

# **Interdiffusion studies in binary Co–Ta system and ternary Co(Ni)–Ta, Co(Ni)–Nb and Fe(Ni)–Nb systems**

M.E. thesis

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## **Synopsis**

Different refractory elements, such as Ta, Nb, Re, W, Cr and Mo are added to various superalloys to improve their mechanical properties. However, during long exposure at elevated temperatures during service, different topological close packed (tcp) phases, such as  $\mu$  ( $\mu$ ),  $\sigma$  ( $\sigma$ ) and the Laves phases grow, which are brittle in nature and deleterious to the structure. These phases grow by the interdiffusion process. In this project, our aim is to study the interdiffusion process in the binary Co–Ta system and ternary Co(Ni)–Ta, Co(Ni)–Nb and Fe(Ni)–Nb systems.

Co–Ta system is considered to estimate the diffusion parameters such as the interdiffusion coefficients and the ratio of the tracer diffusion coefficients are calculated in the  $\text{Co}_2\text{Ta}$  Laves phase. The activation energy for the interdiffusion coefficients is calculated as  $186 \pm 29$  kJ/mol. The ratio of tracer diffusion coefficients indicates that Co has higher diffusion rate than that of Ta. This is explained with the help of possible point defects and the crystal structure of the phase. The phase boundary compositions measured in this study is different from the compositions published previously.

Diffusion couple experiments are conducted to study phase evolutions in the Co–rich part of the Co–Ni–Ta phase diagram. This helps to examine the available phase diagram and propose a correction on the stability of the  $\text{Co}_2\text{Ta}$  phase based on the compositional measurements and X–ray analysis. The growth rate of this phase decreases with an increase in Ni content. The same is reflected on the estimated integrated interdiffusion coefficients of the components in this phase. The possible reasons for this change are discussed based on the discussions of defects, crystal structure and the driving forces for diffusion. Diffusion rate of Co in the  $\text{Co}_2\text{Ta}$  phase at the Co–rich composition is higher because of more number of Co–Co bonds present compared to that of Ta–Ta bonds and the presence of Co antisites for the deviation from the stoichiometry. The decrease in the diffusion coefficients because of Ni addition indicates that Ni preferably replaces Co antisites to decrease the diffusion rate.

Ternary Co(20at.%Ni)–Nb and Fe(20at.%Ni)–Nb systems are also considered to study the effect of Ni alloying addition on the growth and the diffusion rate of the various tcp phases present in their respective binary system viz. Co–Nb and Fe–Nb. In ternary Co(Ni)–Nb, Ni addition increases the growth and the diffusion rate of the  $\text{Nb}_2\text{Co}_7$  phase while the same decreases of the  $\text{NbCo}_2$  and  $\text{Nb}_6\text{Co}_7$  phases. In ternary Fe(Ni)–Nb, the layer thickness of  $\text{Fe}_2\text{Nb}$  decreases while that of  $\text{FeNb}$  increases with Ni addition. The diffusion rate for both phases decreases in ternary.

# **Diffusion-controlled growth of phases in metal-tin systems related to microelectronics packaging**

Ph.D. thesis

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## **Abstract**

The electro-mechanical connection between under bump metallization (UBM) and solder in flip-chip bonding is achieved by the formation of brittle intermetallic compounds (IMCs) during the soldering process. These IMCs continue to grow in the solid-state during storage at room temperature and service at an elevated temperature leading to degradation of the contacts. In this thesis, the diffusion-controlled growth mechanism of the phases and the formation of the Kirkendall voids at the interface of UBM (Cu, Ni, Au, Pd, Pt) and Sn (bulk/electroplated) are studied extensively.

Based on the microstructural analysis in SEM and TEM, the presence of bifurcation of the Kirkendall marker plane, a very special phenomenon discovered recently, is found in the Cu-Sn system (Figure 1). The estimated diffusion coefficients at these marker planes indicate one of the reasons for the growth of the Kirkendall voids, which is one of the major reliability concerns in a microelectronic component. Systematic experiments using different purity of Cu are conducted to understand the effect of impurities on the growth of the Kirkendall voids. It is conclusively shown that increase in impurity enhances the growth of voids.

The growth rates of the interdiffusion zone are found to be comparable in the Cu-Sn and the Ni-Sn systems. EPMA and TEM analyses indicate the growth of a metastable phase in the Ni-Sn system in the low temperature range (Figure 2). Following, the role of Ni addition in Cu on the growth of IMCs in the Cu-Sn system is studied based on the quantitative diffusion analysis (Figure 3). The analysis of thermodynamic driving forces, microstructure and crystal structure of  $\text{Cu}_6\text{Sn}_5$  shed light on the atomic mechanism of diffusion. It does not change the crystal structure of phases; however, the microstructural evolution, the diffusion rates of components and the growth of the Kirkendall voids are strongly influenced in the presence of Ni. Considering microstructure of the product phases in various Cu/Sn and Cu(Ni)/Sn diffusion couples, it has been observed that (i) phases have smaller grains and nucleate repeatedly, when they grow from Cu or Cu(Ni) alloy, and (ii) the same phases have elongated grains, when they grow from another phase.

A difference in growth rate of the phases is found in bulk and electroplated diffusion couples in the Au-Sn system (Figure 4). This is explained in  $\text{AuSn}_4$  based on the estimated tracer diffusion coefficients, homologous temperature of the experiments, grain size distribution and crystal structure of the phase. The

growth rates of the phases in the Au–Sn system are compared with the Pd–Sn and the Pt–Sn systems. Similar to the Au–Sn system, the growth rate of the interdiffusion zone is found to be parabolic in the Pd–Sn system; however, it is linear in the Pt–Sn system. Following, the effect of addition of Au, Pd and Pt in Cu is studied on growth rate of the phases. An analysis on the formation of the Kirkendall voids indicates that the addition of Pd or Pt is deleterious to the structure compared to the addition of Au (Figure 5). This study indicates that formation of voids is equally influenced by the presence of inorganic as well as organic impurities.

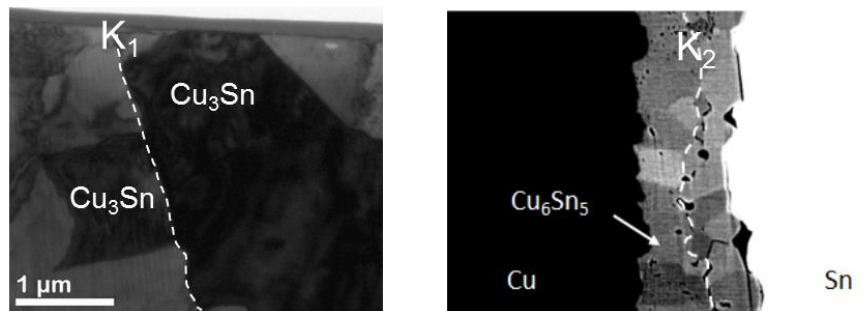


Figure 1: Identification of bifurcation of the Kirkendall marker plane in a binary Cu/Sn diffusion couple, i.e.,  $K_1$  in  $\text{Cu}_3\text{Sn}$  and  $K_2$  in  $\text{Cu}_6\text{Sn}_5$  found in TEM and SEM, respectively, based on duplex morphology.

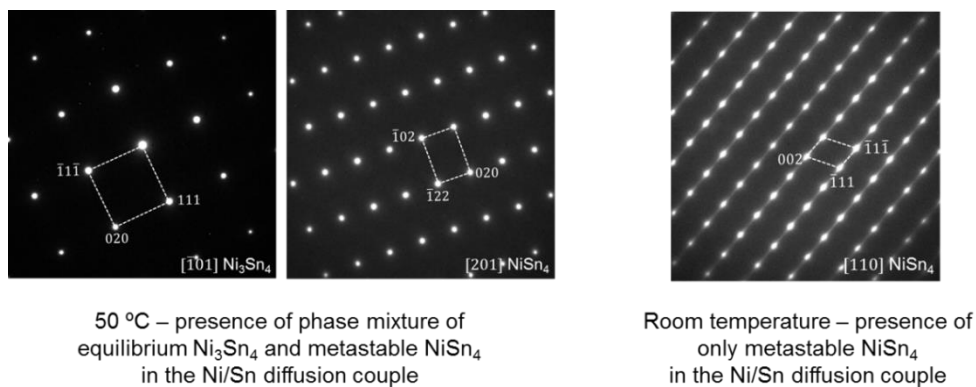


Figure 2: Metastable phase in the Ni–Sn system found in the low temperature range.

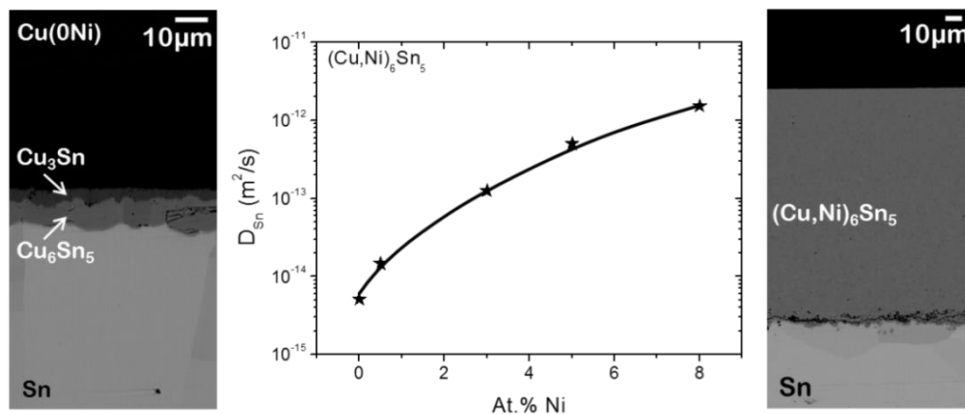


Figure 3: Role of Ni addition in Cu on the growth of phases in the Cu–Sn system.

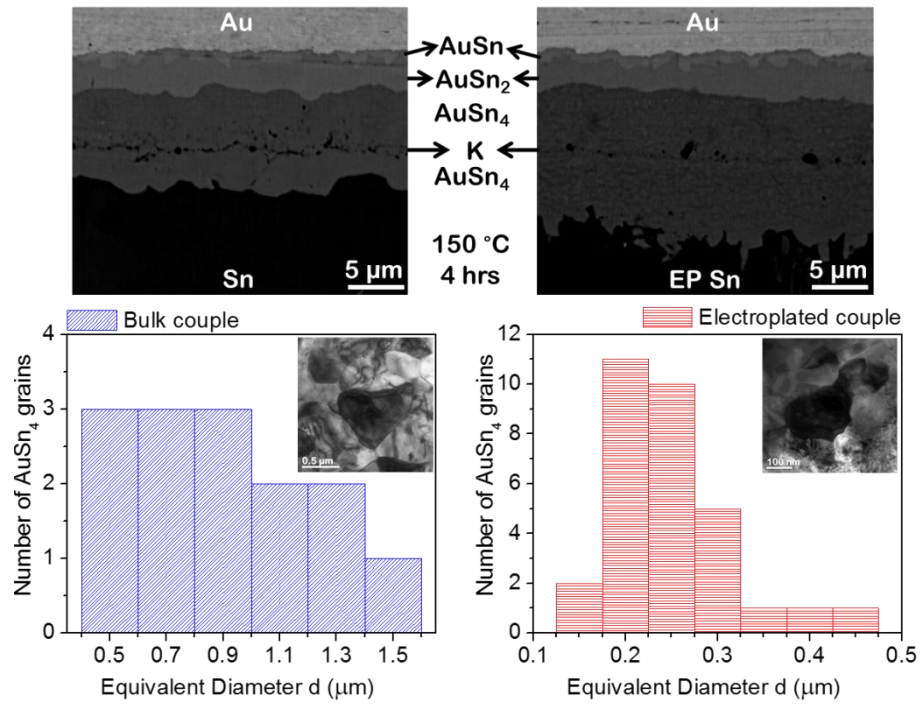


Figure 4: Most prominent difference in growth rate of  $\text{AuSn}_4$  as found in (left) bulk and (right) electroplated diffusion couples in the Au–Sn system is shown along with grain size distribution of  $\text{AuSn}_4$  grains observed in TEM.

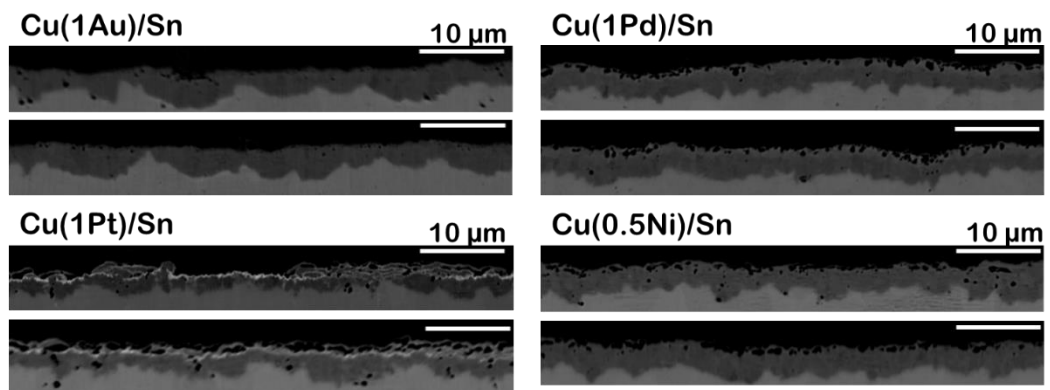


Figure 5: The Kirkendall voids in  $\text{Cu(M)/Sn}$  couples annealed at 200 °C for 81 hrs. Purity is same for all cases: 99.999 wt.% Cu, 99.99 wt.% Sn, 99.95 wt.% M = Au, Pd, Pt and Ni.