

## 中文摘要

由於鉛污染問題，現今已用無鉛錒料取代鉛錒錒料，但無鉛化製程仍有可靠度上的問題，例如封裝適合性、孔洞的形成等。在錒點  $\text{Cu}_3\text{Sn}/\text{Cu}$  界面處，我們有時可以觀察到一整排 Kirkendall's voids，這些孔洞的形成是造成產品失效的主要兇手，而由於 Kirkendall's voids 只會生長在  $\text{Cu}_3\text{Sn}$  介金屬層上，因此， $\text{Cu}_3\text{Sn}$  生長型態與 Kirkendall's voids 的形成是息息相關的，本實驗觀察的重點即在於  $\text{Cu}_3\text{Sn}$  生長。

為了改善無鉛錒料的品質，減少介金屬  $\text{Cu}_3\text{Sn}$  生成，添加微量元素於錒料中將有助於降低  $\text{Cu}_3\text{Sn}$  生成厚度，本實驗室先前研究結果發現，添加 0.1% 的 Ni 於 Sn3.5Ag 錒料中，能有效降低  $\text{Cu}_3\text{Sn}$  生成。在本研究中，將所添加微量元素的量縮小到 0.1% 以下，觀察其是否仍具有相同效果。另一方面，我們也添加 Fe、Co 兩種微量元素和 Ni 做比較，本實驗目的為探討添加微量 Fe、Co、Ni 於錒料中，與 Cu 墊層進行錒接與熱處理反應時對界面生成物的影響。

實驗結果顯示當我們把微量元素 Fe、Co、Ni 的使用量縮小的情況下，仍具有抑制  $\text{Cu}_3\text{Sn}$  生長，但卻增加  $\text{Cu}_6\text{Sn}_5$  形成。在  $160^\circ\text{C}$  下當熱處理時間超過 1000 小時，在 Sn2.5Ag-xNi 與 Cu 墊層反應的試片中， $\text{Cu}_3\text{Sn}/\text{Cu}$  界面處有 Kirkendall's voids 生長，而由於孔洞生長的位置靠近 Cu 墊層，因此我們推測在  $\text{Cu}_3\text{Sn}$  層裡，Cu 原子擴散的速度比 Sn 原子快；另外，在 Sn2.5Ag0.8Cu-xNi 與 Cu 墊層反應的試片中，在錒點界面處並沒有孔洞的生成，本實驗結果推測錒料中 Cu 含量應是其中一個控制孔洞生成的因子。

Sn2.5Ag-xNi 與 Cu 墊層反應中，在界面生成物  $\text{Cu}_6\text{Sn}_5$  上有兩層 Ni 分佈，靠近錐料端的  $\text{Cu}_6\text{Sn}_5$  Ni 含量比靠近 Cu 墊層端的  $\text{Cu}_6\text{Sn}_5$  Ni 含量多，這是由於在冷卻過程中，錐料中部分 Ni 回到界面所致；而在 Sn2.5Ag0.8Cu-xNi 與 Cu 墊層反應中，界面生成物  $\text{Cu}_6\text{Sn}_5$  沒有 Ni 分層情形，因為 Sn2.5Ag0.8Cu 錐料中本身含有 Cu，與 Cu 墊層錐接時錐料內部生成的  $\text{Cu}_6\text{Sn}_5$  多，部分的 Ni 溶解到錐料內的  $\text{Cu}_6\text{Sn}_5$  中，以致於冷卻過程中，回到界面上的 Ni 少，才不會有分層的情形。

本實驗之主要目的即是探討 Fe、Co、Ni 的添加對無鉛錐料與 Cu 界面反應之影響。研究目標是去深入了解加入第四元素對  $\text{Cu}_6\text{Sn}_5$ 、 $\text{Cu}_3\text{Sn}$ 、及 Kirkendall's voids 生長之影響，進而找出最佳之無鉛錐料合金組成。

## ABSTRACT

Owing to the ban of lead, the conventional lead-bearing solder has been replaced by lead-free solder. The drive for lead-free solders in the microelectronics industry presents some reliability challenges. Examples include package compatibility, creep, and Kirkendall's voids. Along the  $\text{Cu}_3\text{Sn}/\text{Cu}$  interface, we can find a series of Kirkendall's voids. These Kirkendall's voids were the true culprit responsible for the weakening of the interface. It is widely accepted that the formation of these Kirkendall's voids is related to the growth of  $\text{Cu}_3\text{Sn}$ .

In order to promote the quality of lead-free solder, minor elements addition can reduce the  $\text{Cu}_3\text{Sn}$  thickness. Recently, our research group showed that a 0.1 wt.% Ni addition to SnAg could reduce the  $\text{Cu}_3\text{Sn}$  thickness during the solder/Cu reaction. We want to extend this past result to find out the minimum level of Ni addition that still retains this beneficial effect. In addition, we will also investigate whether the elements, Fe, and Co will have a similar effect. The objective of this study is to investigate the effects of minor Fe, Co, and Ni on the soldering and aging reactions between lead-free solders and Cu.

The experimental result shows that the presence of Ni can in fact reduce the growth rate of  $\text{Cu}_3\text{Sn}$  but increase the formation of  $\text{Cu}_6\text{Sn}_5$ . Moreover, the presence of Fe and Co can have the some effect. We can find the Kirkendall's voids in the reaction between  $\text{Sn}_{2.5}\text{Ag}-x\text{Ni}$  ( $x=0\sim 0.1\text{wt. \%}$ ) and electroplated Cu at  $160\text{ }^\circ\text{C}$  for excess 1000 hr. The observation of Kirkendall's void formation near the  $\text{Cu}_3\text{Sn}/\text{Cu}$  is direct evidence of Cu diffusion since we can use the voids to serve as diffusion markers. On the side, we didn't find voids in the reaction between  $\text{Sn}_{2.5}\text{Ag}_{0.8}\text{Cu}-x\text{Ni}$  ( $x=0\sim 0.1\text{wt. \%}$ ) and electroplated Cu. The growth of voids is complicated. We consider that the Cu concentration in the solders

is the factor to control the void formation.

In the Sn2.5Ag-xNi solders, the addition of Ni also produces two distinct  $\text{Cu}_6\text{Sn}_5$  regions at the interface. The outer region contains more Ni, and the inner region contains less Ni. Cooling conditions changed the Ni content of the  $\text{Cu}_6\text{Sn}_5$  formed at the interface. Besides, the Sn2.5Ag0.8Cu-xNi solders didn't have two different Ni content in the  $\text{Cu}_6\text{Sn}_5$ . This is because there are more  $\text{Cu}_6\text{Sn}_5$  precipitated in the Sn2.5Ag0.8Cu-xNi than in Sn2.5Ag-xNi solders. A part of Ni could be dissolved in the  $\text{Cu}_6\text{Sn}_5$ . Therefore, a few Ni could come back to interface.