To examine growth behavior of α-CoSn₃ at solid-state temperatures, kinetics of reactive diffusion between Co and Sn was experimentally observed using sandwich Sn/Co/Sn diffusion couples prepared by a diffusion bonding technique. The diffusion couples were isothermally annealed in the temperature range of 433–473 K for various times up to 744 h. Owing to annealing, an intermetallic layer consisting of CoSn₃ was formed at the original interface in the diffusion couple. The mean thickness of the intermetallic layer increases in proportion to a power function of the annealing time. The exponent of the power function takes values of 0.67 and 0.62 at 433 and 473 K, respectively. These values of the exponent indicate that volume diffusion predominantly controls the layer growth and interface reaction partially contributes to the rate-controlling process.

1. Introduction

The scaling-down of three-dimensional integration for electronic device results in decreasing bond pad pitch and smaller solder ball diameters. As an under bump metallization (UBM) material, Cu is widely used in electronics interconnection and packaging. Recently, the capability of Co as a new UBM material for Sn-base solder bump has been investigated by many researchers. If Co is interconnected with a Sn-base solder, Co–Sn compounds may be formed at the interconnection during soldering and then will gradually grow due to solid-state heating under usual energization conditions. Since such intermetallic compounds are generally brittle and possess high electrical resistivities, the compound growth deteriorates the electrical and mechanical properties of the interconnection. Thus, for application of Co, reliable information on kinetics of reactive diffusion between Co and the Sn-base solder at solid-state temperatures is essentially important.

The solid-state reactive diffusion in the Cu/Sn system was experimentally observed in a previous study. In this experiment, sandwich Sn/Cu/Sn diffusion couples were prepared by a diffusion bonding technique and then isothermally annealed at temperatures of T = 433–473 K. At all the annealing temperatures, an intermetallic layer composed of Cu₆Sn₅ and Cu₃Sn is formed at the original Cu/ Sn interface in the diffusion couple. The total thickness of the intermetallic layer increases in proportion to a power function of the annealing time. The exponent of the power function is close to 0.5 at T = 473 K but becomes 0.37 and 0.43 at T = 433 and 453 K, respectively. If the growth of the intermetallic layer is controlled by volume diffusion, the exponent is equal to 0.5. On the other hand, the exponent becomes smaller 0.5, if boundary diffusion contributes to the rate-controlling process of the layer growth and grain growth occurs in the intermetallic layer. Even though the layer growth is purely governed by boundary diffusion, however, the exponent is equivalent to 0.5 unless grain growth takes place in the intermetallic layer. Thus, for the reactive diffusion in the Cu/Sn system, volume diffusion is the rate-controlling process at T = 473 K but boundary diffusion contributes to that at T = 433–453 K.

In a previous study, the solid-state reactive diffusion in the Ni/Sn system was examined experimentally. In this experiment, like the Cu/Sn system, sandwich Sn/Ni/Sn diffusion couples were prepared by a diffusion bonding technique and then isothermally annealed at temperatures of T = 433–473 K. At the interface in the annealed diffusion couple, a layer of Ni₃Sn₄ was observed at T = 453–473 K, but granular particles of Ni₃Sn₄ were recognized at T = 433 K. Also in this case, the Ni₃Sn₄ layer grows according to the power relationship. The exponent of the power function is 0.46 and 0.41 at T = 453 and 473 K, respectively. Hence, the layer growth of Ni₃Sn₄ is controlled by boundary and volume diffusion, and grain growth occurs in Ni₃Sn₄. Therefore, the rate-controlling process of reactive diffusion varies depending on the annealing temperature and the metal system. Although the layer growth of Ni₃Sn₄ may be accelerated by boundary diffusion, the overall growth rate is smaller for Ni₃Sn₄ than for Cu₆Sn₅ and Cu₃Sn.

The reactive diffusion in the Co/ Sn system was experimentally observed by Wang and Chen using Co/Sn diffusion couples prepared by a soldering technique. In their experiment, pure Co specimens were soldered with pure Sn at T = 553 K and then quenched into water. After quenching, the diffusion couple was annealed at temperatures of T = 423–473 K for various periods. At the original Co/Sn interface in the diffusion couple, an intermetallic layer consisting of CoSn₃ is produced during soldering and then grows during annealing. In the binary Co–Sn system, β-CoSn₃ is stable at T = 548–618 K, but α-CoSn₃ becomes stable at T < 548 K. According to their observation, the β-CoSn₃ layer with a thickness of about 0.5 μm is formed at the original Co/Sn interface in the diffusion couple during soldering at T = 553 K. Since β-CoSn₃ transforms into α-CoSn₃ at T < 548 K, the preformation and the transformation of β-CoSn₃ may influence the growth of α-CoSn₃ during annealing at T = 423–473 K. To examine the growth behav-
ior of α-CoSn3 at $T < 548 \text{ K}$, this influence should be eliminated. However, no reliable information on growth behavior of α-CoSn3 without the influence of β-CoSn3 is available. To examine such growth behavior, the solid-state reactive diffusion in the Co/Sn system was experimentally observed at $T = 433–473 \text{ K}$ using a diffusion bonding technique in the present study.

2. Experimental

Polycrystalline plate specimens of pure Sn with a size of 12 mm × 5 mm × 2 mm were prepared by cold rolling and spark erosion from a commercial 1 kg rectangular ingot of pure Sn with purity of 99.99%. The cold-rolled plate specimens were separately annealed in evacuated silica capsules at 1173 K for 2 h, followed by air cooling without breaking the capsules. The annealed Sn plate 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 12 mm × 5 mm of each Sn plate specimen were mechanically polished on # 800 emery paper. One of the two polished surfaces was again mechanically polished on # 1000–4000 emery papers until a depth of 100 µm and then finished using diamond with a diameter of 1 µm.

Sheet specimens with a size of 20 mm × 7 mm × 0.4 mm were cut from a pure Co commercial sheet with dimensions of 50 mm × 50 mm × 0.4 mm and purity of 99.9% 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 nitrohydrochloric acid for 60 s.

After chemical polishing, a Co sheet specimen was immediately sandwiched between the finished surfaces of two freshly prepared Sn plate specimens in ethanol by the technique used in a previous study.15) The sandwiched Sn/Co/Sn couple was fastened between two plates made of 18Cr–8Ni austenitic steel with molybdenum screws; this process generated thermal compressive stress in the couple upon heating because of the lower coefficient of thermal expansion of molybdenum compared with the couple and the austenitic steel. A mica sheet with dimensions of 12 × 5 × 0.2 mm was inserted between the Sn plate and the austenitic steel to avoid diffusion bonding. The fastened couples were dried completely and then diffusion bonded by heat-treating them in an oil bath with silicone oil for 96, 28.5 and 24 h at 433, 453 and 473 K, respectively. After the heat treatment, the diffusion couples were isothermally annealed at 433, 453 and 473 K for various times up to 648, 527.1 and 410 h, respectively. The summation of the heat-treating and annealing times is hereafter merely called the annealing time $t$.

A typical cross-sectional DICOM image of the Sn/Co/Sn diffusion couple annealed at $T = 453 \text{ K}$ for $t = 334 \text{ h}$ (1.20 Ms) is shown in Fig. 1. In this figure, the bottom and top regions are the Co and Sn specimens, respectively. As can be seen, a layer with rather uniform thickness is formed at the Co/Sn interface in the diffusion couple. To identify this layer, concentration profiles of Co and Sn were determined by EPMA along the direction normal to the original Co/Sn interface in the diffusion couple. The cross-sections of the annealed diffusion couple were mechanically polished using diamond with diameters of 15, 3 and 1 µm, and then finished with an OP-S liquid manufactured by Struers Ltd. The microstructure of the cross-section was observed by differential interference contrast optical microscopy (DICOM).

3. Results and Discussion

3.1 Microstructure

Concentrations of Co and Sn in each phase on the cross-section were measured by electron probe microanalysis (EPMA) using 99.99% pure Co and Sn as standard specimens under the following conditions: the accelerating voltage was 20 kV; the probe current was 5 nA; the analyzing crystal was lithium fluoride (LiF) for Co and polyethylene terephthalate (PET) for Sn–La, and the chemical composition was evaluated using a standard ZAF correction technique.

3.2 Concentration Profiles

Fig. 2 Concentration profiles of Co and Sn across the intermetallic layer for the Sn/Co/Sn diffusion couple annealed at $T = 473 \text{ K}$ for $t = 166 \text{ h}$ (568 ks).
According to a recent phase diagram in the binary Co–Sn system,\(^1\) \(\text{Co}_2\text{Sn}_2\), CoSn and CoSn\(_2\) as well as CoSn\(_3\) exist as stable compounds at \(T = 433–473\) K. However, only CoSn\(_3\) was clearly recognized for all the annealed diffusion couples in the present study. If the interdiffusion coefficient of a compound is small at an experimental annealing temperature, the compound cannot grow to visible thicknesses within realistic annealing times.\(^1\) This implies that the interdiffusion coefficient is much smaller for \(\text{Co}_2\text{Sn}_2\), CoSn and CoSn\(_2\) than for CoSn\(_3\) at \(T = 433–473\) K. In Fig. 1, a slightly dark thin layer with a thickness of about 6 \(\mu\)m may be detected on the Co side in the CoSn\(_3\) layer. The detection of the slightly dark thin layer in a DICOM image is attributed to the surface relief of CoSn\(_3\) formed by the OP-S liquid. During annealing at \(T = 433–473\) K, the CoSn\(_3\) layer grows mainly towards the Sn side and merely slightly towards the Co side.

### 3.2 Growth behavior of intermetallic layer

As previously mentioned, the CoSn\(_3\) layer with rather uniform thickness is formed at the original Co/Sn interface in the diffusion couple owing to isothermal annealing at \(T = 433–473\) K. Hereafter, the CoSn\(_3\) layer is called the intermetallic layer. The schematic morphology of the intermetallic layer on cross-section \(i\) is shown in Fig. 3. From DICOM images such as that shown in Fig. 1, the area \(A_i\) of the intermetallic layer corresponding to the partial length \(w_i\) of the original Co/Sn interface in Fig. 3 was measured on each cross-section, and then the sums \(A\) and \(w\) were obtained as\(^2\)

\[
A = \sum_{i=1}^{m} A_i \tag{1a}
\]

and

\[
w = \sum_{i=1}^{m} w_i \tag{1b}
\]

from \(A_i\) and \(w_i\), respectively, where \(m \geq 5\). Using the values of \(A\) and \(w\), the mean thickness \(l\) of the intermetallic layer was evaluated at each annealing time \(t\) by the equation\(^2\)

\[
l = \frac{A}{w}. \tag{2}
\]

The results of \(T = 433–473\) K are plotted as various open symbols in Fig. 4. In this figure, the ordinate and the abscissa show the logarithms of \(l\) and \(t\), respectively. As can be seen, the thickness \(l\) increases monotonically with increasing annealing time \(t\). Furthermore, the plotted points of each annealing temperature are located well on a straight line. Consequently, \(l\) is expressed as a power function of \(t\) as follows.

\[
l = k \left(\frac{t}{t_0}\right)^n \tag{3}
\]

Here, \(t_0\) is unit time, 1 s, which 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 \(l\), and the exponent \(n\) is dimensionless. From the points plotted in Fig. 4, \(k\) and \(n\) were determined by the least-squares method as shown with various straight lines. The determined values are indicated in Fig. 4.

As mentioned in Section 1, the reactive diffusion in the Co/Sn system was experimentally observed by Wang and Chen\(^9\) using Co/Sn diffusion couples prepared by a soldering technique. For the preparation of the Co/Sn diffusion couple in their experiment, pure Co specimens were soldered with pure Sn at \(553\) K and then quenched into water. After quenching, the diffusion couple was annealed at temperatures of \(T = 423–473\) K for various periods. At the original Co/Sn interface in the diffusion couple, an intermetallic layer consisting of CoSn\(_3\) is produced during soldering and then grows during annealing. Their experimental results of \(T = 433, 453\) and \(473\) K are shown as open squares in Fig. 5(a), 5(b) and 5(c), respectively. In Fig. 5, like Fig. 4, the ordinate and the abscissa indicate the logarithms of \(l\) and \(t\), respectively. As can be seen, the power relationship between \(l\) and \(t\) holds also for the open squares in Fig. 5. From the open squares, \(k\) and \(n\) in eq. (3)
were determined by the least-squares method as shown with dashed lines. The determined values are indicated in Fig. 5. On the other hand, the results of $T = 433$, 453 and 473 K in Fig. 4 are represented as open circles with solid lines in Figs. 5(a), 5(b) and 5(c), respectively. As can be seen, the dashed line is located on the upper side of the solid line within the experimental annealing times at each annealing temperature. This means that the growth of the intermetallic layer is faster for the diffusion couple prepared by a soldering technique$^9$ than for that made by a diffusion bonding technique.

According to a recent phase diagram in the binary Co–Sn system,$^{19}$ $\beta$-CoSn$_3$ is stable at $T = 548–618$ K, but $\alpha$-CoSn$_3$ becomes stable at $T < 548$ K. Here, the space groups of $\alpha$-CoSn$_3$ and $\beta$-CoSn$_3$ are Cmca and I4$_1$/acd, respectively. Although $\beta$-CoSn$_3$ is unstable at $T < 548$ K, the electrical resistivity and the magnetic susceptibility of $\beta$-CoSn$_3$ were experimentally measured at $T = 4–300$ K by Lang and Jeitschko.$^{19}$ This implies that the transformation of $\beta$-CoSn$_3$ into $\alpha$-CoSn$_3$ at $T < 548$ K is rather sluggish. In the experiment by Wang and Chen,$^9$ the $\beta$-CoSn$_3$ layer with a thickness of about 0.5 µm is produced at the original Co/Sn interface in the diffusion couple during soldering at $T = 553$ K. On the other hand, during annealing at $T = 423–473$ K, $\beta$-CoSn$_3$ will transform into $\alpha$-CoSn$_3$. When the transformation occurs slowly, however, $\beta$-CoSn$_3$ may remain for long periods during annealing and thus will grow together with $\alpha$-CoSn$_3$. If the interdiffusion coefficient is greater for $\beta$-CoSn$_3$ than for $\alpha$-CoSn$_3$, the overall growth of the $\alpha$-CoSn$_3$ + $\beta$-CoSn$_3$ two-phase layer takes place much faster than that of the $\alpha$-CoSn$_3$ single-phase layer. This is a possible reason why the dashed line is located on the upper side of the solid line within the experimental annealing times at each annealing temperature in Fig. 5. To discuss conclusively this reason, however, more detailed information on microstructure evolution is necessary for the Co/Sn diffusion couple prepared by a soldering technique.

The results of $T = 433$, 453 and 473 K in Fig. 4 are shown again as open circles with solid lines in Figs. 6(a), 6(b) and 6(c), respectively. In Fig. 6, the corresponding results of the Au/Sn,$^{21}$ Cu/Sn$^{15}$ and Ni/Sn$^{18}$ systems are indicated as open squares with dashed-and-dotted lines, open rhombuses with dashed lines and open triangles with dotted lines, respectively. As can be seen, the power relationship between $l$ and $t$ holds for all the metal systems. Since the exponent $n$ varies depending on the metal system, however, the kinetics of reactive diffusion cannot be compared with one another using the proportionality coefficient $k$. Nevertheless, within the experimental annealing times at each annealing temperature, the overall growth of the intermetallic layer is smaller for the Co/Sn system than for the Au/Sn system but greater for the Co/Sn system than for Cu/Sn and Ni/Sn systems.

### 3.3 Rate-controlling process of intermetallic growth

The values of $n$ in Fig. 4 are plotted against $T$ as open circles with error bars in Fig. 7. If the growth of the intermetallic layer is controlled by volume diffusion, $n$ is equal to 0.5.$^{16,22–30}$ On the other hand, $n$ is equivalent to unity, if interface reaction governs the layer growth.$^{31–35}$ According to the results in Fig. 7, $n$ takes intermediate values between 0.5 and unity. This means that both volume diffusion and interface reaction contribute to the rate-controlling process of the layer growth at $T = 433–473$ K. Since the
values $n = 0.62 - 0.67$ are closer to 0.5 than to unity, the contribution of volume diffusion is more predominant than that of interface reaction. As previously mentioned, the intermetallic layer grows mainly towards the Sn side and merely slightly towards the Co side. Therefore, the Sn/CoSn$_3$ interface is mobile, but the Co/CoSn$_3$ interface is rather stationary. Consequently, it is plausible that the interface reaction at the mobile Sn/CoSn$_3$ interface dominantly influences the rate-controlling process of the layer growth.

Diffusion induced recrystallization (DIR) occurs in many metal systems. Here, 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 fine-grain region produced by DIR is hereafter called the DIR region. The kinetics of DIR in the Cu(Ni) system was experimentally examined at $T = 723$–$823$ K in a previous study,$^{36)$ where 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. The experimental result of $T = 823$ K$^{36)$ is represented as open circles in Fig. 8. In this figure, the ordinate shows the logarithm of the thickness $l$ of the DIR region, and the abscissa indicates the logarithm of the annealing time $t$. In that study,$^{36)$ the dependence of $l$ on $t$ was also theoretically calculated using a new extended (NE) model.$^{37)$ The model calculation is shown as a solid curve in Fig. 8. As can be seen, the solid curve is considered straight at $t < 10^4$ s in the early stages and at $t > 10^7$ s in the late stages. In such cases, $l$ is expressed as a power function of $t$ by eq. (3). In Fig. 8, the solid curve is extrapolated as dashed lines with $n = 1$ and $n = 0.446$ at $t < 10^5$ s and $t > 10^7$ s, respectively. From these values of $n$, it is concluded that the growth of the DIR region is controlled by interface reaction in the early stages but by boundary diffusion in the late stages.$^{36)$ In the intermediate stages for $10^4$ s $< t < 10^7$ s, however, the exponent $n$ gradually decreases with increasing annealing time $t$. Thus, the transition of the rate-controlling process occurs in the intermediate stages. For the transition, both interface reaction and boundary diffusion contribute to the rate-controlling process, and the contribution of boundary diffusion gradually increases with increasing annealing time.

![Fig. 6](image_url)

![Fig. 7](image_url)

Fig. 6 The results in Fig. 4 are shown as open circles with solid lines: (a) $T = 433$ K, (b) $T = 453$ K, and (c) $T = 473$ K. The corresponding results of the Au/Sn,$^{21)$ Cu/Sn$^{15)$ and Ni/Sn$^{18)$ systems are indicated as open squares with dashed-and-dotted lines, open rhombuses with dashed lines and open triangles with dotted lines, respectively.

Fig. 7 The exponent $n$ versus the annealing temperature $T$. 

As can be seen in Fig. 8, the open circles are distributed in the intermediate stages. Hence, the mixed rate-controlling process works within the experimental annealing times. If eq. (3) is conveniently used to express the dependence of \( l \) on \( t \) within the experimental annealing times, the values of \( k = 5.86 \times 10^{-9} \) m and \( n = 0.630 \) are estimated from the open circles in Fig. 8 by the least-squares method. Consequently, for the mixed rate-controlling process, the overall value of \( n \) is smaller than unity but greater than 0.446. Also for the growth of the CoSn3 layer in Fig. 4, the value of \( n \) can gradually decrease with increasing annealing time \( t \). Unlike the growth of the DIR region, however, the contribution of boundary diffusion may not be important for the growth of the CoSn3 layer. As a result, the NE model cannot be unfortunately applicable to the theoretical analysis of kinetics for the solid-state reactive diffusion in the Co/Sn system.

As shown in Fig. 7, \( n \) is rather insensitive to \( T \). If \( n \) is considered to be independent of \( T \), \( k \) and \( n \) in eq. (3) are simultaneously evaluated by the least-squares method from all the experimental points plotted in Fig. 4. The evaluated value of \( n \) is shown as a solid circle with error bars in Fig. 7, and those of \( k \) are indicated as open circles with error bars in Fig. 9. In Fig. 9, the ordinate shows the logarithm of \( k \), and the abscissa indicates the reciprocal of \( T \). The dependence of \( k \) on \( T \) is generally expressed by the following equation.

\[
k = k_0 \exp\left(-\frac{Q_k}{RT}\right)
\]

Here, \( k_0 \) is the pre-exponential factor, and \( Q_k \) is the activation enthalpy. From the open circles in Fig. 9, \( k_0 \) and \( Q_k \) were evaluated by the least-squares method as shown with a solid line. The evaluated values are indicated in Fig. 9. The rate-controlling process of the layer growth is usually discussed on the value of \( Q_k \). As mentioned earlier, however, the layer growth of CoSn3 at \( T = 433–473 \) K is controlled by volume diffusion and interface reaction. Therefore, \( Q_k \) contains mixed-information on the temperature dependencies of volume diffusion and interface reaction. In such a case, the rate-controlling process cannot be estimated only from the value of \( Q_k \). It is worth noting that \( n \) is much more useful than \( Q_k \) for the estimation of the rate-controlling process.

4. Conclusions

The reactive diffusion in the Co/Sn system was experimentally observed in a solid-state temperature range. In this experiment, the sandwich Sn/Co/Sn diffusion couple was prepared by a diffusion bonding technique and then isothermally annealed at temperatures of 433–473 K for various periods up to 744 h. During annealing, an intermetallic layer composed of CoSn3 was produced at the original interface in the diffusion couple. The mean thickness of the intermetallic layer is proportional to a power function of the annealing time. The exponent of the power function takes intermediate values between 0.5 and unity under the present annealing conditions. This means that both volume diffusion and interface reaction contribute to the rate-controlling process of the layer growth.

Acknowledgement

The present study was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

REFERENCES

5) W. Zhang, Z. Mai, L. Bogaerts, M. Gonzalez, G. Vakanas, A.