Advancing Bonding Techniques for Electronic Interconnects: Eco-Friendly Cu Nanoparticles and Cu-SAC Hybrid Paste

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ABSTRACT

Recent developments in copper (Cu)-based bonding techniques have shown promising advancements for lowtemperature and pressureless interconnect applications in electronics for both engineered Cu nanoparticles (NPs) and hybrid Cu-SAC pastes. This study synthesizes Cu NPs using an eco-friendly method with ascorbic acid and without capping agents, achieving controlled particle size distribution through pH manipulation. These NPs are then utilized to form Cu NP pastes by mixing with polyethylene glycol (PEG), which is applied in Cu-to-Cu direct bonding. The optimal bonding properties are achieved with proper particle size and packing density, which directly correlate to increased joint strength. This study also utilizes a hybrid paste composed of Cu particles and SAC alloy paste. By varying the SAC fractions and Cu particle sizes, a detailed analysis is conducted on joint microstructures and mechanical properties. A paste that displays superior mechanical characteristics can be attributed to an ideal formation of the Cu3Sn phase, offering high stability and resistance against external forces. This phase is particularly noted for its toughening effect within the intermetallic compound matrix. an effect enhanced by a coherent Cu3Sn/Cu interface. Both approaches demonstrate the potential of Cu-based pastes in achieving efficient, robust, and durable joints suitable for high-temperature applications in electronics manufacturing. These innovative methodologies not only enhance mechanical properties but also contribute to the sustainability of materials, presenting a significant step forward in electronic packaging technologies.

Key words: Cu nanoparticle synthesis; Sintering; Intermetallic; Interdiffusion; Low temperature bonding; Power electronic packaging

INTRODUCTION

The rapid growth in demand for electronic devices, driven by emerging technologies such as machine learning, automotive advancements, and advanced networking, has significantly increased the need for semiconductors. The global semiconductor market was valued at USD 611.56 billion in 2023 and is projected to reach USD 1123.44 billion by 2033 [1]. This increasing demand has created new challenges, particularly in developing reliable interconnect materials for high-temperature power devices. Wide-bandgap (WBG) semiconductors, such as gallium nitride (GaN) and silicon carbide (SiC), have emerged as alternatives to traditional silicon (Si) semiconductors due to their superior performance at high temperatures and ability to handle high voltages [2,3]. GaN power devices are projected to see market growth, reaching USD 200 million by 2025 [2]. However, scaling down transistor sizes and miniaturization have introduced challenges to device efficiency and reliability.

Power device packaging is critical in maintaining stability, particularly in environments with high temperatures and power densities. Devices like insulated gate bipolar transistors (IGBTs), commonly used in electric vehicles, are prone to thermal stress due to mismatched coefficients of thermal expansion (CTE) between different materials, which can lead to cracks and device failure [4]. Moreover, traditional Sn-based solders are unsuitable for use beyond 200°C, limiting their effectiveness in high-power applications [5]. One major issue with traditional soldering materials is the formation of intermetallic compounds (IMCs) at the interface between solder and substrate. Excessive IMC growth degrades the mechanical properties of solder joints, leading to potential failure [6]. As device sizes shrink, the presence of brittle IMCs further compromises the reliability of solder joints in high-performance electronics.

This study focuses on two major bonding techniques: Cu nanoparticle (Cu NP) sintering and Cu-Sn3.0Ag0.5Cu (Cu-SAC305) hybrid paste bonding. Both methods aim to address the limitations of conventional soldering processes, especially in high-temperature, high-power applications. Cu NP bonding is a promising alternative to traditional high-temperature solders. Copper has excellent thermal and electrical conductivity, making it ideal for power device interconnects. However, bulk Cu bonding presents challenges due to oxidation and the high temperatures required to form strong bonds [7]. Cu nanoparticles, with their large surface area, reduce the bonding temperature while maintaining strong mechanical properties. The high chemical potential of the nanoparticles allows bonding at lower

pressures and temperatures compared to bulk Cu, making the process more cost-effective

The Cu NP bonding process is typically conducted under a reductive atmosphere or vacuum to prevent oxidation, which can negatively affect the quality of the bond. Cu NP sintering offers much lower processing temperatures than traditional methods while maintaining excellent mechanical and thermal properties. These reduced conditions make Cu NP bonding suitable for advanced semiconductor applications in high-temperature environments where traditional materials fail. However, challenges such as oxidation prevention and the cost-effectiveness of scaling up Cu NP production remain. Recent advancements have focused on green synthesis methods to mitigate environmental impacts and reduce production costs, further enhancing the viability of Cu NP bonding.

The second bonding technique explored is the use of a hybrid paste made from Cu and SAC305 particles. This method leverages the formation of stable Cu-Sn intermetallic compounds, specifically Cu6Sn5 and Cu3Sn, which are thermally stable at temperatures exceeding 400°C and 600°C, respectively. The Cu-SAC hybrid paste provides a reliable solution for power device interconnects, particularly in hightemperature environments. The hybrid paste undergoes a solid-state interdiffusion process, allowing bonding to occur without the need for high external pressure or protective gases. The low-temperature bonding process is ideal for miniaturized devices that are sensitive to stress. By combining the thermal and electrical properties of Cu with the mechanical properties of SAC alloys, this method offers a balanced solution for advanced packaging technologies.

In this study, the focus will be on optimizing both Cu NP bonding and Cu-SAC hybrid paste bonding techniques. The primary goal is to enhance material properties while reducing bonding temperatures and ensuring long-term reliability under harsh conditions. For Cu NP bonding, the study will address oxidation challenges during the bonding process and explore more environmentally friendly synthesis methods for Cu nanoparticles. Green synthesis techniques will be investigated to reduce production costs while maintaining the strong mechanical and thermal properties needed for hightemperature applications. For Cu-SAC hybrid paste bonding, the study will concentrate on enhancing the solid-state interdiffusion process to create more stable and robust bonds. The relationship between Cu-SAC particle size and intermetallic compound (IMC) formation will be examined to improve bonding reliability in miniaturized devices like 3D ICs.

By focusing on these two bonding methods, this study aims to contribute significantly to the development of advanced packaging solutions for high-temperature power devices. It seeks to ensure better performance, durability, and costeffectiveness for future semiconductor technologies.

EXPERIMENTAL

Copper nanoparticles (Cu NPs) were synthesized using a chemical reduction method with ascorbic acid as the reducing agent. First, 0.10 g of CuO powder was mixed with 5 mL of deionized water and 0.79 g of oxalic acid. The solution was stirred at 20°C for 20 hours, converting CuO into CuC₂O₄. This solution was mixed with 10 mL of ascorbic acid (1.25 M), and sodium hydroxide was added to adjust the pH to between 8 and 11. The mixture was heated to 85°C for 15 minutes, producing Cu NPs. The particles were separated by centrifugation at 5000 rpm for 20 minutes, washed with deionized water and absolute alcohol, and dried in a vacuum tank at room temperature.

For Cu-SAC hybrid paste preparation, commercially available Cu particles $(0.3-5.0 \ \mu\text{m})$ and SAC particles $(1.5 \ \mu\text{m})$ were used. Both Cu and SAC particles were etched with sulfuric acid, washed with ethanol, and dried in a vacuum oven. The paste was created by mixing Cu $(1.0 \ \mu\text{m})$ and SAC $(1.5 \ \mu\text{m})$ particles with PEG 400 in an optimized weight ratio. The mixture was homogenized using a planetary mixer for 10 minutes. Both Cu NP and Cu-SAC pastes were prepared for bonding through screen printing onto Cu substrates.

The bonding process for both pastes involved printing the paste onto a Cu foil substrate ($1 \times 1 \text{ cm}^2$ and 300 µm thick) and placing a 2 mm diameter, 2 mm height Cu pillar on top. The substrates were prepared by grinding with sandpaper, polishing with 1 µm alumina powder, and dipping in 10 vol.% sulfuric acid to remove surface oxides. The bonding was carried out in a tube furnace under nitrogen flow (2.5 L/min) at a heating rate of 10°C/min, with the bonding temperature held for 1 hour.

Mechanical strength of the bonded joints was tested using a bond tester (Dage 4000), with shear tests conducted at a shear height of 200 μ m and a shear speed of 50 μ m/s. The cross-sectional microstructure of the joints was analyzed using SEM (Hitachi S-3000H, 15 kV in BSE mode) and ion milling (SC-1000, Technoorg Linda).

RESULTS AND DISCUSSION

The Cu NPs in this study were synthesized through chemical reduction using copper oxide (CuO) as a precursor. Ascorbic acid acted as the reducing agent, with oxalic acid and sodium hydroxide facilitating the reduction process. Notably, no capping agent was employed, which allowed for the formation of pure Cu NPs. However, the absence of a capping agent also increased the risk of oxidation during the washing and drying phases. The extent of oxidation was more pronounced in samples with smaller particles, as their increased surface area made them more susceptible to oxidation.

The pH of the reducing solution played a critical role in controlling particle size. As the pH increased from 8 to 11, particle size decreased significantly. At pH 8, the particles measured approximately 190 nm, whereas at pH 11, the particles were reduced to around 60 nm. This behavior can be

attributed to the higher reduction potential of ascorbic acid at elevated pH levels, which promotes a higher nucleation rate and thus smaller particles. However, the trade-off for smaller particles was a higher degree of oxidation, which became more significant at higher pH levels.

The synthesized Cu NPs were then used to form pastes by mixing them with polyethylene glycol (PEG), which served as a solvent. These pastes were employed to bond copper substrates and pillars by heating them to 300°C in a nitrogen atmosphere. The heat caused the nanoparticles to sinter, creating a dense layer that bonded the components. SEM images of the cross-sections revealed that the bonding process was successful, but small fractions of void were present in the sintered material. These voids were primarily attributed to the outgassing of PEG during the bonding process. The presence of voids was more pronounced in joints made from Cu NP pastes synthesized at pH 8 and 11, whereas joints made from the pH 9 paste exhibited the fewest voids and the most uniform microstructure.



Figure 1. Cross-sectional microstructure of each Cu NP paste joint

The analysis also revealed that smaller Cu nanoparticles, particularly those synthesized at pH 10 and 11, showed better sintering behavior and connection between the Cu particles and the substrate. However, the smaller particle size also contributed to more significant void formation, which weakened the mechanical strength of the joints. In contrast, the pH 9 sample, which had a moderate particle size and fewer voids, produced the densest microstructure. This suggests that an optimal balance between particle size and void formation is essential for maximizing the performance of Cu NP-based joints.

Mechanical strength tests, specifically shear strength evaluations, were performed on the sintered joints. The joints created from the pH 9 paste exhibited the highest shear strength, exceeding 40 MPa on average. Notably, particle size alone did not directly correlate with mechanical strength. Instead, the void ratio played a more crucial role in determining joint strength. Joints made from pastes with higher void ratios, such as those synthesized at pH 8 and 11, exhibited significantly lower shear strength compared to those made from the pH 9 paste, which had a denser microstructure and fewer voids. Examination of the fracture surfaces post-shear test further supported this finding, as the pH 9 joint retained more sintered Cu particles on the substrate, indicating a stronger bond.



Figure 2. Shear strength of each Cu NP paste joint

In addition to pure Cu NP pastes, the study also explored the use of a Cu-SAC (tin-silver-copper) hybrid paste. This hybrid paste was evaluated under different bonding conditions, including vacuum and nitrogen atmospheres. The vacuum system produced superior joints, as it allowed for better solvent removal, resulting in fewer voids and stronger bonds. The nitrogen atmosphere, on the other hand, trapped solvent residues, weakening the mechanical properties of the joints.

The effectiveness of the Cu-SAC hybrid paste was also influenced by the ratio of SAC to Cu particles. When the SAC fraction was too low (10 wt%), the bond quality was poor due to inadequate intermetallic compound (IMC) formation. As the SAC fraction increased to 20–30 wt%, the microstructure of the joints improved significantly. The formation of a coreshell structure, with Cu particles encased in an IMC shell, provided better mechanical properties, as the IMCs contributed to the overall strength of the joint. However, when the SAC fraction exceeded 30 wt%, the excessive formation of IMCs led to volume shrinkage and void formation, which compromised joint strength.

The bonding atmosphere was optimized using both nitrogen and a vacuum system during the bonding process. Figure 4 presents the results of joint strength under different environments. The joints formed in a vacuum demonstrated superior mechanical performance across all SAC fractions. The vacuum environment enhances the efficiency of solvent release from the paste, leading to lower chemical residue [101]. Without a vacuum, it is difficult to effectively remove the PEG solvent during the process, as its high boiling point exceeds 200°C. Therefore, using a vacuum system to assist with solvent removal is crucial for achieving optimal joint properties in this study.



Figure 3. SEM images and void ratio of cross-sectional joints of various SAC fractions: (a)10, (b) 20, (c) 30, and (d) 50 wt%.

Mechanical tests confirmed that the joints containing 20 wt% SAC had the highest shear strength of 17.3 MPa and the lowest void ratio of 7.6% compared to joints with other Cu–SAC weight ratios. This combination of properties resulted in excellent mechanical performance, attributed to the balanced interaction between the ductile Cu particles and the robust IMC connections. In contrast, joints with higher SAC fractions were more brittle, as the excessive formation of IMCs reduced the joint's ability to absorb external forces. The toughness of the joints with 20 wt% SAC was superior, as they could absorb more energy before failure. This enhanced toughness was attributed to the ductility of the Cu particles embedded in the IMC matrix, which provided additional resilience against mechanical stress.



Figure 4. The shear strength of various SAC fractions in different bonding conditions.

The size of the Cu particles used in the hybrid paste also had a significant impact on joint performance. Smaller Cu particles formed thinner IMC shells, resulting in a more uniform and denser microstructure. This led to fewer voids and higher mechanical strength. In contrast, larger Cu particles produced thicker IMC layers, which increased the void fraction and reduced joint strength. The study found that a Cu particle size of 0.5 μ m provided the best balance between IMC thickness, void fraction, and mechanical strength, with joints exhibiting a shear strength of 19.5 MPa.

The results indicate that the size of the Cu particles and the SAC fraction significantly influenced the joint performance. Smaller Cu particles led to thinner intermetallic compound (IMC) layers and greater interfacial area, which contributed to enhanced joint strength and reduced void formation. The findings also suggest that when the SAC fraction exceeded a critical threshold, the Cu particles were largely consumed, resulting in a joint that was predominantly composed of IMC. This excessive IMC formation made the joints more brittle and prone to failure. Optimal mechanical performance was observed when the SAC fraction was maintained below this threshold, ensuring a balance between the formation of strong IMC layers and maintaining the ductility of Cu particles within the joint.

CONCLUSION

This study demonstrated that controlling the synthesis conditions of Cu NPs, particularly the pH of the reducing solution and the sintering temperature, is crucial for optimizing their microstructure and mechanical performance. The hybrid Cu-SAC paste also showed promise as a bonding material, with the best results achieved using a 20 wt% SAC fraction and a Cu particle size of 0.5 μ m. These findings have significant implications for the development of cost-effective and reliable bonding materials for electronic packaging and other high-performance applications.

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