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# Solid state interfacial reactions in electrodeposited Cu/Sn couples

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**Abstract:** Cu/Sn couples, prepared by sequentially electroplating Cu and Sn layers on metallized Si wafers, were employed to study the microstructures, phases and the growth kinetics of Cu-Sn intermediate phases, when electroplated Cu/Sn couples were aged at room temperature or annealed at temperatures from 373 K to 498 K for various time. Only $Cu_6Sn_5$ formed in aged couples or couples annealed at temperature below 398 K. The $Cu_6Sn_5$ layer was continuous, but not uniform, with protrusions extending into the Sn matrix. When Cu/Sn couples were annealed at temperatures from 423 K to 498 K, two continuous and uniform $Cn_6Sn_5/Cu_3Sn$ layers formed within the reaction region between Sn and Cu. There were many voids near the $Cu_3Sn$/Cu interface and within the $Cu_3Sn$ layer. $Cu_6Sn_5$ and $Cu_3Sn$ formations both follow parabolic growth kinetics with activation energies of 41.4 kJ/mol for $Cu_6Sn_5$ and 90.4 kJ/mol for $Cu_3Sn$, respectively.

**Key words:** Cu/Sn couple; electrodeposition; solid state reaction; microstructure; growth kinetics

## 1 Introduction

In electronic devices, common conducting metals, such as Cu, Ni, Ag, Au and their alloys, form intermetallic compounds (IMCs) with Sn, the major component in Pb-free solders used for packaging applications[1−6]. It was concluded that extensive formation of Cu-Sn IMCs not only degrades mechanical strength of solder joints, but also changes the electrical characteristics of the interconnects because these compounds, in general, are brittle and have high electrical resistivities[7−8]. The microstructure and phase composition of the reaction region and the reaction kinetics for the Cu-Sn binary system are essential for predicting the lifetime and the reliability of chip-to-substrate connections.

Interfacial reaction between Cu and Sn generally results in the formation of $Cu_6Sn_5$ at room temperature, and $Cu_6Sn_5$ and $Cu_3Sn$ at higher temperatures. The onset temperature for $Cu_3Sn$ has been reported to range from 333−363 K[9−10]. For the growth kinetics of these intermediate phases, it is widely recognized that the growth of the $Cu_6Sn_5$ phase may change from a reaction-controlled process to a diffusion-controlled process if the $Cu_6Sn_5$ layer is thick enough so that the atom flux across the layer is reduced and diffusion becomes the rate-limiting process. For example, the submicron-thick $Cu_6Sn_5$ layer in Cu/Sn thin film couples exhibits linear growth, while the thicker $Cu_6Sn_5$ layer in bulk couples usually obeys a parabolic growth law. The formation of $Cu_3Sn$ at elevated temperatures by consumption of $Cu_6Sn_5$ also exhibits parabolic kinetics[11−12]. Activation energy data[11−12], for the growth of both $Cu_6Sn_5$ and $Cu_3Sn$, are quite variable, possibly due to the different Cu/Sn couple fabricating techniques and different annealing methods.

Electrodeposition is frequently used to prepare solders and in some cases metallization because it offers advantages such as simplicity, cost-effectiveness and controllable patterning and it can be applied to fabricating films with thicknesses from $\ll 1$ μm to $> 100$ μm[13−15]. Electrodeposition can also be employed conveniently to prepare two-layer or multi-layer films by sequential plating. For example, TANG et al[16] have successfully prepared Au-rich (Sn-rich) Au-Sn eutectic alloy solders, and Au/Sn (Sn/Au) couples for packaging applications.

In this work, the Cu/Sn couples were prepared by electroplating a Cu layer onto a metallized Si wafer, and followed by plating of a Sn layer. Cu and Sn layers are thick enough to provide a sufficient supply of Cu and Sn for reaction during annealing. The phases and microstructures in the reaction regions of the Cu/Sn

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couples were investigated after aging at room temperature and annealing at higher temperatures (up to 598 K) for various time. The growth kinetics and phase formation mechanisms for the $Cu_6Sn_5$ and $Cu_3Sn$ layers were also analyzed.

## 2 Experimental

The Sn plating aqueous solution contained tribasic ammonium citrate and $SnCl_2 \cdot 2H_2O$ with $\beta$-naphthol and gelatin as levelers, and the Cu plating solution contained tribasic ammonium citrate and $CuCl_2 \cdot 2H_2O$. These solutions were used to sequentially plate Sn and Cu layers on Si pieces sectioned from wafer substrates with 100 mm in diameter. The Si wafers were metallized with 25 nm of TiW (90% W and 10% Ti, mass fraction) and 200 nm of Pt. TiW acted as an adhesion layer and a diffusion barrier layer, while Pt served as a seed layer for plating. The Si substrates were sectioned into about 1 $cm^2$ pieces.

A Dynatronix DuPR 10-0.1-0.3 pulse plating power supply was used for electrodeposition. The forward direction was set at 10 ms, with a forward on-time of 2 ms and a forward off-time of 8 ms. A current density of 25 $mA/cm^2$ was selected to plate the Sn at a rate of about 0.5 μm/min. A current density of 10 $mA/cm^2$ was chosen to deposit the Cu at a rate of about 0.3 μm/min. An RC2400 Bio-Rad alloying furnace was used to anneal the deposited Cu/Sn couples. Plated samples were annealed at temperatures from 373 K to 498 K for 0.5−5.0 h. The annealing process was done in a forming gas (95% $N_2$+5% $H_2$, volume fraction) atmosphere at a heating rate of 100 K/min and a cooling rate of 40 K/min.

Phases in the aged and annealed Cu/Sn couples were identified using a Rigaku Rotaflex rotating anode X-ray diffraction (XRD) system. Specific Cu/Sn couples for XRD were prepared by plating a 1 μm-thick Sn layer on the Cu layer, in order to allow the X-ray to penetrate the Sn layer and reach the reaction region at the Sn/Cu interface. The aged and annealed samples were also examined, in cross-section orientations, using a Hitachi H2700 scanning electron microscope (SEM) equipped with a PGT IMIX energy dispersive X-ray (EDX) detector. For cross-section observations, the samples were cleaved, mounted with epoxy resin, ground with SiC papers in water and then polished with a 0.05 μm $Al_2O_3$ particle-water suspension.

## 3 Results and discussion

### 3.1 Interfacial reaction at room temperature

Fig.1 shows XRD patterns for the same Cu/Sn couple, which consists of a thin Sn layer (1 μm) on a plated Cu layer (9 μm), aged at room temperature for various time. For comparison, XRD measurement was also conducted on a fresh "as-deposited" sample immediately after the sequential electrodeposition without aging, and the XRD pattern is shown as Fig.1(a). This pattern shows peaks corresponding to Cu and Sn, as well as the Pt seed layer, as expected. In addition, there is a weak peak at about 35° (2$\theta$), which corresponds to $Cu_6Sn_5$. Evidently, some reaction occurs between Cu and Sn at room temperature, either during electrodeposition or shortly afterwards. With increasing aging time (Figs.1(b)−(f)), the peaks at 35° increase in intensity, indicating an additional reaction between Cu and Sn, and the formation of more $Cu_6Sn_5$. Other $Cu_6Sn_5$ peaks show up and increase in intensity with aging (e.g., at 2$\theta$ of about 63° and 85°). No $Cu_3Sn$ is detected, even after aging for 76 d.

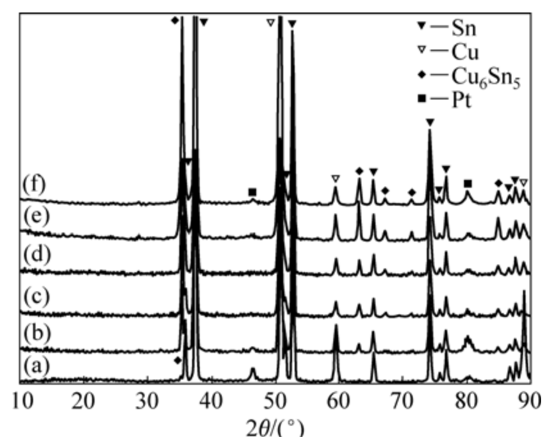


**Fig.1** XRD patterns for Cu/Sn couple with 1 μm-thick Sn layer aged for various time: (a) 0 d; (b) 5 d; (c) 10 d; (d) 20 d; (e) 40 d; (f) 76 d

It is well established that group ⅠB noble metal atoms (e.g., Cu, Ag and Au) can diffuse rapidly into group ⅢA and group ⅣA host metals (e.g., In, Sn and Pb) via an interstitial diffusion process, even at room temperature[17]. The interstitial diffusivity of Cu in Sn at room temperature can be as high as $1.23\times10^{-7}$ $m^2/s$ with an apparent activation energy for diffusion of 0.34 eV (32.8 kJ/mol), and the activation energy for grain boundary diffusion of Sn in Cu has been measured as 0.78 eV (75.3 kJ/mol) by BANDYOPADHYAY et al[10]. As such, the transport of Cu atoms from the Cu layer into the Sn layer should predominate and control the formation of $Cu_6Sn_5$ at room temperature. The presence of $Cu_6Sn_5$ as the only reaction product in as-deposited and aged Cu/Sn couples can be rationalized in terms of the structure of $Cu_6Sn_5$. $Cu_6Sn_5$ has a pseudohexagonal structure, which can form without markedly changing the tetragonal structure of Sn. In addition, $Cu_6Sn_5$ formation follows the empirical rule where the first phase to form should have the composition nearest the lowest temperature eutectic[18−19]. The lowest temperature eutectic occurs at a composition of 99.3% Sn and a

temperature of 405 K (Fig.2)[20]. $Cu_6Sn_5$ is the closest intermetallic phase to the eutectic, compared with other Cu-Sn intermetallic compounds, such as $Cu_3Sn$, $Cu_{10}Sn_3$ and $Cu_{41}Sn_{11}$.

Fig.3(a) shows a cross section backscattered electron (BSE) image of the Cu/Sn couple after aging for 76 d. Sn appears bright, while Cu is dark and the interfacial region has intermediate contrast. The reaction region is determined to be $Cu_6Sn_5$ by EDX analysis (50.2%Sn and 49.6%Cu in molar fraction, Fig.3(b)), which is consistent

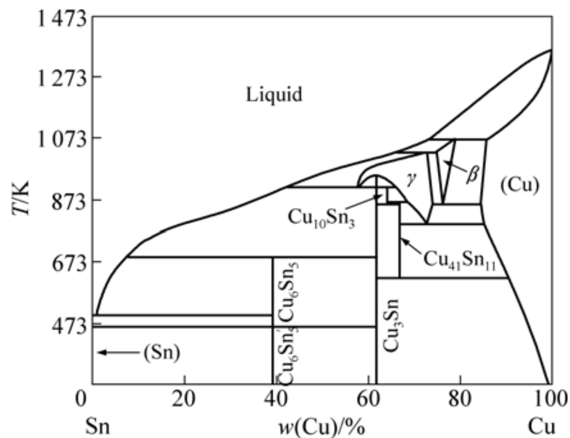


**Fig.2** Cu-Sn phase diagram [20]

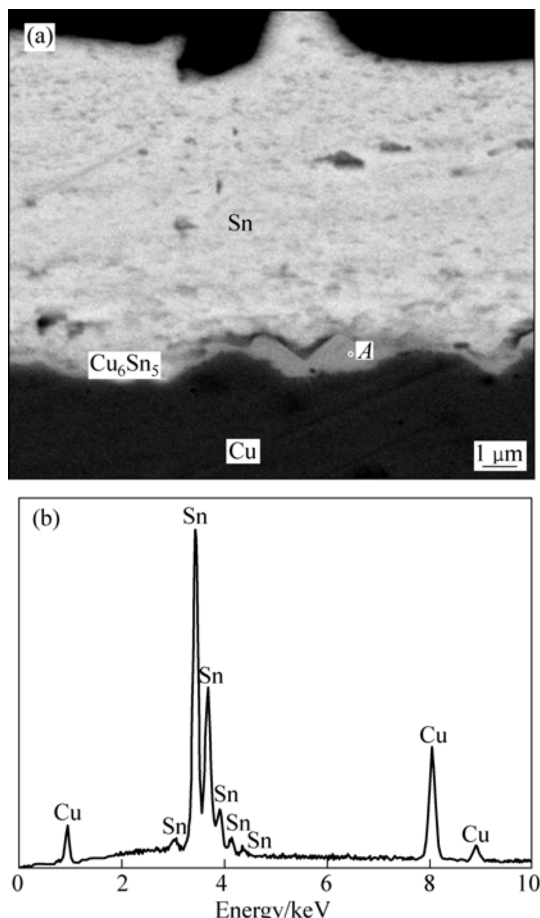


**Fig.3** BSE image (a) and EDX spectrum taken from point *A* (b) of Cu/Sn couple aged at room temperature for 76 d

with the XRD result. The $Cu_6Sn_5$ layer is continuous, but not uniform. At some locations, it is very thin, while at other locations there are some relatively thick protrusions towards the Sn layer. The formation of $Cu_6Sn_5$ protrusions through reaction between molten Sn-based solders and Cu substrates has been reported previously by ZENG et al[21], LIU et al[22] and BADER et al[23], and is attributed to the anisotropic nucleation and growth behavior of $Cu_6Sn_5$. The $Cu_6Sn_5$ protrusions in the current study are formed through solid state reaction between Cu and Sn, which is different from the reaction conditions for the cited literature. Therefore, the formation mechanism for $Cu_6Sn_5$ in the current study may be different from those previously reported[21−23].

### 3.2 Interfacial reaction at elevated temperatures

Fig.4 shows XRD patterns for Cu/Sn couples annealed at different temperatures from 373 K to 473 K. For couples annealed at 373 K and 398 K, respectively, for 1 h, only $Cu_6Sn_5$ is detected as the reaction product (Fig.4(a) and 4(b)), which is the same as the results for the couples aged at room temperature. BSE image for a couple annealed at 373 K is shown in Fig.5, confirming that only $Cu_6Sn_5$ forms. The $Cu_6Sn_5$ layer is still non-uniform with protrusions at some locations. A particularly prominent protrusion extending into the Sn matrix, perhaps along Sn grain boundary, is shown by the arrow in Fig.5. The formation of $Cu_6Sn_5$ protrusions is likely due to a combination of grain boundary diffusion and interstitial diffusion of Cu atoms into the Sn. Similar behavior has also been reported in Ref.[15] for Au/Sn diffusion couples aged at room temperature, where $AuSn_4$ protrusions formed as a result of Au diffusion (both grain boundary and interstitial) into Sn.

When the annealing temperature was increased to 423 K and the Cu/Sn couple was annealed for a short time (0.5 h, Fig.4(c)), weak diffraction peaks for $Cu_3Sn$ are detected. The onset temperature for $Cu_3Sn$ formation

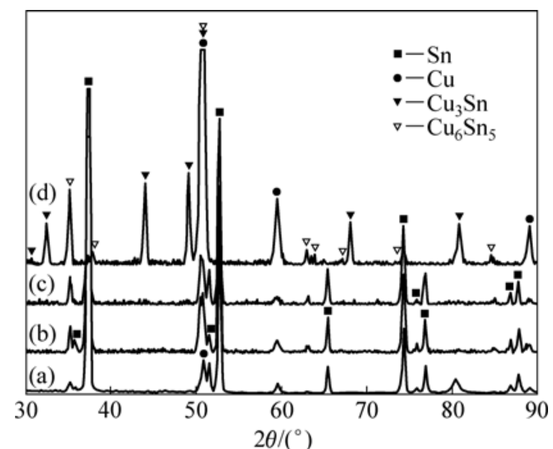


**Fig.4** XRD patterns of annealed Cu/Sn couples with 1 μm-thick Sn layer: (a) 373 K, 1 h; (b) 398 K, 1 h; (c) 423 K, 0.5 h; (d) 473 K, 0.5 h

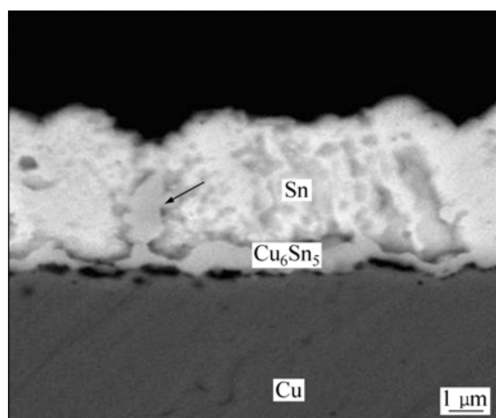


**Fig.5** BSE image of Cu/Sn couple annealed at 373 K for 4 h

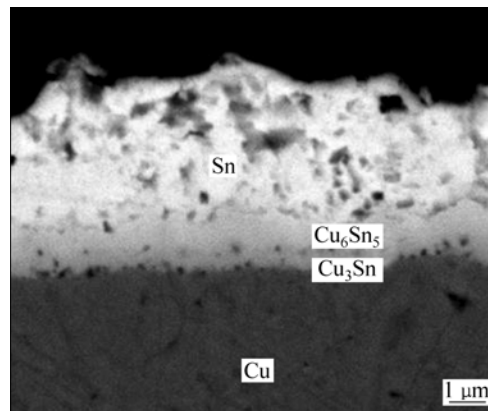


**Fig.6** BSE image of Cu/Sn couple annealed at 423 K for 5 h

appears to be between 398 K and 423 K for the electroplated Cu/Sn couples studied here, which is higher than the onset temperature for $Cu_3Sn$ formation in evaporated Cu/Sn couples (333−363 K) previously reported by TU and THOMPSON[9] and BANDYOPADHYAY and SEN[10], but lower than that for evaporated Cu/Sn thin film couples (457 K) reported by LIAO and WEI[11]. It is clear from the Cu-Sn phase diagram (Fig.2) that solid Sn is in equilibrium with $Cu_6Sn_5$, but solid Cu is not in equilibrium with $Cu_6Sn_5$. Therefore, the $Cu_6Sn_5$/Cu interface is not thermodynamically stable so that a $Cu_3Sn$ layer forms between the $Cu_6Sn_5$ layer and the Cu layer by the following reaction:

$$Cu_6Sn_5+9Cu \rightarrow 5Cu_3Sn \quad (1)$$

Two intermetallic layers are clearly visible for the couple annealed at 423 K for 5 h (Fig.6). The $Cu_3Sn$ layer shows slightly darker contrast relative to the $Cu_6Sn_5$ layer due to its lower Sn content. The morphology of the reaction region is very different from that for the Cu/Sn couples annealed at room temperature and 373 K. The main difference is the lack of $Cu_6Sn_5$ protrusions extending into Sn, i.e., both the $Cu_3Sn$ and $Cu_6Sn_5$ layers are quite uniform. For the Cu/Sn couples annealed at 423 K, $Cu_6Sn_5$ forms initially (as room temperature annealed couples), forming a non-uniform layer. Subsequently, Cu atoms diffuse to the $Cu_6Sn_5$/Sn interface through the $Cu_6Sn_5$ layer to react with Sn, so $Cu_6Sn_5$ continues to grow towards the Sn layer. Since it takes much longer for Cu atoms to diffuse through the thicker protrusions than through the thin regions between neighbouring protrusions, $Cu_6Sn_5$ grows faster in the thin regions than at the protruding locations. As a result, the morphology of $Cu_6Sn_5$ layer evens out over time, producing a uniform $Cu_6Sn_5$/Sn interface. This flattening process is also driven by thermodynamics because of the higher interfacial energy between Sn and $Cu_6Sn_5$ for the uneven $Cu_6Sn_5$/Sn interface.

As shown in Fig.4(d), strong diffraction peaks for $Cu_3Sn$ are detected for the Cu/Sn couple annealed at 473 K for 0.5 h. Therefore, more rapid growth of the $Cu_3Sn$ layer is achieved by increasing the annealing temperature form 423 K to 473 K. The reaction regions are shown in Fig.7 for Cu/Sn couples annealed at 473 K for various time from 0.5 to 3 h. There are two reacted layers, i.e., $Cu_6Sn_5$ and $Cu_3Sn$, as for 423 K. Voids begin to appear for the shorter annealing time (0.5 h, Fig.7(a)), primarily at the $Cu_3Sn$/Cu interface. The number and size of voids increase with increasing annealing time (1 h, Fig.7(b)). As the annealing time is further increased (2 h), the density of voids increases, although the size remains approximately constant, i.e., no coalescence occurs (Fig.7(c)). In addition, as the annealing time is increased, the voids are present within the $Cu_3Sn$ layer as well as near the $Cu_3Sn$/Cu interface. Moreover, the intermetallic thickness ratio ($Cu_3Sn$ to $Cu_6Sn_5$) increases with annealing time, indicating faster growth of the $Cu_3Sn$ layer relative to the $Cu_6Sn_5$ layer.

The voids in the $Cu_3Sn$ layer and near the Cu/$Cu_3Sn$ interface are important because void formation can result in weakening of the joint interface, possibly leading to brittle fracture, between the Sn alloy solder and the Cu substrate and loss of much of the electrical connectivity[24]. Some researchers have attributed the voids to Kirkendall voids, while others attributed void formation to impurities in the Cu layer of the Cu/Sn couple[8]. Recently, PAUL et al[25] have found voids in annealed Cu/Sn bulk couples with high-purity Cu and Sn plates. Their result implies that void formation is primarily due to the Kirkendall effect, as a result of the imbalance in migration of the diffusing species, i.e., Cu diffuses significantly faster than Sn. OH[26] has determined that the diffusivity of Cu in $Cu_3Sn$ is approximately 3 times larger than that of Sn in $Cu_3Sn$, leading to void formation at the $Cu_3Sn$/Cu interface. The voids at the $Cu_3Sn$/Cu interface will remain as long as Cu is the only diffusing species. The voids will be

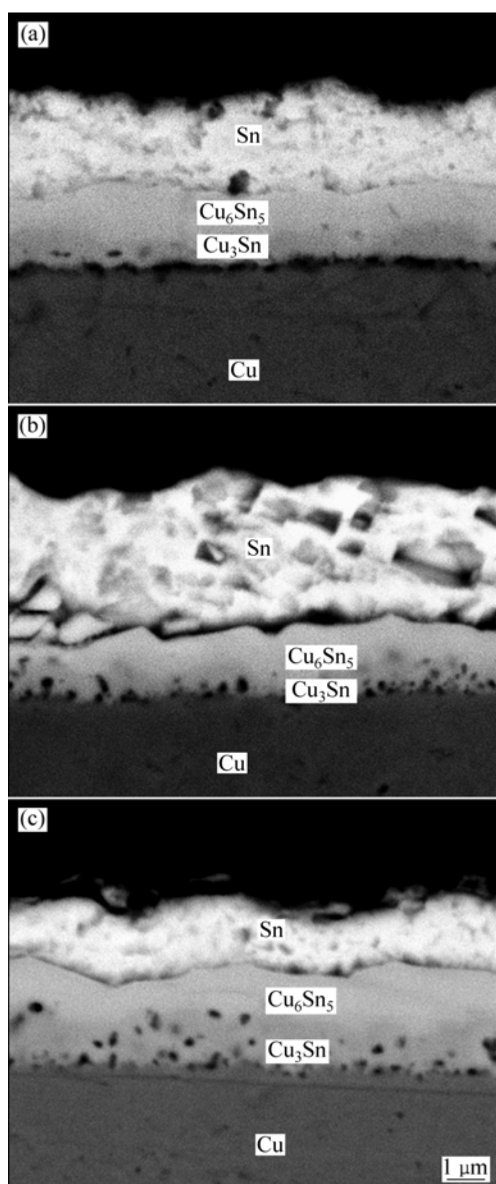


**Fig.7** BSE images of Cu/Sn couples annealed at 473 K for various time: (a) 0.5 h; (b) 1 h; (c) 3 h

displaced into the $Cu_3Sn$ layer, if some of the Sn atoms diffuse to the $Cu_3Sn$/Cu interface to react with the Cu behind the voids. Based on the fact that most of the voids are near the $Cu_3Sn$/Cu interface and within the $Cu_3Sn$ layer in this work, it can be concluded that diffusion of Sn through the $Cu_3Sn$ layer has occurred, with Sn reacting with Cu at the $Cu_3Sn$/Cu interface to form $Cu_3Sn$:

$$3Cu+[Sn] \rightarrow Cu_3Sn \tag{2}$$

where [Sn] refers to the dissolved Sn.

Cu remains the dominant diffusing species in the $Cu_3Sn$ phase. Of course, $Cu_3Sn$ is also formed at the $Cu_3Sn$ side of the $Cu_6Sn_5$/$Cu_3Sn$ interface through reaction between the $Cu_6Sn_5$ layer and diffusing Cu atoms from the Cu layer:

$$Cu_6Sn_5+9[Cu] \rightarrow 5Cu_3Sn \tag{3}$$

where [Cu] refers to the dissolved Cu.

Sn is the main diffusing species in the $Cu_6Sn_5$ phase[8] and the growth of $Cu_6Sn_5$ is based on the following reactions. At the $Cu_6Sn_5$ side of the $Cu_6Sn_5$/$Cu_3Sn$ interface, reaction occurs between the $Cu_3Sn$ layer and the Sn atoms from the Sn layer:

$$2Cu_3Sn+3[Sn] \rightarrow Cu_6Sn_5 \tag{4}$$

At the $Cu_6Sn_5$/Sn interface, reaction occurs between the Sn layer and Cu atoms diffusing from the Cu layer:

$$5Sn+6[Cu] \rightarrow Cu_6Sn_5 \tag{5}$$

In summary, interdiffusion of Sn and Cu atoms during the growth of $Cu_3Sn$ and $Cu_6Sn_5$ intermetallic layers can be schematically illustrated in Fig.8. The larger arrow in this illustration denotes the faster diffusion species in the given phases, i.e., Cu in $Cu_3Sn$ and Sn in $Cu_6Sn_5$.

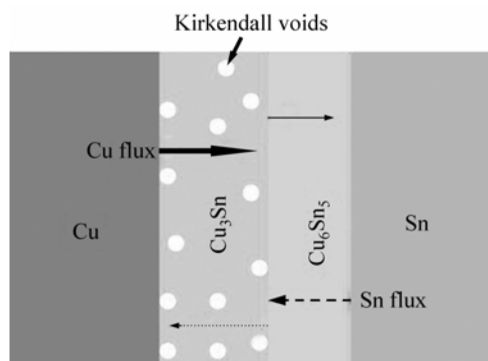


**Fig.8** Schematic illustration of interdiffusion of Cu and Sn in reaction region of electroplated Cu/Sn couple annealed at temperature above 423 K

### 3.3 Reaction kinetics

As mentioned above, the growth of the $Cu_6Sn_5$ layer dominates at lower temperature; however, with increasing temperature, the $Cu_3Sn$ layer grows rapidly at the expense of $Cu_6Sn_5$ and the remaining Cu layer. In general, the growth kinetics of $Cu_6Sn_5$ and $Cu_3Sn$ in the Cu-Sn binary system depends on two types of processes: 1) mass transport through the resultant layers, i.e., the $Cu_6Sn_5$ layer and the $Cu_3Sn$ layer and 2) the reaction at the interfaces, i.e., the Sn/$Cu_6Sn_5$, $Cu_6Sn_5$/$Cu_3Sn$ and $Cu_3Sn$/Cu interfaces.

The reaction rate constant ($k$) is a function of temperature ($T$) as described by an Arrhenius-type equation:

$$k=k_0 \exp[-Q/(RT)] \tag{6}$$

where $k_0$ is the frequency factor; $Q$ is the apparent activation energy; and $R$ is gas constant (8.31 J/(K·mol)). Kinetic plots for the $Cu_6Sn_5$ and $Cu_3Sn$ layers are shown in Figs.9 and 10, respectively. Because the $Cu_6Sn_5$ layer

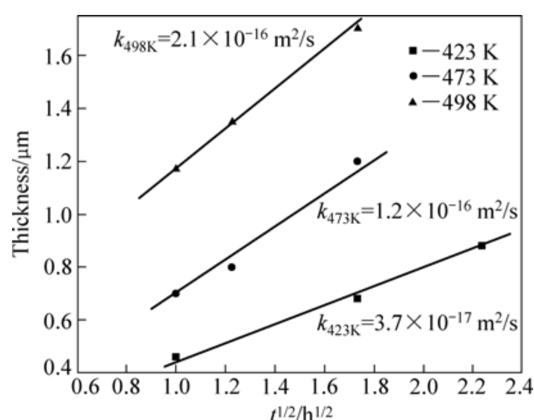


**Fig.9** Average thickness of $Cu_6Sn_5$ layer vs square root of time for Cu/Sn couples annealed at different temperatures

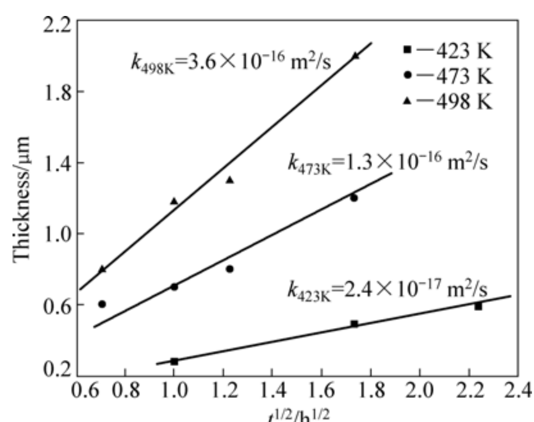


**Fig.10** Average thickness of $Cu_3Sn$ layer vs square root of time for Cu/Sn couples annealed at different temperatures

is not uniform when the Cu/Sn couples are annealed at 398 K and below, the layer thicknesses cannot be measured accurately.

Therefore, only the $Cu_6Sn_5$ layer thicknesses for couples annealed at temperatures from 423 K to 498 K for various time are plotted in Fig.9. The approximate linear relationships, for the $Cu_6Sn_5$ layer and $Cu_3Sn$ layer thicknesses, with the square root of the annealing time indicate diffusion controlled kinetics for the two compounds. The reaction rate constants, $k$, for each temperature for the $Cu_6Sn_5$ and $Cu_3Sn$ layers are marked in Fig.9 and Fig.10, respectively. For the temperatures studied (from 423 K to 498 K), $Cu_6Sn_5$ layer has a higher $k$ value than $Cu_3Sn$ at 423 K, and lower $k$ values than $Cu_3Sn$ at 473 K and 498 K. The kinetic data obtained in this work can be compared with the interdiffusion data for $Cu_6Sn_5$ and $Cu_3Sn$ in Ref.[27]. As shown in Table 1, $k$ values for $Cu_6Sn_5$ at temperatures from 423 K to 498 K are about one order of magnitude less than the interdiffusion coefficients for $Cu_6Sn_5$ in Ref.[27]. This is, at least partially, because some of the $Cu_6Sn_5$ is consumed through reaction (3) to form $Cu_3Sn$. $k$ values for $Cu_3Sn$ at the same temperature are approximately equal to the interdiffusion coefficients for $Cu_3Sn$ in Ref.[24]. Reaction (4) at the $Cu_6Sn_5$ side of the $Cu_6Sn_5/Cu_3Sn$ interface is not significant, perhaps even negligible. In other words, reaction (3) dominates at the $Cu_6Sn_5/Cu_3Sn$ interface during annealing of Cu/Sn couples at 423 K and above, resulting in faster growth for the $Cu_3Sn$ layer compared with the $Cu_6Sn_5$ layer.

The logarithms of the rate constants are plotted vs. the reciprocal of the absolute temperature, for $Cu_6Sn_5$ and $Cu_3Sn$, in Fig.11 and Fig.12. From the linear relationships, the frequency factors and activation energies were determined to be $4.3\times10^{-12}$ m$^2$/s and 41.4 kJ/mol for $Cu_6Sn_5$ and $3.3\times10^{-3}$ m$^2$/s and 90.4 kJ/mol for $Cu_3Sn$, respectively. $Cu_6Sn_5$ growth has a lower activation energy than $Cu_3Sn$ growth, which agrees with most results previously reported[11, 27]. Although kinetic data have been reported previously, the data are quite variable, e.g., 0.67−0.87 eV (64.6−83.9 kJ/mol) for $Cu_6Sn_5$ and 0.77− 1.07 eV (74.3−103.3 kJ/mol) for $Cu_3Sn$. The activation energy obtained here for the growth of $Cu_6Sn_5$, 41.4 kJ/mol, is lower than the reported values of 0.67−0.87 eV (64.6−83.9 kJ/mol). The reasons are not clear yet, but may be related to the initial abnormally rapid growth of $Cu_6Sn_5$ in the annealed Cu/Sn couples. The activation energy obtained here for $Cu_3Sn$, 90.4 kJ/mol, is in reasonable agreement with other data of 0.77−1.07 eV (74.3−103.3 kJ/mol).

**Table 1** Growth rate constants ($k$) and interdiffusion coefficients ($D_{inter}$) for $Cu_3Sn$ and $Cu_6Sn_5$

| Temperature/K | $k^a$/(m$^2$·s$^{-1}$) | | $D^b_{inter}$/(m$^2$·s$^{-1}$) | |
|---|---|---|---|---|
| | $Cu_3Sn$ | $Cu_6Sn_5$ | $Cu_3Sn$ | $Cu_6Sn_5$ |
| 423 | $2.4\times10^{-17}$ | $3.7\times10^{-17}$ | $2.5\times10^{-17}$ | $2.0\times10^{-16}$ |
| 473 | $1.3\times10^{-16}$ | $1.2\times10^{-16}$ | $2.3\times10^{-16}$ | $1.0\times10^{-15}$ |
| 498 | $3.6\times10^{-16}$ | $2.1\times10^{-16}$ | $5.0\times10^{-16}$ | $2.5\times10^{-15}$ |

a: those data came from the present work; b: those data came from Ref.[27].

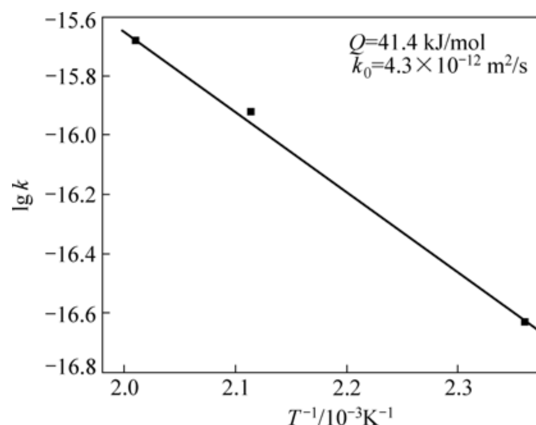


**Fig.11** Plot of $k$ vs annealing temperature for $Cu_6Sn_5$ layer in annealed Cu/Sn couples

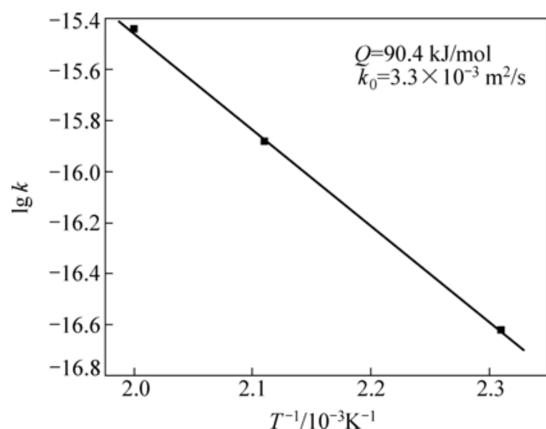


**Fig.12** Plot of $k$ vs annealing temperature for $Cu_3Sn$ layer in annealed Cu/Sn couples

## 4 Conclusions

1) $Cu_6Sn_5$ formed in as-deposited Cu/Sn couples. The amount of $Cu_6Sn_5$ increased with aging time. The $Cu_6Sn_5$ layer was continuous, but non-uniform, with protrusions extending into the Sn matrix. The protrusions were likely due to a combination of grain boundary diffusion and interstitial diffusion of Cu atoms into the Sn layer.

2) When Cu/Sn couples were annealed at 373 K and 398 K, $Cu_6Sn_5$ was still the only intermetallic that formed and the layer was continuous and non-uniform.

3) When Cu/Sn couples were annealed at 423−498 K, two continuous and uniform layers, $Cu_6Sn_5$ and $Cu_3Sn$, formed. The $Cu_3Sn$ phase formed by consuming $Cu_6Sn_5$ phase and the remaining Cu. Kirkendall voids formed near the $Cu_3Sn$/Cu interface and inside the $Cu_3Sn$ layer due to the much faster Cu diffusion rates relative to Sn.

4) The $Cu_6Sn_5$ and $Cu_3Sn$ layers both followed parabolic growth kinetics during annealing of Cu/Sn couples from 423 K to 498 K. The growth rate constants were determined as $k=4.3\times10^{-12}\exp[-41.4\times10^3/(RT)]$ for $Cu_6Sn_5$ and $k=3.3\times10^{-3}\exp[-90.4\times10^3/(RT)]$ for $Cu_3Sn$.

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