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Effects of residual S on Kirkendall void formation at Cu/Sn–3.5Ag solder joints

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Abstract

Solder joints of Cu/Sn–3.5Ag were prepared using Cu foil or electroplated Cu films with or without SPS additive. With a high level of SPS in the Cu electroplating bath, voids tended to localize at the Cu/Cu_3Sn interface during subsequent aging at 150 °C, which was highly detrimental to the drop impact resistance of the solder joints. In situ Auger electron spectroscopy of fractured joints revealed S segregation on the Cu/Cu_3Sn interface and void surfaces, suggesting that segregation of S to the Cu/Cu_3Sn interface lowered interface energy and thereby the free energy barrier for Kirkendall void nucleation. Once nucleated, voids can grow by local tensile stress, originating from residual stress in the film and/or the Kirkendall effect. Vacancy annihilation at the Cu/Cu_3Sn interface can induce tensile stress which drives the Kirkendall void growth.

Keywords: Soldering; Electroplating; Auger electron spectroscopy (AES); Segregation; Diffusion

1. Introduction

Soldering is a fundamental method for joining chip and substrate in flip chip or ball grid array (BGA) applications, and copper under bump metallurgy (UBM) is widely used due to the good wettability with solder materials. With the implementation of Pb-free solders, numerous works have been conducted on the UBM/Pb-free solder reaction, including the kinetics of intermetallic compound (IMC) growth, calculation of the multicomponent phase diagram, etc. [1–5]. Currently, a critical issue in the solder joint reliability is Kirkendall void formation, which can seriously degrade reliability. In binary couples, the vacancy flux caused by the difference in intrinsic diffusivities of two diffusing species was known to be responsible for Kirkendall void formation [6]. Kirkendall voids were frequently observed in Cu/Pb–Sn, Cu/Sn–Ag and Ni(P)/Sn–Ag–Cu solder joints [7–11]. However, previous results on Kirkendall void formation in Cu/Sn system were not always consistent [8–11]. Yang et al. [9] found voids in the Cu_3Sn IMC layer of an electroplated Cu/Sn–3.5Ag solder joint (aged for 3 days at 190 °C), but was unable to do so in a rolled Cu/Sn–3.5Ag joint even after prolonged aging (12 days), and assumed that excess H in the Cu film introduced during electroplating condensed into voids in Cu_3Sn. On the other hand, Laurilla et al. [10], without identifying the species responsible, suggested that impurity atoms in electroplated Cu film assisted void formation. In this study, the process parameters of Cu UBM were varied and the effects of residual impurities in electroplated Cu UBM on Kirkendall void formation were analyzed systematically.

2. Materials and methods

Four types of Cu metallizations – rolled foil (A) and electroplated films made without using SPS (B) and with SPS (C and D) – were prepared over FR4 PCB and reacted with Pb-free Sn–3.5Ag solder. The electroplating baths contained 1 M $CuSO_4{\cdot}5H_2O$, 0.7 M H_2SO_4 and

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varying amounts of SPS (bis-sodium sulfopropyldisulfide, $C_6H_{12}O_6S_4Na_2$): 1.5×10^{-5} and 3.0×10^{-5} M for specimens C and D, respectively, as shown in Table 1. The chemical composition of the Cu films (A, B and D) was analyzed using secondary ion mass spectroscopy (SIMS) and the results are listed in Table 1. It can be seen that the S content of the film increased with SPS (up to 17 ppm in the D film), while the C content remained unchanged (~23 ppm). Then, solder balls with the diameter of 760 μm were reflowed over Cu foil or electroplated films (20 μm in thickness) for 1 min at 260 °C and subsequently aged at 150 °C for further observations of IMC and Kirkendall voiding by scanning electron microscopy (SEM). The surface chemistry of Kirkendall voids at the Cu/Cu_3Sn interface was studied by in situ Auger electron spectroscopy (AES) using specimen D. Here, two Cu blocks, one of which was pre-electroplated with D film (20 μm), were immersed in a liquid Sn–3.5Ag solder bath (260 °C) for 5 min before air cooling. Typically, specimens were fractured under 3×10^{-9} Torr vacuum and the bottom Cu block was analyzed as described in Ref. [12]. The effects of Kirkendall voids on the solder joint reliability were evaluated by conducting drop impact tests using specimens where two printed circuit boards (PCBs) were joined by 12 Sn–3.5Ag solder balls. Experimental details of SEM, AES and drop tests are provided in the parallel paper [13].

3. Results

3.1. TEM characterization of Cu films

Bright-field transmission electron microscopy (TEM) images of aged Cu films (30 min at 400 °C), unreacted with solder, are presented in Fig. 1. It can be seen that aged Cu foil showed no microvoids, whereas electroplated Cu films showed microvoids, and that voids were larger and more numerous in specimen D with a high level of SPS than in the SPS-free specimen B. Thus, excess point defects such as vacancies and ions of S (D specimen), C and Cl, introduced into Cu film during electroplating, assisted homogeneous nucleation of voids [14,15]. SIMS analyses of electroplated Cu films showed only C and S peaks, and the amount of residual S in the film increased with SPS content of the bath as shown in Table 1.

Table 1
Characterizations of Cu UBMs, SPS content in the electroplating bath, results of chemical analyses by SIMS

Specimen code	UBM type	SPS content ($\times 10^{-5}$ M)	S content (ppm)	C content (ppm)
A	Cu foil	–	0.18	11.2
B	EP Cu	0	0.31	22.3
C	EP Cu	1.5	–	–
D	EP Cu	3.0	16.8	23.8

EP, electroplated.

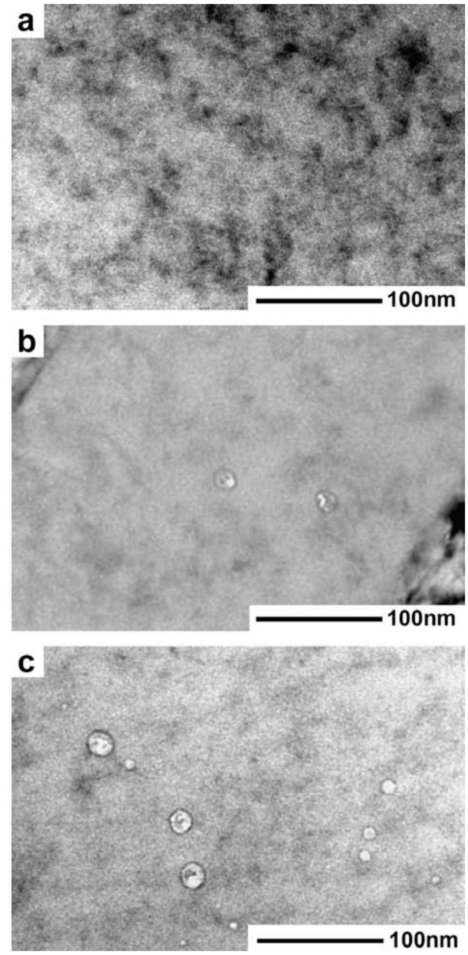

Fig. 1. TEM images of various Cu films aged for 30 min at 400 °C: (a) Cu foil (A), (b) electroplated Cu film without SPS (B), and (c) with SPS (D).

3.2. Microstructures of solder joints

3.2.1. As-reflowed specimens

When molten Sn–3.5Ag solder contacted the Cu pad, Cu_6Sn_5 IMC started to form at the interface right away, and cross-sectional SEM micrographs of the Cu/Sn–Ag joints after a reflow of 1 min at 260 °C are presented in Fig. 2. Only Cu_6Sn_5 was observed at the interface without Kirkendall voids in the IMC layer of all specimens regardless of the film fabrication methods.

3.2.2. Aged specimens: 240 h at 150 °C

After thermal aging of the solder joint A made of Cu foil, two void-free IMC layers, Cu_6Sn_5 and Cu_3Sn, developed as shown in Fig. 3a, and the initially scallop-shaped Cu_6Sn_5 IMC became flatter. In contrast, electroplated films all contained Kirkendall voids, suggesting that these are related to the electroplating process. Note subtle differences in the location of voids and characteristics of Cu_3Sn growth between joints C and D with varying SPS content as shown in Fig. 3b–d. When Cu film was electroplated without using SPS (B specimen), voids formed uniformly in the Cu_3Sn phase, but tended to localize at the Cu/Cu_3Sn