The Kinetics of Formation of Ternary Intermetallic Alloys in Pb-Sn and Cu-Ag-Sn Pb-free Electronic Joints

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Abstract

A simple model of the formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ in Pb-Sn solder/Ni interconnects is examined by numerical simulation. Previous experimental observation has shown that after reflow the interface consists of the Ni_3Sn_4 alloy between Pb-Sn solder and Ni, with Au distributed through the PbSn solder ball. $Au_{0.1}Ni_{0.1}Sn_{0.8}$ was observed to form at the Pb-Sn solder/Ni_3Sn_4 interface during annealing at 150 °C in a number of studies. The numerical simulation was used to calculate the maximum flux of Au to the interface, and with the assumption that this Au was immediately incorporated in to $Au_{0.1}Ni_{0.1}Sn_{0.8}$, a maximum rate of formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ was calculated. This rate was found to be similar to measured rates of formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ from two different studies. The formation of $(CuNi)_6Sn_5$ in Sn-Ag-Cu/Ni solder interconnects was discussed within the context of these observations.

Introduction

Changes in constituents, geometry and processing of solder joints create new metallurgical problems to be solved in order to ensure interconnect reliability. Changes in the constituents of solder and metallization metallurgies, combined with decreases in package sizes and increases in the process temperatures of solder joints provide significant challenges. The complete effect of the addition of Au to solder joints in the form of oxidation barriers for Ni metallizations is just being understood. At the same time, the advent of Pb free solders has resulted in the addition of other species such as Ag and Cu to the Sn matrix. Reflow temperatures are apparently to increase by up to forty degrees, while diffusion distances decrease with shrinking component sizes. The new constituents of the solder joint are able to combine with Sn and the metallization to form ternary alloys. Thus new processes are occurring during the reflow and heat treatment of solder joints which must be understood to ensure joint reliability and to optimize manufacturing practices.

While the frequency of use of no-Pb solder continues to increase, electronic solder joints are still generally fabricated using Pb-Sn eutectic solder reflowed in contact with the metallic surfaces to be joined. Upon reflow new intermetallic alloys grow at the interface solder/pad and ensure bonding. For instance for Cu metallizations, Cu_6Sn_5 with some Cu_3Sn forms at the Sn/Cu interface [1,2,3]. If these alloy layers are too thick, they have deleterious effects on the mechanical reliability of the joints [4]. Therefore, over the years, the composition of electronic leads has changed from a single metal, usually Cu, to multi-layered structures with two or more metallic layers stacked on top of each other. A thin coating of a noble metal such as Au or Pd is frequently used to protect the surface from oxidation, while a second layer, commonly Ni, is used as a diffusion barrier to prevent the Cu underneath it from interacting with solder. A number of investigators have shown that Ni/solder intermetallics grow more slowly than Cu/solder intermetallics during reflow [5,6,7].

The introduction of metals such as Pd, Au and Ni, which diffuse at very high rates in solder, and the reduction of the dimensions of the joints have dramatically altered the mechanisms of formation of solder alloys. For example, Au dissolves very quickly into molten Pb-Sn solder (1.33 μm/s) [8] and if present in concentrations above the solubility limit at the melting temperature it combines with Sn to form $AuSn_4$ precipitates which are dispersed in the solder [9,10, 11]. Mei. et al. in their study of Pb-Sn solder joints reflowed on Au/Ni metallizations [12] reported that during long term aging (336 h at 150 °C), Au-Sn alloys form at the solder/ Ni_3Sn_4 interface and degrade the strength of the joints. Other studies of similar systems [13-16] with lower Au concentrations (less than 0.34 at% versus 1.5 at% for Mei et al.) found that Au diffuses back to the interface. It was found that Au combines with Ni and Sn to form a ternary phase of nominal composition $Au_{0.5}Ni_{0.5}Sn_4$. [13-16] This indicates that even very low concentrations of Au in the joint might have a considerable effect on both the microstructure of the joint and the formation of different solder alloys, and thus the reliability of the solder interconnect.

In addition to the variety of materials used in the metallizations, the advent of Pb-free solders is expected to further complicate the metallurgy of these joints. In fact, the alternatives to Pb-Sn solders are mainly Sn based alloys which contain small additives of a number of metals [17,18], such as Cu, Ag, Bi, or Au, used to reduce the melting temperature of the solder and improve its mechanical properties [19] (creep, tensile strength, fatigue...etc). The introduction of numerous metals to the solder joints with anomalously high diffusion coefficients in Sn, even though present in small amounts, can fundamentally affect phase selection criteria at the interface. For example $(Cu,Ni)_6Sn_5$ forms at Pb free Sn-Ag-Cu solder/Ni interconnect interfaces, rather than the Ni_3Sn_4 phase observed in Pb-Sn solder/Ni interconnects [23].

The mechanisms of formation of ternary intermetallic compounds which were observed to form in previous investigations [13-16,23] in electronic joints made with Au/Ni metallizations and either Pb-Sn solder or Cu-Ag-Sn Pb-free solder are further examined. In the case of PbSn/Ni solder interconnects, a numerical simulation was performed in order to determine whether the supply of Au atoms to the

solder/metallization interface controls the growth of the ternary alloy $Au_{0.1}Ni_{0.1}Sn_{0.8}$.

Samples preparation

We examined studies of two sets of samples, one Pb-Sn solder [13,14] and one Pb-free solder [23]. Both sets of samples were built using printed circuit boards with Cu/Ni/Au metallizations. However the thicknesses of both Au and Ni were different for the different sets. While Pb-Sn Ball Grid Array (BGA) spheres (500 μm in diameter) were reflowed over Au/Ni metallizations with respective thicknesses of 0.75 μm and 12 μm, Pb-free Cu-Ag-Sn flip-chip bumps (50 μm in diameter) were reflowed on 0.3 μm Au/5μm Ni metallizations. The flip-chip samples had a (Ni,V) underbump metallization and a solder composition of $Cu_{1.85}Ag_{3.8}Sn_{94.35}$ (the compositions will all be given in atomic percentage if not otherwise mentioned). The two sets of samples were reflowed in a nitrogen atmosphere with two different thermal profiles according to vendor recommendations. The peak temperature for Pb-Sn samples was 209 °C and the samples remained for approximately 40s above the liquidus while Pb-free samples were maintained above the liquidus for approximately 74s with a peak temperature of 244°C. The assemblies were then air cooled and those to be annealed were sealed in glass tubes in an Ar atmosphere under a pressure of 10 psi. The annealing temperature used for both batches was 150 °C. Pb-Sn samples were annealed for 1h, 4h, 9h, 40h and 150h, while Pb-free samples were annealed for 16h, 36h, 64h and 261h.

Annealed and non-annealed samples were subsequently mounted in epoxy, ground and polished. After polishing, we examined the samples with both optical and electron microscopy to identify and locate the different phases. For quantitative analysis we used Wavelength Dispersive Spectroscopy (WDS) techniques. Phase precipitates with sub-micron dimensions were analyzed with a beam current set to 1nA and an accelerating voltage of 5kV while coarser phases were analyzed using a current of 47nA and a voltage of 15kV.

Numerical simulations were performed using a student version of commercial software (FlexPDE 2.19b)[24], which uses a finite element method (Galerkin) to solve partial differential equations. The software uses an automatic adaptive refinement mesh technique to meet the required accuracy in the solution. The software was used to solve the diffusion equation in a two-dimensional domain.

## Results and Discussion

A. Ni/Au/PbSn Solder Joints

The examination of cross-sections of as reflowed samples with optical and electron microscopy together with WDS analyses revealed the composition of the phases in the solder interconnect[13,14]. A layer of Ni_3Sn_4 with an average thickness of 0.2 μm formed at the Pb-Sn solder/Ni interface during reflow(Figure 1). It appeared from micro-chemical analyses carried out both near the interface and in the bulk of the solder, that the Au initially protecting Ni from oxidation completely dissolved into solder and on this scale was homogeneously distributed within the solder sphere. For thicker Au layers and thus higher concentrations of Au dissolved in to the solder, precipitates of $AuSn_4$ are typically visible. For instance, in a previously reported case [15], for an

initial Au layer of 1.5 μm (compared to 0.75 μm with similar size solder balls in the present study) finely dispersed $AuSn_4$ were revealed in electron micrographs.
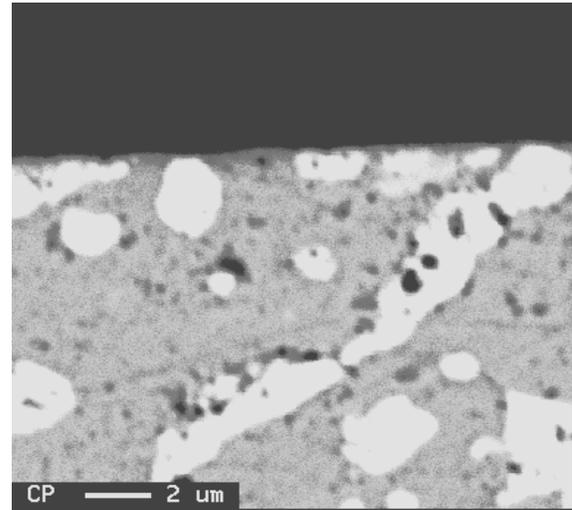

Figure 1 SEM image of the interface of an as reflowed eutectic Pb-Sn/Au/Ni/Cu joint showing solder on the bottom, a layer of Ni_3Sn_4 in the middle (dark grey) and Ni on the top (black) [13,14].

Although after reflow we did not detect the presence of any Au-Sn alloys at the solder/metallization interface, after only 4 h of annealing at 150°C, a new intermetallic layer was observed growing adjacent to the 0.5μm thick layer of Ni_3Sn_4[13,14]. This compound was found to be a ternary Au-Ni-Sn intermetallic with an average atomic composition of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ Figure 2. Like $AuSn_4$, the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ alloy is not stable at reflow temperatures. At lower temperatures, such as our annealing temperature of 150 °C, this ternary alloy can grow at a relatively rapid rate [13-16].
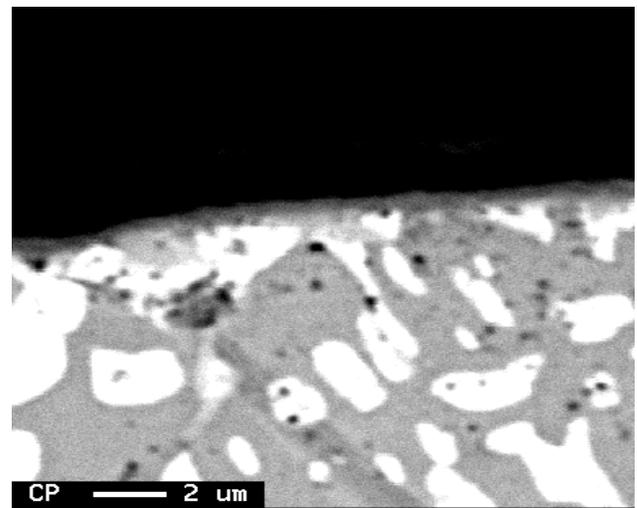
Figure 2 SEM image of the interface of a Pb-Sn/Au/Ni/Cu joint annealed for 4h at 150 °C showing Ni on the top (black)a layer of Ni_3Sn_4 in the middle (dark grey), small islands of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ start growing on top of Ni_3Sn_4 and solder on the bottom [13,14].

An examination of the kinetics of growth of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ at a temperature of 150 ^{o}C provides some insight in to the mechanisms controlling the formation of this alloy. Plots of the thickness of the ternary alloy and of the thickness of the Ni_3Sn_4 layer as a function of time are presented in Figure 3[13,14]. The $Au_{0.1}Ni_{0.1}Sn_{0.8}$ alloy grows more quickly than the Ni_3Sn_4 layer, surpassing the thickness of the Ni_3Sn_4 layer after 4 h. After 150 h of annealing, the thickness of the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ alloy is more than three times that of the Ni_3Sn_4 layer. The thickness of the ternary compound versus aging time can be well approximated with a parabolic growth ($x^2=k^2*t$), where k^2 is the reaction constant of the alloy. However, the reaction constant estimated for $Au_{0.1}Ni_{0.1}Sn_{0.8}$ (10^{-13} cm^2/s) is much less than that found for $PdSn_4$, an alloy of similar structure. At a temperature of 150 °C the reaction constant for $PdSn_4$ was found to be 1.4×10^{-10} cm^2/s [20], three orders of magnitude larger than the value indicated for the averaged interdiffusion coefficient of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ by the data of Figure 3. An important difference in this case is the ternary nature of the growing alloy and the limited supply of Au atoms. Au, present in the solder after reflow at relatively low concentration (0.1at%) atomic percent for these samples) must diffuse long distances in order for the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ to grow. The diffusion rate of Au atoms may limit the rate of growth of the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ alloy.
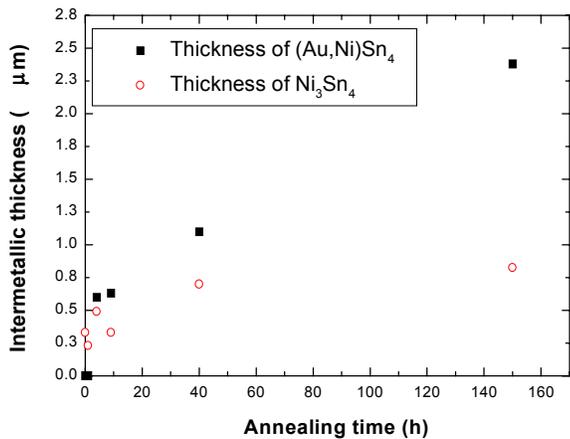
Figure 3 Variation of the measured thickness of Ni_3Sn_4 and $Au_{0.1}Ni_{0.1}Sn_{0.8}$ with annealing time[13,14].

A numerical simulation was performed in order to determine whether the supply of Au atoms to the solder/metallization interface controls the growth of the ternary alloy $Au_{0.1}Ni_{0.1}Sn_{0.8}$. The diffusion equation was solved for the concentration of Au in a two dimensional domain (cross section of the solder sphere). Previously measured values of the tracer diffusion coefficient of Au in polycrystalline Sn were used for the diffusion constant in the solder [21]. The initial condition for the problem is a uniform Au concentration within the joint, as observed for these samples[13,14]. The boundary conditions consist of an impermeable outermost surface with a zero flux normal to the boundary and a Dirichlet zero boundary concentration

condition at the solder interface. The Dirichlet boundary condition reflects the assumption that all the Au that reaches the interface is immediately consumed to form the ternary alloy. This simulation included a calculation of the flux of Au atoms at the interface as a function of time. From this flux a rate of formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ was calculated by assuming that a Au atom reaching the interface immediately combined with Ni and Sn to form $Au_{0.1}Ni_{0.1}Sn_{0.8}$. A comparison of the results of this calculation, which has no adjustable parameters, and the data of Figure 3, is provided in Figure 4. The observed good agreement between experimental and numerical data indicates that the growth of the ternary $Au_{0.1}Ni_{0.1}Sn_{0.8}$ is diffusion controlled and that Au is the controlling species.
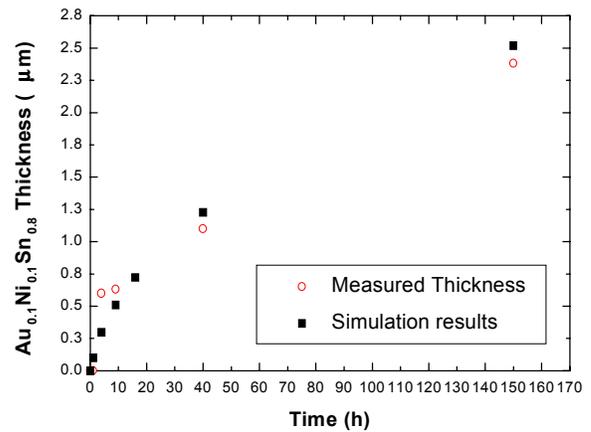
Figure 4 Comparison of simulated and measured $Au_{0.1}Ni_{0.1}Sn_{0.8}$ thicknesses versus annealing time.

Confirmation of the concept that the rate of diffusion of Au controls the rate of growth of the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ alloy at the solder interface in such Ni/Au/PbSn solder joints is provided by examination of the data of Minor et al. [15]. These data were provided along with the thickness of the Au layer on the Ni metallization, and the ball geometry, making possible a calculation of the rate of formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ (with no adjustable parameters, assuming again that the diffusion rate of Au limits the rate of growth). The data from Minor et al. for this different geometry is plotted in Figure 5 along with calculations of the Au diffusion limited rate of growth. A calculation for a 1.5 µm layer of Au on the Ni metallization (the thickness reported [15]) is provided. Calculations for 1.7 µm and 1.9 µm layers are provided for comparison as well. Reasonably good agreement is observed between model and data, particularly at longer times. The observed growth at shorter times is significantly faster than the prediction of the simple Au diffusion limited model; this may reflect observed inhomogenties in the initial Au distribution. The influence of such inhomogeneities would clearly decrease as time and diffusion distances increase. The limitation of the rates of growth of the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ alloy by the rate of diffusion of Au provides a simple means to calculate the rate of growth of this alloy for different geometries.

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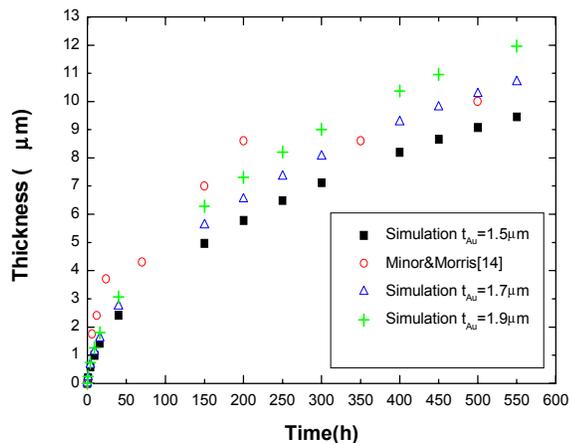
Figure 5 Comparison of simulated and measured [15] $Au_{0.1}Ni_{0.1}Sn_{0.8}$ thicknesses versus annealing time.

B. Ni/Au/SnAgCu Solder Joints

A comparison of the formation of $(Cu,Ni)_6Sn_5$ to the growth of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ at solder/metallization interfaces provides some insight on the mechanisms controlling these processes. In both cases the two major species at the interface, Sn and Ni, combine with a third species distributed through the solder at relatively low concentrations. Although limited amounts of these species (Cu or Au) are available, these species diffuse rapidly in Sn at relevant temperatures. Thus these species (Cu or Au) are available for the formation of a ternary alloy which can grow more quickly than the Ni_3Sn_4 phase.

An important difference between the two systems is that the $(Cu,Ni)_6Sn_5$ phase is stable at reflow temperatures, while the $Au_{0.1}Ni_{0.1}Sn_{0.8}$ is not. Thus, if it is kinetically favored, $(Cu,Ni)_6Sn_5$ can start to grow during reflow. In fact, Ni/SnAgCu solder joints did not exhibit the Ni_3Sn_4 intermetallic layer at the interface after reflow[23]. In example, Figure 6 provides an electron microscope image which reveals a 2 μm thick layer of the $(Cu,Ni)_6Sn_5$ phase at the Ni/solder interface after reflow (244 °C for approximately 74s). Many previous studies [5, 6, 7] proved that Cu_6Sn_5 grows very fast during reflow in PbSn solder/Cu joints; specifically, faster than Ni_3Sn_4 (which is one of the reasons Ni is used in metallizations as a diffusion barrier between Cu and solder). Anomalously high diffusion rates of Cu in Sn have been observed at temperatures below the melting point of Sn. Apparently Cu atoms have a high mobility in liquid Sn as well [3], and $(Cu,Ni)_6Sn_5$ can grow significantly faster than Ni_3Sn_4.

Metallic species such as Au, Ni, and Cu dissolved in the solder matrix dramatically changes the phase evolution of both Pb-free and Pb-Sn solder interconnects. Whether initially present in small amounts as additives to the solder or used as protective coatings on metallization, these metals diffuse so rapidly during annealing that they are available in sufficient quantity at the solder/metallization interface to facilitate the formation of ternary solder alloys. This phenomenom may affect the mechanical reliability of the joints in at least three ways. First, depletion from the solder of constituent can weaken the joint and lead to failure. Second,

some of the ternaries such as $Au_{0.1}Ni_{0.1}Sn_{0.8}$ are fast growing compounds, which might lead to an undesirable thickening of intermetallics at the interface and hence brittle failure by crack propagation. Finally, as different solder alloys compete to grow at the interface, one risks growing multilayered structures of intermetallics with poor adhesion properties to each other which lead to mechanical failure of the joint.
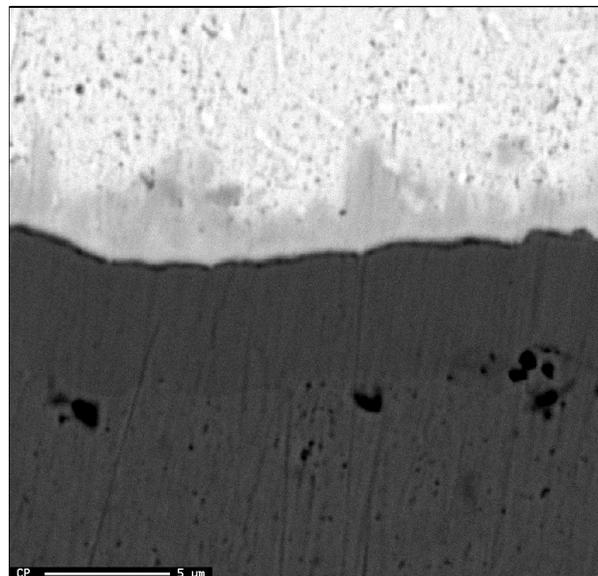
Figure 6 Compositional map of the interface of a Pb-free Cu-Ag-Sn solder/Au-Ni-Cu metallization right after reflow. It illustrates the ternary $Cu_{0.27}Ni_{0.26}Sn_{0.47}$ compound growing upon solidification of the joint at the interface solder/Ni. The upper phase is solder with Ag_3Sn needle-like precipitates, the middle layer scalloped layer is $Cu_{0.27}Ni_{0.26}Sn_{0.47}$ and on the bottom we have Ni and Cu.

Conclusion

We considered the formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$ at the PbSn solder/Ni interfaces, and of $(Cu,Ni)_6Sn_5$ at the Pb-free $Cu_{1.85}Ag_{3.8}Sn_{94.35}$ solder/Ni interfaces, in solder joints. A simple model indicated that the diffusion of Au controls the rate of formation of $Au_{0.1}Ni_{0.1}Sn_{0.8}$. It is likely that the diffusion of Cu in Pb-free $Cu_{1.85}Ag_{3.8}Sn_{94.35}$ solder/Ni joints controls the rate of formation of $(Cu,Ni)_6Sn_5$.

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