Kinetics of Reactive Diffusion in the Co/Zn System at Solid-State Temperatures

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The kinetics of reactive diffusion in the Co/Zn system was experimentally examined at solid-state temperatures. In this experiment, sandwich Zn/Co/Zn diffusion couples were prepared by a diffusion bonding technique, and then isothermally annealed in the temperature range of 523–573 K for various times up to 211 h. Owing to annealing, an intermetallic layer consisting of the γ, γ1 and γ2 phases formed at the original interface in the diffusion couple, where the thickness is much smaller for the γ and γ1 phases than for the γ2 phase. Thus, the γ2 phase predominantly governs the overall growth of the intermetallic layer. The total 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 0.54–0.56 at 523–548 K and that of 0.85 at 573 K. Consequently, volume diffusion mainly controls the layer growth at 523–548 K, but interface reaction as well as volume diffusion contributes to the rate-controlling process at 573 K. [doi:10.2320/matertrans.M2016416]

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1. Introduction

In the binary Sn–Zn system, the eutectic reaction \( L \rightarrow Sn + Zn \) occurs at a temperature of \( T_e = 472 \text{ K} \).\(^1\) Here, the concentration of Zn in the liquid (L) phase is 15 at% (9 mass%), the solubility of Sn in the Sn phase is smaller than 1 at%, and that of Sn in the Zn phase is negligible. Since the eutectic temperature \( T_e \) is much lower than the melting temperature of pure Sn with \( T_m = 505 \text{ K} \), the eutectic Sn–Zn alloy is used as a Pb-free Sn-base solder with low-melting temperature in the electronics industry.\(^2–8\) On the other hand, the scaling-down of three-dimensional integration for electronic device results in decreasing bond pad pitch and smaller solder ball diameter. As an under bump metallization (UBM) material, Cu is widely used in electronics interconnection and packaging.\(^9–13\) Recently, the capability of Co as a new UBM material for Sn-base solder bump has been investigated by many researchers.\(^14–22\) If Co is interconnected with the Sn–Zn solder, Co–Sn and Co–Zn 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 the kinetics of reactive diffusion between Co and the Sn–Zn solder at solid-state temperatures is essentially important.

The solid-state reactive diffusion in the Co/Sn system was experimentally observed in a previous study.\(^23\) In that experiment, Sn/Co/Sn diffusion couples were prepared by a diffusion bonding technique, and then isothermally annealed in the temperature range of \( T = 433–473 \text{ K} \). In this temperature range, an intermetallic layer composed of CoSn3 is formed at the original Co/Sn interface in the diffusion couple. The mean thickness of the CoSn3 layer is proportional to a power function of the annealing time. The exponent of the power function takes a value of 0.67 at 433–453 K and that of 0.62 at 473 K. These values of the exponent indicate that volume diffusion predominantly controls the layer growth and interface reaction partially contributes to the rate-controlling process.

In contrast, the reactive diffusion in the Co/Zn system was experimentally observed by Duchenko et al.\(^24\) In their experiment, Co/Zn diffusion couples were prepared by a soldering technique, and then annealed at temperatures of \( T = 523–673 \text{ K} \). Due to soldering and annealing, an intermetallic layer consisting of the γ, γ1 and γ2 phases is produced at the original Co/Zn interface in the diffusion couple. The total thickness of the \( γ + γ_1 + γ_2 \) three-phase layer increases almost in proportion to the square root of the annealing time at \( T = 623 \text{ K} \). Such a relationship is usually called a parabolic relationship. At the other annealing temperatures, however, raw experimental results for thicknesses of the γ, γ1 and γ2 layers are not reported in their article.\(^24\) Nevertheless, they mention that the parabolic relationship mostly holds at all the annealing temperatures. This means that the layer growth is controlled mainly by volume diffusion at \( T = 523–673 \text{ K} \). In a soldering technique,\(^24\) the γ, γ1 and γ2 phases will be produced between the solid-Co and liquid-Zn specimens during soldering. The existence of these phases at the Co/Zn interface in the diffusion couple may affect subsequent growth of the intermetallic layer during annealing and thus the rate-controlling process of the layer growth. On the other hand, in a diffusion bonding technique,\(^23\) diffusion bonding is conducted at the same temperature as isothermal annealing, and hence formation and growth of the intermetallic layer occurs at the equivalent temperature. Therefore, for experiment in solid-state reactive diffusion, a diffusion bonding technique is more suitable than a soldering technique. In the present study, a diffusion bonding technique\(^23\) was used to examine experimentally the kinetics of solid-state reactive diffusion in the Co/Zn system at temperatures of \( T = 523–573 \text{ K} \). The rate-controlling process was discussed on the basis of the experimental result.

2. Experimental

Sheet specimens with size of 12 mm × 5 mm × 1 mm were
cut from a pure Zn commercial sheet with dimensions of 200 mm × 200 mm × 1 mm and purity of 99.5% and then separately annealed in evacuated silica capsules at 523 K for 2 h, followed by air cooling without breaking the capsules. The two surfaces with area of 12 mm × 5 mm of each annealed Zn sheet specimen were mechanically polished on # 800 emery paper. One of the two polished surfaces was again mechanically polished on # 1500–4000 emery papers until depth of 100 μm, and then finished using diamond with diameter of 1 μm.

Sheet specimens with 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 Zn sheet specimens in ethanol by the technique used in a previous study.23) The sandwich Zn/Co/Zn couples were completely dried, and then heat treated for diffusion bonding in an evacuated silica tube at temperatures of 523 K, 548 K and 573 K for times of 8 h, 4 h and 2 h, respectively, followed by air cooling. After the heat treatment, the diffusion couples were isothermally annealed at 523 K, 548 K and 573 K for various times up to 203 h. Hereafter, the summation of the heat-treating and annealing times at the equivalent temperature 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 diamond with diameters of 15 μm, 3 μm 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). Concentrations of Co and Zn in each phase on the cross-section were measured by electron probe microanalysis (EPMA) using pure Co and Zn with purity of 99.99% 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–Kα and Zn–Kα; and the chemical composition was evaluated by a standard ZAF correction technique.

3. Results and Discussion

3.1 Microstructure

A typical cross-sectional DICOM image of the diffusion couple annealed at \( T = 573 \) K for \( t = 24 \) h (86.4 ks) is shown in Fig. 1. For this DICOM image in Fig. 1, the top and bottom regions are the Zn and Co specimens, respectively. As can be seen, layers with slightly different contrasts are formed at the original Co/Zn interface. To identify each layer, concentration profiles of Co and Zn were measured by EPMA along the direction normal to the original interface. A result of the diffusion couple with \( T = 573 \) K and \( t = 30 \) h (108 ks) 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 \( x \) measured from an arbitrary origin, respectively, and open circles and squares represent the mol fractions \( y_{Co} \) and \( y_{Zn} \), respectively. As can be seen, the layers are the \( \gamma \), \( \gamma_1 \) and \( \gamma_2 \) phases from the Co side to the Zn side. The thickness is much smaller for the \( \gamma \) and \( \gamma_1 \) phases than for the \( \gamma_2 \) phase. Similar results were obtained for all the diffusion couples annealed at \( T = 523–573 \) K. If we observe the edge of diffusion couple on the cross-section, we can find the location of the original Co/Zn interface. This observation indicates that the \( \gamma + \gamma_1 + \gamma_2 \) three-phase layer grows mainly into the Zn specimen but slightly towards the Co specimen.

According to a recent phase diagram in the binary Co–Zn system,25) the \( \beta_1 \) phase as well as the \( \gamma \), \( \gamma_1 \) and \( \gamma_2 \) phases should appear as a stable compound phase at \( T = 523–573 \) K. However, the \( \beta_1 \) phase was not recognized in any annealed diffusion couples in the present study. For reactive diffusion in binary alloy systems, the growth rate of a compound phase is predominantly determined by the interdiffusion coefficient and the solubility range of the growing phase.26–30) If the interdiffusion coefficient or the solubility range of a compound phase is small at an experimental annealing temperature, the compound phase cannot grow to visible thicknesses within realistic annealing times.26–30) At \( T = 523–573 \) K, the solubility range is greater for the \( \gamma \) phase than for the \( \beta_1 \), \( \gamma_1 \) and \( \gamma_2 \) phases, and close to one another among the \( \beta_1 \), \( \gamma_1 \) and \( \gamma_2 \) phases.25) Consequently, the interdiffusion coefficient of the \( \beta_1 \) phase must be much smaller than those of the \( \gamma \), \( \gamma_1 \) and \( \gamma_2 \) phases. Furthermore, according to the result in Fig. 2, the interdiffusion coefficient has to be smaller for the \( \gamma \) phase than...
for the $\gamma_1$ phase but greater for the $\gamma_2$ phase than for the $\gamma_1$ phase.

3.2 Growth behavior of intermetallic layer

As shown in Fig. 1, a three-phase layer consisting of the $\gamma$, $\gamma_1$ and $\gamma_2$ phases is formed at the original Co/Zn interface in the diffusion couple due to isothermal annealing at $T = 523$–573 K. Hereafter, the three-phase layer is merely called the intermetallic layer. From DICOM images, such as that indicated in Fig. 1, the area $A_j$ of the intermetallic layer corresponding to the partial length $w_j$ of the original Co/Zn interface was measured for cross-section $j$. The sums $A$ and $w$ were obtained by the equations\(^{23}\)

\[
A = \sum_{j=1}^{m} A_j \quad (1a)
\]

and

\[
w = \sum_{j=1}^{m} w_j \quad (1b)
\]

from $A_j$ and $w_j$, respectively, where $w_j = 422 \mu$m and $m \geq 5$. Using the values of $A$ and $w$, the total thickness $l$ of the intermetallic layer was evaluated at each annealing time $t$ as follows:\(^{23}\)

\[
l = \frac{A}{w} \quad (2)
\]

The results for $T = 523$, 548 and 573 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, at $T = 523$–573 K, the experimental points for each annealing temperature lie well on a straight line. Consequently, $l$ is expressed as a power function of $t$ as follows

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

where $t_0$ 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. The dimensionless argument of the power function is essentially important; otherwise the dimension of $k$ varies depending on the value of $n$. From the experimental points in Fig. 3, $k$ and $n$ were evaluated by the least-squares method as indicated with various straight lines. The evaluated values of $k$ and $n$ are also shown in Fig. 3. According to the evaluation at $T = 523$–573 K, the overall growth rate of the intermetallic layer monotonically increases with increasing annealing temperature $T$.

According to Fig. 1, the interface between the $\gamma_2$ and $\gamma_1$ phases is rather distinguishable, but that between the $\gamma_1$ and $\gamma$ phases is almost invisible. From DICOM images, such as that shown in Fig. 1, the total thickness $l_1$ of the $\gamma + \gamma_1$ two-phase layer and the mean thickness $l_2$ of the $\gamma_2$ single-phase layer were evaluated using the relationships similar to eqs. (1a), (1b) and (2). Thus, there exists the following relationship among $l_1$, $l_2$ and $l$.

\[
l = l_1 + l_2 \quad (4)
\]

The results of $l_1$, $l_2$ and $l$ for $T = 573$ K are shown as open rhombuses, squares and circles, respectively, in Fig. 4. In this figure, the ordinate and the abscissa indicate the logarithms of $l_1$ and $t$, respectively. Since $l_1$ is much smaller than $l$ and $l_2$, reliable measurement of $l_1$ was possible only just at $T = 573$ K but not at $T = 523$–548 K. Even at $T = 573$ K, however, the open rhombuses in Fig. 4 are rather scattered due to small values of $l_1$. In contrast, the open squares and circles are located well on each straight line. Therefore, we consider that $l_1$ is expressed as a power function of $t$ by the following equation of the same formula as eq. (3).

\[
l_1 = k_1 \left( \frac{t}{t_0} \right)^n \quad (5)
\]

From the experimental points in Fig. 4, $k_1$ and $n$ for $l_1$ in eq. (5) were evaluated by the least-squares method as shown with various straight lines. Since $l_1$ and $l_2$ are smaller than $l$, however, the values of $k_1$, $k_2$ and $n$ for $l_1$ and $l_2$ cannot be estimat-
ed with the same reliability as those of \( k \) and \( n \) for \( l \). Consequently, using the same value of \( n \) as \( l, k_1 \) and \( k_2 \) for \( l_1 \) and \( l_2 \) in eq. (5) were estimated from the open rhombuses and squares by the least-squares method as indicated with dotted and dashed lines, respectively. The values of \( n, k, k_1 \) and \( k_2 \) for \( l_1 \) and \( l_2 \) in eq. (5) were estimated from the open rhombuses and squares by the least-squares method as indicated with dotted and dashed lines, respectively. The values of \( n, k, k_1 \) and \( k_2 \) are shown in Fig. 4. As can be seen, \( k_1 \) is smaller than \( k_2 \) at \( T = 573 \) K. Although the identical value of \( n \) was adopted for \( l, l_1 \) and \( l_2 \) and \( k, k_1 \) and \( k_2 \) were independently evaluated from the corresponding experimental points in Fig. 4 as mentioned earlier. As a result, the relationship \( k = k_1 + k_2 \) does not necessarily hold, even though eq. (4) holds at each experimental annealing time.

3.3 Rate-controlling process of intermetallic growth

The values of \( n \) in Fig. 3 are plotted against \( T \) as open circles with error bars in Fig. 5. Here, the error bar shows the standard error. If the growth of the intermetallic layer is controlled by volume diffusion, \( n \) is equal to 0.5.26–36) On the other hand, \( n \) is equivalent to unity, if interface reaction governs the layer growth.37–43) The temperature dependencies of the diffusion coefficient for the volume diffusion across the intermetallic layer and the interface reaction rate at the moving interface of the intermetallic layer are schematically drawn as straight lines in Fig. 6. In this figure, the ordinates on the left-hand and right-hand sides show the logarithms of the diffusion coefficient and the interface reaction rate, respectively, and the abscissas on the top and bottom sides indicate the temperature \( T \) and the reciprocal of \( T \), respectively. The temperature dependence of the diffusion coefficient is more remarkable than that of the interface reaction rate in Fig. 6(a), and \( \text{vice versa} \) in Fig. 6(b). Hereafter, as depicted in Fig. 6, the temperature range higher than \( A \) is called the high temperature range, and that lower than \( B \) is designated the low temperature range. On the other hand, the temperature range between \( A \) and \( B \) is denoted by the intermediate temperature range. If volume diffusion and interface reaction participate in the rate-controlling process for the layer growth, the relatively sluggish process governs the layer growth. In Fig. 6(a), interface reaction is much slower than volume diffusion in the high temperature range, and \( \text{vice versa} \) in the low temperature range. In such a case, the layer growth is controlled by interface reaction in the high temperature range but by volume diffusion in the low temperature range. In the intermediate temperature range, however, both volume diffusion and interface reaction contribute to the rate-controlling process. Such a process is called a mixed rate-controlling process. The contribution of interface reaction increases with increasing temperature from \( B \) to \( A \). In contrast, in Fig. 6(b), volume diffusion is much slower than interface reaction in the high temperature range, and \( \text{vice versa} \) in the low temperature range. In this case, the layer growth is governed by volume diffusion in the high temperature range but by interface reaction in the low temperature range. In the intermediate temperature range, the contribution of volume diffusion increases with increasing temperature from \( B \) to \( A \).

According to the result in Fig. 5, \( n \) is close to 0.5 at \( T = 523–548 \) K, but takes a value of 0.85 at \( T = 573 \) K. As a consequence, volume diffusion predominantly controls the layer growth at \( T = 523–548 \) K, but interface reaction and volume diffusion contribute to the rate-controlling process at \( T = 573 \) K. The value \( n = 0.85 \) is closer to unity than to 0.5, and hence the contribution of interface reaction is more remarkable than that of volume diffusion. Such a mixed rate-con-
controlling process of solid-state reactive diffusion was observed for various metal systems in previous studies.\textsuperscript{23,37–43} For the Co/Zn system, the contribution of interface reaction increases with increasing temperature from $T = 523$ K to $T = 573$ K according to the temperature dependence of the rate-controlling process in Fig. 6(a). This is the case also for the reactive diffusion in the Ni/Zn\textsuperscript{24} and Ag/Zn\textsuperscript{30} systems. On the other hand, the temperature dependence of the rate-controlling process in Fig. 6(b) was recognized for the reactive diffusion in the (Cu–Sn)/Nb system.\textsuperscript{37–39} As mentioned earlier, for the reactive diffusion in the Co/Zn system, the intermetallic layer grows mainly into the Zn specimen and merely slightly towards the Co specimen. Therefore, the $\gamma_2$/Zn interface is mobile, but the $\gamma$/Co interface is rather stationary. Consequently, it is plausible that the interface reaction at the mobile $\gamma_2$/Zn interface dominantly influences the rate-controlling process of the layer growth at $T = 573$ K.

As can be seen in Fig. 3, $n = 0.54\pm0.56$ at $T = 523$–548 K, and $n = 0.85$ at $T = 573$ K. Since $n$ is smaller for $T = 523$–548 K than for $T = 573$ K, the dotted and dashed lines may intersect the solid line at very short annealing times. According to a phase diagram in the binary Co–Zn system,\textsuperscript{25} however, the phase relationship among the stable phases does not vary at $T = 523$–578 K. As a result, the growth rate of the intermetallic layer should be a monotonical increasing function of the annealing temperature, and thus such intersection cannot be realized. In the early stages of reactive diffusion, the intermetallic layer is very thin, and hence the interdiffusion across the intermetallic layer occurs very fast. In this case, the interface reaction at the moving interface is the bottleneck for the layer growth, and the exponent becomes unity. As the annealing time increases, the layer thickness increases, and the interdiffusion slows down. In such a case, the interface reaction is no longer the bottleneck, and the exponent decreases from unity. Consequently, the transition of the rate-controlling process has to occur at an intermediate annealing time between the early and late stages. This type of transition was actually observed in previous studies.\textsuperscript{30,41}

### 3.4 Comparison with other results

The results for $T = 523$ and 573 K in Fig. 3 are represented as open circles with solid lines in Fig. 7(a) and 7(b), respectively. In contrast, as mentioned in Section 1, the reactive diffusion in the Co/Zn system was experimentally observed also by Duchenko \textit{et al.}\textsuperscript{24} Unlike the present study, however, they used a soldering technique to prepare Co/Zn diffusion couples. In their experiment, pure Co was soldered with pure Zn at $T = 733$–743 K for 30 s, and then cooled down to room temperature during 60 s. After cooling, the diffusion couple was annealed at temperatures of $T = 523$, 573, 623 and 673 K for various times up to 60 h (216 ks). At the original Co/Zn interface in the diffusion couple, an intermetallic layer composed of the $\gamma$, $\gamma_1$ and $\gamma_2$ phases was formed owing to soldering and annealing. According to their result, the square of the total thickness $l$ of the intermetallic layer is almost proportional to the annealing time $t$ at $T = 623$ K. Such a relationship is called a parabolic relationship as mentioned earlier. On the other hand, at $T = 523$, 573 and 673 K, raw experimental results of $l$ are not reported in their article.\textsuperscript{24} Nevertheless, they mention that the parabolic relationship holds also at $T = 523$, 573 and 673 K. This means that the layer growth is mainly controlled by volume diffusion at $T = 523$–673 K. In their article,\textsuperscript{24} the parabolic relationship is described as

$$ l^2 = 2Kt, \quad (7) $$

and $K = 2.7 \times 10^{-15}$ and $1.4 \times 10^{-14} \text{ m}^2/\text{s}$ are estimated for $T = 523$ and 573 K, respectively. Inserting these values of $K$ into eq. (7), we obtain dashed lines in Fig. 7(a) and 7(b) for $T = 523$ and 573 K, respectively. At $T = 573$ K in Fig. 7(b), $l$ is close to each other between the solid and dashed lines within the experimental annealing times of the open circles, though $n$ is smaller for the dashed line than for the solid line. In contrast, at $T = 523$ K in Fig. 7(a), $l$ is greater for the dashed line than for the solid line, but $n$ is not dissimilar to each other between the solid and dashed lines. As mentioned above, pure Co was soldered with pure Zn at $T = 733$–743 K for 30 s in the experiment by Duchenko \textit{et al.}\textsuperscript{24} Since the $\gamma$, $\gamma_1$ and $\gamma_2$ phases are stable also at $T = 733$–743 K,\textsuperscript{25} they will be produced by the reactive diffusion between solid-Co and molten-Zn during soldering. The existence of these phases at the Co/Zn interface in the diffusion couple may influence subse-
quent growth of the intermetallic layer during annealing at $T = 523–673 \text{ K}$. On the other hand, a diffusion bonding technique was used to prepare the Zn/Co/Zn diffusion couple in the present study. In this technique, diffusion bonding is conducted at the same temperature as isothermal annealing, and thus formation and growth of the intermetallic layer occurs at the equivalent temperature. Such difference in the bonding technique may be the reason why $l$ is greater for the dashed line than for the solid line in Fig. 7(a) and $n$ is smaller for the dashed line than for the solid line in Fig. 7(b).

The solid-state reactive diffusion in the Cu/Zn system was experimentally observed in a previous study. In that experiment, Zn/Cu/Zn diffusion couples were also prepared by a diffusion bonding technique, and then isothermally annealed in the temperature range of $T = 523–623 \text{ K}$ for various times up to 49 h (176.4 ks). Owing to annealing, an intermetallic layer consisting of the $\gamma$ and $\epsilon$ phases was formed at the original Cu/Zn interface in the diffusion couple, where the thickness is much smaller for the $\epsilon$ phase than for the $\gamma$ phase. The total thickness of the intermetallic layer increases in proportion to a power function of the annealing time. The exponent $n$ of the power function takes values of 0.60–0.62 at $T = 523–623 \text{ K}$. The values $n = 0.60–0.62$ indicate that volume diffusion predominantly controls the layer growth and interface reaction partially contributes to the rate-controlling process. The results for $T = 523$ and 573 K are represented as open squares with dashed lines in Fig. 8(a) and 8(b), respectively. As can be seen, the growth rate of the intermetallic layer is much smaller for the Co/Zn system than for the Cu/Zn system. Therefore, Co works more effectively than Cu as a diffusion inhibitor against the reactive diffusion between UBM and the Zn phase in the eutectic Sn–Zn solder during solid-state heating under usual energization conditions.

4. Conclusions

The solid-state reactive diffusion in the Co/Zn system was experimentally observed using the Zn/Co/Zn diffusion couples prepared by the diffusion bonding technique. The diffusion couples were isothermally annealed at temperatures of $T = 523, 548$ and 573 K for various periods up to $t = 211 \text{ h}$. During annealing, an intermetallic layer composed of the $\gamma$, $\gamma_1$ and $\gamma_2$ phases forms at the original Co/Zn interface in the diffusion couple, where the thickness is much smaller for the $\gamma$ phases than for the $\gamma_1$ phase. The total thickness of the three-phase layer is proportional to a power function of the annealing time. The exponent of the power function takes values of 0.54–0.56 at 523–548 K and that of 0.85 at 573 K under the present annealing conditions. This means that the layer growth is controlled mainly by volume diffusion at 523–548 K but by interface reaction and volume diffusion at 573 K.

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