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Investigation of diffusion behavior in Cu–Sn solid state diffusion couples

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ABSTRACT

The diffusion behaviors and diffusion parameters of intermetallic compounds (IMCs) formed in Cu–Sn diffusion couples were investigated at the temperature range of 130 °C–200 °C. Interdiffusion coefficients of IMCs were calculated based on the measured composition profiles of the diffusion zones. Considering the wavy type of the diffusion layers and the narrow homogeneity range of the IMCs (Cu_3Sn and Cu_6Sn_5), the integrated method was performed to evaluate the integrated interdiffusion coefficients based on the measured thicknesses of the IMCs layers. The transient initial growth stage was excluded by considering two diffusion times where the growths of both IMCs are in the diffusion control stage. The activation energies for diffusion of the IMCs were evaluated from the integrated diffusion coefficients. The growth behavior of Cu_3Sn suggested the existence of a transient growth regime for Cu_3Sn at the initial stage in cold-bonded Cu–Sn diffusion couple. The intrinsic diffusion coefficients of Cu and Sn in Cu_6Sn_5 were estimated based on the integrated diffusion coefficients. Sn was found to be the faster diffusion component in the Cu_6Sn_5 phase. Phase-field simulations combined with the experimentally measured diffusion coefficients and steady-state growth-rate coefficients were performed to estimate the homogeneity range of IMCs. The estimated results are consistent with the experimental results from this study as well as those from literature experimental values and showed that the homogeneity ranges of Cu_3Sn and Cu_6Sn_5 phases in the Cu–Sn system are almost temperature independent.

1. Introduction

In the electronic industry, the formation and growth of intermetallic compounds (IMCs) between solder and substrate greatly affects the reliability of the joints. The interfacial reactions between Sn (or Sn-rich solders), and common metal substrates, such as Cu, are important for the solder alloy design and processing [1–3]. Cu–Sn couples set by cold-bonding, where only the solid-state interdiffusion reactions are involved, were studied many times [4–13]. The work reported by Onishi and Fujibuchi [13] focused on a relatively high temperature range of 190–220 °C, where the Cu_6Sn_5 high temperature variant Cu_6Sn_5_HT was involved. Paul et al. [6] investigated the diffusion properties of Cu_3Sn and Cu_6Sn_5 using Cu–Sn diffusion couples at 200 °C and incremental diffusion couples at different temperatures and derived the temperature dependent expressions of the diffusion coefficients based on the data obtained from incremental diffusion couples. Kumar et al. [7] studied the reactions in Cu–Sn diffusion couples and in incremental diffusion couples too. However the activation energies for diffusion in Cu_3Sn and Cu_6Sn_5 reported by Kumar et al. [7] are much lower than those reported in Refs. [6,13]. There is still no consensus on which is the faster diffusing component in the Cu_3Sn and Cu_6Sn_5 phase. Kumar et al. [7] suggested that Cu diffuses faster in both the Cu_3Sn and Cu_6Sn_5 phase, whereas other works [6,13] reported that Sn diffuses faster in the Cu_6Sn_5 phase.

Furthermore, in several studies, simulations of IMC growth in Cu–Sn joints have been carried out [11,14–20], to obtain a better understanding of the microstructure evolution and failure processes in solder/Cu joints, where the accuracies of the diffusion coefficients are critical for the fidelity and validity of the simulation outcomes.

A more detailed study, especially at lower temperatures, is thus

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still required. In this work, the simultaneous growth of Cu_3Sn and Cu_6Sn_5 in Cu–Sn couples over a wide temperature range 130–200 °C is considered. The corresponding diffusion parameters and growth rates were derived as a function of temperature from the experimental diffusion couples. Simulations with relation to the homogeneity range of the IMCs and their growth rates were then carried out based on the parameters from this work and the method proposed in Ref. [20].

2. Experimental processes

Sn (99.9999 wt%) and Cu (99.999 wt%) bars, purchased from ChemPur company, were used as starting materials. Sn and Cu plates with dimensions of 2*7*5 mm were cut from the raw materials. These plates were polished and cleaned with ethanol in an ultrasonic bath to obtain flat and clean surfaces.

The Cu–Sn diffusion couples were assembled by cold pressing together one Cu plate and one Sn plate using a hydraulic pressing machine. A small amount of alumina powder with 1 μm diameter was distributed in the interface as markers for tracking the original contacting interface. The diffusion couples were sealed in argon-filled quartz ampoules and subsequently annealed at 130 °C, 150 °C, 170 °C and 200 °C for certain periods. The temperatures were calibrated and controlled in the error range of ±2 °C using a K-type thermocouple.

After the annealing heat-treatment, the diffusion couples together with the quartz ampoules were quenched in water. The diffusion couples were taken out of the quartz ampoules and cold-mounted in Epofix resin. The interfaces of diffusion couples were kept perpendicular to the resin surface with clippers. Mounted samples were grinded, polished and ultrasonic cleaned using standard metallographic techniques.

PHILIPS XL30 FEG Scanning electron microscope (SEM) was used to analyze the phase structure and morphology in the diffusion zone. The composition of the phase in the diffusion layer was analyzed using JXA-8530F field emission electron probe micro-analyzer (EPMA) with wavelength dispersive spectroscopy (WDS) mode. Pure Cu and Sn, remained in the region far away from the interface in the diffusion couples, were employed as the standard materials to calibrate the EPMA results. The quantitative line-scanning module with step sizes of 0.25, 0.5 and 1 μm was utilized to obtain the concentration profiles of Cu and Sn in the corresponding diffusion zone.

Auger electron spectroscopy (AES) analysis, using PHI 680 Xi Auger Nanoprobe, was performed to obtain the composition profile with a higher resolution near the phase interface. Quantitative line-scanning measurements of the diffusion zone were carried out using a step size of 100 nm and beam size of 24 nm. The performed accelerating voltage was 10 kV and the current was 20 nA. Sputtering etching using Ar ion beam with etching rate as ~10 nm/min was continuously applied on the surface of the sample to get rid of accumulated carbon during the analysis. The AES sensitivity factors were calibrated using the elemental data obtained in EPMA analysis on the same sample.

3. Methods of analysis of binary diffusion couple

3.1. Determination of the parabolic growth constants of the IMCs

The diffusion couple method is commonly used to investigate the interdiffusion behavior between two metals or alloys [21]. If diffusion is the rate-limiting factor, the thickness of the diffusion layer is proportional to the square root of the diffusion time. When reaction at the interface is the rate-limiting factor, the thickness of the diffusion layer is linearly proportional to time [22]. Normally the reaction at the interface is very rapid compared with the rate of diffusion [23]. The growth of the phases is thus diffusion-controlled and following the Fick's law. The square of the thickness of the phase layers linearly increases with time, as interpreted by Equation (1) [24], which is also applicable to multi-phase system [25].

$$k^{(j)} = \frac{\left(\Delta x^{(j)}\right)^2}{2t} \tag{1}$$

where superscript j denotes the investigated phase; $\Delta x^{(j)}$ is the thickness of j phase layer in the diffusion zone after annealing for a time t and $k^{(j)}$ is the parabolic growth constant of phase j in the diffusion couple.

However, the linear extrapolation using Equation (1) for IMCs doesn't always pass the origin if an initial transient or non-diffusion-controlled stage existed. in As clarified in Refs. [22], the growth kinetics will always change to diffusion–controlled growth kinetics with a parabolic time dependence if the phase layer has grown to a sufficiently large thickness. Therefore the parabolic equation can still be applied to the later stage growth of the IMC layer [26]. As interpreted by Paul et al. [27], the growth curves can be expressed with a correction applied to the thickness or the time depending on its early starting stage. In our case, the growth curves intersect with the time axis. Therefore, the effect of an initial transient t_0 is considered, resulting in Equation (2). The time of t_0 can be attributed to the incubation time for nucleation of IMC or more generally to an initial transient stage. One should notice that t_0 doesn't stand for the real time of the initial non diffusion-controlled stage.

$$k^{(j)} = \frac{\left(\Delta x^{(j)}\right)^2}{2(t - t_0)} \tag{2}$$

Diffusion coefficients typically show a temperature dependence following the Arrhenius equation over an temperature range [28]. However as clarified in Refs. [25], $k^{(j)}$, being a complex function of the diffusion coefficients of the different phases present in the diffusion couple, does not show a simple Arrhenius temperature dependence.

3.2. Determination of interdiffusion coefficients

In diffusion couple, the motion of one constituent causes a counter flow of the other constituents or vacancies. An interdiffusion coefficient describing the intermixing effect of the diffusion, $\widetilde{D}$, is defined [29]. The most widely used method is the Boltzmann-Matano method [30], in which the interdiffusion coefficient is determined based on the experimentally measured composition profile in the diffusion zone of a diffusion couple. To avoid possible errors introduced in the process of the evaluation of the position of the Matano plane, Sauer and Freise [31] defined an auxiliary variable, which was further developed by Wagner [24], *via* equation:

$$Y(x) = \frac{N_i(x) - N_i^{+\infty}}{N_i^{+\infty} - N_i^{-\infty}} \tag{3}$$

where N_i is the mole fraction of specie i at the position x; superscripts $+\infty$ and $-\infty$ denote the corresponding values in the left and right end-boundaries of the diffusion couple.

With this variable Y, the equation to evaluate the interdiffusion coefficient is then given by Equation (4):