Film growth characterization of pulse electrodeposited Au/Sn thin films

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ABSTRACT

One of the more promising lead-free solders currently being used in GaAs-based and InP-based optoelectronic and microelectronic packaging applications is eutectic Au/Sn (30 at%Sn). The film growth characteristics were studied to better understand the deposition mechanisms for Au₅Sn and AuSn. AuSn deposits more rapidly and the process is growth controlled. Au₅Sn deposition is slower and is nucleation controlled.

INTRODUCTION

The gold/tin eutectic alloy (30 at%Sn), like all hard solders, has excellent thermal and mechanical properties improving overall device reliability [1]. The advantage of the Au/Sn alloy over other hard solders is its comparatively low melting temperature (280ºC) allowing it to be used when packaging temperature sensitive materials.

Electroplating is a cost effective alternative to current solder deposition processes, such as solder preforms and evaporation. Co-deposition of Au/Sn, from a slightly acidic, chloride-based solution, using pulsed currents has been demonstrated to be effective at plating eutectic and near-eutectic compositions directly onto metallized wafers or carriers [2,3]. Two separate Au/Sn compositions, 16 at%Sn (Au₅Sn) and 50 at%Sn (AuSn), can be deposited under the plating current density conditions shown in Figure 1: <1.0mA/cm² and >2.0 mA/cm² respectively. By varying the plating time at each current density, it is possible to deposit solder layers with an overall composition ranging from 16-50 at%Sn.

In order to obtain reliable and reproducible deposits, it is important to understand the film nucleation and growth mechanisms. The purpose of the current work is to study the nucleation and growth behavior of both phases, using electron microscopy techniques to characterize the film structure, morphology and composition.

EXPERIMENTAL PROCEDURE

In order to study the growth mechanisms of the solder deposition, a series of electrodeposition experiments were carried out and stopped at different stages of growth. In this way, a sequential picture of the growth processes for each phase could be studied. Deposition was done on standard Ti/Au metallized wafers using a Dynatronix DuPR 10-0.1-0.3 Pulse Plating Power Supply. For all plating experiments, the pulse on-time was set at 2ms and the off-time was set at 8ms with a forward direction of 10ms.

Based on previous work, the Au₅Sn phase, ξ, was produced using average current densities <1.0 mA/cm². The AuSn phase, δ, was deposited using average current densities >2.0 mA/cm² [3]. Deposition time was varied for each phase, and the resulting film structure, morphology, and composition were studied using the scanning electron microscope (SEM) and the transmission electron microscope (TEM).

The plating solution had five major constituents; the solution development details have been published elsewhere [2,3]. The KAuCl₄ and SnCl₂·2H₂O salts were
the sources of the Au(III⁺) and Sn(II⁺) ions respectively. Tri-ammonium citrate was added as a buffer to maintain a nearly neutral solution pH. Sodium sulfite acted as a complexing agent for the gold, and to some degree the tin, while l-ascorbic acid was used to prevent the hydrolysis of the tin in water.

**PHASE MORPHOLOGY**

Before experimentation, it is important to establish standards against which the results can be compared. Figure 2 is a topographical image of the Ti/Au metallized blanket wafer that was used for deposition. The image reveals a flat, uniform surface. It is also important to note that the grain structure is too fine to be viewed in this image. Figures 3a and 3b show topographical images of a continuous and uniform layer for each phase. Note that like the gold seed layer, the Au₅Sn phase possesses grains that are too fine to resolve in the SEM and it is a flat deposit. This is likely due to the high gold content of the phase. The AuSn also appears topographically flat, although its grain structure is coarser.

**SEM RESULTS**

Figures 4a-d show the progression of particle growth for the Au₅Sn phase. Prior to 66s, no particles were observed on the surface of the wafer. A gradual coarsening of the particles can be seen as time progresses. Initially, the particles are small and finely dispersed. However, in the subsequent images, the particles have become larger. At 180s, there is evidence of two particles having grown together to form one larger particle, suggesting islanding is the primary growth mechanism. This type of growth is similar to Volmer-Weber growth used to describe epitaxial growth [4]. This type of coarsening behaviour continues and is seen at both 400s and 600s. By 600s there is evidence of a continuous layer. Although there are still distinct particles visible, it is apparent that they are a part of a continuous matrix that spans the wafer area. What has not happened at this stage,
is the leveling effect that is seen in the final deposit in Figure 3a.

Figures 4a-d show a similar progression of film growth for the AuSn phase. Again, no particles were observed prior to 18s. Unlike the growth mechanism for the Au5Sn phase where particle coarsening was slow, the AuSn particles coarsen quickly without agglomeration. Instead, more particles form filling the gaps between other particles. By 60s, although a continuous layer has not quite formed, the entire wafer surface is almost completely covered. At 180s, although the particles have grown larger, there are still many voids between various particles. Indeed, it is not until 300s that the particles begin to grow together and form a structure that resembles Figure 3b.

A different growth mechanism for each phase is expected because of the difference in deposition current density. At the higher current density (2.4mA/cm²) for depositing Au5Sn, many more atoms impinge upon the surface of the wafer allowing for easy nucleation. This results is a situation where there are many small nuclei that form and grow until a complete layer is deposited as seen in Figure 5. However, at the lower current density (0.8mA/cm²) for depositing AuSn, there are comparatively fewer atoms impinging on the surface of the wafer. This makes nucleation more difficult resulting in fewer, but often larger, nuclei that will tend to grow together at the expense of forming more nuclei. This trend is seen in the coarsening behavior of the Au5Sn that is illustrated in Figure 4. The lower current density will also result in a slower plating rate, accounting for the longer time required to produce visible particles and a continuous layer.

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**TEM RESULTS**

The TEM was used to obtain cross-section images of the particles and layers that are forming. Figure 6 shows a sample of a deposit that has been growing for 1200s at a deposition rate of 0.8mA/cm². On the gold seed layer is a fairly large solder particle exhibiting a multi-grain structure. What is important to observe is that there
are few voids along the growth interface. Although the solder layer is not uniform, it is definitely continuous. The structure is similar to the one seen in Figure 4d showing a larger particle protruding from a continuous matrix.

Figure 6. TEM cross-sectional image of particle deposited at 0.8mA/cm² for 1200s.

Figure 7 is an image of smaller particles that have just nucleated after plating at 2.4mA/cm² for 18s. This corresponds to the finely dispersed structure seen in Figure 5a. Figure 8, at 300s, clearly shows that the deposit has become a continuous and uniform layer confirming the SEM results.

Figure 7. TEM cross-sectional image of particles deposited at 2.4mA/cm² for 18s.

Figure 8. TEM cross-section image of deposit at 2.4mA/cm² for 300s

CONCLUSIONS
The nucleation and growth characteristics of Au/Sn films electrodeposited from a chloride-based plating solution have been studied. Two phases form during deposition, Au₅Sn at lower plating current densities (<1 mA/cm²) and AuSn at higher current densities (>2 mA/cm²). The Au₅Sn formation process has been shown to be nucleation controlled, while AuSn formation is growth controlled and considerably faster.

ACKNOWLEDGEMENTS
The authors would like to acknowledge the funding received for this project from Nortel Networks and the Natural Sciences and Engineering Research Council (NSERC) of Canada.

REFERENCES