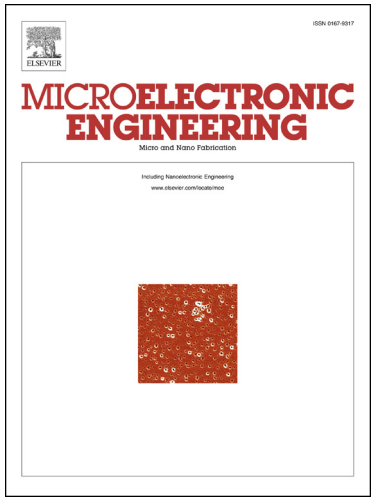

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Formation of compounds and Kirkendall vacancy in the Cu-Sn system

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The Cu/Sn system is one of the simplest metallurgical options for three-dimensional (3D) microbumps. Even at room temperature, however, intermetallic compounds of Cu_3Sn and Cu_6Sn_5 are formed at the interconnection between Cu and Sn, and voids are produced inside the microbump. The formation of compounds and voids deteriorates mechanical and electrical properties of the microbump and thus causes potential reliability issues. Among various root causes of voids in microbumps, the void formation due to Kirkendall effect was examined in the present study. The Kirkendall effect provides the lower limit of the void formation in the Cu/Sn microbump. In order to develop a criterion for the maximum vacancy concentration in the Cu/Sn system, the growth of intermetallic compounds and the formation of Kirkendall vacancy in the binary Cu-Sn system were studied by simulation using an analytical diffusion model and experimental results under an assumption of atomic exchange mechanism for diffusion. The fraction of Kirkendall vacancy was calculated and then plotted against the distance representing the Cu/Cu_3Sn, Cu_3Sn/Cu_6Sn_5 and Cu_6Sn_5/Sn interfaces in semi-infinite diffusion couples. Among these three interfaces, a maximum vacancy fraction of about 0.0125 was realised at the location close to the initial Cu/Cu_3Sn interface at an annealing temperature of T = 473 K for an annealing time of t = 1 h. The penetration depth of vacancy is much greater on the Cu_3Sn side than on the Cu side. This implies that Kirkendall voids may be predominantly formed on the Cu_3Sn side of the Cu/Cu_3Sn interface. To confirm validity of the simulation, the growth behaviour of intermetallic compounds and the formation of Kirkendall voids were experimentally observed using Cu/Sn diffusion couples prepared by an electroplating technique. The fraction of Kirkendall void in the diffusion couple annealed at T = 473 K for t = 1 h was measured by binary large objects (Blob) analysis. According to the observation, a row of Kirkendall voids is formed in Cu_3Sn along the direction parallel to the Cu/Cu_3Sn interface, where the measured value of void fraction is 0.0112. If most of Kirkendall vacancies are used to form Kirkendall voids, the void fraction is almost equal to the vacancy fraction. Thus, the simulation satisfactorily reproduces the experiment. The growth behaviour of the intermetallic compounds in the present Cu/Sn diffusion couple well coincides with that observed for a semi-infinite Cu/Sn diffusion couples in a previous study.

Introduction

The binary Cu/Sn system is one of the simplest metallurgical options for various methods of the interconnection in 3D integration. Even at room temperature, however, intermetallic compounds of Cu_3Sn and Cu_6Sn_5 are formed at the interconnection of Cu/Sn microbumps, and voids with various sizes and shapes are produced inside the microbump. The formation of compounds and voids deteriorates mechanical and electrical properties of the microbump and thus causes potential reliability issues [12-13]. The void formation in the Cu/Sn system is attributed to many sources such as contamination from electrolyte additives during electroplating process, oxidation of Cu and Sn, flux or underfill entrapments, the Kirkendall effect and so on.

In the Cu/Sn system, the diffusion of Cu into Sn occurs much faster than that of Sn into Cu. The difference between the diffusion rates of Cu and Sn results in the formation of atomic vacancies on the Cu side due to the Kirkendall effect [1-4]. The atomic vacancies aggregate to generate Kirkendall voids inside the compound and at the interface between Cu and Cu_3Sn. The Kirkendall effect provides the lower limit of the void formation in the Cu/Sn microbumps. Therefore, in order to optimize the integration flow by reducing the processing-related voids, it is essentially important to evaluate the concentration of the atomic vacancy formed by the Kirkendall effect.

The Kirkendall shift and the fraction of Kirkendall void in the binary Fe-Ni system were studied by Strandlund and Larsson using a computer simulation technique [8]. In their study, three different models were adopted to estimate the fraction of Kirkendall vacancy using thermodynamic and kinetic data in the Fe-Ni system. Among the three models, the analytical model was derived by approximation and simplification of the diffusion equation [9]. In the analytical model, the interdiffusion coefficient and the difference between the intrinsic

diffusion coefficients are assumed to be constant to integrate analytically the equation of time evolution. The fraction of Kirkendall vacancy was calculated and plotted against the distance in a semi-infinite Fe/Ni diffusion couple. The simulation of the maximum vacancy fraction and the Kirkendall shift agrees well with the simulation and the observation reported by Bongenstam and Hillert [10].

The growth behaviour of the compound layers due to reactive diffusion between Cu and Sn was experimentally observed using in a semi-infinite Cu/Sn diffusion couple in a previous study [11]. In this experiment, sandwich Sn/Cu/Sn diffusion couples were prepared by an isothermal bonding technique and then annealed in the temperature range of T = 433-473 K. Owing to annealing, compound layers of Cu_3Sn and Cu_6Sn_5 are produced at the Cu/Sn interface in the diffusion couple. The total thickness of the compound layers monotonically increases in a proportion of a power function of the annealing time. The rate-controlling process of the layer growth was discussed from the exponent of the power function.

To develop a criterion for the maximum vacancy concentration in the Cu/Sn system, the growth of intermetallic compounds and the formation of Kirkendall vacancy in the binary Cu-Sn system were examined by simulation using an analytical diffusion model and experimental results in the present study. On the basis of an analytical diffusion model for Kirkendall-vacancy formation [8], the simulation was conducted using the intrinsic diffusion coefficients of Cu and Sn reported in literatures [4-7]. To test reliability of the simulation, the growth behaviour of intermetallic compounds and the formation of Kirkendall void were experimentally observed using Cu/Sn diffusion couples prepared by an electroplating technique. The fraction of Kirkendall void in the diffusion couple was measured by binary large objects analysis. The simulation was compared with the corresponding experimental result.

Analytical model

For a solid-solution phase in a substitutional binary A-B system, the interdiffusion between components A and B occurs by a vacancy mechanism. If the diffusional fluxes of component A, component B and vacancy in the lattice fixed frame of reference are denoted by J_A, J_B and J_{Va}, respectively, the following relationship holds among J_A, J_B and J_{Va} for the vacancy mechanism [16-17].

$$J_{Va} + J_A + J_B = 0 \tag{1}$$

In the lattice fixed frame of reference, the intrinsic diffusion coefficient D_A of component A is usually different from that D_B of component B. If the molar volume V_m is constant and equivalent between components A and B, the net diffusional flux of components A and B is expressed by the following equation.

$$J_A + J_B = (D_A - D_B)\frac{1}{V_m}\frac{\partial x_B}{\partial z} \tag{2}$$

Here, x_B is the mol fraction of component B, and z is the distance along the diffusional direction. The following relationship is readily obtained from Eq. (1).

$$J_{Va} = -J_A - J_B \tag{3}$$

Combining Eqs. (2) and (3) with the continuity relationship, we obtain the equation

$$\frac{1}{V_m}\frac{\partial x_{Va}}{\partial t} = -\frac{\partial J_{Va}}{\partial z} = \frac{\partial}{\partial z}\left\{(D_A - D_B)\frac{1}{V_m}\frac{\partial x_B}{\partial z}\right\}, \tag{4}$$

where x_{Va} is the mol fraction of vacancy. Equation (4) shows that time evolution of the vacancy fraction is attributed to the difference between D_A and D_B. If there is no composition dependence of the interdiffusion coefficient D, the Fick's second law is described as follows.

$$\frac{\partial x_B}{\partial t} = D\frac{\partial^2 x_B}{\partial z^2} \tag{5}$$

For a semi-infinite single-phase diffusion couple consisting of binary A-B specimens with initial mol fractions of $x_B = x_1$ and $x_B = x_2$, an analytical solution of Eq. (5) is expressed by the equation.

$$x_B = \frac{x_2 + x_1}{2} + \frac{x_2 - x_1}{2}\,\mathrm{erf}\left(\frac{z}{2\sqrt{Dt}}\right) \tag{6}$$

At $t = 0$, the specimens with $x_B = x_1$ and $x_B = x_2$ are located at $z < 0$ and $z > 0$, respectively. The gradient of the mol fraction x_B is calculated from Eq. (6) as follows.

$$\frac{\partial x_B}{\partial z} = \frac{x_2 - x_1}{2\sqrt{\pi Dt}}\exp\left(-\frac{z^2}{4Dt}\right) \tag{7}$$

Inserting Eq. (7) into Eq. (4), we obtain the following time evolution of the fraction of vacancies.

$$\frac{\partial x_{Va}}{\partial t} = \frac{\partial}{\partial z}\left\{\frac{(x_2 - x_1)(D_A - D_B)}{2\sqrt{\pi Dt}}\exp\left(-\frac{z^2}{4Dt}\right)\right\} = -\frac{(x_2 - x_1)(D_A - D_B)z}{4\sqrt{\pi}(Dt)^{3/2}}\exp\left(-\frac{z^2}{4Dt}\right) \tag{8}$$

Assuming that the difference between D_A and D_B is constant independent of z in the composition range of $x_B = x_1$-x_2, Eq. (8) is analytically integrated as follows. The fraction of vacancy can be expressed by integrating Eq. (8) and introducing the complementary error function.

$$x_{Va} = \frac{(x_2 - x_1)(D_A - D_B)}{2D}\,\mathrm{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) + K \tag{9}$$

Here, K is the integration constant. If x_{Va} is initially equal to 0 at $t = 0$ for $z > 0$, $K = (x_2\text{-}x_1)(D_B\text{-}D_A)/2D$. Consequently, the fraction x_{Va} of Kirkendall vacancy is calculated as a function of z and t from Eq. (9). In the binary Cu-Sn system, however, intermetallic compounds of Cu_3Sn and Cu_6Sn_5 exist as stable phases [15]. Hence, Cu/Sn diffusion couples become multi-phase diffusion couples during annealing. In such a case, Eq. (9) cannot be used in a straightforward manner. As a result, the following assumptions were adopted for the calculation in the Cu/Sn diffusion couple: (a) the concentration profile in each phase is discontinuous at the interface, and (b) the interdiffusion coefficient and the intrinsic diffusion coefficients are constant in each intermetallic compound as well as each solid-solution phase.

Experimental

Blanket film Cu/Sn diffusion couples were prepared by an electroplating technique on a substrate of unpatterned p-Si (001) wafer. A Cu/Ti seed layer was sputtered on the Si substrate, and then Cu and Sn double-layers were sequentially electroplated on the Cu/Ti seed layer. The thicknesses of the Cu and Sn layers in the diffusion couple were 3 and 5 μm, respectively. The electroplated wafer was cut into a square coupon with area of 8 × 8 mm^2. Each square-coupon was isothermally annealed at temperatures of T = 453–493 K for various times up to t = 48 h to observe growth behaviour of intermetallic compounds. Some square-coupons were heat-treated with a temperature profile of reflow, where the peak temperature was 533 K.

Cross-sections of the annealed square-coupon were mechanically polished using # 800-4000 emery papers and diamond with sizes of 3 and 1 μm and then finished with colloidal silica liquid. The microstructure of the cross-section was observed by optical microscopy (OM) and scanning electron microscopy (SEM). The fraction of Kirkendall voids on the cross-section was measured by binary large objects (Blob) analysis. Here, the Blob analysis is a technique to obtain statistical information of particles and defects. In this technique, the original image is transformed into the binary image by a threshold process. The threshold process was carefully conducted to improve accuracy of the transformation.

Results and discussion

Simulation

The fraction x_{Va} of Kirkendall vacancy was numerically calculated as a function of the distance z and the annealing time t across the Cu/Cu_3Sn, Cu_3Sn/Cu_6Sn_5 and Cu_6Sn_5/Sn interfaces in the Cu/Sn diffusion couple. As mentioned earlier, the interdiffusion coefficient D and the difference between the intrinsic diffusion coefficients D_{Cu} and D_{Sn} are assumed to be constant for each phase. The values of D, D_{Cu} and D_{Sn} for the Cu, Cu_3Sn, Cu_6Sn_5

and Sn phases were carefully selected from literatures. The results with T = 473 K and t = 1 h (3.6 ks) are shown in Fig. 1. Here, the abscissa indicates the distance z, and the ordinate represents the fraction x_{Va} of Kirkendall vacancy. The value z = 0 shows the initial position of the interface. The thickness of each phase is considered semi-infinite. Figure 1(a), 1(b) and 1(c) indicates the results across the Cu/Cu_3Sn, Cu_3Sn/Cu_6Sn_5 and Cu_6Sn_5/Sn interfaces, respectively. As can be seen, the peak value of x_{Va} is 0.0125, 0.007 and 1.5×10^{-4} for Fig. 1(a), 1(b) and 1(c), respectively. Hence, the peak value is greater for Fig. 1(a) than for Fig. 1(b) and 1(c). In Fig. 1(a), the value x_{Va} = 0.0125 is realised in Cu_3Sn close to the Cu/Cu_3Sn interface, and the penetration depth of the x_{Va}-z curve is much larger on the Cu_3Sn side than on the Cu side. In Fig. 1(b) and 1(c), the position for the peak value of x_{Va} is shifted towards Cu_3Sn and Cu_6Sn_5, respectively. As a consequence, it is concluded that the Kirkendall vacancy is predominantly formed in Cu_3Sn in the neighbourhood of the Cu/Cu_3Sn interface.

In an actual semi-infinite Cu/Sn diffusion couple, however, the thickness of each compound is finite but not semi-infinite. Thus, the simulation was carried out for finite thicknesses of Cu_3Sn and Cu_6Sn_5. The result with T = 473 K and t = 1 h is shown in Fig. 2. As can be seen, the maximum value of x_{Va} is recognised in Cu_3Sn near by the Cu/Cu_3Sn interface also in Fig. 2. To increase the reliability of simulated results, the limited distances were defined by the growth of the intermetallic thickness during given annealing condition in the present study.

Observation

A typical SEM photograph for the cross-section of the annealed diffusion couple is shown in Fig. 3. This figure indicates the photograph for the diffusion couple with T = 473 K and t = 1 h. In Fig. 3, the lowest region is the Si substrate, the layer on the upper side of the Si substrate is the Cu layer, and the upper region is the Sn layer. Although the Cu/Ti seed layer exists between the Cu layer and the Si substrate, it is invisible due to the small thickness. As can be see, compound layers of Cu_3Sn and Cu_6Sn_5 are formed between the Cu and Sn layers. Severe cracks and elongated voids are observed in Cu_6Sn_5, and small voids are distributed in Cu_3Sn in the neighbourhood of the Cu/Cu_3Sn interface. Since Cu_6Sn_5 is more brittle than Cu_3Sn, the cracks can be easily formed in Cu_6Sn_5 [12-14]. To measure the fraction x_{Vo} and the mean size d_{Vo} of the small void in Cu_3Sn, the Blob analysis was conducted using ImageJ software. According to the analysis, x_{Vo} = 0.0112 and d_{Vo} = 0.198 μm. The experimentally determined value of x_{Vo} = 0.0112 is close to the calculated value of x_{Va} is 0.0125. When we assume that all Kirkendall vacancies transform to voids and pores, the evaluated fraction of vacancy can be used to void fraction. It means that the fraction of Kirkendall vacancy implies the maximum fraction of voids by Kirkendall effect. Thus, this guarantees that the small void in Cu_3Sn is produced by the Kirkendall effect.

During annealing, the Cu_3Sn and Cu_6Sn_5 layers are formed at the initial Cu/Sn interface in the diffusion couple as mentioned earlier. Hereafter, the Cu_3Sn and Cu_6Sn_5 layers are merely called the intermetallic layer. From SEM photographs like Fig. 3, the total thickness l of the intermetallic layer was evaluated by the equation

$$l = \frac{A}{w}, \tag{10}$$

where w and A are the total length parallel to the initial Cu/Sn interface and the total area of the intermetallic layer, respectively, on the cross-section. The results of T = 453, 473 and 493 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 and t, respectively. As can be seen, the total thickness l monotonically increases with increasing annealing time t. Furthermore, the plotted points for each annealing temperature are located well on a straight line. As a consequence, l is expressed as a power function of t as follows:

$$l = k\left(\frac{t}{t_0}\right)^n. \tag{11}$$

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 open symbols in Fig. 4, k and n were determined by the least-squares method as represented with the straight lines. As can be seen, n is slightly smaller than 0.5. This implies that boundary diffusion as well as volume diffusion contributes to the rate-controlling process of the layer growth.

As mentioned in Introduction, the reactive diffusion in the Cu/Sn system was experimentally observed in a previous study [11]. In this experiment, sandwich Sn/Cu/Sn diffusion couples were prepared by a diffusion bonding technique, and then isothermally annealed in the temperature range of T = 433-473 K for various times up to 1128 h. Due to annealing, the intermetallic layer composed of Cu_3Sn and Cu_6Sn_5 is formed at the initial interface in the Sn/Cu/Sn diffusion couple. The results of T = 453 and 473 K for the relationship between l and t are shown as open triangles and rhombuses, respectively, in Fig. 5. The corresponding results of T = 453 and

473 K in Fig. 4 are also indicated as open squares and circles, respectively, in Fig. 5. Although the type of diffusion couple is dissimilar in the previous and present studies, the open symbols for each annealing temperature lie well on a straight line. Hence, from the open symbols in Fig. 5, k and n in Eq. (11) were determined by the least-squares method as shown with the straight lines. As can be seen, unlike Fig. 4, n is slightly greater than 0.5 in Fig. 5.

According to the result in Fig. 4, n is rather insensitive to T and close to 0.5. Thus, from all the open symbols in Fig. 4, k and n were simultaneously determined by the least-squares method. The values of k are plotted against the annealing temperature T as open circles with error bars in Fig. 6. In this figure, the ordinate shows the logarithm of k, and the abscissa indicates the reciprocal of T. As can be seen, the plotted points are located well on a straight line. Thus, the dependence of k on T is expressed by the equation

$$k = k_0 \exp\left(-\frac{Q_k}{RT}\right), \tag{12}$$

where 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 the least-squares method as represented with the solid line. The evaluated values are shown in Fig. 5.

Conclusions

To develop a criterion for the maximum vacancy concentration in the Cu/Sn system, the growth of intermetallic compounds and the formation of Kirkendall vacancy in the binary Cu-Sn system were studied by the simulation using the analytical diffusion model and the experimental results. The assumption of atomic exchange mechanism for diffusion was adopted in the present simulation. The fraction of Kirkendall vacancy was calculated and then plotted against the distance for the semi-infinite Cu/Cu_3Sn, Cu_3Sn/Cu_6Sn_5 and Cu_6Sn_5/Sn diffusion couples. According to the simulation, the maximum vacancy fraction is realised in Cu_3Sn in the vicinity of the Cu/Cu_3Sn interface. This implies that Kirkendall voids are predominantly formed in Cu_3Sn. This was experimentally confirmed using the Cu/Sn diffusion couple prepared by an electroplating technique.

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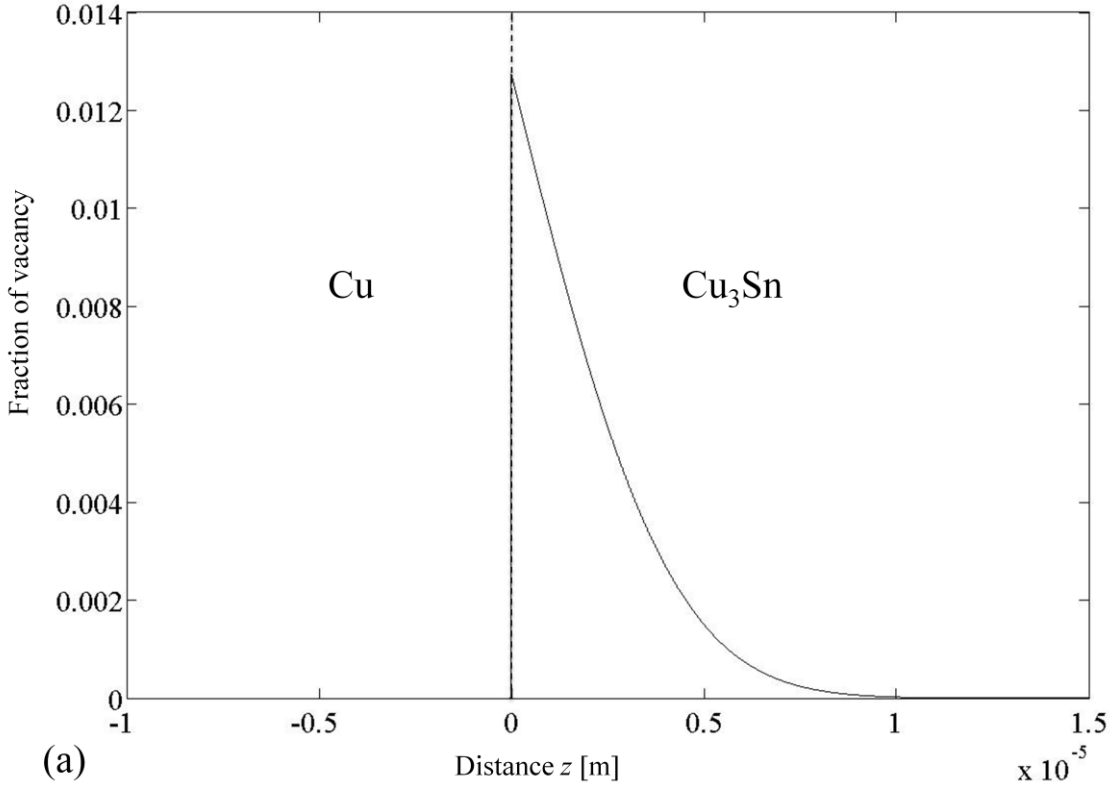
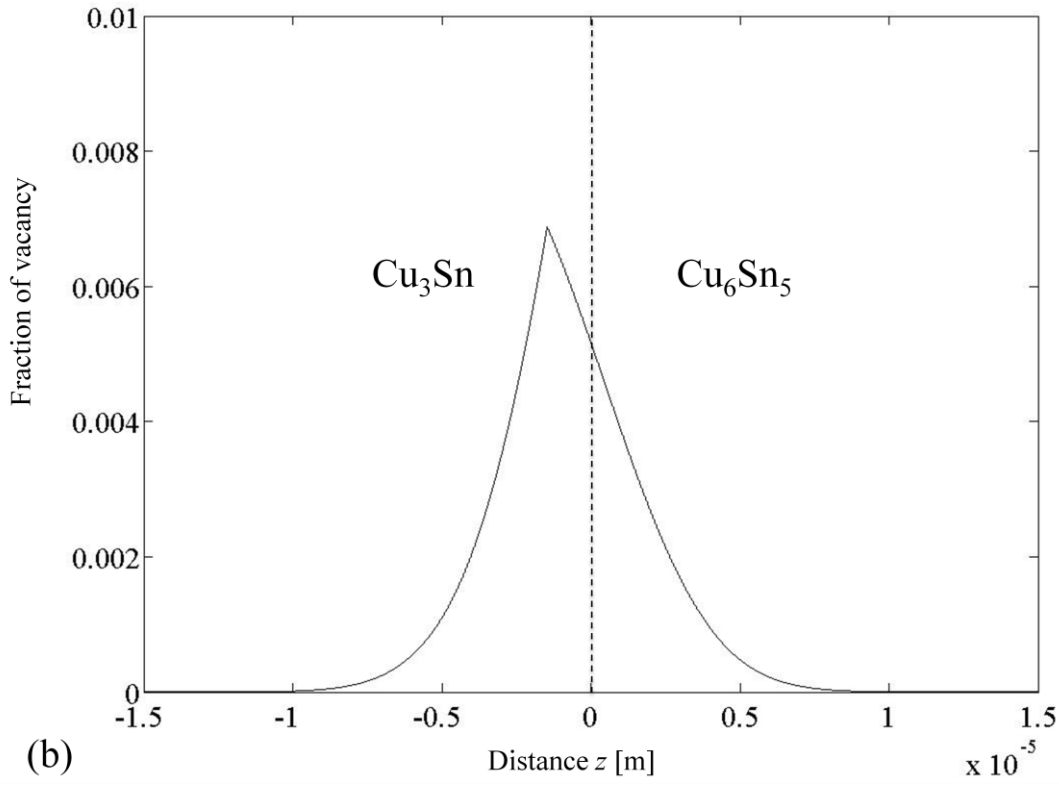


(a)



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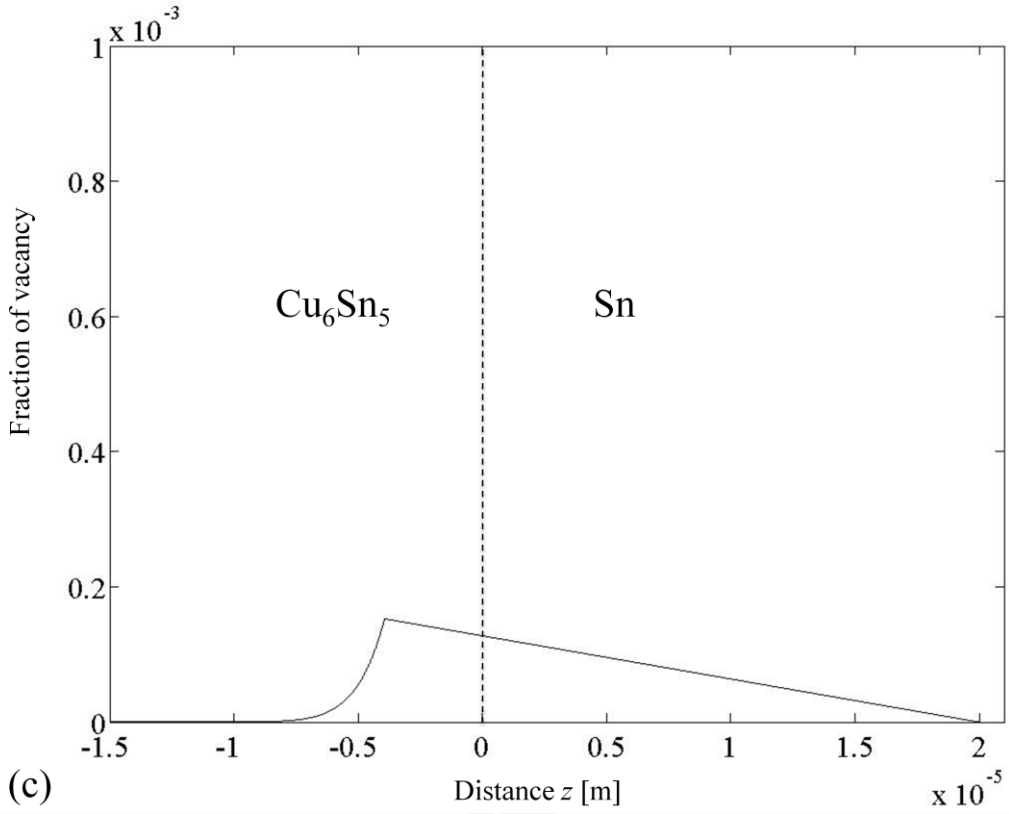


Fig. 1 Simulation for the Kirkendall vacancy fraction versus the distance for various semi-infinite diffusion couples under the annealing conditions of T = 473 K and t = 1 h (3600 s): (a) Cu/Cu_3Sn diffusion couple, (b) Cu_3Sn/Cu_6Sn_5 diffusion couple, and (c) Cu_6Sn_5/Sn diffusion couple.

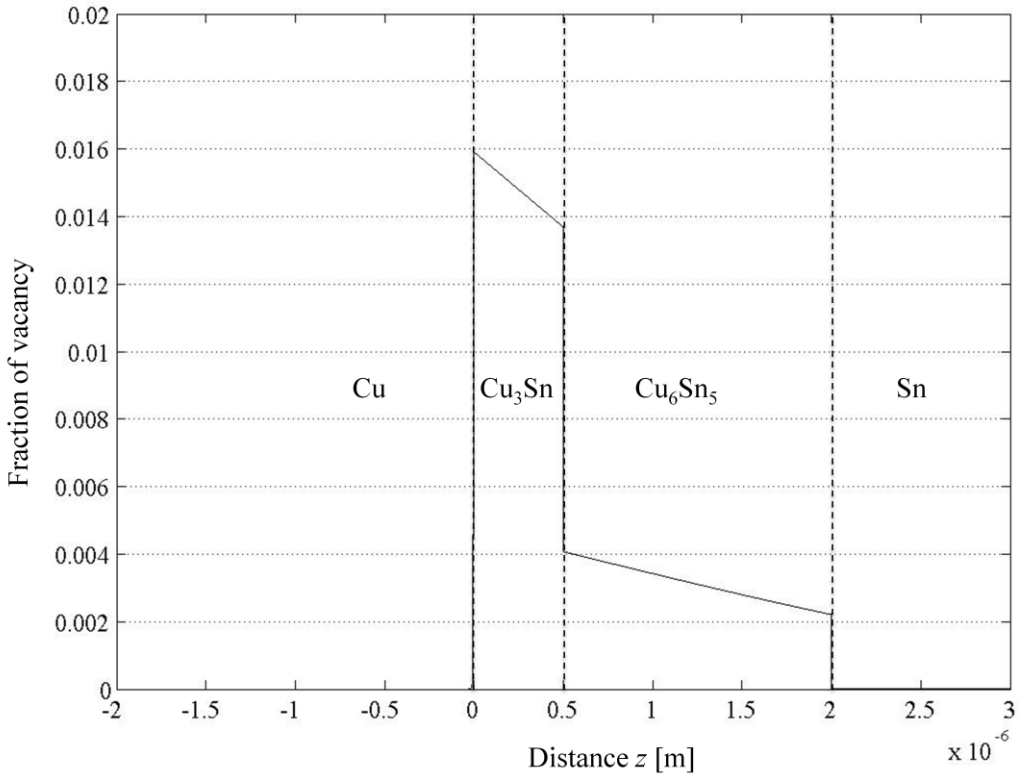


Fig. 2 Simulation for the Kirkendall vacancy fraction versus the distance for the semi-infinite Cu/Sn diffusion couples under the annealing conditions of T = 473 K and t = 1 h (3600 s).

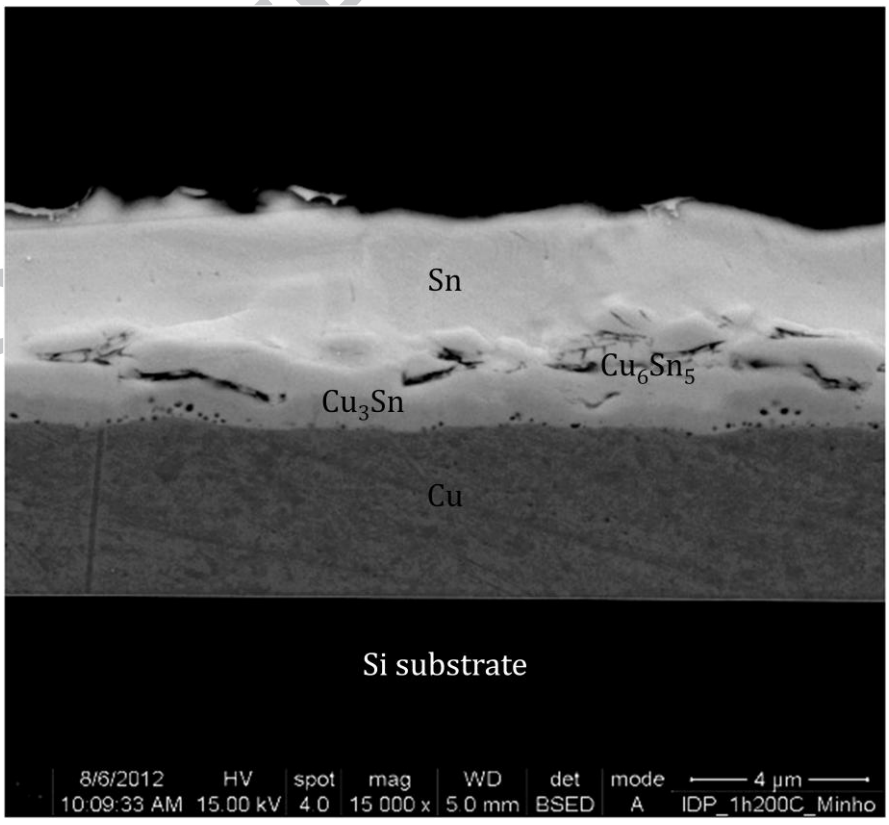


Fig. 3 SEM photograph of the Cu/Sn diffusion couple annealed at T = 473 K for t = 1 h.

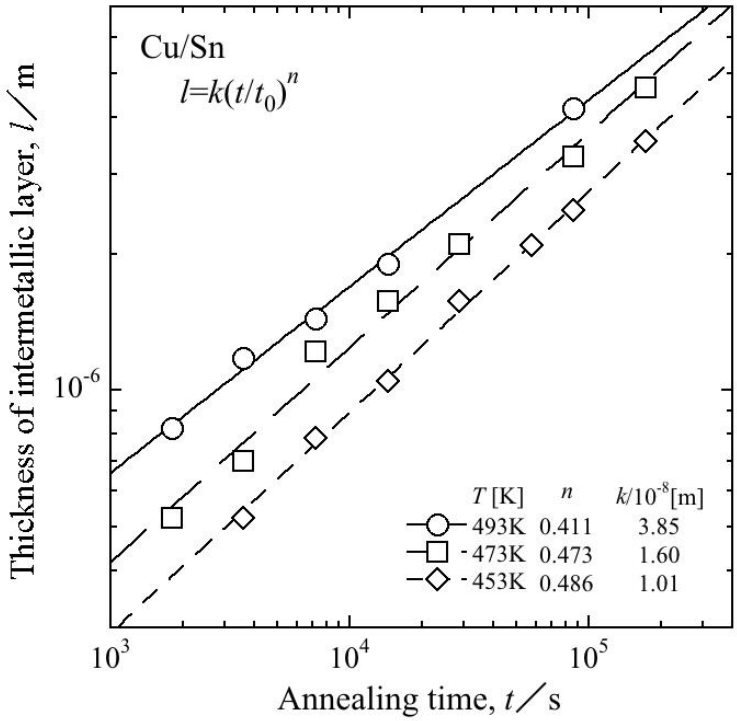


Fig. 4 The total thickness l of the intermetallic layer versus the annealing time t shown as open rhombuses, squares and circles for T = 453, 473 and 493 K, respectively. Straight lines indicate the calculations from Eq. (11).

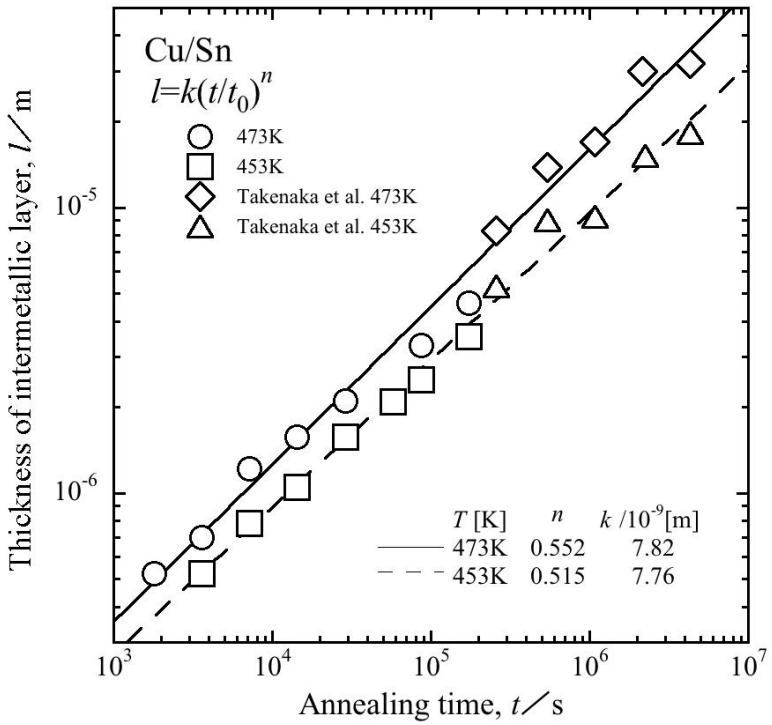


Fig. 5 The total thickness l of the intermetallic layer versus the annealing time t shown as open squares and circles for T = 453 and 473 K, respectively. Open triangles and rhombuses indicate the corresponding results of T = 453 and 473 K, respectively, in a previous study [11]. Straight lines represent the calculations from Eq. (11).

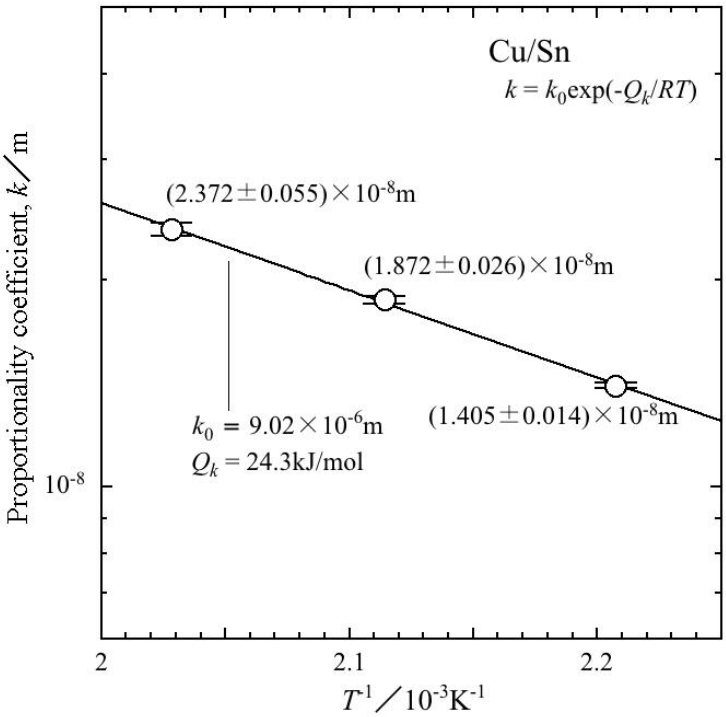


Fig. 6 The logarithm of the proportionality coefficient k versus the reciprocal of the annealing temperature T shown as open circles with error bars.

The Kirkendall effect provides the lower limit of the void formation in the Cu/Sn.

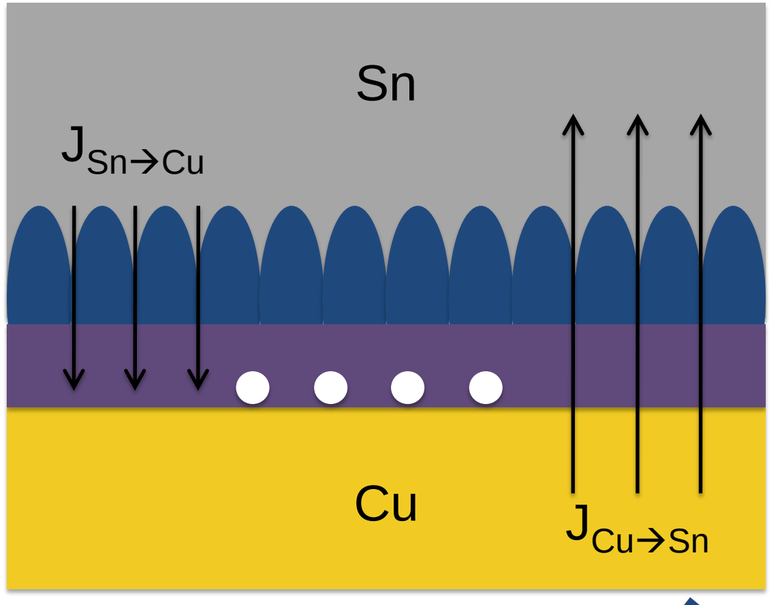
A criterion for the maximum vacancy concentration in the Cu/Sn system was developed.

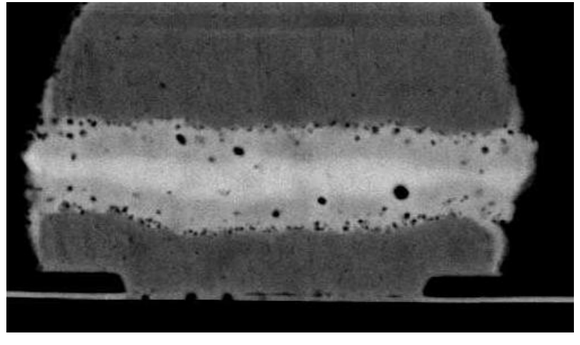
The fraction of Kirkendall vacancy was calculated by an analytical diffusion model.

Kirkendall voids were experimentally observed using Cu/Sn diffusion couples.

The simulation result satisfactorily reproduces the experiment.

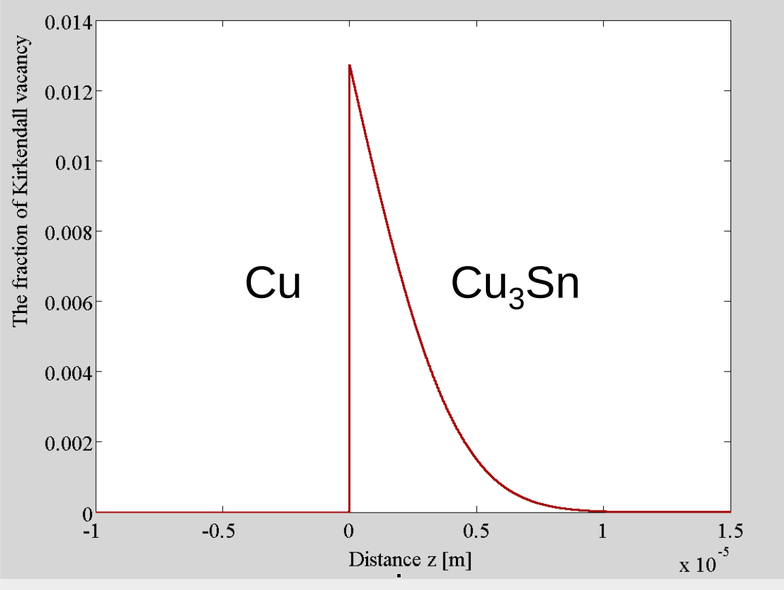
Mechanism of Kirkendall voids in Cu/Sn system





Voids in microbumps of Cu/Sn system

Simulation for Kirkendall voids



Analytical diffusion model