Effects of residual impurities in electroplated Cu on the Kirkendall void formation during soldering

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(Received 29 November 2007; accepted 11 February 2008; published online 5 March 2008)

Additions of bis-(sodium sulfopropyl)-disulfide (SPS) to the Cu electroplating bath strongly affected the characteristics of Kirkendall void formation when the Cu film is soldered with Sn–3.5Ag solder and subsequently aged. Voids were predominantly distributed near the Cu3Sn/Cu interface with SPS, but randomly distributed in the Cu3Sn layer without SPS. In situ Auger electron spectroscopy of voids at the Cu3Sn/Cu interface revealed surface segregation of S atoms, which came from SPS put into the bath as an additive. The S segregation to Cu3Sn/Cu interface lowers the interface energy, thereby accelerating the void nucleation. Assisted by the high surface diffusivity of Cu and the presence of excess vacancies arising from the Kirkendall effect, voids tend to localize at the interface, which would result in serious degradation of the joint reliability. © 2008 American Institute of Physics. [DOI: 10.1063/1.2890072]

Soldering is a fundamental method to join chip and substrate in flip chip or ball grid array applications, and copper metallization is widely used due to good wettability with solder materials. With the implementation of Pb-free solders, solder materials. With the implementation of Pb-free solders, metallization is widely used due to good wettability with substrate in flip chip or ball grid array applications, and copper reported.1–5 A critical issue affecting the solder joint reliability is Kirkendall void formation, which can degrade mechanical and electrical reliability seriously. In binary systems, the vacancy flux caused by the difference of intrinsic diffusivities between two species was known to be responsible for the Kirkendall void formation.6,7 However, previous results on Kirkendall void formation in Cu/Sn system are not always consistent.8–12 According to Yang and Messler,9 voids were found in Cu3Sn IMC layer of electroplated Cu/Sn–3.5Ag solder joint which was aged for 3 days at 190 °C, while voids were not found in the case of rolled Cu/Sn–3.5Ag joint even after 12 days at 190 °C. The results were ascribed to the presence of excess hydrogen introduced in the metal layers during the electroplating process, which subsequently accelerated void formation in the Cu3Sn IMC layer. On the other hand, impurity atoms in electroplated Cu film were suggested to assist the void formation,10 which was yet to be verified. In this study, electroplating conditions of Cu were systematically studied and effects of impurities in electroplated Cu, which originally came from electroplating bath, on the Kirkendall void formation are discussed.

Three types of Cu metallization, rolled Cu foil (A) and electroplated Cu films using an additive (B) and without an additive (C), were prepared and reacted with Pb-free Sn–3.5Ag solder. The electroplating bath of the B and C specimens was composed of 1M CuSO4·5H2O and 0.7M H2SO4, and contained 3.0 × 10−2M bis-(sodium sulfopropyl)-disulfide (SPS), C6H12O6S4Na2 as an additive in the case of the B specimen. For the Kirkendall void observations, solder balls (760 μm in diameter) were refloved over Cu foils or electroplated films (20 μm in thickness) at 260 °C for 1 min, and subsequently aged at 150 °C. The surface chemistry of Kirkendall voids on the Cu3Sn/Cu interface was studied by in situ Auger electron spectroscopy (AES) using B specimens with schematic diagram described in Fig. 1(a). Here, two Cu blocks were connected by Sn–Ag solder, and electroplating was conducted on the bottom Cu block before soldering. Typically, specimens were fractured under 3 × 10−9 Torr vacuum, and primary electron beam energy and current were 5 keV and 200 nA, respectively. AES depth profilings were conducted under 5 × 10−8 Torr vacuum with the primary ion beam energy of 3 keV and current density of 80 μA/cm2.

Figure 2 shows cross-sectioned images of the Cu/Sn–3.5Ag joint after thermal agings of 240 h at 150 °C. It can be seen clearly that void formation and Cu3Sn IMC growth characteristics were significantly different among specimens. In the solder joint with a Cu foil (A specimen), two layers of IMC, Cu3Sn, and Cu6Sn5 formed, but none of them showed observable amount of voids. The solder joint with an electroplated Cu film from a bath without SPS (C specimen) showed two layers of IMC and a small amount of voids was randomly distributed in the Cu3Sn layer. In contrast, a joint with an electroplated Cu film from a bath with SPS (B specimen) showed pronounced Cu3Sn5 with nominal Cu3Sn, and numerous voids were concentrated at the Cu3Sn/Cu interface. In literature, Kirkendall void formation was associated with electroplated Cu films,8–12 but the

FIG. 1. Schematic diagrams of in situ AES specimens (a) before and (b) after fracture. AES was conducted on the fracture surface of the bottom Cu block.
amount and distribution of voids differed substantially even under the same aging condition. It is interesting to note that Kirkendall voids formation at the Cu/Cu₃Sn interface suppressed the growth of Cu₃Sn layer, presumably by blocking Cu diffusion into Cu₃Sn. According to Zeng et al., Cu₂₃Sn layer converted to Cu₆Sn₅ as Cu diffusion into IMC layer.

Bright field transmission electron microscopy (TEM) images of aged Cu films (30 min at 400 °C) are presented in Fig. 3. It can be seen that aged Cu foil showed no microvoids while electroplated Cu films showed microwoids and that voids were larger and more numerous in the B specimen (with SPS) than in the C specimen. Since an excess amount of vacancies was introduced and ions of S (B specimen), C, and Cl were codeposited along with metal ions during the electroplating process, electroplated Cu films were expected to have more vacancies than Cu foil, and the impurity concentration in the film tends to increase with the SPS concentration in the electroplating bath. During subsequent reflow and thermal aging treatment, excess vacancies can form microvoids.

As mentioned in the previous section, the surface chemistry of the Cu/Cu₃Sn interface was analyzed by AES. Figure 4 shows scanning electron microscopy (SEM) micrographs of the joint cross section and fracture surface, AES spectra, and depth profilings of the as reflowed B specimen. Here, only Cu₆Sn₅ IMCs formed at the solder joint and fracture occurred along grain boundaries and cleavage planes of Cu₆Sn₅, as shown in Figs. 4(a) and 4(b). An AES spectrum out of a smooth facet in Fig. 4(b) showed only Cu and Sn peaks originating from the underlying IMC, as shown in Fig. 4(c), which was consistent with subsequent AES depth profiling of Fig. 4(d). After an isothermal aging treatment of 192 h at 150 °C after the reflow, the solder joint fractured along the Cu/Cu₃Sn interface where numerous Kirkendall voids with the diameters ranging between 0.1 and 1 μm formed as shown in Fig. 5(a). An AES spectrum out of voids and subsequent depth profiling shown in Figs. 5(b) and 5(c) clearly demonstrated S segregation on the surface of Kirkendall voids located at the Cu/Cu₃Sn interface. The amount of S atoms segregated at the Cu/Cu₃Sn interface estimated from the Auger spectra of Fig. 5(b) was ~0.26. It is interesting to find Sn segregation here, which came from Sn atoms dissolved in Cu [Note that sputtering profiles of Sn differed between Figs. 5(c) and 5(d)]. Without more data, it is difficult to know whether site competitions between S and Sn atoms occurred on the Cu₆Sn₅/Cu interface, but it remained as a possibility which needs further study.

Sulfur segregation to grain boundaries and surfaces of copper was reported at various temperatures and expected to lower the interface energy according to the Gibbs isotherm. The surface segregation studies of S showed that the kinetics were controlled by the bulk diffusion of Cu (Xₘ = ΔX/Δt), and that the surface coverage of S (Xₛ^S) was related to the bulk content of S (Xₘ^S) by the Langmuir–McLean theory

\[ \frac{X_{s}^{S}}{1 - X_{s}^{S}} = \frac{X_{m}^{S}}{1 - X_{m}^{S}} \exp \left( \frac{- \Delta G_{S}}{RT} \right). \]  

(1)

Here, Gₛ is the free energy of sulfur segregation on the copper surface, which was estimated to be 0.18–0.31 eV by Singh et al. and 1.56 eV by Militzer and Hofmann. At the same time, site competitions between S and other elements, Ag (Ref. 20) and P, respectively, on the copper surface were reported.

Surface segregation of S to the Cu/Cu₃Sn interface can affect the nucleation and growth of Kirkendall voids simultaneously. The free energy barrier for the void nucleation is given by

\[ \Delta G = \frac{4\gamma_{SV}f_{V}}{\sigma}, \]  

(2)

where σ is local stress acting at the interface during the void nucleation and f₉ is a geometric factor of void. There being
no applied stress, $\sigma$ in Eq. (2) can be taken as the residual stress in the as-plated film plus internal gas pressure $P$ coming from excess vacancies or $H_2$ gas molecules produced in the Cu film during the electroplating process.\textsuperscript{23,24} According to Lee and Park,\textsuperscript{25} high tensile in the range of 0.6 GPa was found in which tended to increase with additive concentration in the Cu film. When S segregates to the Cu/Cu$_3$Sn interface, interface energy ($\gamma_b$) will be lowered according to the Gibbs isotherm and the energy barrier for the void nucleation will be reduced thereby increasing the steady state nucleation rate of voids. Once nucleated, voids will grow by diffusion of atoms from the void surface to the Cu/Cu$_3$Sn interface driven by the stress gradient on the interface. When the surface diffusion process is much faster than the interface diffusion, the diffusive growth of equilibrium voids is directly proportional to the diffusivity of Cu atoms at the interface ($D^m_{Cu}$) which can vary orders of magnitude by the presence of adsorbents. Another complicating factor is the high concentration of vacancies near the interface due to the Kirkendall effect, which results from the difference between the Cu flux into Cu$_3$Sn and Sn flux into Cu. A continuous supply of vacancies to the interface voids by the Kirkendall effect can be an important mechanism of void growth, which can deteriorate the joint reliability seriously.

Characteristics of Kirkendall void formation at the Cu/Sn–3.5Ag joint were investigated by reacting the Pb-free solder with Cu foil (A), electroplated Cu films with (B), and without SPS (C), respectively. Kirkendall voids formed only when electroplated Cu films were used, showing that the existence of large tensile stress and excess vacancies in the films during the electroplating process was crucial. Between the two electroplated films, Kirkendall voids were more abundant and concentrated at the Cu/Cu$_3$Sn interface when SPS was added to the electroplating bath. Subsequent AES analyses of Cu/Sn–3.5Ag joints revealed S segregation to the void surface, which would lower the interface energy and thereby the critical energy for the void nucleation. In addition to the internal pressure coming from vacancies or gas produced in the Cu film during the electroplating process, void growth can be also assisted by the presence of excess vacancies created by the Kirkendall effect and by high interface diffusivity of Cu. Localized voids at the Cu/Cu$_3$Sn interface were expected to be most detrimental from the reliability standpoint.

This work was supported by the Center for Electronic Packaging Materials (ERC) of MOST/KOSEF. (Grant No. R11-2000-085-08001-0)