

**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). The 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.

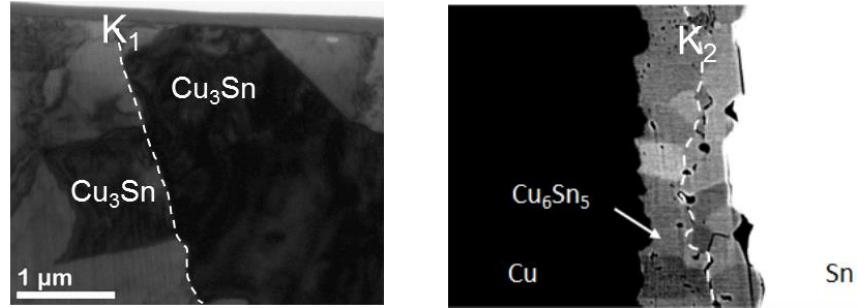


Figure 1: Identification of bifurcation of the Kirkendall marker plane in a binary Cu/Sn diffusion couple, i.e.,  $K_1$  in  $\text{Cu}_3\text{Sn}$  and  $K_2$  in  $\text{Cu}_6\text{Sn}_5$  found in TEM and SEM, respectively, based on duplex morphology.

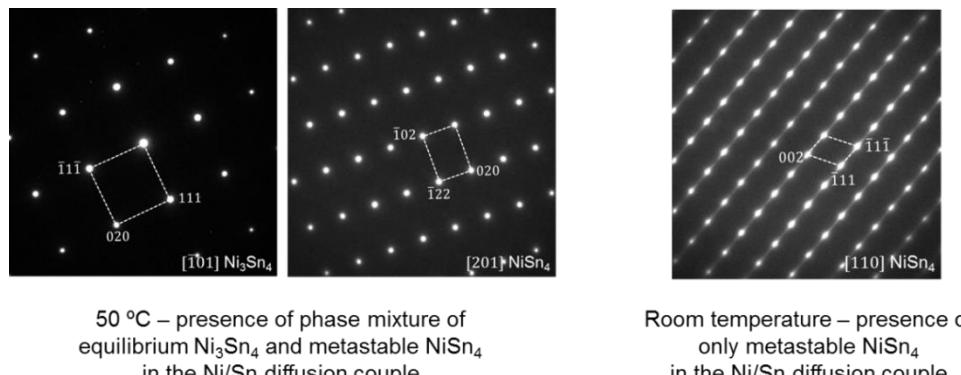


Figure 2: Metastable phase in the Ni–Sn system found in the low temperature range.

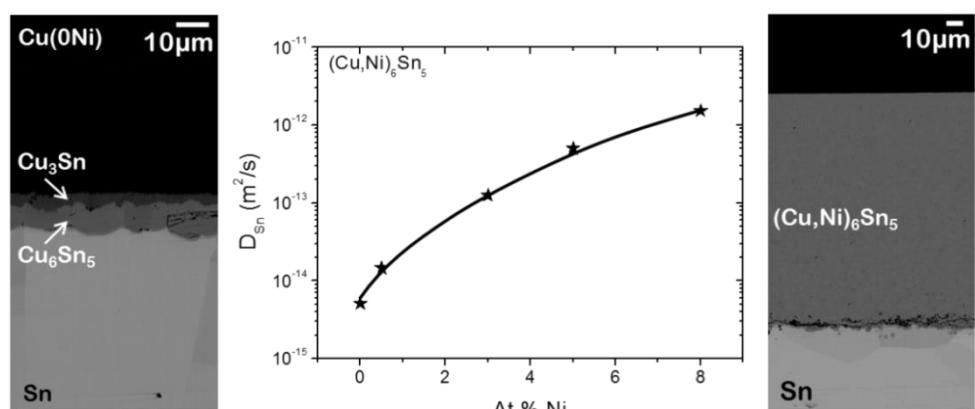


Figure 3: Role of Ni addition in Cu on the growth of phases in the Cu–Sn system.

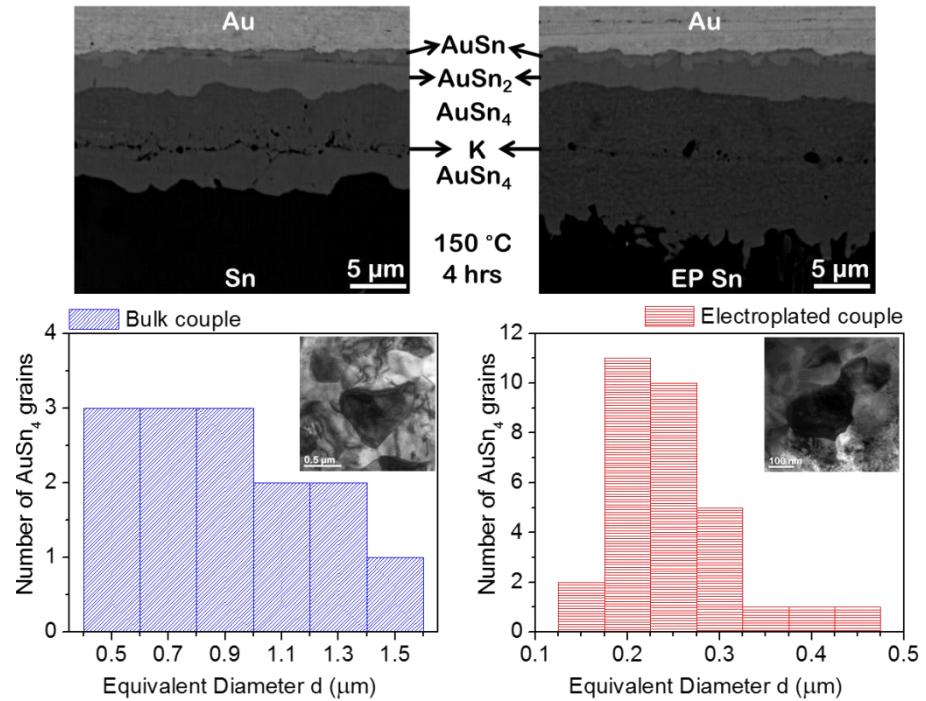


Figure 4: Most prominent difference in growth rate of AuSn<sub>4</sub> as found in (left) bulk and (right) electroplated diffusion couples in the Au–Sn system is shown along with grain size distribution of AuSn<sub>4</sub> grains observed in TEM.

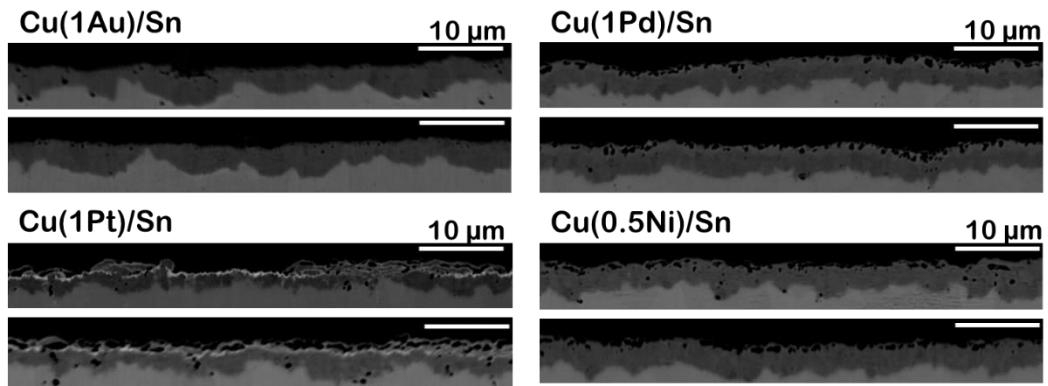


Figure 5: The Kirkendall voids in Cu(M)/Sn couples annealed at 200 °C for 81 hrs. Purity is same for all cases: 99.999 wt.% Cu, 99.99 wt.% Sn, 99.95 wt.% M = Au, Pd, Pt and Ni.

**List of Publications**  
(Based on this Ph.D. thesis)

[1] V.A. Baheti, S. Kashyap, P. Kumar, K. Chattopadhyay, A. Paul, Bifurcation of the Kirkendall marker plane and the role of Ni and other impurities on the growth of Kirkendall voids in the Cu–Sn system, *Acta Materialia* 131 (2017) 260-270.  
<http://doi.org/10.1016/j.actamat.2017.03.068>

[2] V.A. Baheti, S. Kashyap, P. Kumar, K. Chattopadhyay, A. Paul, Effect of Ni on growth kinetics, microstructural evolution and crystal structure in the Cu(Ni)–Sn system, *Philosophical Magazine* 97(21) (2017) 1782-1802.  
<http://doi.org/10.1080/14786435.2017.1313466>

[3] V.A. Baheti, S. Islam, P. Kumar, R. Ravi, R. Narayanan, H. Dong, V. Vuorinen, T. Laurila, A. Paul, Effect of Ni content on the diffusion–controlled growth of the product phases in the Cu(Ni)–Sn system, *Philosophical Magazine* 96(1) (2016) 15-30.  
<http://doi.org/10.1080/14786435.2015.1119905>

[4] V.A. Baheti, S. Kashyap, P. Kumar, K. Chattopadhyay, A. Paul, Solid–state diffusion–controlled growth of the phases in the Au–Sn system, *provisionally accepted*, *Philosophical Magazine* (2017).

[5] V.A. Baheti, P. Kumar, A. Paul, Effect of Au, Pd and Pt addition in Cu on the growth of intermetallic compounds and the Kirkendall voids in the Cu–Sn system, *provisionally accepted*, *Journal of Materials Science: Materials in Electronics* (2017).

[6] V.A. Baheti, S. Kashyap, P. Kumar, K. Chattopadhyay, A. Paul, Solid–state diffusion–controlled growth of the intermediate phases from room temperature to an elevated temperature in the Cu–Sn and the Ni–Sn systems, *under review*, *Journal of Alloys and Compounds* (2017).

[7] V.A. Baheti, P. Kumar, A. Paul, Growth of phases in the solid–state from room temperature to an elevated temperature in the Pd–Sn and the Pt–Sn systems, *under review*, *Journal of Materials Science: Materials in Electronics* (2017).

[8] V.A. Baheti, A. Paul, Different approaches and their efficiencies for the estimation of diffusion parameters, *under preparation* (2017).