

Growth behavior of compound layers in Sn/Cu/Sn diffusion couples during annealing at 433–473 K

T. Takenaka^a, S. Kano^a, M. Kajihara^{b,*}, N. Kurokawa^c, K. Sakamoto^c

^a Graduate School, Tokyo Institute of Technology, Yokohama 226-8502, Japan

^b Department of Materials Science and Engineering, Tokyo Institute of Technology, Nagatsuta 4259-G3-21, Midori-ku, Yokohama 226-8502, Japan

^c Tyco Electronics AMP Co., Ltd., Kawasaki 214-8533, Japan

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Abstract

The kinetics of the reactive diffusion between Cu and Sn at solid-state temperatures was experimentally examined using Sn/Cu/Sn diffusion couples prepared by a diffusion bonding technique. The diffusion couples were isothermally annealed at temperatures between $T=433$ and 473 K for various times in an oil bath with silicone oil. Due to annealing, compound layers consisting of Cu_3Sn and Cu_6Sn_5 are formed at the Cu/Sn interface. In most of the annealed diffusion couples, grains of CuSnO exist in the Cu_6Sn_5 layer. However, the CuSnO grain scarcely influences the growth behavior of the compound layers. The thickness of the Cu_6Sn_5 layer is around twice greater than that of the Cu_3Sn layer. The difference between their thicknesses slightly increases with increasing annealing temperature. At a constant temperature, the ratio of the thicknesses remains constant independent of the annealing time. The total thickness l of the compound layers monotonically increases with increasing annealing time t according to equation $l=k(t/t_0)^n$, where t_0 is unit time, 1 s. The observations provide $n=0.37$, 0.43 and 0.50 at $T=433$, 453 and 473 K, respectively. The value $n=0.5$ indicates that the volume diffusion is the rate-controlling process for the reactive diffusion at $T=473$ K. As the annealing temperature decreases, the grain boundary diffusion will contribute to the rate-controlling process. Thus, the values of n smaller than 0.5 yield that there is the contribution of the grain boundary diffusion and the grain growth occurs at certain rates at $T=433$ and 453 K. Since the ratio between the thicknesses of the compound layers is kept constant during isothermal annealing, the same rate-controlling process is expected to work in both compound layers.

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1. Introduction

Copper-base alloys are widely used as conductor materials owing to high electrical conductivity. When the Cu-base conductor alloy is interconnected with a Sn-base solder alloy with or without Pb, binary Cu–Sn intermetallic compounds are produced at the interface between the conductor and solder alloys during soldering and then gradually grows due to heating under usual energization conditions [1–9]. The Cu–Sn compounds are very brittle and possess high electrical resistivities. Hence, such growth of the compounds edgingly

deteriorates the electrical and mechanical properties of the interconnection.

The reactive diffusion between Cu and Sn was experimentally studied by Vianco et al. [7] using Cu/Sn diffusion couples. In their experiment, pure Cu specimens were soldered with pure Sn at about 540 K for 5 s and then annealed at temperatures between $T=343$ and 478 K for various times. Here, T is the annealing temperature. At the Cu/Sn interface in the diffusion couple, a Cu_6Sn_5 compound layer was observed after soldering, and then a Cu_3Sn compound layer as well as the Cu_6Sn_5 layer was recognized after annealing at $T=373$ – 478 K. The annealing time dependence of the total thickness of the compound layers was determined at $T=408$ – 478 K but could not be measured reliably due to

* Corresponding author. Tel.: +81 45 924 5635; fax: +81 45 924 5173.
E-mail address: kajihara@materia.titech.ac.jp (M. Kajihara).

small absolute values of the total thickness at $T = 373$ K. If the volume diffusion of the constituent elements in each phase is the rate-controlling process of the reactive diffusion, the total thickness is mathematically described as a power function of the annealing time with an exponent of 0.5. However, their experimental results indicate that the exponent is slightly smaller than 0.5 at $T = 443$ and 478 K. Such small values of the exponent imply that the grain boundary diffusion contributes to the rate-controlling process.

Onishi and Fujibuchi [10] also observed the reactive diffusion between Cu and Sn experimentally. In that experiment, Cu/Sn diffusion couples were prepared by a diffusion bonding technique and then annealed at $T = 463$ – 493 K up to 900 h in an argon gas. After annealing, the Cu_3Sn and Cu_6Sn_5 compound layers were discerned to form at the Cu/Sn interface. Their observations indicate that the exponent of the power function is equal to 0.5 and thus the volume diffusion is the rate-controlling process. Therefore, there exists a difference between the rate-controlling processes deduced from the observations by Vianco et al. [7] and those by Onishi and Fujibuchi [10]. In the diffusion couple prepared by the soldering technique, the Cu_6Sn_5 compound layer with a certain thickness exists even before annealing. The existence of the Cu_6Sn_5 layer will affect the growth behavior of the Cu_3Sn layer during annealing at solid-state temperatures. Actually, the ratio between the thicknesses of the Cu_3Sn and Cu_6Sn_5 layers varies during solid-state annealing in this type of diffusion couple [7]. Thus, the soldering technique may not be appropriate for observation of the kinetics of the reactive diffusion.

Recently, the reactive diffusion between Au and Sn at solid-state temperatures was experimentally studied by the present authors using Sn/Au/Sn diffusion couples [11–13]. The diffusion couples were prepared by a diffusion bonding technique and then annealed at $T = 393$ – 473 K for various times in an oil bath with silicone oil. After annealing, AuSn, AuSn₂ and AuSn₄ compound layers were observed to form at the Au/Sn interface in the diffusion couple. According to the observations, the exponent of the power function is 0.48, 0.42 and 0.36 at $T = 393$, 433 and 473 K, respectively. Such temperature dependence of the exponent indicates that the grain boundary diffusion contributes to the rate-controlling process and grain growth occurs in the compound layers at certain rates at higher annealing temperatures. As the annealing temperature decreases, the contribution of the grain boundary diffusion becomes more remarkable, but the grain growth slows down. This is the reason why the exponent is smaller than 0.5 at $T = 473$ and 433 K but becomes close to 0.5 at $T = 393$ K [12,13].

In the present study, the temperature dependence of the kinetics was experimentally examined for the reactive diffusion between Cu and Sn at solid-state temperatures in a similar manner to previous studies [11–13]. Sn/Cu/Sn diffusion couples were prepared by the diffusion bonding technique and then annealed at $T = 433$ – 473 K in the oil bath. This temperature range is lower than that in the experiment by Onishi and

Fujibuchi [10]. The growth behavior of the binary Cu–Sn compound layers was observed metallographically. On the basis of the observations, the rate-controlling process of the reactive diffusion will be discussed.

2. Experimental

Pure Sn plates with a size of $12\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$ were prepared by cold rolling and spark erosion from a commercial 1 kg rectangular ingot of pure Sn with purity of 99.997%. The cold-rolled Sn plates were annealed at 473 K for 2 h in an oil bath with silicone oil and then chemically polished in an etchant composed of 25 vol.% of hydrochloric acid and 75 vol.% of distilled water. The two surfaces with an area of $12\text{ mm} \times 5\text{ mm}$ of each chemically polished Sn plate were mechanically polished on 800-emery paper. This kind of pure Sn specimen is called Specimen A. One of the two polished surfaces of Specimen A was again mechanically polished on 1500–4000 emery papers until a depth of 100 μm and then finished using diamond with a diameter of 1 μm . This kind of pure Sn specimen is designated Specimen B.

A pure Cu specimen was prepared as a 300 g ingot by argon induction melting from pure Cu with purity of 99.99%. Plate specimens with a dimension of $10\text{ mm} \times 4\text{ mm} \times 2\text{ mm}$ were cut from the ingot and then cold rolled to a thickness of 0.1 mm. Sheet specimens with a size of $20\text{ mm} \times 7\text{ mm} \times 0.1\text{ mm}$ were cut from the cold rolled specimens and then separately annealed in evacuated silica capsules at 1223 K for 2 h, followed by air-cooling without breaking the capsules. The annealed sheet specimens were chemically polished in an etchant consisting of 50 vol.% of nitric acid and 50 vol.% of distilled water.

After chemical polishing, a Cu sheet specimen was immediately sandwiched between two freshly prepared pieces of Specimen A in methanol by a technique used in previous studies [11–13]. The Sn/Cu/Sn couples were completely dried and then heat treated for diffusion bonding in the oil bath at $T = 473$ K for 120 h. This sort of diffusion couple is called Diffusion Couple A. Similar Sn/Cu/Sn couples were prepared by sandwiching a Cu sheet specimen between the finely polished surfaces of two pieces of Specimen B. Such couples were heat treated for diffusion bonding in the oil bath for 72 h at $T = 433$, 453 and 473 K. This sort of diffusion couple is designated Diffusion Couple B. After the heat treatment, Diffusion Couple B was annealed at $T = 433$, 453 and 473 K for various times up to 1128 h. The summation of the heat-treating and annealing times is hereafter merely called the annealing time. Cross-sections of the annealed diffusion couples were mechanically polished using diamond with diameters of 15, 3 and 1 μm and then finished with an OP-S liquid by Struers Ltd. The microstructure of the cross-section was observed with a differential interference contrast (DIC) optical microscope. Concentration profiles of Cu and Sn were measured on the cross-section along the direction normal to the interface by electron probe microanalysis (EPMA).

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