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1.0% Zn, Ni 对 Sn－3.5Ag/Cu 界面反应及化合物生长的影响

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摘 要: 在微电子互连结构中, 反应界面化合物层的形貌及厚度是决定焊点可靠性的一个重要因素。通过向 Sn－3.5Ag 共晶钎料中添加第三元素, 分别研究元素 Zn 和 Ni 对 Sn－3.5Ag/Cu 界面反应的影响。结果表明, 对于 Sn－3.5Ag/Cu 界面, 液态反应初始生成物为 Cu_6Sn_5, 在随后的热老化阶段形成 Cu_3Sn 化合物层; Zn 元素不影响界面的初始生成相及其厚度, 但在 150 ℃老化阶段, Cu_3Sn 化合物的形成受到抑制, 取代的是非连续的 Cu_5Zn_8 化合物层, 并且, 化合物层增厚速度减慢; 然而, 当添加 1.0%(质量分数)的 Ni 元素后, 界面初始生成相为 $(Cu, Ni)_6Sn_5$, 该化合物层厚度明显大于前者, 老化阶段界面无其它相生成。

关键词: 无铅钎料; 合金元素; 界面反应; 金属间化合物
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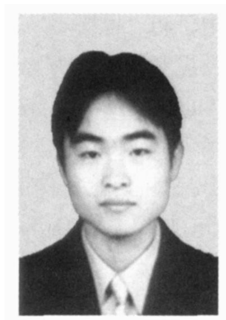
余 春

0 序 言

随着无铅化进程的延续, 无铅钎料将逐渐取代 Sn－37Pb 共晶钎料。SnCu, SnAg 和 SnAgCu 共晶或近共晶钎料是最有希望的替代品[1]。这类钎料的特点是, 合金元素的含量较低, 而 Sn 元素的含量达 95%(不做特殊说明, 均为质量分数)以上, 其性质明显区别于 SnPb 共晶钎料。因此, 无铅钎料取代 SnPb 共晶钎料, 会带来一系列问题, 如熔点、润湿性、耐腐蚀性、界面可靠性等等。特别是倒装焊(flip chip)、芯片级封装(chip scale packaging)技术的广泛应用, 要求互连焊点尺寸不断减小, 以适应高性能电子产品的发展。目前焊点尺寸已达到 100 μm 以下。因此, 界面可靠性问题成为制约钎料推广及封装技术发展的主要因素之一[2]。

Sn－3.5Ag 共晶钎料具有优良的润湿性、耐腐蚀性和耐疲劳冲击性, 被用于许多特殊场合[3]。近年来, 国内外学者通过向 Sn－3.5Ag 钎料中添加 Cu, Sb, Ni, In, Bi, Zn 以及稀土元素, 以期进一步改善该钎料的性能, 并取得了不错的效果。特别是当添加 1.0% Zn 元素后, Sn－3.5Ag 钎料的晶粒得到细化, 组织分布均匀, 同时, 屈服强度和抗剪强度得到提高[4]。然而, 很少有关于 Zn 元素如何影响 Sn－3.5Ag/Cu 界面反应的报道。另外, Ni 是钎料接头界面常见的一种元素, 其对界面反应的影响也值得探讨。

作者通过向 SnAg 共晶钎料中分别添加 1.0% Zn, Ni 元素, 重点研究 SnAg/Cu, SnAg－Zn/Cu, SnAg－Ni/Cu 界面反应物随老化时间的演变情况, 为该钎料的推广应用提供试验数据。

1 试验方法

在加热炉中, 将纯 Sn, 纯 Ag 和纯 Zn 以及纯 Sn, 纯 Ag 和纯 Ni 分别混合熔炼, 生成如表 1 所示配比的钎料。熔炼过程中, 熔融金属采用共晶配比的 KCl＋LiCl 混合盐进行保护, 熔炼温度为 600 ℃, 保温时间为 4 h, 充分搅拌。液态钎料在冷却到约 300 ℃时浇注入直径 6 mm 的不锈钢模具, 自然冷却。随后, 将钎料棒切割成尺寸为 ϕ5 mm×2 mm 的小圆盘, 置于丙酮中用超声波清洗, 吹干后备用。将圆盘状钎料浸入活性松香助焊剂中, 随后放置于 20 mm×20 mm×0.2 mm 的铜箔上, 在加热炉加热至 260 ℃, 并在钎料液态温度以上保温 60 s。以上试样在 150 ℃恒温炉中进行恒温热老化 0～20 d。之后, 将试样进行冷镶嵌, 在 SiC 细砂纸上打磨后, 采用 0.05 μm 的 Al_2O_3 悬浮液进行抛光, 表面经轻腐蚀之后, 采用扫描电镜及能谱分析仪分析反应界面的微观组织形貌及成分。

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表 1 钎料成分(质量分数, %)

Table 1 Components of solder

	Zn	Ag	Sn
Sn-3.5Ag	0	3.5	余量
Sn-3.5Ag-1.0Zn	1.0	3.5	余量
Sn-3.5Ag-1.0Ni	1.0	3.5	余量

2 结果及分析

图 1 为 Sn-3.5Ag/Cu 界面反应物演变情况的二次电子相。根据 Cu-Sn 二元相图可知, Cu/Sn 界面的反应产物主要为 Cu_6Sn_5 和 Cu_3Sn 两种化合物, 由于 Cu_6Sn_5 的 Gibbs 自由能更低, 因此在液态反应阶段最先形成 Cu_6Sn_5。但是, Cu 和 Cu_6Sn_5 处于不平衡状态, 在热老化条件下, 会促发反应, $Cu+Cu_6Sn_5 \rightarrow Cu_3Sn$, 从而形成 Cu_3Sn, 降低界面自由能, 使体系稳定。在焊态下, 如图 1a 所示, 反应界面形成了一层连续的扇贝状化合物层, 能谱分析表明该化合物为 Cu_6Sn_5。150 ℃条件下保温一段时间后, 在 Cu_6Sn_5/Cu 界面形成了一层新的化合物, 图 1b 为保温 20 d 后的界面形貌电子相, 能谱分析表明, 该化合物层为 Cu_3Sn。

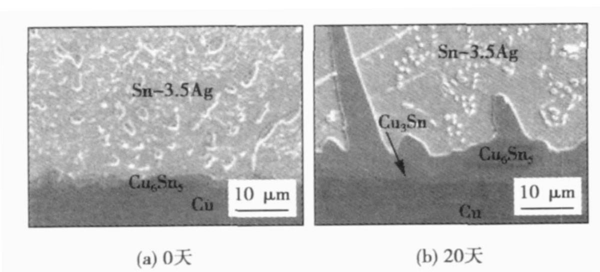

图 1 Sn-3.5Ag/Cu 界面 150 ℃老化条件下化合物的演变情况

Fig. 1 Evolution of intermetallics (IMCs) at Sn-3.5Ag/Cu interface aged at 150 ℃

另外, 在热老化阶段, 总的化合物层厚度随老化时间的延长而增加。并且, Cu_6Sn_5 化合物层的增厚速度明显快于 Cu_3Sn。

图 2 反映了 Sn-3.5Ag-1.0Zn/Cu 界面微观组织的二次电子相。焊态下, 如图 2a 所示, 反应界面同样形成了一层扇贝状化合物层, 能谱分析表明该化合物层为 Cu_6Sn_5。文献[5] 的研究结果表明, 当 Sn-0.7Cu 钎料中 Zn 元素的含量为 1.0%时, 焊态下最先形成的化合物为 Cu_5Zn_8。并且, Sn-9Zn/Cu 反应界面上最先生成的化合物也是 Cu_5Zn_8[6]。然而, 当 Sn-9Zn 钎料中添加了适量的 Ag 元素后, 界面上的初始生成相就变成了 Cu_6Sn_5[7]。因此, 试验结果表明, 少量的 Zn 元素并不会改变界面初始化合物的形貌和物相。

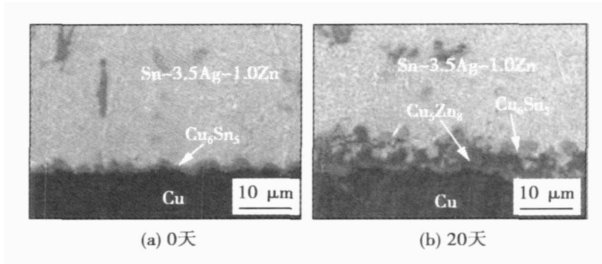

图 2 Sn-3.5Ag-1.0Zn/Cu 界面在 150 ℃老化条件下化合物的演变

Fig. 2 Evolution of IMCs at Sn-3.5Ag-1.0Zn/Cu interface aged at 150 ℃

然而, 在 150 ℃条件下对以上试样进行老化试验后发现, Cu_3Sn 化合物层并没有出现在反应界面, 并且, 反应界面发生了显著的变化。图 3b 为热老化 20 d 后的界面微观形貌, 由图可见, 化合物由深色和浅色两相交错组成。能谱分析表明, 深色化合物为 Cu_5Zn_8, 浅色为 Cu_6Sn_5。

图 3 反映了 Sn-3.5Ag-1.0Ni/Cu 界面微观组织的二次电子相。很明显, 液态反应层的厚度比前两种反应界面都要厚, 如图 3a 所示, 能谱分析表明该化合物为 $(Cu, Ni)_6Sn_5$。随着保温时间的延长, 化合物层的厚度不断增加, 如图 3b 所示, 但并未出现新的化合物层。由于化合物生长过快, 化合物层中弥散着一些未反应的钎料。

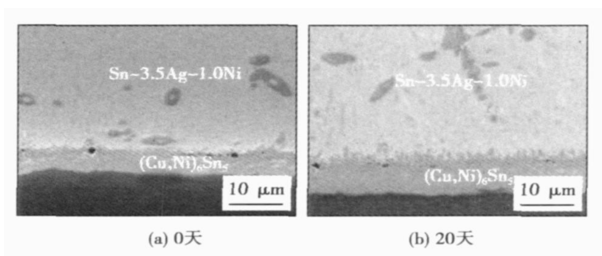

图 3 Sn-3.5Ag-1.0Ni/Cu 界面在 150 ℃老化条件下化合物的演变

Fig. 3 Evolution of the IMCs at Sn-3.5Ag-1.0Ni/Cu interface aged at 150 ℃

图 4 为化合物层的厚度与老化时间及钎料成分的关系曲线。其中, 化合物层的厚度是用反应界面化合物层的总面积除以界面的水平长度得到的。从图中可以看到, 在焊态下, 金属间化合物层的厚度与

Zn 元素的含量基本上无关。随着老化时间的延长，Sn3.5Ag/Cu 界面金属间化合物层的厚度迅速增加。然而，添加了 Zn 元素后，化合物层的增厚速度有所减缓。说明 Zn 元素的添加对界面化合物的生长有一定的抑制作用。从生长动力学角度来看，界面化合物的生长受反应原子的扩散速度控制。Cu 是 Cu/Sn 界面反应及化合物生长的主要元素。Cu 经过化合物层向钎料中扩散，并与 Sn 反应形成新相，从而化合物层不断增厚。Cu 在 Cu_6Sn_5 和 Cu_5Zn_8 中的扩散速度分别为 4.3×10^{-13}，2.95×10^{-15} cm^2/s[8]。因此，在反应界面形成 Cu_5Zn_8 化合物层后，Cu 的扩散系数降低了 2 个数量级，从而制约了化合物层的生长。

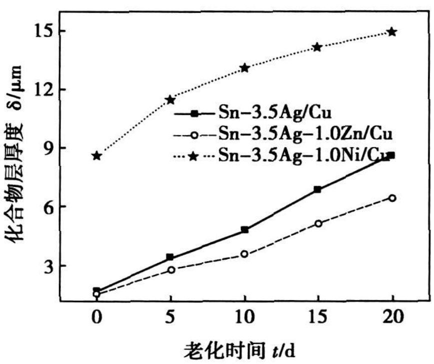

图 4　界面化合物层生长曲线

Fig 4　Growth rule of total IMCs layer at different interfaces

然而，当添加 1.0% 的 Ni 元素后，界面初始化合物的厚度约为 Sn－3.5Ag/Cu 界面的 5 倍。但是在随后的老化阶段，化合物的生长速度逐渐减缓。Gao 等人在研究 Sn－3.5Ag－0.2Ni/Cu 界面时发现，Sn－3.5Ag－0.2Ni/Cu 界面初始化合物层的厚度是 Sn－3.5Ag/Cu 界面化合物层厚度的 3 倍。主要原因是 Ni 元素促进界面化合物的形核率，并且，Ni 元素的含量越多，作用越明显。

3　结　　论

（1）Sn－3.5Ag/Cu 界面的初生相为扇贝状 Cu_6Sn_5，老化阶段化合物层不断增厚，同时在铜侧界面形成 Cu_3Sn 化合物层。

（2）钎料中添加 1.0% 的 Zn 元素对 Sn－3.5Ag/Cu 界面的初始生成相无影响，但在随后的热老化阶段，Cu_3Sn 的形成受到抑制，取代的是 Cu_5Zn_8。化合物层的生长速度相对减慢。

（3）当钎料中添加 1.0% 的 Ni 元素后，Sn－3.5Ag/Cu 界面的初始生成相为 $(Cu, Ni)_6Sn_5$，化合物层的厚度是原来的 5 倍。

参考文献：

[1]　Laurila T, Vuorinen V, Kivilahti J K. Interfacial reactions between lead-free solders and common base materials [J]. Materials Science and Engineering R, 2005, 49(1—2): 1—60.

[2]　Choi S, Lucas J P, Subramanian K. N, *et al*. Formation and growth of interfacial intermetallic layers in eutectic Sn－Ag solder and its composite solder joints [J]. Journal of Materials Science: Materials in Electronics, 2000, 11(3): 497—502.

[3]　Ochoa F, Williams J J, Chawla N. Effects of cooling rate on the microstructure and tensile behavior of a Sn3.5wt.% Ag solder[J]. Journal of Electronic Materials, 2003, 32(12): 1414—1420.

[4]　Kariya Y, Otsuka M. Mechanical fatigue characteristics of Sn－3.5Ag－X(X=Bi, Cu, Zn and In) solder alloys[J]. Journal of Electronic Materials, 1998, 27(11): 1229—1235.

[5]　Wang F J, Ma X, Qian Y Y. Improvement of microstructure and interface structure of eutectic Sn－0.7Cu solder with small amount of Zn addition [J]. Scripta Materialia, 2005, 53(6): 699—702.

[6]　Lee B J, Hwang N M, Lee H M. Prediction of interface reaction products between Cu and various solder alloys by thermodynamic calculation [J]. Acta Materialia, 1997, 45(5): 1867—1874.

[7]　Chang T C, Wang M C, Hon M H. Growth and morphology of the intermetallic compounds formed at the Sn－9Zn－2.5Ag/Cu interface [J]. Journal of Alloys and Compounds, 2005, 402(1—2): 141—148.

[8]　Chao B, Chae S H, Zhang X F, *et al*. Electromigration enhanced intermetallic growth and void formation in Pb-free solder joints [J]. Journal of Applied Physics, 2006, 100: 084909—084910.

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strength test. According to the microstructure analysis, thin TiC layer generated due to the reaction of filler metal and graphite, which formed high-strength interface. Brazing seam was mainly consisted of solid solution, with intermetalic compound distributing in it.

Key words: copper; graphite; brazing

Microstructure and strength of aluminum and aluminum alloy joint brazed with rapidly-cooled Al—Si—Cu—Zn filler metals

ZOU Jiasheng, LV Sicong, ZHAO Hongquan, LUO Xinfeng (Provincial Key Laboratory of Advanced Welding Technology, Jiangsu University of Science and Technology, Zhenjiang 212003, Jiangsu, China). p77—80

Abstract: The microstructure and strength of aluminum and 6063 aluminum alloy joints brazed with Al70Si7.5Cu20Zn2.5 and Al65Si10Cu20Zn5 rapidly-cooled filler metals were studied. The result indicates that the brazed joint is composed of base metal, center of brazing seam and interface region. The microstructure of interface is α Al solid solutions, while the center of brazing seam is α Al solid solutions, Si and θ (Al_2Cu). The resnlt also indrcates that the strength of the joint brazed with Al65Si10Cu20Zn5 is higher that the one brazed with Al70Si 7.5Cu20Zn2.5, and the strength of the joint using chloride flux is hgher that the one usding fluoried flux. Under the same technological conditions, shear strength of aluminum joint brazed with rapidly cooled fillers is better than the one of conventional fillers, which increased about 40%.

Key words: Al—Si—Cu—Zn brazing filler metal; rapidly-cooled ribbon fillers; aluminum and aluminum alloy; interface construction; shear strength

Effects of 1.0% Zn or Ni additions on interfacial reaction and growth of intermetallics in Sn-3.5Ag/Cu joint

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Abstract: The morphology and thickness of the intermetallic compounds (IMCs) layer become one of the dominant factors which determine the reliability of the soldered joints in integrate circuit. The effects of Zn and Ni on the reaction of Sn—3.5Ag/Cu interface were investigated by adding 1.0% Zn or Ni addition into the eutectic Sn—3.5Ag solder. It is found that, for Sn—3.5Ag/Cu interface, the initial product was Cu_6Sn_5 IMC, and Cu_3Sn IMC layer was formed at the following 150 ℃ thermal aging period. Although Zn addition had little effect on the thickness of reaction lagers, the Cu_3Sn IMC in the reaction layer was found to be depressed, at the some time, non-continuous Cu_5Zn_8 IMC layer was formed, moreover, the thickening rate of the IMC layer decreased. Whereas, the original product was $(Cu, Ni)_6Sn_5$ as Ni was added, in addition, the initial thickness of the IMC layer was much thicker. However, there was no other product at the aging stage.

Key words: lead free solder; alloying element; interfacial reaction; intermetallic compound

Stress intensity factor of interfacial crack between metal-base ceramic coating and steel

XU Lianyong, JING Hongyang (School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China). p84—88

Abstract: The three-point bending fracture mechanics experiments and finite element analysis had been used to compute the complex stress intensity factor (K) of the interfacial crack between LX88A coating and Q345 steel. It was found that the K-dominant zone exist near the crack tip only for some specimens. The result indicates that K_C can not be used as the single fracture parameter to evaluate the interface fracture behavior for three-point bending specimen. Therefore, it is necessary that the elastic-plastic fracture mechanics and probabilistic fracture mechanics are used to analyze such interface cracks.

Key words: interfacial crack; complex stress intensity factor; 3-point bend test; finite element analysis

Microstructure and strength analysis of IC10 alloy TLP-DB joint

HOU Jinbao, ZHANG Lei, WEI Youhui (Beijing Aeronautical Manufacturing Technology Research Institute, Beijing 100024, China). p89—92

Abstract: TLP-DB (transient liquid phase diffusion bonding) experiments were carried out on IC10 alloy, which is one kind of intermetallic compound based on Ni_3Al. Experimental results showed that with proper interface layer and welding parameters, microstructure of TLP-DB joints could be the same as the matrix, which consists of γ and γ′ phases. Endurance strengths of the joints under 980 ℃ were above 128 MPa, and had reached 80% of the matrix. Employed for a long time at high temperature, tensile strengths of the joints under room temperature and high temperature were mostly close to the matrix. Fracture of room temperature tensile samples was mainly made up of quasi-cleavage pattern, and fracture of high temperature tensile samples was mainly made up of dimple pattern.

Key words: IC10 alloy; transient liquid phase diffusion bonding; fracture pattern

Analysis of characteristic zones of isothermal superplastic welded joint of heterogeneous steels

ZHANG Keke, SHI Hongxin, YU Hua, YANG Yunlin (School of Materials Science and Engineering, Henan University of Science & Technology, Luoyang 471003, Henan, China). p93—96

Abstract: Through such ultra-fining-pretreatment of 40Cr and T10A steels as salt-bath cyclic quenching, high frequency hardening and laser hardening, the microstructure appearance, the superplastic microstructure characteristic and their forming characteristic of isothermal superplastic welded joint of heterogeneous steels are systematically studied by the metallurgical microscope and electron microscope. And the characteristic zone forming model of the joint is established. The experimental results indicate that it occurs obviously the diffusive behavior in the isothermal superplastic welded interface and the characteristic zones of the joint are divided into three zones