Reactive Diffusion between Ag and Sn at Solid State Temperatures

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The reactive diffusion at solid-state temperatures was experimentally studied for the binary Ag–Sn system. Sn/Ag/Sn diffusion couples were prepared by a diffusion bonding technique and then annealed at temperatures between T = 433 and 473 K for various periods in an oil bath with silicone oil. After annealing, layers of the ζ(Sn/Ag) and ξ compounds were observed to form at the Sn/Ag interface. Furthermore, a thin layer alloyed with Sn was produced into the Ag specimen from the Sn/Ag interface owing to diffusion induced recrystallization (DIR). The thickness is about one order of magnitude greater for the ζ layer than for the ξ and DIR layers. The total thickness l of the ζ and ξ layers is described as a function of the annealing time t by the equation l = k(t/t₀)ⁿ. Here, t₀ is unit time, 1 s. The exponent n is 0.40, 0.38 and 0.36 at T = 433, 453 and 473 K, respectively. If the reactive diffusion is controlled by the volume diffusion, n is equal to 0.5. However, n is actually smaller than 0.5 at all the annealing temperatures. This indicates that the grain boundary diffusion contributes to the reactive diffusion and the grain growth occurs at certain rates. As the annealing temperature decreases, the contribution of the grain boundary diffusion should be more remarkable, but the grain growth will become sluggish. This is the reason why the value of n increases with decreasing annealing temperature.

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1. Introduction

Tin-base solder alloys are widely used to interconnect Cu-base conductor alloys in electronic industry. However, Cu–Sn intermetallic compounds are produced at the interface between the solder and conductor alloys during soldering and then soakingly grow owing to healing under usual energization conditions.¹–⁹) The Cu–Sn compounds are very brittle and possess high electrical resistivities. Hence, the growth of such compounds gradually deteriorates the electrical and mechanical properties of the interconnection. The Cu-base conductor alloy is usually plated with Au to improve the corrosion resistance. When the Au-plated conductor alloy is soldered with the Sn-base solder alloy, Au–Sn intermetallic compounds are formed at the interface. Like the Cu–Sn compounds, the Au–Sn compounds are brittle and possess high electrical resistivities. Thus, the growth of the Au–Sn compounds also causes the deterioration of the electrical and mechanical properties of the interconnection during heating. However, the growth rate is much faster for the Au–Sn compounds than for the Cu–Sn compounds.³,⁴,¹⁰–¹²) Thus, the Au plating remarkably accelerates the deterioration of the interconnection.

Recently, the reactive diffusion between Au and Sn at solid-state temperatures was experimentally observed by the present authors using Sn/Au/Sn diffusion couples prepared by a diffusion bonding technique.¹³–¹⁵) The diffusion couples were isothermally annealed at temperatures between T = 393 and 473 K for various periods in an oil bath with silicone oil. Here, T is the annealing temperature. After annealing, compound layers composed of AuSn, AuSn₂ and AuSn₃ were observed to form at the Au/Sn interface in the diffusion couple. According to the observations, the total thickness of the compound layers is mathematically described 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 K, respectively. Such temperature dependence of the exponent indicates that the grain boundary diffusion contributes to the rate-controlling process and grain growth occurs in the compound layers at certain rates at higher annealing temperatures. As the annealing temperature decreases, the contribution of the grain boundary diffusion becomes remarkable, but the grain growth slows down.

In order to examine whether such a temperature dependency of the rate-controlling process is usually recognized in semblable binary systems, the reactive diffusion between Ag and Sn was experimentally observed in the present study. Sn/Ag/Sn diffusion couples were prepared by the diffusion bonding technique and then isothermally annealed at T = 433–473 K in the oil bath in a similar manner to previous studies.¹³–¹⁵) The growth behavior of Ag–Sn compound layers was metallographically observed, and then the rate-controlling process of the reactive diffusion was discussed.

2. Experimental

Polycrystalline pure Sn plates with a size of 12 × 5 × 2 mm² 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, and then chemically polished in an etchant composed of 20 vol% of hydrochloric acid, 20 vol% of nitric acid and 60 vol% of distilled water. The two surfaces with an area of 12 × 5 mm² of each chemically polished plate were mechanically polished on 1000 emery paper. One of the two surfaces was again mechanically polished on 1500 emery paper until a depth of 100 µm and then finished using diamond with a diameter of 3 µm.

Polycrystalline pure Ag plates with a dimension of
10 × 4 × 2 mm³ were cut by spark erosion from a commercial 100 g 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 size of 20 × 7 × 0.1 mm³ 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 consisting of 10 vol% of nitric acid and 90 vol% of methanol.

After chemical polishing, a Ag sheet specimen was immediately sandwiched between two freshly prepared Sn plate specimens in methanol by a technique used in previous studies.13–15) The Sn/Ag/Sn couples were completely dried and then heat treated for diffusion bonding in the oil bath for 72 h at T = 433, 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 µm, and then finished utilizing an OP-S liquid by Struers Ltd. The microstructure of the cross-section was observed with a differential interference contrast (DIC) optical microscope. 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 Growth behavior of compound layers

A typical DIC optical micrograph for the cross-section of the Sn/Ag/Sn diffusion couple is shown in Fig. 1. This figure indicates the micrograph of the diffusion couple annealed at 473 K for 550 h. As can be seen, slightly dark layers with a thickness of about 20 µm are observed at both Sn/Ag interfaces on the upper and lower sides. In order to identify the dark layer, concentration profiles of Ag and Sn were measured by EPMA along the direction normal to the interface. A result for the diffusion couple in Fig. 1 is shown as open circles in Fig. 2. In this figure, the ordinate and the abscissa indicate the mol fraction of Ag and the distance, respectively. As can be seen in Fig. 2, two compound layers are recognized between the Sn and Ag specimens. They are the ε (Ag₃Sn) and ζ phases on the Sn and Ag sides, respectively. According to a recent phase diagram in the binary Ag–Sn system,16) the ε and ζ phases are the only stable intermetallic compounds. Furthermore, a thin layer alloyed with Sn is discerned in the Ag specimen adjacent to the ζ phase. Such an alloyed layer was produced by diffusion induced recrystallization (DIR). The thickness is about 30, 3 and 3 µm for the ε, ζ and DIR layers, respectively. 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.17–19)

The solubility range at T = 473 K16) is shown as thin solid lines for the Ag and ζ phases in Fig. 2. As can be seen, the maximum concentration of Sn in the DIR layer is close to the solubility of Sn in the Ag phase. The tracer diffusion coefficient D for the volume diffusion of Sn in Ag is evaluated to be 1.9 × 10⁻²² m²/s at T = 473 K.20) Using this value of D, the penetration distance x of Sn in Ag was roughly estimated from the equation \( x^2 \approx 4Dt \). The estimation gives a value of x ≈ 0.01 µm. Thus, the thickness of the DIR layer is about 300 times greater than the penetration distance for the volume diffusion of Sn in the Ag specimen.

As already shown in Fig. 1, the compound layers are discriminable from the Ag and Sn specimens in the DIC optical micrograph of the cross-section. However, it was difficult to distinguish the ε and ζ layers. Thus, the total thickness l of the compound layers was evaluated by the following equation from the cross-sectional micrographs.

\[
l = A/w
\]

The layer consisting of the ε and ζ layers is hereafter designated the intermetallic layer. In eq. (1), A and w are the total area and the total length of the intermetallic layer, respectively, in the cross-section. The results at annealing temperatures of T = 433, 453 and 473 K are plotted as open triangles, squares and circles, respectively, in Fig. 3. As can be seen in this figure, the total thickness l monotonically increases with increasing annealing time t at all the temperatures. Furthermore, the plotted points at each annealing
temperature lie well on a straight line. As a consequence, $l$ is mathematically described as a function of $t$ by the equation

$$l = k(t/t_0)^n.$$  

Here, $t_0$ is unit time, 1 s. It is adopted to make the ratio $t/t_0$ dimensionless. The proportionality coefficient $k$ has the same dimension as the total thickness $l$, but the exponent $n$ is dimensionless. The values of $k$ and $n$ were determined from the plotted points in Fig. 3 by a least-squares method. The determination gives $k = 3.39 \times 10^{-8}$ m and $n = 0.384$ at $T = 433$ K, and $k = 1.17 \times 10^{-7}$ m and $n = 0.364$ at $T = 473$ K. Using these values, the total thickness $l$ was calculated as a function of the annealing time $t$ from eq. (2). The results are shown as solid straight lines in Fig. 3. As can be seen, most of the experimental points at each annealing temperature are located well on the corresponding straight line.

The results at $T = 433$ and 473 K in Fig. 3 are represented as open circles with solid lines in Figs. 4(a) and (b), respectively. As already mentioned in Introduction, the reactive diffusion between Au and Sn was experimentally studied by the present authors using Sn/Au/Sn diffusion couples at $T = 393$–473 K. The experimental results for the total thickness $l$ of the AuSn, AuSn$_2$, and AuSn$_3$ compound layers at $T = 433$ and 473 K are plotted as open squares against the annealing time $t$ in Figs. 4(a) and (b), respectively. Here, dashed lines indicate the calculation by eq. (2) with $k = 2.71 \times 10^{-7}$ m and $n = 0.415$ at $T = 433$ K and that with $k = 9.55 \times 10^{-7}$ m and $n = 0.362$ at $T = 473$ K. Furthermore, the reactive diffusion between Cu and Sn was experimentally observed by Onishi and Fujibuchi in their experiment, Cu/Sn diffusion couples were prepared also by a diffusion bonding technique and then annealed at $T = 463$–493 K for various periods. Their observations show that Cu$_3$Sn and Cu$_6$Sn$_5$ compound layers are formed at the interface during annealing. In this case, however, $n$ is equal to 0.5 independently of $T$, whereas $k$ varies depending on $T$. From its temperature dependence, $k = 8.73 \times 10^{-9}$ and $1.69 \times 10^{-8}$ m are obtained at $T = 433$ and 473 K, respectively. The calculations by eq. (2) with these values of $k$ and $n$ are indicated as dotted lines, and those for the Cu/Sn diffusion couple by the present authors are indicated as open squares with dashed lines.
3.2 Rate controlling process

The values of the exponent \( n \) for the Sn/Ag/Sn and Sn/Au/Sn\(^{14,15}\) diffusion couples are plotted as open circles and squares, respectively, with error bars against the annealing temperature \( T \) in Fig. 5. When the reactive diffusion is controlled by the volume diffusion of the constituent elements in each phase, the exponent \( n \) is equal to 0.5. On the other hand, the grain boundary diffusion across the intermetallic layer will govern the reactive diffusion at low temperatures where the volume diffusion is practically frozen out. If the reactive diffusion is purely controlled by the grain boundary diffusion and grain growth takes place in the intermetallic layer according to the parabolic law, the exponent takes a value of \( n = 0.25 \).\(^{22}\) Here, the parabolic law means that the grain size in the intermetallic layer is proportional to the square root of the annealing time. According to the results for the Sn/Au/Sn diffusion couple, \( n \) is equal to 0.36 at \( T = 473 \text{ K} \) and increases with decreasing annealing temperature. At \( T = 393 \text{ K} \), \( n \) becomes close to 0.5. Even if the reactive diffusion is purely controlled by the grain boundary diffusion, \( n \) is equal to 0.5 unless the grain growth occurs.\(^{15}\)

Hence, for the reactive diffusion between Au and Sn, the grain boundary diffusion contributes to the rate-controlling process, and the grain growth takes place at a certain rate at \( T = 473 \text{ K} \). However, at \( T = 393 \text{ K} \), the grain growth will slow down, though the contribution of the grain boundary diffusion becomes more remarkable.\(^{15}\) As can be seen in Fig. 5, the open circles well coincide with the open squares. This indicates that the same rate-controlling process as the reactive diffusion between Au and Sn works also in the reactive diffusion between Ag and Sn at each annealing temperature.

The values of the logarithm of \( k \) are plotted against the reciprocal of \( T \) as open circles with error bars in Fig. 6. As can be seen, the open circles are located well on a straight line. This means that \( k \) is expressed as a function of \( T \) by the equation

\[
k = k_0 \exp(-Q_k/RT).
\]

Here, \( k_0 \) is the pre-exponential factor, \( Q_k \) is the activation enthalpy, and \( R \) is the gas constant. From the open circles in Fig. 6, \( k_0 \) and \( Q_k \) were evaluated by a least-squares method. The evaluation provides \( k_0 = 7.10 \times 10^{-2} \text{ m} \) and \( Q_k = 52.6 \text{ kJ/mol} \). Using these parameters, the temperature dependence of \( k \) was calculated from eq. (3). The result is shown as a solid line in Fig. 6. In this figure, the corresponding results for the Sn/Au/Sn\(^{14,15}\) and Cu/Sn\(^{21}\) diffusion couples are indicated as open squares with a dashed line and open triangles with a dotted line, respectively. According to the results in Fig. 5, \( n \) is almost identical for the Sn/Ag/Sn and Sn/Au/Sn diffusion couples at each annealing temperature. However, \( l \) is one order of magnitude greater for the Sn/Au/Sn diffusion couple than for the Sn/Ag/Sn diffusion couple as shown in Fig. 4. Therefore, \( k \) is also one order of magnitude greater for the former diffusion couple than for the latter diffusion couple. On the other hand, \( l \) is close to each other for the Sn/Ag/Sn and Cu/Sn diffusion couples at the present annealing times, but \( n \) is smaller for the former diffusion couple than for the latter diffusion couple. As a result, \( k \) becomes greater for the Sn/Ag/Sn diffusion couple than for the Cu/Sn diffusion couple. The rate-controlling process varies depending on the annealing temperature for the reactive diffusion between Ag and Sn and that between Au and Sn as mentioned earlier. Thus, complex information for the temperature dependencies of the volume diffusion, the grain boundary diffusion and the grain growth in each phase is included in the activation enthalpy \( Q_k \). In order to account for the physical meaning of \( Q_k \), these temperature dependencies should be known separately. Unfortunately, however, such information is not available for the Sn/Ag/Sn and Sn/Au/Sn diffusion couples. Consequently, it is not appropriate to estimate the rate-controlling process only from the value of \( Q_k \).
4. Conclusions

The kinetics of the reactive diffusion between Ag and Sn was experimentally examined at solid-state temperatures using Sn/Ag/Sn diffusion couples. The diffusion couples were prepared by a diffusion bonding technique and then annealed at temperatures of $T = 433$ to $473$ K for various periods in the oil bath with silicone oil. Owing to annealing, the $\varepsilon$ (Ag$_3$Sn) and $\zeta$ compound layers are formed at the Sn/Ag interface in the diffusion couple. In the Ag specimen adjacent to the $\zeta$ layer, a thin layer alloyed with Sn is produced by diffusion induced recrystallization (DIR). Thickness of the DIR layer is close to that of the $\varepsilon$ layer but one tenth of that of the $\zeta$ layer. The total thickness $l$ of the compound layers monotonically increases with increasing annealing time $t$ according to the equation $l = k(t/t_0)^n$, where $t_0$ is unit time, 1 s. The proportionality coefficient $k$ and the exponent $n$ were determined from the experimental results by a least-squares method. The determination provides $k = 3.39 \times 10^{-8}$ m and $n = 0.404$ at $T = 433$ K, $k = 5.36 \times 10^{-8}$ 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. Such a temperature dependency of the exponent $n$ indicates that the grain boundary diffusion contributes to the reactive diffusion and the grain growth occurs at certain rates at higher annealing temperatures. At lower annealing temperatures, however, the grain boundary diffusion becomes more predominant, but the grain growth will slow down. This type of rate-controlling process has been observed also for the reactive between Au and Sn.$^{14,15}$

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