change of n is attributed to the transition of the rate-controlling process for the layer growth. Such transition of the rate-controlling process in the reactive diffusion is realized also for other alloy systems.^{16,22,23)} For instance, the reactive diffusion between Ta and a bronze was experimentally observed in a previous study.¹⁶⁾ In this experiment, diffusion couples composed of Ta and a Cu-9.3 at% Sn-0.3 at% Ti alloy were isothermally annealed at $T = 973$ – 1053 K for various times up to $t = 1462$ h (5.26×10^6 s). During annealing, a uniform Ta_9Sn layer is formed at the initial Ta/(Cu-Sn-Ti) interface in the diffusion couple. The mean thickness of the Ta_9Sn layer is proportional to a power function of the annealing time. The exponent of the power function is equal to unity at $t < t_c$ but smaller than 0.5 at $t > t_c$. Thus, like the result of $T = 623$ K in Fig. 3, the transition of the rate-controlling process occurs for the growth of Ta_9Sn . In this case, $t_c = 1.83 \times 10^6$ s, 4.63×10^5 s and 5.98×10^5 s at $T = 973$ K, 1023 K and 1053 K, respectively. The growth of Ta_9Sn is controlled by the interface reaction at the migrating $\text{Ta}_9\text{Sn}/\text{Ta}$ interface in the early stages with $t < t_c$. In the late stages with $t > t_c$, however, the interdiffusion across the Ta_9Sn layer governs the layer growth and boundary diffusion remarkably contributes to the interdiffusion.¹⁶⁾

If l is expressed as a power function of t by eq. (2) for the growth of a compound layer during solid-state reactive diffusion in a certain alloy system, the growth rate v of the compound layer is calculated for given values of k and n by the following equation as reported in a previous study:¹⁶⁾

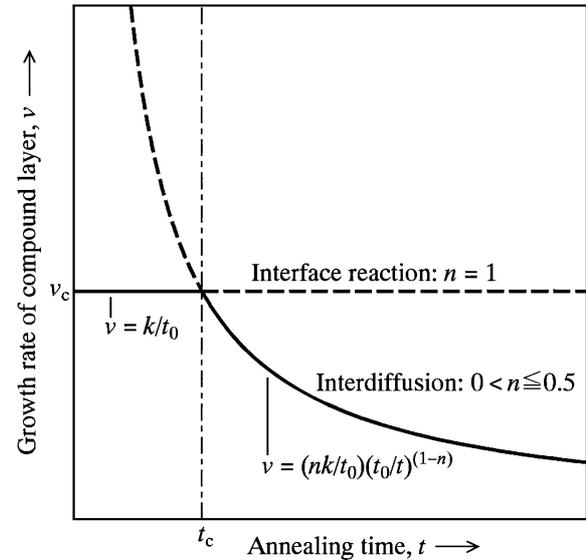


Fig. 9 Schematic relationships for the growth rate v of the compound layer versus the annealing time t obtained from eq. (6).¹⁶⁾ A horizontal line shows the result with $n = 1$, and a smooth curve indicates that with $0 < n \leq 0.5$.

$$v = \frac{dl}{dt} = \frac{nk}{t_0} \left(\frac{t_0}{t} \right)^{1-n}. \quad (6)$$

The dependencies of v on t for $n = 1$ and $0 < n \leq 0.5$ evaluated from eq. (6)¹⁶⁾ are schematically drawn as a horizontal line and a smooth curve, respectively, in Fig. 9. In the case of $n = 1$, eq. (6) gives $v = k/t_0$, and hence v is constant independent of t . In contrast, for $0 < n \leq 0.5$, v is infinitely large at $t = 0$ and monotonically decreases with increasing value of t . As a consequence, the smooth curve intersects the horizontal line at $t = t_c$, where t_c is the critical annealing time as mentioned earlier. Nevertheless, t_c may not necessarily appear within experimental annealing times. Under realistic experimental conditions, the appearance of t_c depends on the alloy system.

As reported in a previous study,²⁴⁾ the growth of the compound layer is determined by the mass transport across the compound layer. In the case of the diffusion rate-controlling process, the mass transport is governed by the interdiffusion. Since the diffusional flux J_i of component i is proportional to the gradient $\Delta\mu_i/l$ of the chemical potential across the compound layer,¹⁷⁾ J_i is in inverse relation to l . Here, $\Delta\mu_i$ is the difference between the chemical potentials of component i at the two parallel interfaces sandwiching the compound layer with the thickness l . When the growth of the compound layer proceeds in a semi-infinite diffusion couple, the chemical potential μ_i of component i at each interface remains constant during the growth. Thus, $\Delta\mu_i$ is also constant independent of t . At $t < t_c$, l is very small, and thus $\Delta\mu_i/l$ is considerably large. In such a case, J_i is large, and hence the growth of the compound layer should be fast. Therefore, v may vary depending on t along the dashed curve indicated in Fig. 9. If J_i is very large, however, the interface reaction becomes an obstacle of the interface migration and thus the bottleneck for the layer growth. Consequently, at $t < t_c$, v cannot take

infinitely large values but becomes equal to k/t_0 as shown with the solid line in Fig. 9. On the other hand, at $t > t_c$, l is large, and hence $\Delta\mu_i/l$ is relatively small. Under such conditions, J_i is small, and thus the interface reaction is no longer the bottleneck. As a result, at $t > t_c$, v varies depending on t along the solid curve indicated in Fig. 9. This is the reason why the growth of the compound layer is controlled by the interface reaction at $t < t_c$ but by the interdiffusion at $t > t_c$.

4. Conclusions

The growth behavior of the Au-Al compounds during the solid-state reactive diffusion between Au and Al was experimentally examined using the sandwich Al/Au/Al diffusion couple prepared by the diffusion bonding technique. The diffusion couple was isothermally annealed in the temperature range of $T = 623\text{--}723$ K for various times up to $t = 103$ h. Due to annealing, the compound layers composed of Au_8Al_3 , AuAl and AuAl₂ are produced at the Au/Al interface in the diffusion couple. Among these compounds, Au_8Al_3 is predominantly formed in the early stages and then replaced by AuAl and AuAl₂ in the late stages. However, the volume fraction of each compound does not systematically vary depending on the annealing time and temperature. The total thickness l of the compound layers increases in proportion to a power function of the annealing time t . The exponent n of the power function is smaller than 0.5 at $T = 673\text{--}723$ K. This indicates that the growth of the compound layers is controlled by the interdiffusion across the layers and the interdiffusion is predominantly governed by boundary diffusion. In contrast, at $T = 623$ K, $n = 1$ for $t < 8$ h, but $n < 0.5$ for $t > 8$ h. The value $n = 1$ means that the interface reaction at the migrating interface controls the growth of the compound layers. Therefore, at $T = 623$ K, the transition of the rate-controlling process takes place at a critical annealing time of $t_c = 8$ h. Such transition should universally appear also at $T > 623$ K. Since the shortest annealing time is 1 h at both $T = 673$ K and 723 K, however, t_s is shorter than 1 h at $T = 673\text{--}723$ K.

Acknowledgements

The present study was supported by the Iketani Science and Technology Foundation in Japan. The study was also partially 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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