Suppression of Interdiffusion in Copper/Tin Thin Films

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Copper/tin thin film couples are often used in microelectronics assembly as device backside coatings for die attach and also as circuit board coatings to maintain solderability. In this article, we report a temperature treatment that slows down the room temperature reaction of these two metals and therefore can extend the storage life of the devices significantly. It was found by x-ray diffraction that during an anneal at 473 K for 1 minute a thin layer of the Cu/Sn ε-phase is formed which introduces an additional interface to the system. The diffusion suppressing effect of this treatment was studied by focused ion beam microscopy.

1. Introduction

Tin coatings on copper are widely used in microelectronics as surface finishes of circuit boards (Ref 1) as well as wafer backside metallization for diffusion soldering (Ref 2). In case of the former, the purpose of the tin coating of the copper pads is to promote component soldering by preventing copper oxidation. For the latter, copper and tin are deposited directly on the backside of the wafer to serve as a solder material for die attach. Due to governmental regulations (Ref 3) the previously used lead/tin alloys have to be replaced by pure tin which is electrochemically deposited directly on copper. A problem that arises with the omission of lead is the faster diffusivity of copper in pure tin. The layer thickness of tin can be reduced significantly by diffusion processes (Ref 4). Even at room temperature, copper diffuses into the Sn layer (Ref 5). At 300 K, the diffusion coefficient of Cu along the crystalline axes of tin is 5×10^{-9} and 2×10^{-6} cm^2/s, respectively (Ref 6). The rapid diffusion between those two metals occurs by an interstitial mechanism (Ref 7) and the growth speed of the intermetallic zone depends on temperature during storage and processing of the device. It was found that that two different intermetallic compounds (IMC) form at the interface (Ref 8, 9): On the Cu side the Cu-rich Cu_3Sn phase grows in a uniform layer, whereas the Sn-rich Cu_6Sn_5 phase on the Sn side has scallop-type morphology (Ref 10). These IMCs have a higher melting point than pure tin and the material therefore does not melt during soldering, which means that it is not available as solder material. It was found empirically that for good wetting of a circuit board surface, at least 0.3 μm of pure tin are necessary (Ref 4). In diffusion soldering these high melting point IMCs can act as a solid spacer during die attach. Due to a certain roughness of the leadframe these spacers can prevent the liquid solder from touching the contact surface, which can result in voids in the joint and failure of the device. In this study, an easily implemented annealing step is introduced to efficiently slow down the undesired Cu/Sn interdiffusion. The microstructure of the Cu/Sn bilayers, annealed and unannealed, was studied by x-ray diffraction (XRD) phase analysis, XRD texture measurements, and focused ion beam (FIB) cross-sectional micrographs.

2. Sample Preparation

The Cu was electrodeposited on a silver-coated silicon wafer from industrial electrolytes at room temperature and a current density of 3 A/dm^2. This corresponds to a deposition rate of 0.66 μm/min. Tin was deposited at a current density of 2 A/dm^2 and a rate of 1 μm/min. For the characterization of the IMCs at the interface by XRD, a 1 μm layer Sn film was deposited on a 5 μm thick layer of copper. This way the x-rays could penetrate to the interface. The FIB cross sections were done on a specimen with a 1.8 μm layer of Cu and a 2.4 μm layer of Sn. For the texture measurements of copper, only a 1 μm thick layer of Cu was deposited without the Sn on top. The annealing was done in an industrial oven under N$_2$-atmosphere for 1 min at 473 K within 24 h after electrodeposition.

2.1 Focused Ion Beam

The layer thickness of the IMCs was measured in a FEI Vectra 200 FIB microscope. The FIB was chosen over an electron microscope for its superior orientation contrast. For FIB imaging the silicon wafer was broken along a preferred orientation to produce a smooth edge. The surface was thereafter polished with the gallium ion beam. This way the image could be taken parallel to the surface without distortions. The thicknesses were measured at multiple positions on every sample with digital image processing software at magnifications of 20,000× or 35,000×.

Some representative micrographs are shown in Fig. 1. Twenty four hours after deposition, some grains of Cu_6Sn_5

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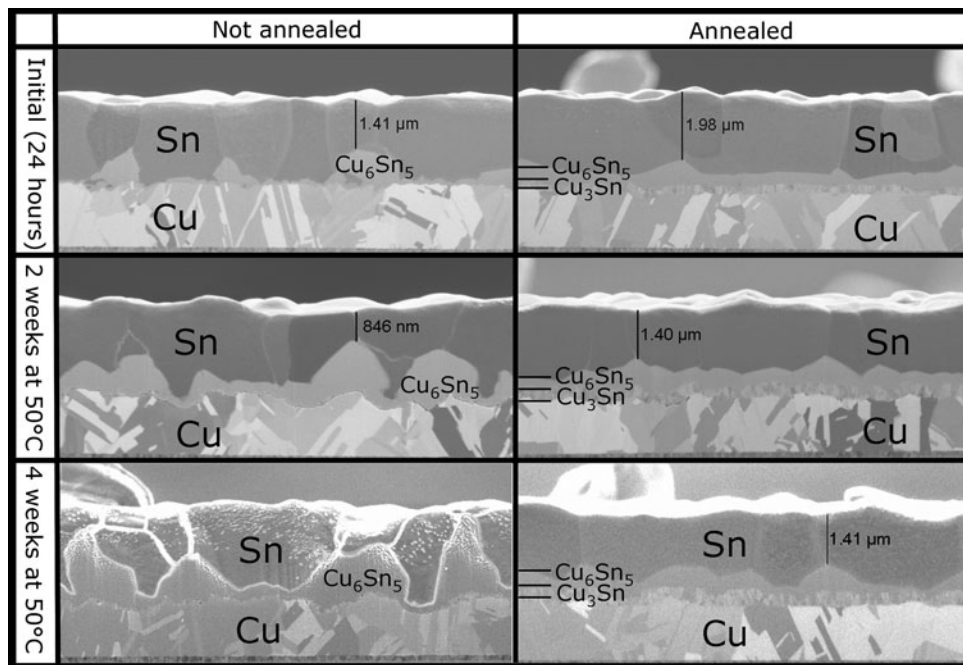
Fig. 1 FIB micrographs of Cu/Sn-couples on an Ag seed layer. The left column shows the evolution of unannealed, as deposited, couples and the right column shows couples that were annealed at 473 K for 1 min. The top row shows the couples after 24 h. In the unannealed sample, the Cu_6Sn_5 phase is present and extends mainly along the grain boundaries into the Sn. The middle row shows couples after 2 weeks of storage at 323 K. The bottom row shows couples after 4 weeks of storage at 323 K. After 4 weeks, the Cu_6Sn_5 phase penetrates the Sn layer reaching the surface of the unannealed sample. The annealing produces a planar layer of Cu_3Sn at the Cu/Sn interface which inhibits the diffusion of Cu into the Sn. Consequently, the annealed sample is nearly unchanged after 4 weeks of storage at 323 K

were observed along the grain boundaries of tin. This inhomogeneous growth can be explained by the fact that mass transport at moderate temperatures can be several orders of magnitude faster along grain boundaries than through the lattice (Ref 11).

When the specimen was annealed at 473 K for 1 min, there was enough thermal energy for both phases, Cu_3Sn and Cu_6Sn_5, to form. A 0.3 μm thick layer of the Cu-rich Cu_3Sn phase formed on the Cu-side and a 0.4 μm thick layer of the Sn-rich Cu_6Sn_5 phase formed on the Sn-side. At 473 K, the process is dominated by bulk diffusion rather than grain boundary diffusion, thus the IMCs grow in a more homogeneous manner.

Annealed and unannealed samples were stored at 323 K, a temperature that was low enough to prohibit the formation of the Cu_3Sn phase, but high enough to speed up diffusion (Ref 12). After 2 weeks, the Cu_6Sn_5 phase had grown significantly along the grain boundaries of tin in the unannealed sample, nearly reaching the surface. However in the annealed sample, the thicknesses of the IMC layers only increased marginally. The continuous Cu_3Sn layer blocks the diffusion of Cu along the grain boundaries of Sn thus inhibiting the aging of the Cu/Sn couple.

After 4 weeks of storage, Cu_6Sn_5 grains reached the surface in parts of the unannealed sample. This leaves insufficient pure tin for a proper wetting of the contact surface for diffusion soldering. The annealed sample, on the other hand, was hardly affected even after 6 weeks of storage at 323 K. The Cu_3Sn layer produced by the short anneal is an effective diffusion inhibitor.

2.2 X-ray Diffraction

Phase composition and crystalline texture of the annealed and unannealed samples were determined by XRD. The analyses were performed within 7 days after deposition. The identification of the different phases was done in a Siemens D501 powder diffractometer in coupled Bragg-Brentano reflection mode with Cu Kα radiation. The x-ray beam passed through a graphite monochromator on the secondary side. As a detector, a scintillation counter with an entrance angle of 0.6° was used. The specimens were mounted symmetrically to the incident and to the diffracted beam. This method detects only (hkl) reflections of crystal planes parallel to the surface. The qualitative phase analysis was performed, using data from the Powder Diffraction File (International Center for Diffraction Data) and the Inorganic Crystal Structure Database (Fachinformationszentrum Karlsruhe).

The results of the XRD phase analysis are shown in Fig. 2. For both the annealed and the unannealed samples, the hexagonal Cu_6Sn_5 phase was observed. The orthorhombic Cu_3Sn phase was only present in the annealed sample. The Cu-rich Cu_3Sn phase was found to form only in bimetallic Cu-Sn films annealed at more than 330 K, which is in very good agreement with the observations made in the FIB micrographs (Ref 12).

The crystalline texture of the electrodeposited Cu and Sn layers was examined by XRD texture measurements. The pole figures were obtained using a Philips X'Pert System with Cr Kα radiation and a graphite monochromator on the secondary side. The defocusing of the pole figures was corrected via powder normals. For Cu, only the 200 reflex was scanned, whereas for Sn the recording of the 200 and the 211 reflex was necessary to clearly assign the texture. Representative pole figures are shown in Fig. 3. It was found that the annealing of the samples did not change the texture of the metal films, so this influence could be ruled out for being responsible for the observed
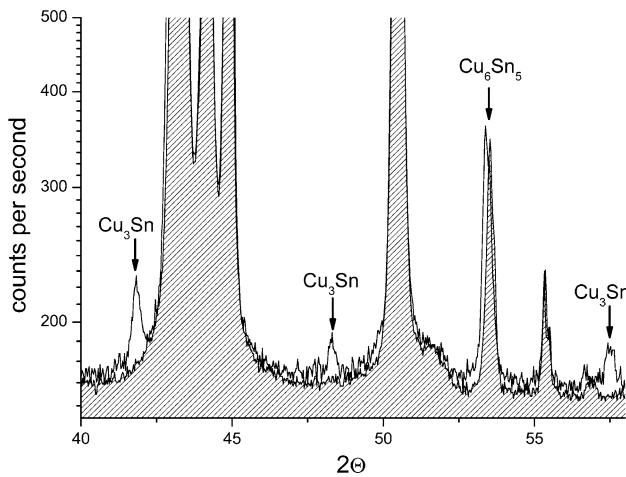
Fig. 2 Detail of the specular x-ray diffraction scan of the unannealed (shaded) and the annealed specimen. The annealed sample has peaks at the predicted positions for Cu_3Sn and Cu_6Sn_5, whereas for the unannealed sample the Cu_3Sn peak is missing

suppression of interdiffusion. The electrodeposited Cu has no preferred orientation of the grains. The tin grows on this substrate with a very well-defined 112 texture, i.e., the majority of the tin grains are oriented with their ⟨112⟩ direction perpendicular to the surface.

3. Discussion

Of the two intermetallic phases of copper and tin that are stable at room temperature only the Sn-rich phase (Cu_6Sn_5) can be formed in binary diffusion couples at temperatures below 330 K. The formation of the Cu_3Sn phase is inhibited by a nucleation barrier that has to be overcome by a sufficient thermal budget (Ref 13). By a short anneal above this critical temperature a thin layer of this Cu-rich phase is formed, introducing an additional interface. In the untreated samples, there is only one layer of intermetallic and thus two interfaces present, whereas there are two compounds and three interfaces in the annealed system. Each interface is representing a reaction barrier that has to be overcome to form the intermetallic compound (Ref 14). The effective reaction barrier of the system is just the sum of the single reaction barriers at the interfaces. Thus the reaction rate is reduced by the anneal.

4. Conclusion

The effect of an annealing step on the growth dynamics of IMCs in Cu/Sn couples was investigated by x-ray diffraction and FIB micrographs.

By heating Cu/Sn couples to 473 K for 1 min, a layer of the Cu-rich Cu_3Sn phase is formed at the Cu/Sn interface, leaving the fiber texture of the films unaffected. This layer introduces an additional interface to the system, thus increasing the effective reaction barrier. The treatment slows down the growth of the undesirable Cu_6Sn_5 phase, which can extend the storage life time of effected devices significantly.
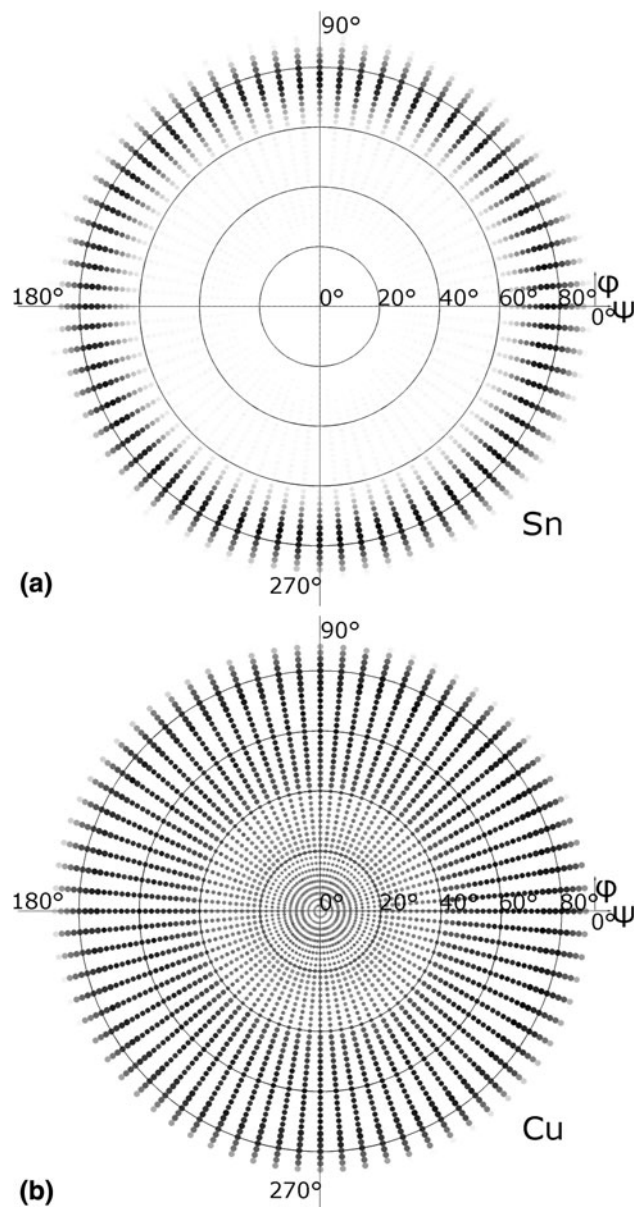

Fig. 3 Pole figures of the 200 reflex of electrochemically deposited Sn (a) and Cu (b). The grayscale is proportional to the intensity. Cu shows no preferred crystal orientation, whereas Sn grains grow preferentially with the ⟨112⟩ direction perpendicular to the surface

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