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The Influence of Barrel Plating Process Parameters on the Composition of Sn-Ag-Cu Deposits

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Abstract: *In response to the new demands for lead-free solder deposit preparation technology brought about by the miniaturization and high-density integration of electronic components, this study, based on a self-developed methanesulfonate-based barrel plating solution, systematically investigated the effects of key barrel plating process parameters-including current density, plating solution temperature, pH value, barrel rotation speed, and plating time-on the composition of Sn-Ag-Cu deposits. The results indicate that current density and temperature are the predominant factors influencing deposit composition, while pH value and rotation speed exhibit a comparatively negligible impact. Prolonged plating time leads to a slight decrease in the Ag and Cu content within the deposit due to concentration depletion. Through the optimized barrel plating process, a uniform alloy deposit with a composition close to the eutectic composition of Sn-3.0Ag-0.5Cu was successfully achieved on 1mm copper spheres.*

Keywords: *Barrel plating, Sn-Ag-Cu alloy, Deposit Composition, Process optimization*

1. Introduction

SnPb solder has been strictly restricted by international regulations such as the European Union's Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) due to the environmental and health hazards arising from its lead content[1]. Among various lead-free alternatives to Sn-Pb solders, Sn-Ag-Cu alloy solder is considered one of the most promising substitute materials due to its solderability being the closest to traditional Sn-Pb solder, particularly its excellent soldering reliability, wettability, and corrosion resistance[2-3]. Sn-Ag-Cu alloy deposits are primarily applied to solderable surface finishes for electronic components, including die-to-substrate interconnections in semiconductor packaging (e.g., QFP, BGA packaging), flip-chip interconnects, micro-bump fabrication, and interconnections for miniature components in high-density integrated circuits[4-7].

Current research on Sn-Ag-Cu alloy deposits predominantly focuses on rack plating processes, which typically employ methanesulfonate-based plating solutions[8-13]. Joseph et al[8]. electrodeposited a Sn2.7Ag0.9Cu alloy deposit from a methylsulfonate solution at approximately pH 4, using thiourea as the complexing agent and incorporating the surfactant octylphenoxypolyethoxyethanol (OPPE). Tsai et al[9]. achieved the electrodeposition of a Sn2.7Ag0.7Cu ternary alloy deposit from an electrolyte at pH 3, employing citric acid as the sole complexing agent. Although significant advances have been made in the preparation of Sn-Ag-Cu alloy deposits via rack plating, this traditional technique struggles to meet the demands of efficient, high-volume production of miniature parts in the context of the trend towards miniaturization and high-density integration of electronic components[14]. Barrel plating, in contrast, offers advantages such as high production efficiency and superior uniformity of the deposit, making it suitable for processing small, high-volume components[15]. However, systematic studies on its application to Sn-Ag-Cu alloy deposits are scarce. Therefore, based on a self-developed barrel plating solution system, this paper focuses on investigating the influence of barrel plating process parameters (such as current density, barrel rotation speed, plating solution pH, plating temperature, and plating time) on the composition of Sn-Ag-Cu alloy deposits. The aim is to optimize the deposition process to produce Sn-Ag-Cu alloy deposits with uniform composition (targeting the eutectic composition of Sn-3.0Ag-0.5Cu), dense structure, and excellent performance, thereby addressing the pressing industrial need for highly reliable and environmentally friendly surface mount technologies.

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2. Experiment Content

2.1 Barrel Plating Process and Plating Solution Preparation

The barrel plating experiments were conducted using a ZL10060-C-3L small-scale barrel plating machine (barrel length: 100 mm, diameter: 60 mm) to deposit Sn-Ag-Cu alloy coatings onto 1 mm diameter copper spheres, with a pure tin plate serving as the anode. The plating solution (2L) was prepared as follows: 1) 232.2g of sodium citrate was dissolved in water, followed by the addition of 59.4g of stannous methanesulfonate and 0.76g of copper methanesulfonate; 2) 83.8g of thiourea was dissolved in water, and 1.62g of silver methanesulfonate was added to this solution; 3) 4g of ascorbic acid was added to the mixed solution from steps 1) and 2). The pH was subsequently adjusted using citric acid and sodium hydroxide solutions, and the final volume was brought to 2L with deionized water.

2.2 Deposit Composition Characterization

The composition of the Sn-Ag-Cu alloy deposit on the surface of the copper spheres was analyzed using the Energy Dispersive Spectrometer (EDS) attached to a ZEISS EVA-10 scanning electron microscope. For each group, five copper sphere samples were selected for testing. Three distinct areas on the surface of each copper sphere were measured, and the average value was calculated.

3. Result and Discussion

3.1 Effect of Current Density on Deposit Composition

Figure 1 illustrates the composition of the Sn-Ag-Cu alloy deposits obtained at different current densities under the following constant conditions: a plating solution temperature of 25 ℃, a pH of 5.0, a barrel rotation speed of 10 $r \cdot min^{-1}$, and a plating time of 5 min. The results indicate that the current density significantly influences the composition of the deposits within a specific range. As the current density increases, the Sn content in the deposit gradually increases, while the Ag and Cu contents decrease and gradually stabilize. At a current density of 0.5 $A \cdot dm^{-2}$, the Ag and Cu contents in the deposit were 18.87% and 4.32%, respectively, significantly higher than the corresponding proportions in the eutectic Sn-Ag-Cu alloy. When the current density was increased to 3 $A \cdot dm^{-2}$ and 4 $A \cdot dm^{-2}$, the Ag content decreased to 3.78% and 2.83%, and the Cu content decreased to 1.01% and 0.91%, respectively. At these levels, the composition of the deposit approached that of the eutectic alloy.

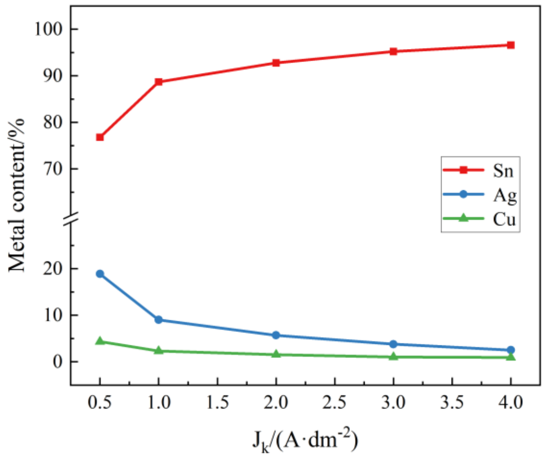

Figure 1. Effect of Current Density on Deposit Composition

This phenomenon can be attributed to the preferential reduction and deposition of the more noble metals Ag and Cu at lower current densities, where electrode polarization is minimal. As the current density increases, enhanced cathodic polarization causes a negative shift in the electrode potential, favoring the reduction of Sn^{2+}/Sn. Concurrently, a concentration polarization develops because Sn^{2+} ions consumed at the cathode inside the barrel cannot be replenished timely by ions from the bulk solution outside the barrel. This concentration difference intensifies with increasing current density[16]. Under the combined effects of these two polarization mechanisms, the Sn content in the deposit increases with rising current density. Furthermore, studies have shown that excessively high current densities can lead to rough and uneven deposit surfaces[17]. Therefore, considering both the compositional influence and surface quality, a current density of 3 A·dm^{-2} is deemed optimal.

3.2 Effect of Plating Solution pH on Deposit Composition

Figure 2 illustrates the composition of Sn-Ag-Cu alloy deposits obtained at different temperatures under constant conditions: a current density of 3 A·dm^{-2}, pH of 5.0, barrel rotation speed of 10 r·min^{-1}, and plating time of 5 min. The results demonstrate that as the temperature increases, the Sn content in the deposit gradually rises, while the Ag and Cu contents decrease. Compared to the influence of current density, the effect of temperature on the individual components of Sn-Ag-Cu is relatively minor. At 20 ℃, the Ag and Cu contents in the deposit were 4.24% and 1.32%, respectively. When the temperature increased to 40 ℃, the Ag content decreased to 2.63% and the Cu content dropped to 0.52%.

Generally, the deposition of the more noble metals Ag and Cu, with their relatively positive deposition potentials, would be expected to be favored at higher temperatures. However, the observed decrease in Ag and Cu content with increasing temperature suggests that the concentration of Ag and Cu complexes within the cathode diffusion layer does not increase but rather decreases. This phenomenon may be attributed to the larger ionic radii of the Ag and Cu complexes, which results in their lower diffusion and migration rates compared to Sn complexes[16]. Concurrently, an increase in temperature can lead to higher porosity in the deposit, resulting in a less dense structure[17]. Considering both the compositional influence and deposit quality, a temperature of 25°C is determined to be optimal.

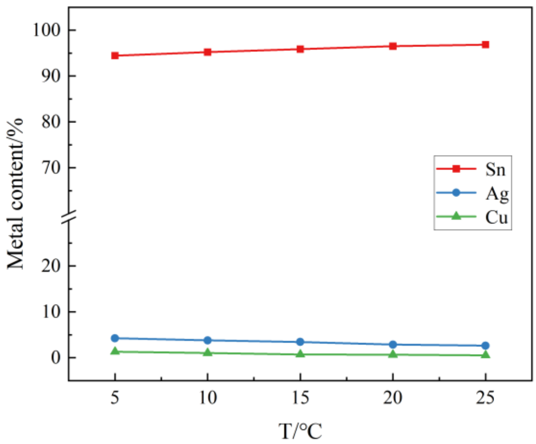

Figure 2. Effect of Plating Solution pH on Deposit Composition

3.3 Effect of Plating Solution pH on Deposit Composition

Figure 3 illustrates the composition of Sn-Ag-Cu alloy deposits obtained at different pH values under constant conditions: a current density of 3 A·dm^{-2}, plating solution temperature of 25 ℃, barrel rotation speed of 10 r·min^{-1}, and plating time of 5 min. The results indicate that the pH of the plating solution has a relatively minor influence on the elemental composition of the deposit. As the pH varies, the Ag and Cu contents fluctuate within a narrow range, with Ag content ranging between 3.14% and 4.57%, and Cu content between 1.01% and 2.05%. The absence of significant trends in deposit composition with pH changes suggests that, under these experimental conditions, solution pH is not a predominant factor affecting deposit composition.

The pH value may indirectly influence the co-deposition process by altering the speciation, stability, and transport behavior of metal complexes. However, due to the complexity of the plating solution composition-which contains various complexing agents and metal ions forming diverse coordination compounds with coupled behaviors-a precise analysis of its influence mechanism remains challenging. In the methanesulfonate-based plating system, both excessively low and high pH values have been shown to result in rough and porous deposits[17]. Considering its limited effect on composition and the critical impact on deposit quality, a pH value of 5.0 is determined to be optimal.

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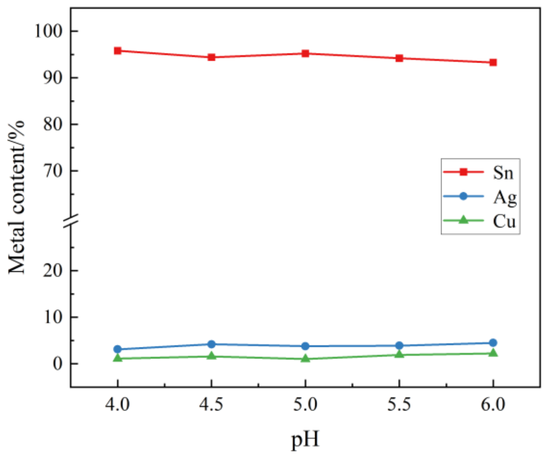

Figure 3. Effect of Plating Solution pH on Deposit Composition

3.4 Effect of Barrel Rotation Speed on Deposit Composition

Figure 4 illustrates the influence of barrel rotation speed on the composition of Sn-Ag-Cu alloy deposits obtained under constant conditions: a current density of 3 $A \cdot dm^{-2}$, temperature of 25°C, pH of 5.0, and plating time of 5 min. The results indicate that the rotation speed has a relatively minor effect on the elemental composition of the deposit. As the rotation speed increases, the contents of Ag and Cu do not exhibit a clear trend but fluctuate within a certain range. At a rotation speed of 12 $r \cdot min^{-1}$, the Ag and Cu contents in the deposit were 3.46% and 1.47%, respectively. When the rotation speed increased to 16 $r \cdot min^{-1}$, these values rose to 4.83% and 1.97%, respectively.

Variations in rotation speed primarily affect the convective transport of the plating solution and the mass transfer process at the electrode surface. However, since the deposition behaviors of Ag^{+} and Cu^{2+} are predominantly governed by current density rather than being entirely mass transfer-controlled, the composition exhibits limited sensitivity to changes in rotation speed. Furthermore, the speciation and stability of metal complexes in the plating system may partially buffer the impact of rotation speed on the co-deposition process, resulting in irregular compositional fluctuations. While increasing the rotation speed can improve deposit uniformity to some extent, excessively high speeds may reduce the deposition rate and increase energy consumption[17]. Considering its marginal effect on composition and the operational trade-offs, a rotation speed of 12 $r \cdot min^{-1}$ is determined to be optimal.

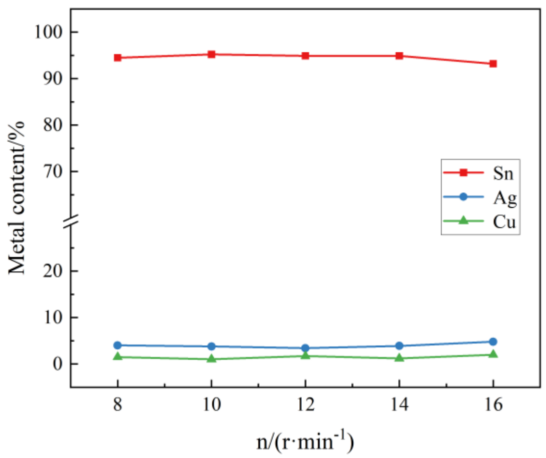

Figure 4. Effect of Barrel Rotation Speed on Deposit Composition

3.5 Effect of Plating Time on Deposit Composition

Figure 5 illustrates the influence of plating time on the composition of the Sn-Ag-Cu alloy deposit under constant conditions: a current density of 3 $A \cdot dm^{-2}$, temperature of 25°C, pH of 5.0, and barrel rotation speed of 12 $r \cdot min^{-1}$. The results indicate that plating time exerts a relatively minor influence on the overall composition of the deposit. However, as the deposition time prolongs, the contents of Ag and

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Cu in the deposit exhibit a progressively decreasing trend. When the plating time is 15 min, the Ag and Cu contents are 3.11% and 0.7%, respectively. Upon extending the time to 25 min, these values decrease to 2.57% and 0.61%, respectively.

This phenomenon is attributed primarily to the continuous consumption of Ag^{+} and Cu^{2+} ions in the plating solution due to their ongoing deposition throughout the process. Without replenishment during barrel plating, their concentrations in the solution gradually decline, leading to a reduction in the corresponding metal content within the deposit. Furthermore, prolonged deposition time may exacerbate the concentration polarization of metal ions within the diffusion layer, further influencing the co-deposition behavior of the alloy.

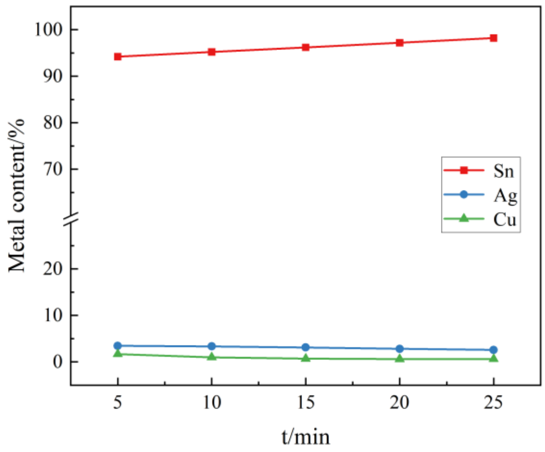

Figure 5. Effect of Plating Time on Deposit Composition

4. Conclusions

This study systematically investigated the effects of key barrel plating parameters-including current density, temperature, pH, rotation speed, and plating time-on the composition of Sn-Ag-Cu alloy deposits. It successfully fabricated a deposit with a composition close to the eutectic ratio of Sn-Ag-Cu on a copper substrate. This process is particularly suitable for environmentally friendly surface finishing of small, high-volume electronic components.The results indicate that current density and bath temperature are the dominant factors influencing co-deposition behavior. Increasing either parameter led to a higher tin content and a reduction in silver and copper within the deposit. In contrast, bath pH and rotation speed did not exhibit significant systematic effects on deposit composition within the tested range. Prolonged plating time slightly decreased the silver and copper content in the deposit, attributable to the gradual consumption of Ag^{+} and Cu^{2+} ions in the electrolyte.The optimized process parameters were determined as follows: current density of 3 $A \cdot dm^{-2}$, bath temperature of 25°C, pH of 5.0, and rotation speed of 12 $r \cdot min^{-1}$. Under these conditions, a dense and uniform alloy deposit with a composition approaching the Sn-Ag-Cu eutectic point was achieved.

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