

Ni Interdiffusion Coefficient and Activation Energy in Cu_6Sn_5

KUAN-CHIH HUANG,¹ FUH-SHENG SHIEU,^{1,3} Y.H. HSIAO,²
and C.Y. LIU²

1.—Department of Materials Science and Engineering, National Chung-Hsing University, Taichung 402, Taiwan, ROC. 2.—Department of Chemical and Materials Engineering, National Central University, Zhongli 32001, Taiwan, ROC. 3.—e-mail: fsshieu@dragon.nchu.edu.tw

Ni diffusion in Cu_6Sn_5 intermetallic compound was investigated. First, we successfully fabricated preferred-orientation Cu_6Sn_5 crystal by liquid-phase electroepitaxy (LPEE). Then, Ni/ Cu_6Sn_5 diffusion couples were produced by sputtering from a Ni thin film onto the Cu_6Sn_5 crystal. Ni/ Cu_6Sn_5 diffusion couples were annealed at different temperatures of 120°C, 160°C, 200°C, 255°C, 290°C, and 320°C for 2 h in a vacuum. The Ni atomic profile across the Ni/ Cu_6Sn_5 interface was obtained by electron spectroscopy for chemical analysis (ESCA). From the Ni atomic profiles, the Matano method was used to evaluate the Ni interdiffusion coefficients (D_{Ni}) in the Cu_6Sn_5 crystal obtained with different annealing temperatures, which then yields the activation energy for Ni diffusion in the Cu_6Sn_5 crystal at a particular Ni content. We found that, as Ni diffuses in the ternary $\text{Cu}_{6-x}\text{Ni}_x\text{Sn}_5$ compound phase, the activation energy of Ni interdiffusion decreases with the Ni content.

Key words: Activation energy, interdiffusion coefficient, LPEE

INTRODUCTION

Flip-chip technology has been widely used because it can accommodate a high input/output (I/O) count.¹ In flip-chip technology, Cu-based under bump metallization (UBM) is utilized to fabricate a solderable metal bonding pad on the chip side.² Ni and Ni(P) are the two under bump metallization (UBM) layers most commonly utilized on the other, packaging side.^{3–5} It has been reported that, when Pb-free solders such as Sn(Cu) and Sn(CuAg) are used for solder bumps joined with Cu-based and Ni-based UBMs, an interfacial ternary Cu-Sn-Ni compound layer will form on the Ni bond pads.^{6–8}

It has been reported in many studies that growth of the ternary compound layer is closely related to diffusion of Ni in that layer. However, little research work has been done to determine how growth of the ternary compound layer is controlled by Ni diffusion.^{7–9} To understand the growth kinetics in the interfacial ternary Cu-Sn-Ni compound layer, Ni diffusion in that layer has to be understood. How-

ever, so far, Ni diffusion in a ternary Cu-Sn-Ni (or binary Cu_6Sn_5) compound layer has not been studied. In this work, we investigated Ni diffusion in the ternary Cu-Sn-Ni compound layer and calculate the interdiffusion coefficient and activation energy of Ni in that layer.

EXPERIMENTAL PROCEDURES

To study Ni diffusion in Ni-Cu-Sn compound phase, a binary Cu_6Sn_5 compound phase has to be produced. In the past, a Cu-Sn compound phase was produced by a simple alloying process. However, the binary Cu_6Sn_5 compound phase does not melt congruently. This means that, when the molten Cu_6Sn_5 compound solidifies, the Sn and Cu_3Sn phases precipitate out along the Cu_6Sn_5 compound phase. In addition, the Cu_6Sn_5 compound product has polycrystalline microstructure.

In this work, we used a new approach to produce a crystalline Cu_6Sn_5 compound, namely liquid-phase electroepitaxy (LPEE).¹⁰ The fabrication of the preferred-orientation Cu_6Sn_5 crystal is described in the following and also in previous work.¹¹ As shown in Fig. 1, Cu/Sn/Cu sandwich samples were placed on a hot-plate and current-stressed by high electrical

(Received May 1, 2011; accepted November 8, 2011;
published online November 30, 2011)

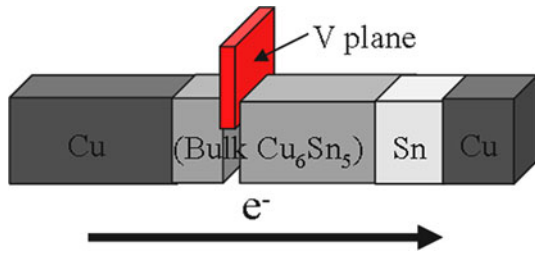


Fig. 1. Schematic representation of the LPEE setup for producing bulk crystalline Cu_6Sn_5 .

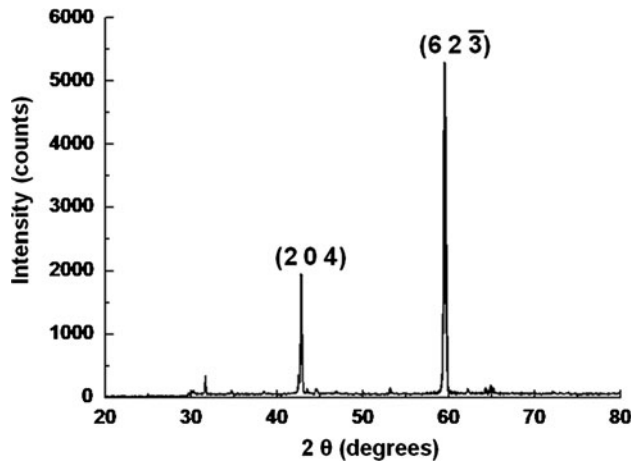


Fig. 2. XRD of LPEE-produced bulk Cu_6Sn_5 disc.

current (10^3 A/cm^2) for 14 days. At high temperature of 400°C and high current stressing, the Cu_6Sn_5 compound phase is a favored stable phase to form at the anode interface, as shown in Fig. 1. The LPEE-produced bulk Cu_6Sn_5 slugs formed at the anode interface were cut into rectangular discs with dimensions of $5 \text{ mm} \times 5 \text{ mm} \times 1 \text{ mm}$ by filament cutting, as shown in Fig. 1.

X-ray diffraction (XRD) was used to analyze the crystallography of the LPEE-produced bulk Cu_6Sn_5 . A disc of LPEE-produced bulk Cu_6Sn_5 was carefully cut out from the interfacial LPEE-produced bulk Cu_6Sn_5 compound layer at the anode side. XRD was used to examine the preferred orientation of the LPEE-produced bulk Cu_6Sn_5 disc. As seen in Fig. 2, only two diffraction peaks, (204) and (623), appear in the XRD diffraction pattern. This implies that the LPEE-grown Cu_6Sn_5 compound does not have polycrystalline structure. Instead, it has preferred orientation, particularly in (204) and (623) planes. The cutoff LPEE-produced Cu_6Sn_5 discs were then polished with sandpaper and finished with polishing cloths to smoothness of $0.3 \mu\text{m}$ using alumina powders. After polishing, the samples were cleaned ultrasonically by acetone, isopropanol (IPA), and de-ionized (DI) water for 5 min, 2 min, and 5 min, respectively. A $0.2 \mu\text{m}$ Ni film was deposited on the

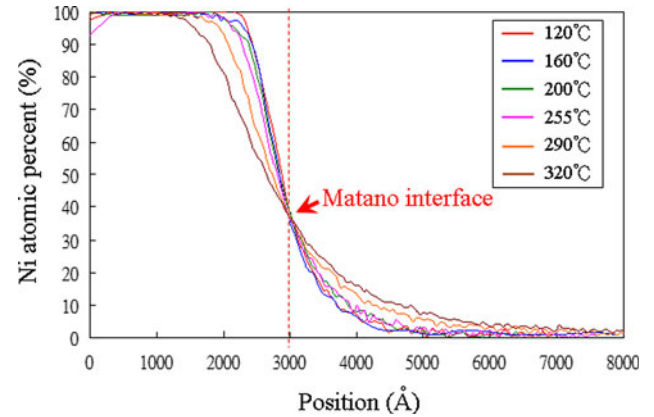


Fig. 3. Atomic profile of Ni across the Ni/ Cu_6Sn_5 interface after 2 h of annealing at different temperatures.

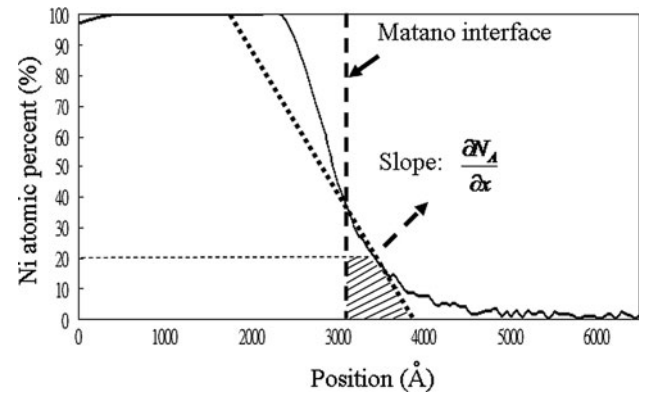


Fig. 4. Interdiffusion coefficient, \tilde{D}_{Ni} , calculated by the Matano method.

Cu_6Sn_5 discs by sputtering. Then, Ni/ Cu_6Sn_5 samples were annealed at 120°C , 160°C , 200°C , 255°C , 290°C , or 320°C for 2 h in an ambient vacuum. After annealing, the Ni atomic depth profile was analyzed by electron spectroscopy for chemical analysis (ESCA).

RESULTS AND DISCUSSION

The Ni atomic profile across the Ni/ Cu_6Sn_5 interface obtained after annealing at different temperatures for 2 h is shown in Fig. 3. It can be observed that all the atomic profiles intercept at a single point, which defines the initial Ni/ Cu_6Sn_5 interface, i.e., the Matano interface. The interdiffusion coefficient (\tilde{D}_{Ni}) of Ni in the Cu_6Sn_5 phase can be calculated from the Ni atomic profiles using the well-known Matano method and the Boltzmann equation, which is formulated as follows:

$$\tilde{D}(N_A) = -\frac{1}{2t} \frac{\partial x}{\partial N_A} \int_{A1}^{N_A} x dN_A, \quad (1)$$

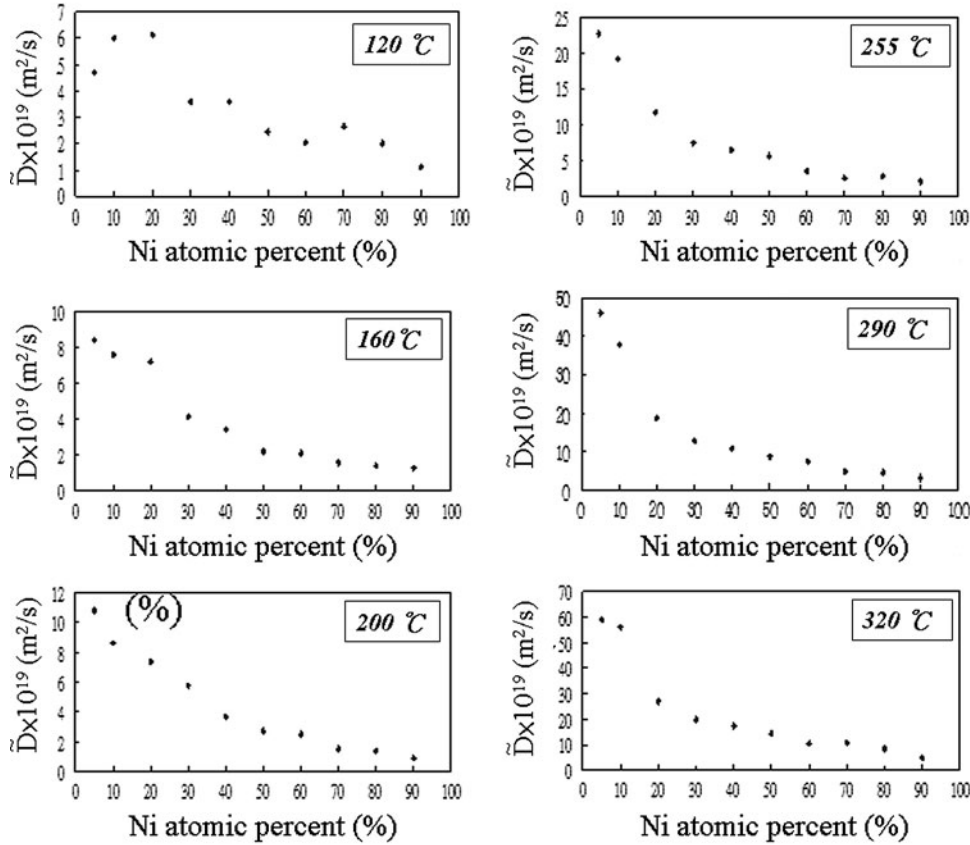


Fig. 5. Interdiffusion coefficients at different annealing temperatures plotted in relation to Ni content.

where t is the annealing time, x is the distance from the Matano interface, N_A is the atomic percentage at distance x from the Matano interface, and N_{A1} is the atomic percentage at infinite distance from the Matano interface.¹²

To compute the interdiffusion coefficient using Eq. (1), two parameters should be obtained, as shown in Fig. 4. The first is the reciprocal of the slope ($\frac{\partial x}{\partial N_A}$) at a particular composition (N_A). The other is the integral value of $\int_{N_{A1}}^{N_A} x dN_A$, which is the crosshatched area in Fig. 4. The two obtained values are plugged into Eq. (1). The interdiffusion coefficient can then be calculated at any Ni composition point.

Using the Ni atomic profiles shown in Fig. 3 and the approach described above, the interdiffusion coefficients of Ni in the Cu_6Sn_5 compound were calculated and are plotted against Ni content for different temperatures in Fig. 5. We find that: (1) the value of the Ni interdiffusion coefficient in the Cu_6Sn_5 binary compound is on the order of 10^{-18} m^2/s to 10^{-19} m^2/s ; (2) the Ni interdiffusion coefficient in the Cu_6Sn_5 binary compound increases with temperature from 120°C to 320°C ; (3) in addition, all the Ni interdiffusion coefficients decrease with the Ni content. This suggests that Ni diffusion

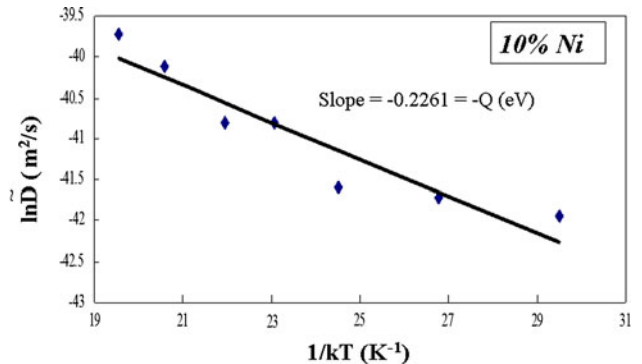


Fig. 6. Activation energy Q calculated at 10 at.% Ni content.

occurs much faster in the Cu_6Sn_5 binary compound when the Ni content is lower.

From the Ni interdiffusion coefficients (Fig. 5) obtained at a given certain Ni composition and different temperatures, the activation energy (Q) of Ni interdiffusion can be determined by using an Arrhenius plot, i.e., $\ln \bar{D}$ versus $\frac{1}{kT}$.^{13–16} In Fig. 6, the Ni interdiffusion coefficient is plotted against Ni composition for different temperatures. The slope of the curve in Fig. 6 gives the activation energy

(0.226 eV) of Ni diffusion in the Cu_6Sn_5 binary compound at Ni composition of 10 at.%, in the temperatures range from 120°C to 320°C. Using the same approach as for 10 at.% Ni above, the activation energies of Ni interdiffusion for the 5 at.% Ni case can be calculated to be about 0.25 eV. Interestingly, we found that the activation energy of Ni interdiffusion in the Cu_6Sn_5 binary compound decreases with the Ni content.

CONCLUSIONS

Ni diffusion in Cu_6Sn_5 intermetallic compound is investigated. First, we successfully fabricated preferred-orientation Cu_6Sn_5 crystal using liquid-phase electroepitaxy (LPEE). Then, a Ni thin film was sputtered onto the Cu_6Sn_5 crystal to produce Ni/ Cu_6Sn_5 diffusion couples, which were annealed at different temperatures of 120°C, 160°C, 200°C, 255°C, 290°C, or 320°C for 2 h in a vacuum. The Ni atomic profile across the Ni/ Cu_6Sn_5 interface was obtained by electron spectroscopy for chemical analysis (ESCA). Given the Ni atomic profile, the Matano method was used to evaluate the Ni interdiffusion coefficient (D_{Ni}) in the Cu_6Sn_5 crystal for different annealing temperatures, which was then used to obtain the activation energy for Ni diffusion in the Cu_6Sn_5 crystals with a particular Ni content. We found that, as Ni diffuses in the ternary $\text{Cu}_{6-x}\text{Ni}_x\text{Sn}_5$ compound phase, activation energy of Ni interdiffusion decreases with the Ni content.

ACKNOWLEDGEMENTS

The authors are appreciative of the financial support of this research received from National Science Council (NSC) of Taiwan under Project No. NSC100-3113-E-008-001.

REFERENCES

1. J.H. Lau, *Flip Chip Technologies* (New York: McGraw-Hill, 1996).
2. C.S. Huang, J.G. Duh, Y.M. Chen, and J.H. Wang, *J. Electron. Mater.* 32, 89 (2003).
3. M.O. Alam, Y.C. Chan, K.N. Tu, and J. Kivilahti, *Chem. Mater.* 17, 2223 (2005).
4. D.R. Frear, J.W. Jang, J.K. Lin, and C. Zhang, *J. Mater.* 53, 28 (2001).
5. Y.H. Hsiao, Y.C. Chuang, and C.Y. Liu, *Scripta Mater.* 54, 661 (2006).
6. S.W. Chen and C.H. Wang, *J. Mater. Res.* 21, 2227 (2006).
7. S.J. Wang and C.Y. Liu, *J. Electron. Mater.* 32, 1303 (2003).
8. S.J. Wang and C.Y. Liu, *Scripta Mater.* 55, 347 (2006).
9. Y. Hao, V. Vuorinen, and J. Kivilahti, *IEEE Trans. Electron. Packag. Manuf.* 30, 293 (2007).
10. S. Dost and B. Lent, *Single Crystal Growth of Semiconductors from Metallic Solution* (The Netherlands: Elsevier, 2007).
11. S.L. Cheng, H.W. Tseng, T.S. Huang, Y.H. Hsiao, Y.C. Chuang, and C.Y. Liu, *135th TMS Conf.* (San Antonio, 2006).
12. E. Robert, R. Hill, and R. Abbaschian, *Physical Metallurgy Principles*, 3rd ed. (Boston: PWS-Kent, 1992).
13. F. Gao and T.J. Takemoto, *J. Alloys Compd.* 421, 283 (2006).
14. K.S. Kim, S.H. Huh, and K. Suganuma, *J. Alloys Compd.* 352, 226 (2003).
15. K.J. Zeng, V. Vuorinen, and J. Kivilahti, *IEEE Trans. Electron. Packag. Manuf.* 25, 162 (2002).
16. L.H. Xu and J.H.L. Pang, *Thin Solid Films* 504, 362 (2006).