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Solid-state interfacial reactions of Sn and Sn–Ag–Cu solders with an electroless Co(P) layer deposited on a Cu substrate

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ABSTRACT

In this study, an electroless Co(P) layer with 5 wt.% P was deposited as a diffusion barrier to prevent the rapid reaction of Cu with Pb-free solders. The electroless Co(P) layer exhibited a mixed amorphous/nanocrystalline structure. Solid-state interfacial reactions of a 6-μm-thick Co(P) layer deposited on a Cu substrate with pure Sn and Sn–3.5Ag–0.7Cu (wt.%) solders were examined at temperatures of 160, 180, and 200 °C. For reactions with Sn, the primary reaction product was identified as a metastable $CoSn_4$ phase. In addition, a thinner uniform layer of Co–Sn–P phase with a nanocrystalline structure was formed at the $CoSn_4$/Co(P) interface, which was likely a mixed phase of $CoSn_3$, Co_2P, and Sn_4P_3. Notably, the growth of the $CoSn_4$ layer was linearly proportional to the aging time, implying that it was reaction-limited in the initial stage. Moreover, the growth kinetics of the Sn/Co(P)/Cu interfacial reactions were systematically studied. The growth rate constants and activation energy were determined. Furthermore, the reaction phases and microstructure in the reactions with the Sn–3.5Ag–0.7Cu solder were clearly different from those with Sn. The thin $(Cu,Co)_6Sn_5$ layer was first formed at the interface and the $CoSn_3$ growth was considerably suppressed. After a specific aging period, the dominant phase changed to a $CoSn_3$ phase with a fast growth rate.

1. Introduction

Electroless plating processes have been extensively applied for surface finishing in electronic packaging industries. Compared with electroplating, electroless plating has the advantage of forming deposits with a uniform thickness over all surfaces. The most prevalent example of electroless plating is electroless Ni plating (i.e., electroless nickel/immersion gold (ENIG) plating), which is extensively used as a diffusion barrier for Cu pads [1,2]. To fabricate solder joints for electrical and mechanical interconnections, Pb-free solders are reflowed in contact with ENIG-finished Cu pads. Eutectic Sn–Ag–Cu or near-eutectic alloys are the most prominent and commonly used Pb-free solders [3,4].

Solder joining technology is used in various packaging applications such as ball grid array and flip chip technology. Interfacial reactions occur between solders and ENIG metallization or Cu pads during soldering and product use stage, resulting in an intermetallic compound (IMC) growth at the interface [3–8]. Nevertheless, forming excessive IMCs deteriorates the mechanical properties of solder joints and even causes brittle fracture. Moreover, when electric currents pass through solder joints, electromigration (EM) may cause severe damage to such joints because of massive atomic transport. Void formation and under-bump metallization (UBM) consumption are typical EM failures in flip-chip solder joints [9–11]. Cu and Ni UBMs inherently incur EM-induced dissolution, particularly Cu, leading to substantial substrate consumption and considerable amounts of IMC formation in solders [12–15].

Compared with Cu and Ni, Co or Co-based alloys, which are potential material candidates for diffusion barriers, have been demonstrated to possess excellent resistance to EM-induced dissolution [16–19]. Fundamental information on the interfacial reactions between Co-based alloys and Pb-free solders is crucial for evaluating the reliability of solder joints. Recently, studies have been conducted on IMC formation and growth between Co and Pb-free solders [19–23]. In addition, electroless plating techniques for Co and its alloys have been developed [24–30]. For electroless plating processes, sodium hypophosphite (NaH_2PO_2) is typically used as a reducing agent. Thus, P and Co are co-deposited in electroless Co(P) layers. Lu et al. [26] characterized that the interfacial reactions between Sn–Ag–Cu solder and three types of electroplated Co(P) UBMs involving various microstructures by tuning the P contents, ranging from 2.7 wt.% (nanocrystalline) to 9.7 wt.%

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(amorphous). Our recent study [27] revealed that in Sn/Co(P) reactions, the P content considerably influenced the formed IMC phases. The $CoSn_3$ phase was significantly suppressed in the Sn/Co-0.7 wt.%P reaction and the $CoSn_4$ phase was formed in the Sn/Co-6 wt.%P reaction.

This study investigated IMC growths and microstructure evolutions in solid-state interfacial reactions of Sn and Sn–Ag–Cu solders with an electroless Co(P) layer on a Cu substrate. An electroless Co(P) layer containing 5 wt.% P was deposited on the Cu substrate and the deposited substrate was soldered with pure Sn and Sn–Ag–Cu solders. In addition, the IMC growth kinetics were thoroughly studied. Different Sn–Co IMCs were formed at the interfaces with the Sn and Sn–Ag–Cu solders. A possible formation mechanism was also proposed.

2. Experimental procedures

Cu sheets with 0.5 mm in thickness were prepared as substrate pieces (5 mm × 10 mm) for electroless Co(P) plating. Prior to electroless plating, Cu substrates were mechanically polished and ultrasonically cleaned in deionized (DI) water. They were sensitized in a $SnCl_2$ solution for 1.5 min, and followed by activating in a $PdCl_2$ solution for 2 min. Electroless Co(P) plating process was conducted at 90 °C in a electrolytic bath (100 ml), consisting of 0.12 M $CoSO_4\cdot 7H_2O$ (Co source), 0.38 M $NaH_2PO_2\cdot H_2O$ (reducing agent) and 0.5 M H_3BO_3, 0.53 M $(NH_3)_2SO_4$, and 0.53 M $Na_3C_6H_5O_7\cdot 2H_2O$ (complexing agent). The pH value of the plating bath was adjusted at 7.5 with a 3 M NaOH solution. It was performed for a period of 4 h and the thickness of the Co(P) layer was controlled to be about 6 μm, which was similar to the thickness of the electroless Ni coating layer in ENIG process.

1 g of pure Sn or Sn–3.5Ag–0.7Cu (wt.%) solder was prepared with the respective elements (99.99% purity). The Sn–Ag–Cu alloy was homogenized in a vacuum of below 10^{-2} torr at 700 °C for 3 days and then quenched in water. The solder was placed in a quartz tube crucible (6 mm inner diameter and 15 mm length) and it was melted in a box furnace at 260 °C. The prepared Co(P)/Cu substrate was cleaned and rinsed with mild activated rosin flux. It was immersed into the molten solder and quenched immediately. The as-joined specimen was cut into several smaller pieces (2 mm thick). Subsequently, they were annealed in a furnace for a predetermined duration of time. The aging temperature was set at 160, 180 and 200 °C, respectively. After heat treatment, the specimens were mounted in epoxy, cross-sectioned, ground and polished. The solder was slightly etched with a Sn-etching solution to clearly reveal interfacial microstructure.

The interfacial zone of the specimen was observed using scanning electron microscopy (SEM) with backscattered electron imaging (BEI). The composition of the formed IMC layer was analyzed using electron probe microanalysis (EPMA, JEOL JXA-8200). Grazing incidence X-ray diffraction (GIXRD, Bruker D8) with Cu K_α radiation was used to identify the deposited Co(P) layer and the interfacial IMCs. The thickness of the IMC layer was measured from SEM micrographs with image analysis software. The average thickness was statistically obtained from the data of at least seven measurements. Additionally, transmission electron microscope (TEM, JEOL JEM-2100F) was also utilized for examination. The dual beam-focused ion beam microscopy (DB-FIB, FEI Quanta 3D FEG) was used to prepare TEM samples. A thin Pt layer was deposited on the surface of the sample as a protection layer during FIB milling. The cross-sectional microstructure of the Co(P) layer and the formed IMCs were also characterized using FIB. The grain structure can be distinctly revealed in ion-induced secondary electron (ISE) mode due to different crystal orientations.

3. Results and discussion

3.1. Sn/Co(P)/Cu interfacial reaction

Fig. 1(a) shows a FIB cross-sectional image of the 6-μm-thick Co(P) layer deposited on the Cu substrate. The electroless Co(P) layer clearly exhibited a uniform fine-grained structure with grain sizes of approximately 100–200 nm. The average composition of the Co(P) layer determined using EPMA was Co-9.2 at.%P-1.1 at.%Cu (Co-5.1 wt.%P-1.2 wt.%Cu). The minor Cu content is attributed to the dissolution of the Cu substrate in the electroless plating bath at the initial deposition stage. The deposited sample was also characterized by XRD. However, no sharp characteristic diffraction peaks were detected, except for a single broad peak of 2θ between 40° and 50°, suggesting that the Co(P) deposit was amorphous.

The microstructure of the as-deposited Co(P) layer was further characterized by TEM. Fig. 1(b) illustrated a bright field TEM image of the Co(P) layer, also indicating that it consisted of fine-grains. Fig. 1(c) depicts the selected area electron diffraction (SAED) pattern of the layer; a typical halo of an amorphous phase was observed. In addition, some diffraction spots were observed, which can correspond to the hcp-Co phase. These analyzed results indicated that the Co(P) layer had a mixed structure of amorphous and nanocrystalline phases. Furthermore, a high-resolution TEM (HRTEM) observation revealed that most grains had amorphous or low-crystallinity phases with short-range ordering. The HRTEM image (Fig. 1(d)) was captured from a small selected region with high crystallinity, as indicated by a dashed circle in Fig. 1(b). A layered lattice structure was clearly visible with an interplanar spacing of 0.217 nm, corresponding to the distance between (100) planes of hcp-Co. Accordingly, the Co(P) layer prepared in this study was confirmed to exhibit a mixed amorphous/nanocrystalline structure.

The interfacial reaction of Sn with the Co(P) layer deposited on the Cu substrate was conducted at 180 °C. Fig. 2(a)–(d) show the interfacial microstructures observed after aging for 3, 12, 24, and 36 h, respectively. After aging for 3 h, one bright IMC layer with a thickness of approximately 4.5 μm was formed at the interface. When the aging time was prolonged to 12 h, in addition to the bright phase, one thin and uniform layer of dark phase was observed at the Co(P) side. The EPMA analysis revealed that the bright phase was composed of Sn-19.4 at.%Co-0.3 at.%Cu, suggesting it to be the $CoSn_4$ phase according to the stoichiometric ratio. However, the $CoSn_4$ phase was not an equilibrium phase according to the Sn–Co phase diagram [31]. Notably, no P content was detected. By contrast, minor Cu content (0.3 at.%) was present, which could be attributed to the aforementioned fact that a little amount of Cu was unintentionally doped in the Co(P) layer during the electroless plating process. In addition, the composition of the dark phase was determined to be Sn-48.3 at.%Co-17.3 at.%P, which was presumed to be the Co–Sn–P phase layer according to the prior studies [26,27]. The P atoms were inherently inert and immobile. When the Co of the Co(P) layer reacted with Sn, P atoms were accumulated at the interface, resulting in the formation of the Co–Sn–P phase layer with high P content. Furthermore, it can be noted that a thin darker IMC layer, i.e., Co–Sn–P layer, was formed at the $CoSn_4$/Co(P) after aging for 3 h (Fig. 2(a)). This indicated that the formation of the Co–Sn–P layer depends on the P content of the Co(P) layer and was not related to the deposited thickness and the reaction time.

XRD characterization was further conducted to identify the $CoSn_4$ phase. Fig. 3(a) depicts the GIXRD pattern obtained from the reaction couple after aging at 180 °C for 12 h and then completely etching out the Sn solder to expose the IMC layer. The crystal structure of the metastable $CoSn_4$ phase was identified as the