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Kinetics of interface reaction and intermetallics growth of Sn-3.5Ag-0.7Cu/Au/Ni/Cu system under isothermal aging

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The environmental concern of Pb toxicity and the "soft error" failure in silicon device caused by the decay of Pb isotopes have propelled the search for Pb-free replacements of Sn-Pb eutectic solders for the surface mount attachment in microelectronic packaging applications [1]. Most of Pb-free solders, similar to Sn-Pb eutectic solders, react with the base metal and form intermetallic compounds, which result in severe reliability issues in microelectronic packages [2]. Many studies have been performed on different solder/metal systems, such as Sn-Cu/Ni, Sn-Bi/Cu, and Sn-Ag/Au/Ni/Cu, etc. [3–5]. This work aims to study the effect of isothermal aging on the growth of intermetallic compound (IMC) and to further explore the kinetics of interdiffusion and develop a physical model for the description of the growing rate of IMC in Sn-Ag-Cu/Au/Ni/Cu system during the isothermal aging.

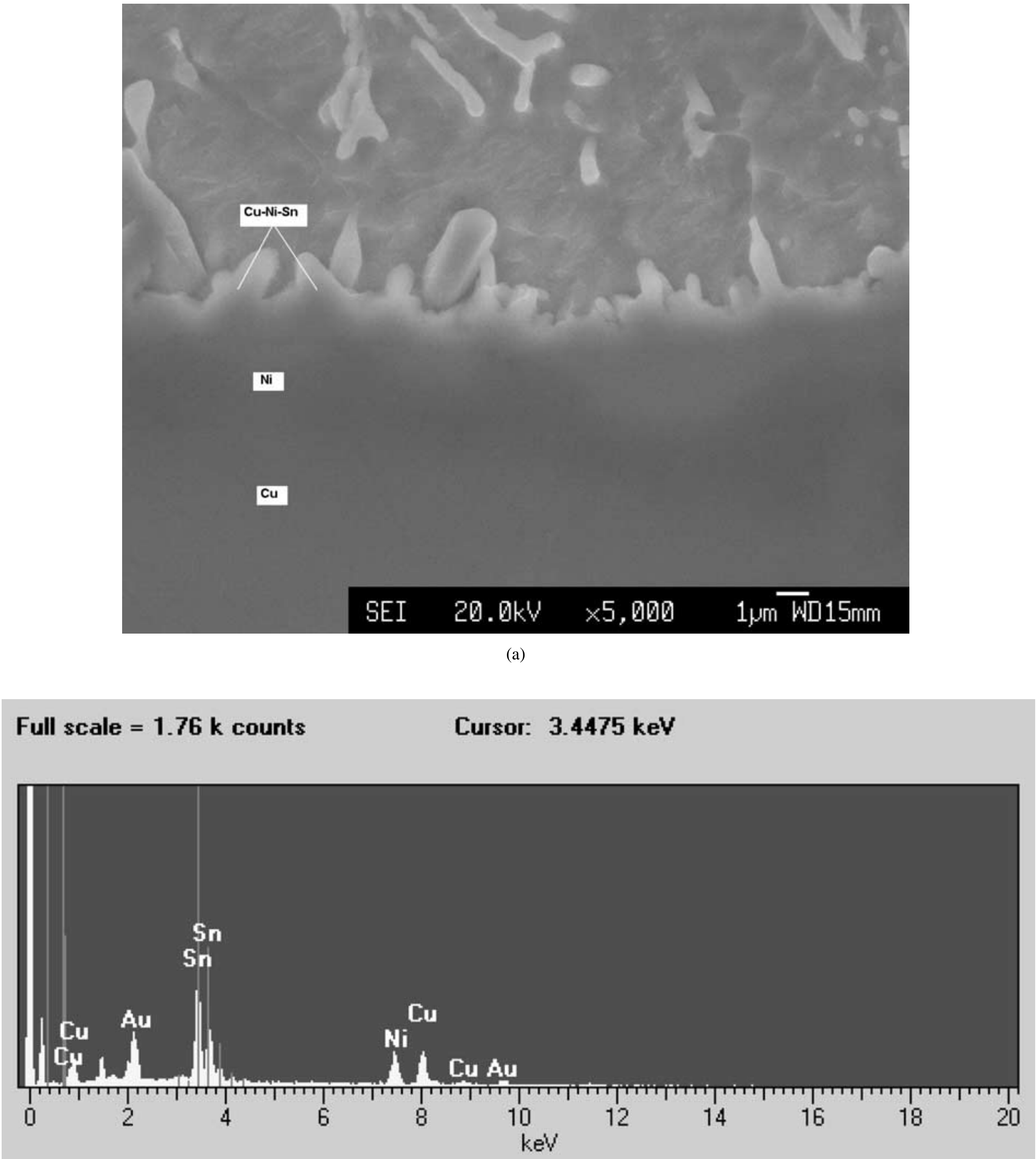
The Pb-free solder used in this work was Sn-3.5Ag-0.7Cu solder paste. The Cu sheet used as the base metal was fabricated from 99.9% pure cold rolled copper plate. The sheet was then electroless-plated with a thin layer of Ni with thickness of about 3 μm following with a thin layer of Au with thickness of about 0.2 μm. With a specially designed fixture, two pieces of Cu sheet were located in the fixture with a constant gap. The solder paste was then filled in the gap. An optimized temperature profile, with a peak temperature of 247 °C, a duration of 115 s for the temperatures above 217 °C and a total reflow time of 10.5 min, was used in this study to fabricate Cu/Sn-Ag-Cu/Cu lap-shear solder joint specimen. The specimen has a uniform rectangular solder joint with thickness of 0.2 mm. It could eliminate the strain concentration at the corner of solder joint and further avoid the crack initiation and propagation, which usually stop the growth of IMC and lead to misunderstanding of interface reaction mechanism [6]. Moreover, it could test the fatigue resistance of solder joint and correlate the growth of IMC with the fatigue life [2].

After reflow, the solder joint specimens were put into a thermal oven and isothermally aged at three temperatures of 130, 150 and 185 °C for three different time durations of 24, 72 and 120 h. The as-reflow and after-aged specimens were then cross-sectioned, molded and polished. The polished specimens were etched with 5% HCl in methanol for about 5 s in order to distinguish the growing IMC from the Sn-Ag-Cu solder layer. Finally, the etched specimens were coated with a thin layer of Au and a field-emission scanning electron microscope (FE-SEM) with an energy dispersive X-ray (EDX) system was employed to observe the IMC growth and to conduct the elementary analysis.

Fig. 1a shows typical FE-SEM micrograph of the Sn-Ag-Cu/Au/Ni/Cu system after reflow. EDX tests were performed across the Sn-Ag-Cu/Au/Ni/Cu interfaces at different positions over the system. It was found that the protective Au layer dissolved completely into the solder and formed $AuSn_4$ IMC. Meanwhile, a rough but continuous thin layer of IMC was formed at the interface between the solder joint and base metal. The IMC was identified by EDX spectrum to be $(Cu,Ni)_6Sn_5$, as shown in Fig. 1b. Typical FE-SEM micrographs, obtained from the three aging temperatures of 130, 150 and 185 °C for constant time duration of 72 h, are shown in Fig. 2. It was observed that the IMC layer grew slowly at lower aging temperatures (i.e., 130 and 150 °C) and there was no obvious change in the morphology of the layer (see Fig. 2a and b). However, the IMC layer grew significantly at high aging temperature (i.e., 185 °C) and the morphology of the layer became planar (see Fig. 2c).

Since the differences of grey-level among the solder joint, IMC and Ni layer are quite significant, ANSYS image analyzer was then employed in this work to calculate the thickness of IMC, h, by

$$h = \frac{A}{L} \times M \tag{1}$$



(a)

(b)

Figure 1 Formation of IMC in the Sn-Ag-Cu/Au/Ni/Cu system after reflow: (a) FE-SEM micrograph of solder/metal interface and (b) EDX spectrum of IMC.

where A is the area of the IMC layer over the total length L of the micrograph taken and M is the magnification used to take the micrograph. For each test condition, at least four micrographs were taken and four measurements were conducted. The average thickness of IMC for the as-reflow specimen was obtained to be 0.826 μm. By subtracting this thickness, the values of averaged growing IMC thickness for each isothermal aging condition were determined, as presented in Fig. 3. It was noted that for any given isothermal aging temperature, the growing IMC thickness had a good linear relationship with square root of aging time. The linear regression coefficients were calculated to be 0.987, 0.991 and 0.939 for the three temperatures of 130, 150 and 185 °C, respectively. The results indicated that the growth of IMC was governed by the interdiffusion process [7].

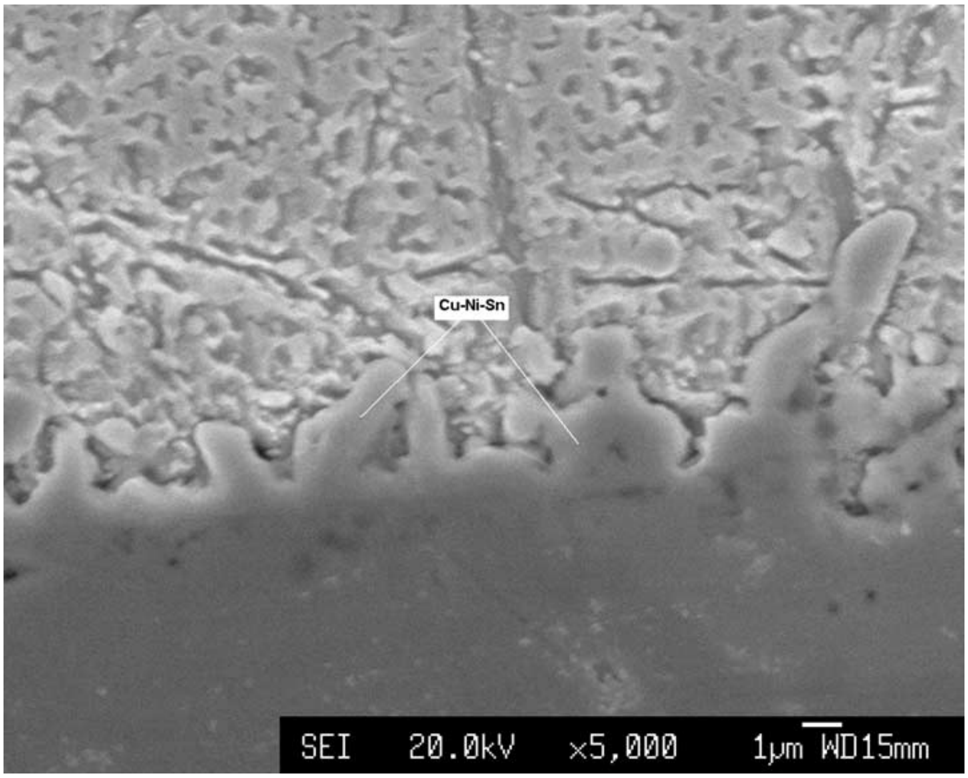
By taking the solder and nickel layer as diffusion parent phases, according to the theory of diffusion couples, when the interface reaction kinetics are governed by the interdiffusion processes, the diffusion limited IMC growth rate $\mathrm{d}h/\mathrm{d}t$ in the solid state can be determined by [7]

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{k^2}{2h} \tag{2}$$

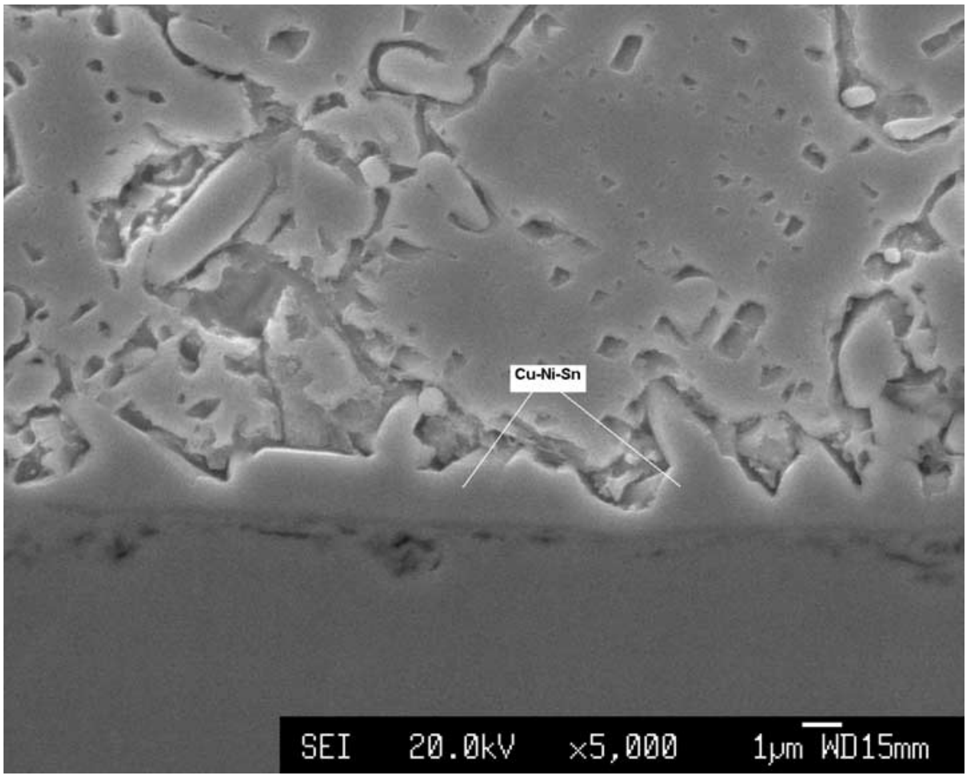
where h is the thickness of the growing IMC layer, and k^2 is the temperature dependent interface reaction constant, given by [8]

$$k^2 = 2\Delta C G_\beta D_{\text{eff}} \tag{3}$$

where ΔC is the steady-state concentration differences across the growing IMC layer, G_β is related to the concentration change across the interfaces, and D_{eff} is the effective interdiffusion coefficient, which follows the thermally activated Arrhenius diffusion

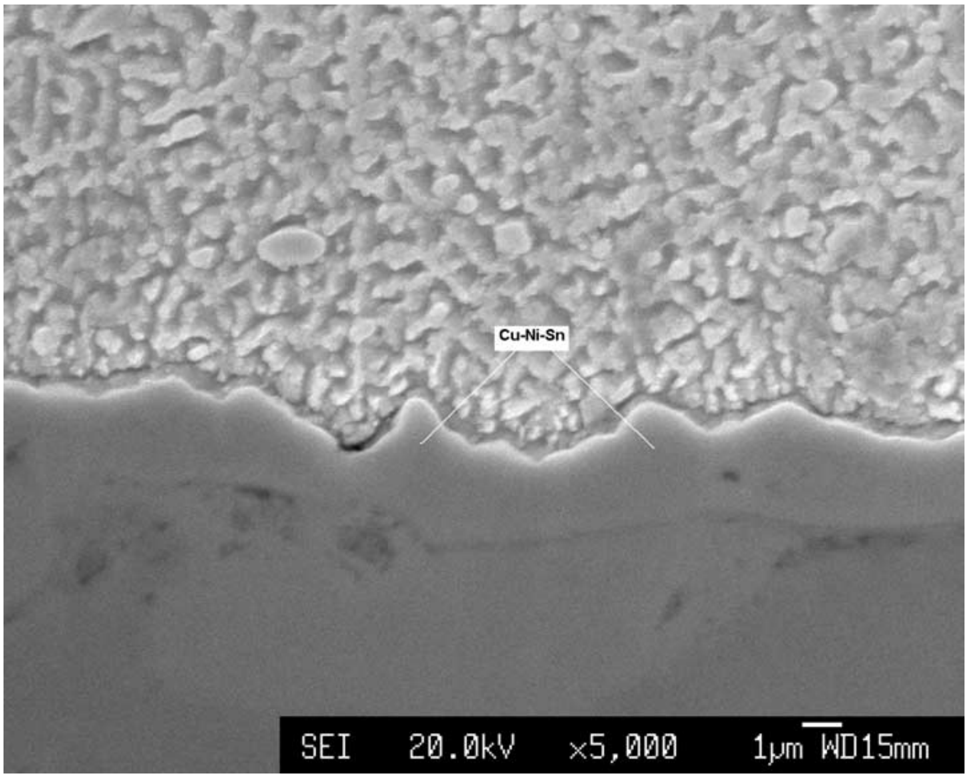


(a)



(b)

Figure 2 FE-FEM micrographs, obtained from the specimens isothermally aged at the three temperatures of (a) 130 °C, (b) 150 °C, and (c) 185 °C for constant time duration of 72 h, show the growth of IMC with increasing aging temperature. (*Continued*)



(c)

Figure 2 (*Continued*)

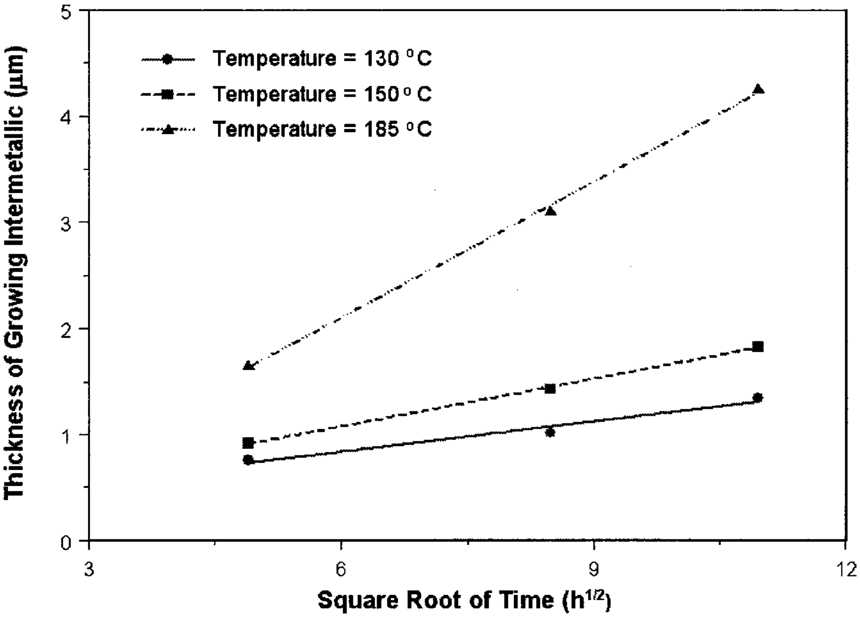


Figure 3 Thickness of growing IMC as functions of square root of time for different aging temperatures.

model [9]

$$D_{\mathrm{eff}} = D_{\mathrm{o}} \exp\left(-\frac{Q_{\mathrm{eff}}}{RT}\right) \quad (4)$$

where D_{o} is the pre-exponential constant; Q_{eff} is the effective thermal activation energy, T is the absolute temperature, and R is gas constant. For the given diffusion couples of solder/Ni, the value of Q_{eff} was then determined from the interdiffusion phases to be 64.20 KJ/mol [10, 11]. The X-ray diffraction (XRD) results showed that the concentration gradient over the IMC layer was time-independent constant [3]. Hence the concentration ratio ΔCG_{β} could be determined and the following IMC growth physical model was established by solving Equations 2–4

$$h^2 = 789 * \exp\left(-\frac{64200}{RT}\right) * t \quad (\mu\mathrm{m})^2 \quad (5)$$

It was noted that Equation 5 has the similar format of $h = \sqrt{Dt}$ to other empirical IMC growth formula

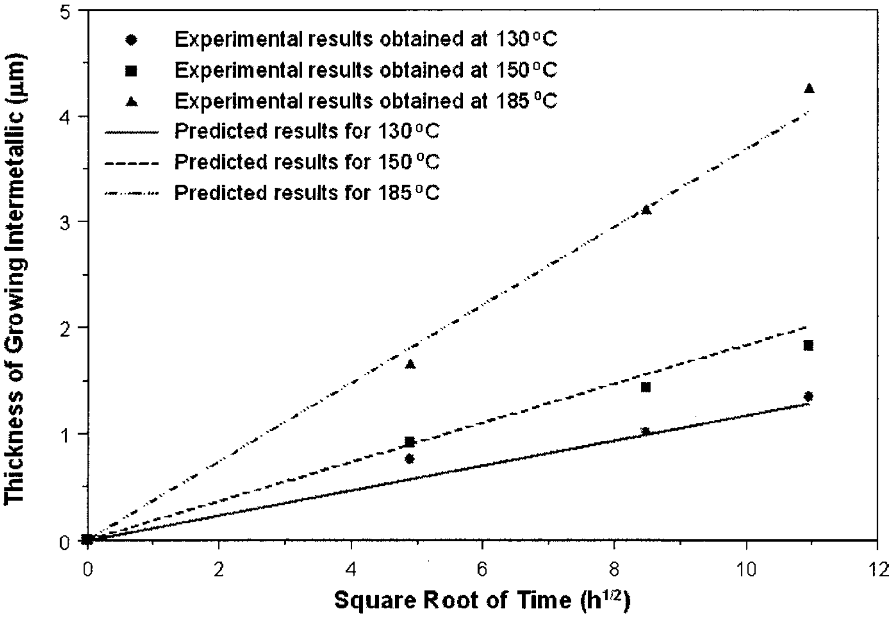


Figure 4 Comparison of growing thickness of IMC obtained from experimental measurement and predicted by the physical model.

[4, 12], where D is the diffusion coefficient. With this physical model, the growing IMC thickness was predicted for each aging condition. The results were plotted in Fig. 4. It was noted that the results were in good agreement with those obtained from the experimental tests. It meant that the interdiffusion couple theory could be used to describe the formation mechanism and the model was able to predict the growth of IMC accurately. Finally, it would be interesting to point out that the tension-shear and low cycle fatigue tests are performed on those as-reflow and isothermal aged specimens. The preliminary experimental results showed that the shear strength and fatigue resistance reduced but with a non-linear trend as the IMC thickness increased.

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