Short communication

Phase evolutions and growth kinetics in the Co–Sn system

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Abstract
Co/Sn diffusion couples are annealed at 175–220 °C. The reaction phase $CoSn_3$ is found to have a narrow homogeneity range of 2 at% with composition 74–76 at% Sn. The growth of this phase is found to be reaction–controlled initially followed by diffusion–controlled later. The marker experiment indicates that Sn is the faster diffusing element in this phase. The $CoSn_2$ phase is found to grow in the Co/$CoSn_3$ incremental couples at 200–220 °C.

Keywords Co–Sn phase diagram · Intermetallic compounds · Incremental diffusion couple · Electron probe micro analyser (EPMA)

1 Introduction

It is important to understand the growth of intermetallic compounds (IMC) at under bump metallization (UBM)—solder interface, for solder joint reliability. Ni, due to its slower growth rate of IMC formation, is commonly used as the diffusion barrier layer for Cu metallization. Co has been considered as a promising alternative material for the diffusion barrier layer in UBM for various solder alloys [1]. Sn being major solder component, in this work Co–Sn interfacial reactions are studied. To authors' knowledge, one related study is available [2] with $CoSn_3$ found as reaction phase. However, the earlier Co–Sn phase diagrams show no $CoSn_3$ phase as reported in Reference [2], and this phase has been added in the latest phase diagram shown in Fig. 1 [3, 4]. Thus, the aim of this work is to study the phase evolutions in the Co–Sn system and the growth kinetics of phases.

2 Experimental procedure

Pure Co (99.95 wt%) and Sn (99.99 wt%) were used as starting materials to make diffusion couples. They were prepared metallographically to obtain a flat and smooth surface. Then, they were cleaned in acetone and dried. The couple halves were joined by clamping in a special fixture with minimum required external pressure. Diffusion couples were annealed in the temperature range of 175–220 (± 2) °C for 100 h in a calibrated oven in high vacuum (~ 10^{-4} Pa). Prior to annealing at 200 °C, more or less evenly distributed Y_2O_3 particles (average size of 4.4 μm) were introduced at the contact interface to act as inert 'Kirkendall' markers. The bonded specimens were removed from the oven and cross sectioned by a slow speed diamond saw. After the standard metallographic preparation, the interdiffusion zone was examined in a scanning electron microscopy (SEM) and the composition profiles were measured in electron probe micro–analyzer (EPMA) equipped with a field emission gun (FEG). The location of the marker plane was identified in electron dispersive spectrometer (EDS) with the help of X–ray peak originating from Y and O.

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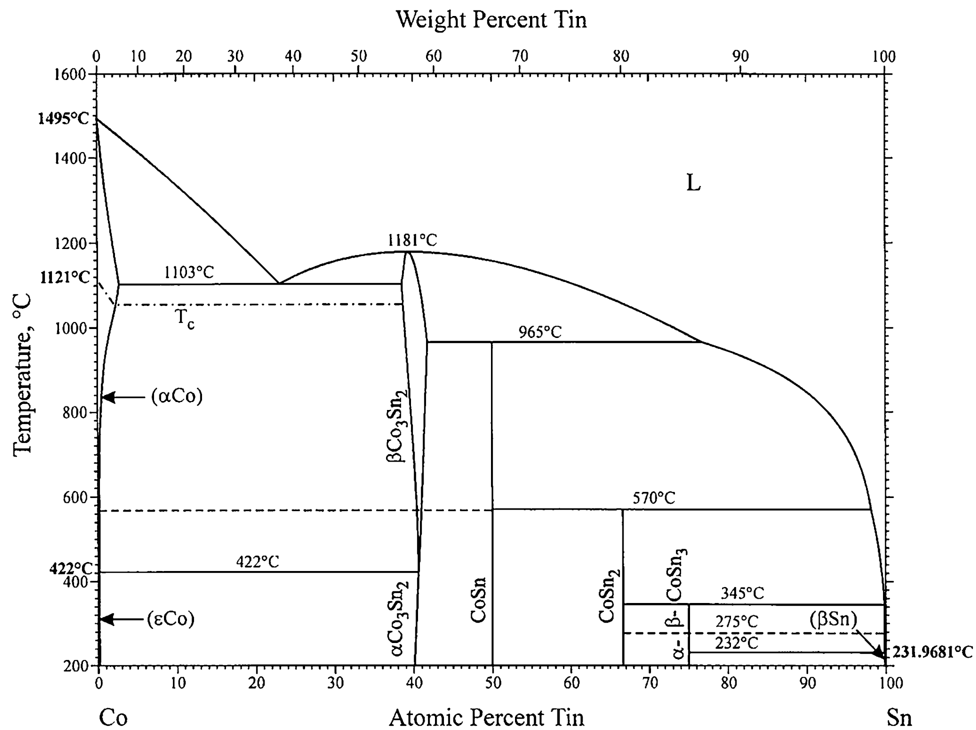

Fig. 1 The latest binary Co–Sn phase diagram published by Okamoto [3], in which the $CoSn_3$ phase found through X-ray analysis by Lang and Jeitschko [4] has been added

3 Results and discussion

Co/Sn diffusion couples are studied in the higher temperature range 220–175 °C because of the joining issues at 150 °C and below. The maximum temperature for the annealing was selected based on the melting point of Sn, so as to meet our objective of studying solid/solid interactions. Before discussing results on the evolution of phases, it is important to refer the Co–Sn phase diagram shown in Fig. 1 [3, 4]. It is be noted here that in this latest binary phase diagram, the newly found $CoSn_3$ phase is added. Total 4 phases viz. Co_3Sn_2, CoSn, $CoSn_2$ and $CoSn_3$ are present in the phase diagram.

3.1 Phase evolutions

The SEM micrograph and the corresponding composition profile of Co/Sn couple annealed at 175 °C for 100 h are shown in Fig. 2a, b, respectively. Interestingly, out of 4 intermetallic compounds present in the phase diagram (Fig. 1), only the $CoSn_3$ phase grows in the interaction zone of Co/Sn couple, which is the newly found phase in the Co–Sn system, as mentioned above. Very frequently in a multiphase growth, one or more phases are not found to grow mainly because of their sluggish growth kinetics. Similar to the Co–Sn system, in general, the missing phases are rich in the higher melting point component, i.e., these missing phases are closer to the higher melting point component (Co in the present case) in the phase diagram. Now, under such circumstances of multiphase growth, to check the growth of other phases in the interaction zone, we conduct the 'incremental' diffusion couple experiments. To prepare an incremental diffusion couple [5], usually one of the end–members is removed either by etching or polishing, such that other phases are allowed to grow as per the phase diagram. Figure 2c shows the BSE micrograph of Co/Sn couple annealed at 200 °C for 625 h. After Sn polishing, Co/$CoSn_3$ incremental diffusion couple is annealed at the same temperature for same time. The experimental result is shown in Fig. 2d. Based on the phase diagram, now the $CoSn_2$ phase is found to grow in the interaction zone of Co/$CoSn_3$ couple. It should be noted that this phase was absent earlier in the interaction zone of Co/Sn couple, shown in Fig. 2c. This indicates that the growth rate of $CoSn_2$ is much slower compared to $CoSn_3$ phase (which has much higher growth rate, as evident from Fig. 2c). It shall be clear from this fact, at 200 °C for 625 h, that the layer thickness of $CoSn_3$ is 350 µm compared to 3.5 µm for $CoSn_2$. Similarly, at 220 °C after 100 h annealing, the layer thickness of $CoSn_3$ is 200 µm in Co/Sn couple compared to 1 µm for $CoSn_2$ in Co/$CoSn_3$ couple. It is to be noted here that even if $CoSn_2$ phase would grow in Co/Sn couple its thickness would be much less than that found in the Co/$CoSn_3$ incremental couple, after annealing at the same temperature and time.

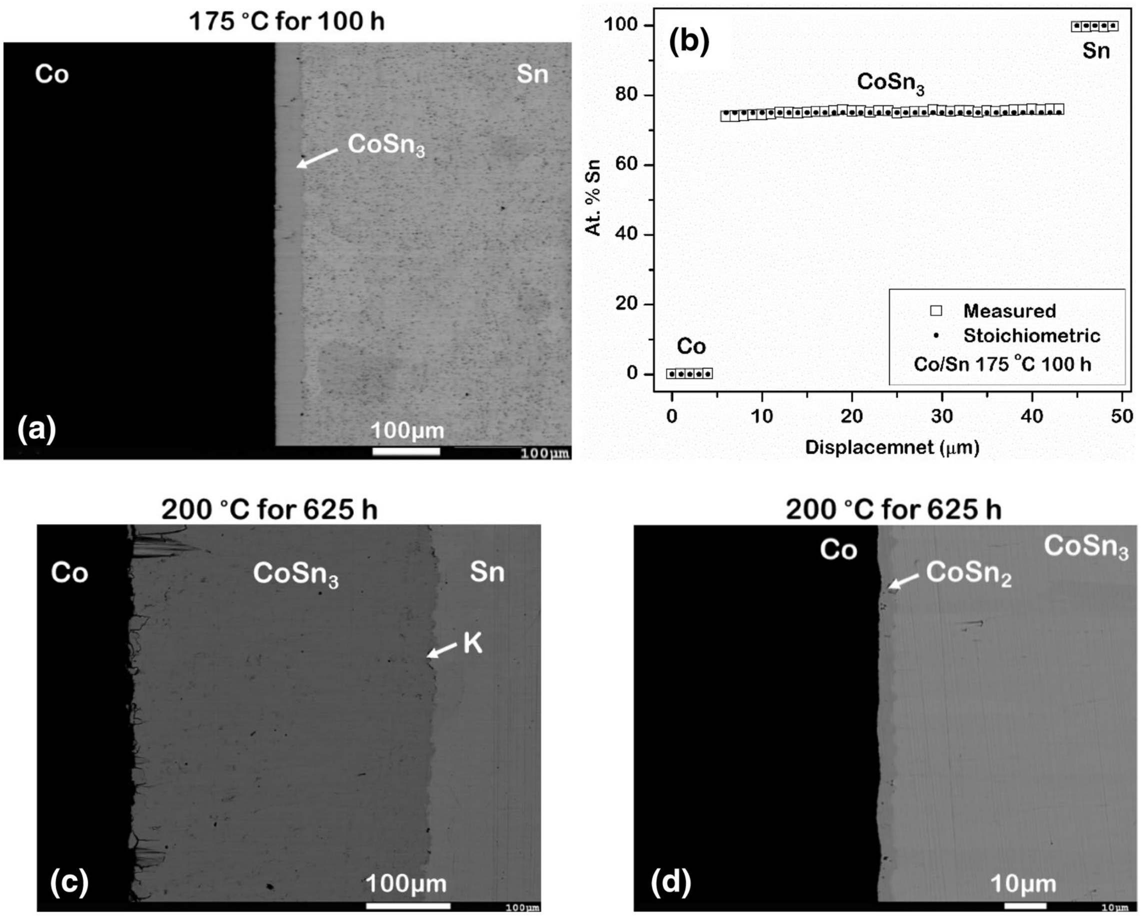

Fig. 2 **a** BSE micrograph and **b** composition profile measured, in EPMA, across the interaction zone of Co/Sn couple annealed at 175 °C for 100 h; BSE micrographs of couple annealed at 200 °C for 625 h **c** Co/Sn and **d** the Co/$CoSn_3$ incremental diffusion couple

Further, the line profiles measured (in EPMA) show the similar trend at all the temperatures. Solid circles in the graph (Fig. 2b) show the compositions of the phases reported in the phase diagram, whereas the open squares represent the actual compositions measured in EPMA. It indicates that the dissolution of other elements in the end–members is minor or negligible. It also indicates the off–stoichiometry in the composition of $CoSn_3$, which has narrow homogeneity range composition, measured as 74–76 at% Sn. Diffusion couple technique (which is employed in this study) is one of the reliable techniques to validate the phase diagram [5], in particular, when the composition does not change sharply near the phase boundaries (like in the present system) in the interaction zone. By careful point analysis in an EPMA equipped with FEG, we have measured the phase boundary compositions (PBC) within 2–3 µm from the interface since the interaction volume is ~ 1 µm. Moreover, the PCB measured, in this manner, when compared with the line profiles (e.g., Fig. 2b) are found to be same. In past, diffusion couple technique is used to validate PBC in Co–Ta [6], Co–Mo [7] and Au–Sn [8] systems, in a similar fashion as done here.

3.2 Growth kinetics of the $CoSn_3$ phase

To check whether the growth kinetics is reaction–controlled or diffusion–controlled, respectively, it is well–known that we need to confirm the linear or parabolic growth by examining the time dependent growth of a phase of interest. Only $CoSn_3$ is found to grow in all the time dependent experiments, which are conducted at 200 °C for 25–625 h. Thickness (x) and time (t) with respect to log x versus log t is plotted in Fig. 3. We know that $x = k \times t^n$, where n is growth exponent and k is growth constant. The slope of log x versus log t curve gives n from the linear fit. It is estimated as 1.12 ± 0.06 for 25–100 h indicating reaction–controlled (linear, $n \sim 1$) growth and as 0.47 ± 0.03 for 100–625 h indicating diffusion–controlled (parabolic, $n \sim 0.5$) growth. Similar growth nature has been reported earlier by Wang and Chen [2], based on their data

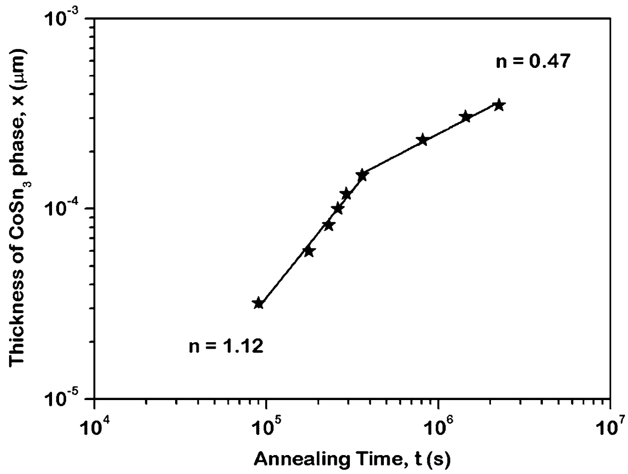

Fig. 3 Time dependent growth of the $CoSn_3$ phase at 200 °C in the Co/Sn couples

n is found to be 0.9 and 0.6 indicating transition from reaction–controlled to diffusion–controlled growth.

Hence, to gain further insights on the growth mechanism, inert Y_2O_3 particles were used as markers at the contact interface of Co/Sn prior to annealing at 200 °C. After the annealing treatment, the location of the marker plane is found at $CoSn_3$/Sn interface, marked as "K" in Fig. 2c. This indicates that the growth of $CoSn_3$ phase would be mainly by the diffusion of Sn atoms (faster diffusing species), and the diffusion of Co atoms through the $CoSn_3$ phase layer could be considered as negligible. In this study, based on the time dependent experiments, we have found transition from reaction–controlled to diffusion–controlled growth. It means that during initial stages of the growth of $CoSn_3$, the phase layer thickness is thin enough such that Sn atoms can diffuse easily across the layer. Thus, the growth rate is limited mainly by the chemical reactions which occurs at the interface, and the layer thickness increases linearly with the holding time. This means that the diffusion rate is relatively faster at the beginning of the phase layer growth, and the formation of the reaction phase (i.e., $CoSn_3$) is the rate–controlling process. The time for diffusion of species across the phase layer would increase with the thickness. Therefore, later (i.e., after holding time of say 100 h) when the layer thickness increases, it would reduce the supply of Sn atoms at Co/$CoSn_3$ interface (growth front) and since diffusion rate has decreased, now the growth of phase is parabolic with the duration of holding time. This means that the diffusion rates of components through the reaction phase (i.e., $CoSn_3$) is the rate–controlling process, and the rate of formation of the reaction phase is relatively faster. Since the main barrier for the reaction to take place now changes to the atomic diffusion, there is transition in the growth mechanism of $CoSn_3$ phase from reaction–controlled to diffusion–controlled.

4 Conclusion

1. Only $CoSn_3$ phase, which has been recently added in the latest Co–Sn binary phase diagram available in the literature, is found to grow in the Co/Sn diffusion couples annealed at 175–220 °C.
2. Based on the binary phase diagram, 3 more phases are expected to grow in the interaction zone. In the Co/$CoSn_3$ incremental diffusion couples, an additional phase $CoSn_2$ is found to grow at 200–220 °C.
3. $CoSn_3$ is found to have a narrow homogeneity range composition, i.e., 74–76 at% Sn, based on line profiles measurements and spot analysis in an EPMA equipped with FEG.
4. The growth of $CoSn_3$ phase is found to be reaction–controlled upto 100 h with growth exponent $n=1.12$ followed by diffusion–controlled till 625 h with $n=0.47$ in this study. Sn is found to be faster diffusing element based on inert marker experiments.

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Compliance with ethical standards

Conflict of interest The author declare that he has no conflict of interest.

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