

Polymer-Protected Cu-Ag Mixed NPs for Low-Temperature Bonding Application

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A simple method has been proposed to prepare polymer-protected Cu-Ag mixed nanoparticles (NPs), which are suitable for use as low-temperature bonding materials. The polymer coated on the Cu-Ag mixed NPs can protect them from oxidation effectively when heated in air at temperature lower than 280°C. The low-temperature bonding process utilizing Cu-Ag mixed NPs as the bonding material is investigated. The bonding experiments show that robust joints are formed using Cu-Ag mixed NPs at 160°C in air. The shear test shows that addition of copper to silver is helpful for improving joint strength. This novel sintering-bonding technology using Cu-Ag mixed NPs as an interconnection material has potential for application in the electronics packaging industry.

Key words: Cu-Ag mixed NPs, lead-free, low-temperature bonding, electronics packaging

INTRODUCTION

Tin-lead solders have been widely used as joining materials in the electronics industry for many years. However, because lead and its compounds do harm to natural resources and human health, legislation has proposed to limit the use of lead in solders in many countries.¹ This situation has stimulated substantial research and development efforts to discover alternative, lead-free solder alloys.² Many lead-free solder alloys have been developed, such as Sn-Zn, Sn-Cu, Sn-Bi, and Sn-Ag systems.³ However, there are still some drawbacks that limit their extensive application, such as high melting point, poor wettability, and limited solderability.

Recently, there has been an increasing focus on low-temperature processing technology with metal nanoparticles (NPs) (Ag NPs, Cu NPs, etc.) as an alternative technique to soldering with lead.⁴⁻⁹ The

novel bonding method using metal NPs has significant advantages over conventional tin-lead solder, including: (1) This low-temperature interconnection process has potential applications for flexible electronics, including flat-panel displays, organic electronics, and low-cost disposable microelectronics devices on plastic substrates;^{7,10,11} (2) This advanced bonding technology, which allows a lower temperature process, can withstand a higher working temperature.¹² These advantages make them suitable for applications such as high-power chips and automotive electronics and high-power electronic devices, frequently working at temperature near 200°C;¹²⁻¹⁴ (3) This bonding technology is environmentally friendly and will not generate pollution to the environment or do harm to human health. However, there are still some concerns over this low-temperature bonding technology in practical applications. Usually, silver NPs have been developed by metallo-organic decomposition to avoid the unstable contact resistance and low working temperature of conventional, electrically conductive adhesives with addition of silver NPs.¹⁵

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Most Ag NP pastes have been shown to be capable of bonding and curing at temperatures ranging from 200°C to 300°C.^{5,16,17} Morisada et al.¹⁸ reported the bonding process with mixed Cu-Ag NPs at 350°C. Lower temperature is still required.^{7,10,11} Another concern is silver migration, which deteriorates interconnect reliability, since migration can produce silver dendrites which may undesirably bridge electrodes.^{19,20} Addition of Cu NPs to Ag NPs could increase the electrical migration resistance. However, it was difficult to obtain strong joints, due to the easy oxidation of the Cu NPs.¹⁸

Herein, we propose a simple method for synthesis of polymer-coated Cu-Ag mixed NPs, which can be used as a low-temperature interconnect material. The polymer coated on the Cu-Ag mixed NPs can protect them from oxidation. Joints were fabricated using Cu-Ag mixed NPs at low bonding temperatures. The joint strength and corresponding fracture characteristics were analyzed.

EXPERIMENTAL PROCEDURES

Preparation of Cu-Ag Mixed NPs

Copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), silver nitrate (AgNO_3), polyvinylpyrrolidone (PVP, K-30), sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), and ethylene glycol (EG) were all analytical grade and used without further purification.

Cu NPs were synthesized in ambient atmosphere by the polyol method.^{8,21,22} PVP K-30 was used as a protecting agent. Sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) was used to reduce copper nitrate pentahemihydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). In the polyol method, 2.5 g PVP and 4 g sodium hypophosphite were mixed with 40 mL EG inside a round-bottomed flask. The mixture was heated to 90°C at a rate of 5°C/min. Then, 10 mL of 1 M solution of copper nitrate in EG liquid at 90°C was added to the PVP/sodium hypophosphite solution while stirring vigorously. The color of the suspension turned from blue to henna within 4 min to 5 min, indicating formation of Cu NPs. These Cu NPs were concentrated by centrifugation. Clean solvent was extracted from the centrifuge pipes using a pipette, leaving highly concentrated Cu NPs for use.

The Ag NPs used in this study were synthesized by the modified polyol method.²³ The typical synthesis method is as follows: 10 mL EG of silver nitrite (0.15 M) in a conical flask and 40 mL EG solution of PVP (0.45 M) in a beaker were prepared. These solutions were heated to the reaction temperature of 160°C, at a constant heating rate of 20°C/min. Then the solution of PVP was injected into the silver nitrite solution at a constant rate of 0.3 mL/s using a syringe pump. The color of the solution changed from colorless water to gray after 30 min, indicating precipitation of Ag NPs. When the reaction was complete, the solution was rapidly cooled by adding deionized (DI) water to 200 mL. These Ag NPs were concentrated by centrifugation and used in the following work. The Cu-Ag mixed NPs used were obtained by mixing the highly concentrated Cu NPs and Ag NPs according to different molar ratios.

Bonding Process Using Cu-Ag Mixed NPs

The bonding process using Cu-Ag mixed NPs was performed in air as shown in Fig. 1. The concentrated NP paste was dropped onto oxygen-free copper pads with thickness of 100 μm using a pipette. Then, oxygen-free copper wire with diameter of 500 μm was put on top of the Cu pad when enough NPs were gathered. Afterwards, these prepared bonding specimens were heated up to the bonding temperature in air under bonding pressure of 10 MPa, which was measured using a load cell.^{7,17} The bonding strength was evaluated as the shear strength measured using a shear strength test machine (ZWICK/ROELL Z005) with displacement speed of 5 mm/min at room temperature. The shear strength was calculated by dividing the maximum force by the area of the bond.

Characterization

The synthesized Cu NPs and Ag NPs were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a computer-controlled thermal analyzer in air atmosphere. The

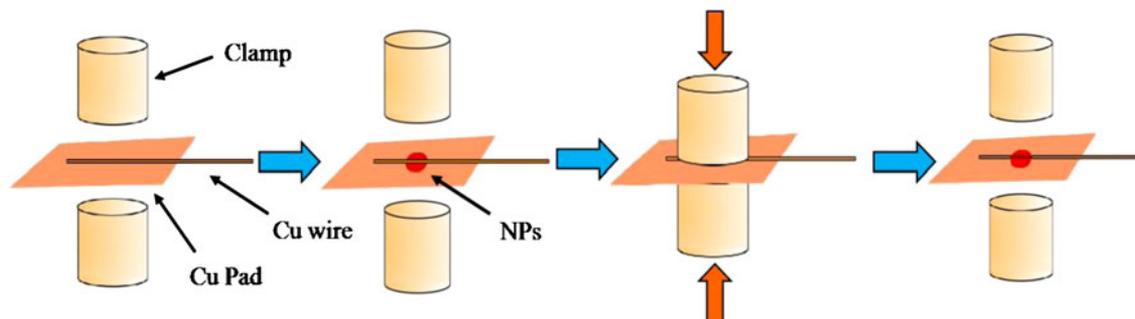
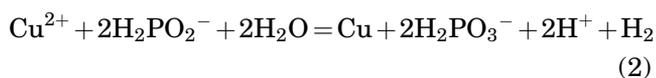


Fig. 1. Schematic illustration of the bonding process using metal NPs.

temperature range was 25°C to 400°C and the heating rate was 10°C/min. The crystal structure of the NPs after sintering at different temperatures was identified using x-ray diffraction (XRD) with Cu K_α radiation ($\lambda = 0.15418$ nm). The microstructure of the joints was observed using SEM.

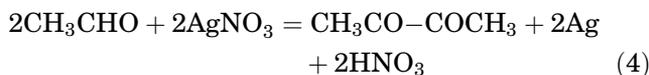
RESULTS AND DISCUSSION

During the synthesis of Cu NPs, PVP K-30 was used as a protecting agent. Sodium hypophosphite monohydrate (NaH₂PO₂·H₂O) was used to reduce copper sulfate pentahydrate (CuSO₄·5H₂O). The mechanism of metal reduction by hypophosphite ions has been described by various schemes.²¹ The copper ions may be reduced by atomic hydrogen evolving from the reaction of hypophosphite with water, as in the following chemical reactions:⁸



For the synthesis of Ag NPs, the polyol acts as both a solvent and reducing agent, since silver ion is easier to reduce. The reduction mechanism of silver

by EG probably involves the following chemical reactions:²⁴



The morphologies of the as-prepared metal NPs are displayed in the SEM images and TEM images in Fig. 2. Most of the Cu NPs and Ag NPs reveal spherically shaped particles. The thin polymer layer coated on the surface of the metal NPs can be detected in the TEM images. It is reasonable to assume that the thin polymer layer of PVP can protect them from oxidation when heated in air.⁸

The precondition for using Cu-Ag mixed NPs as a bonding material is to effectively solve the problem of oxidation. It is necessary to investigate the thermal and sintering behaviors of Cu-Ag mixed NPs. Figure 3 shows SEM images of Cu-Ag mixed NPs after sintering at different temperatures for 30 min. After annealing in air, the mixed Cu-Ag NPs aggregated together gradually. With increasing heating temperature, more Cu-Ag NPs were sintered together. When the temperature increased to 280°C, all the Cu-Ag mixed NPs sintered together. It is clear that

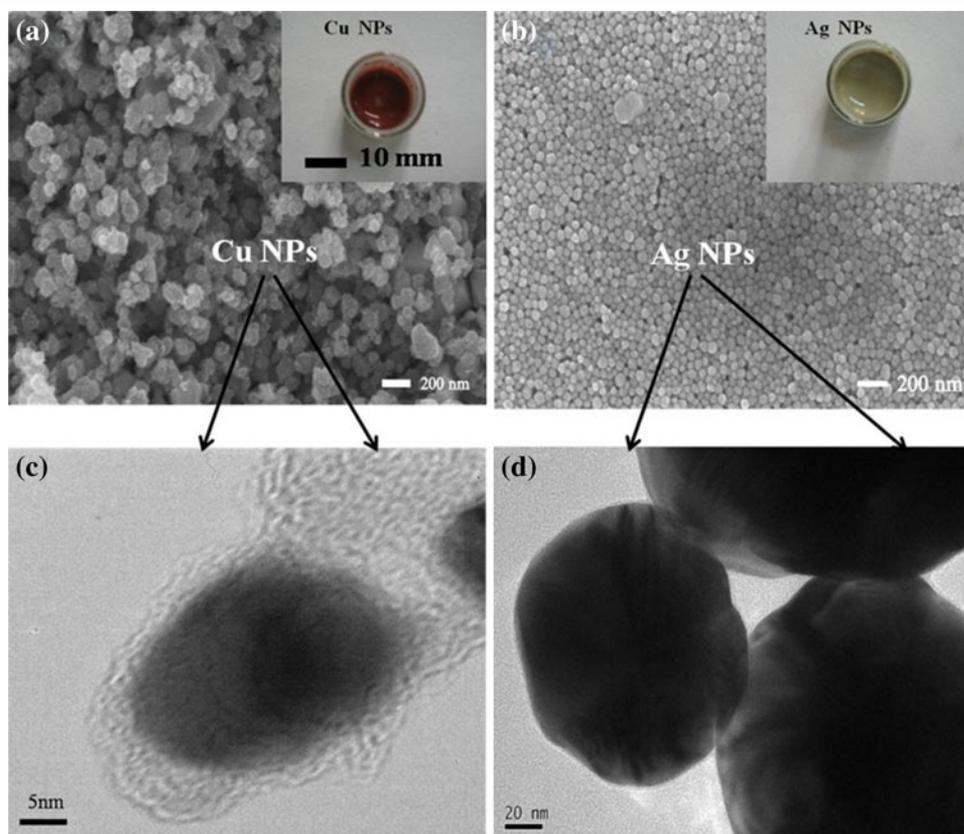


Fig. 2. SEM images of Cu NPs (a), Ag NPs (b) and TEM images Cu NPs (c), Ag NPs (d).

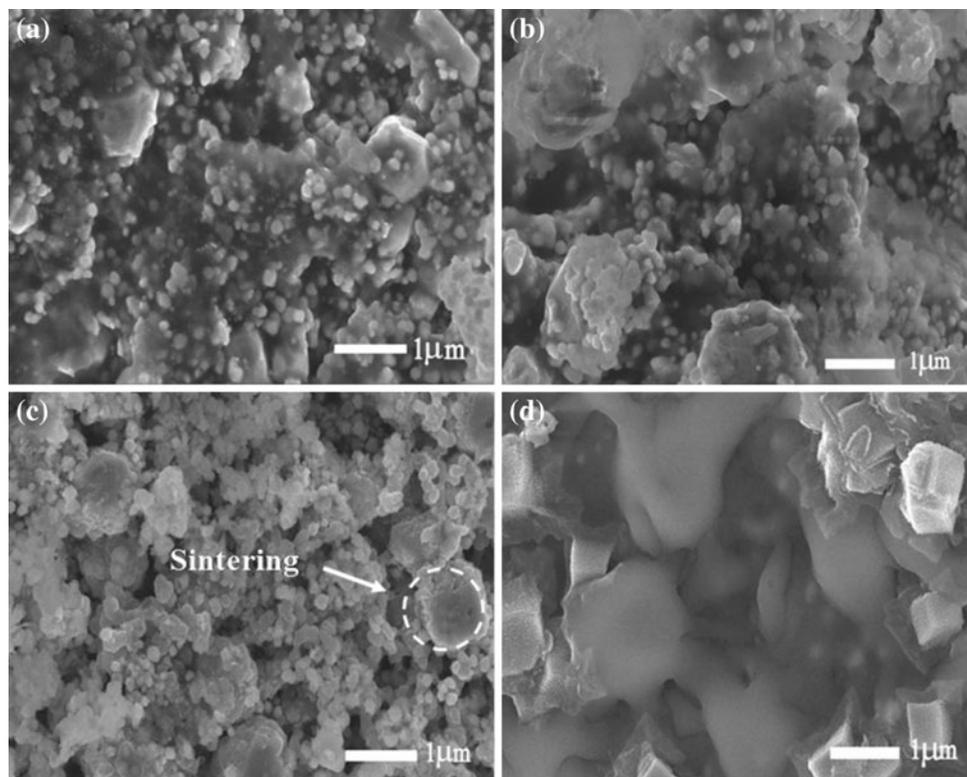


Fig. 3. SEM images of Cu-Ag mixed NPs sintered at various temperatures for 30 min: (a) 160°C, (b) 200°C, (c) 240°C, and (d) 280°C.

the Cu-Ag NPs became much denser after sintering at higher temperatures. It is found that the surface of the Cu NPs becomes rough after annealing at 280°C. This increase of surface roughness may be related to the formation of Cu_2O and CuO .⁸

The thermodynamic properties of Cu-Ag mixed NPs were characterized by TG and DSC. Figure 4 displays the TG and DSC curves of the as-synthesized Cu-Ag NPs (molar ratio 1:1) (temperature increasing ramp 10.00°C/min). The TG results show that the Cu-Ag mixed NPs were covered with surfactants to about 15% particle weight. It can be seen that no obvious exothermic peak is detected at temperatures below 250°C, indicating that no oxidation of Cu-Ag mixed NPs happens at this stage. When the Cu-Ag NPs were sintered at temperature in the range from 250°C to 280°C, the weight of Cu-Ag NPs decreased significantly, as shown in the TG curve. The corresponding DSC curve shows an obvious exothermic peak. These results indicate significant decomposition of organic content. After decomposition of mostly organic component, oxidation of Cu will occur. Above 280°C, slight weight gain was observed. This may be attributed to thermal oxidation of the Cu NPs after decomposition of the polymer. This further confirms that the polymer functions to protect the Cu-Ag mixed NPs from oxidation at temperature below 280°C.

The results of XRD on the mixed Cu-Ag NPs after sintering at different temperatures in air are shown in Fig. 5. At low annealing temperature, no oxida-

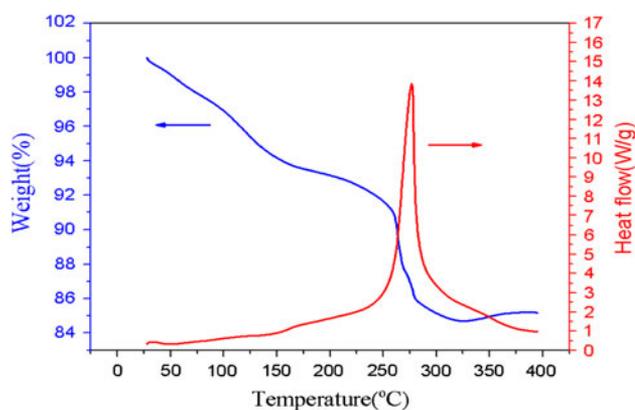


Fig. 4. TG and DSC traces (temperature increasing rate 10.00°C/min).

tion peak appears, which illustrates that the polymer provides good protective action for metal NPs. After annealing at higher temperature of 280°C, the slight CuO peaks indicate that oxidation of Cu NPs occurs. These results are consistent with the TG and DSC curves, which illustrate that decomposition of organic content occurs at temperature around 280°C. Combined the SEM/TEM, DSC/TG, and XRD results, it is hence safe to deduce that the polymer coated on the metal NP surface protects them from oxidation. After decomposition of organic content (heating above 280°C), oxidation of Cu NPs occurs and the surface of Cu changes to Cu_2O and CuO .

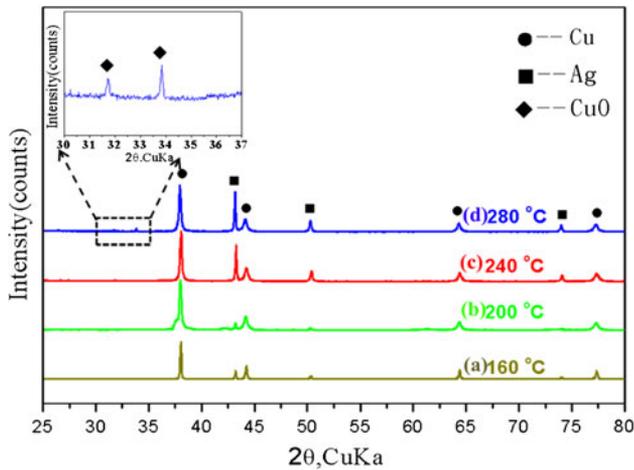


Fig. 5. XRD diffraction patterns of mixed Cu-Ag NPs after sintering at different temperatures in air: (a) 160°C, (b) 200°C, (c) 240°C, and (d) 280°C (holding time 30 min).

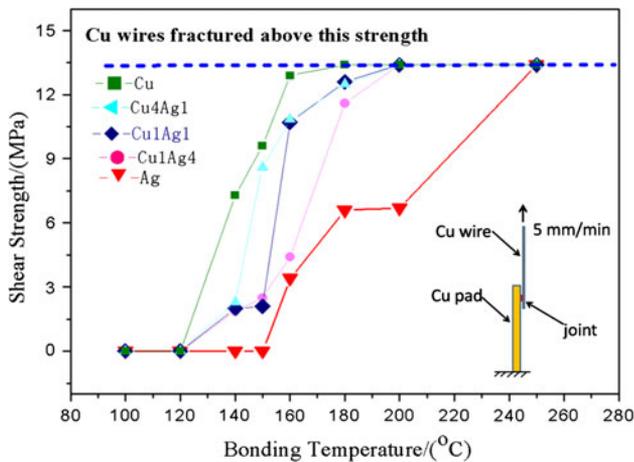


Fig. 6. Shear strength of Cu wires bonded to Cu pads using Cu-Ag mixed NPs as a function of bonding temperature. Inset shows a schematic diagram of a shear sample.

Since the Cu-Ag mixed NPs coated by the polymer have good resistance to oxidation, these Cu-Ag mixed NPs can be used as bonding material. Figure 6 shows the shear strength of joints bonded using different molar fractions of Cu-Ag mixed NPs as a function of bonding temperature. It should be noted that the joints are fabricated at lower bonding temperature than in our previous study. This is attributed to the fact that the assistant bonding pressure is larger than in the previous study.⁸ When bonded using Cu-Ag mixed NPs (molar ratio 1:1) at 160°C, the shear strength is about 10 MPa. By slightly increasing the temperature to 180°C, the strength can be enhanced significantly. When bonding at temperature of 200°C, the fracture position is the Cu wire instead of the joint area, indicating the good quality of the fabricated joint. The strength of the joints exhibits a trend similar to

that in reported results.⁷ The shear testing also shows that the joint becomes stronger with increasing copper content in the Cu-Ag mixed NPs. Morisada's work shows that Cu-Ag (50:50 mass%) displays higher strength than that of joints bonded using only Cu NPs.¹⁸ However, the mean diameter of the Cu NPs was much larger and they were easily oxidized in that study. The higher strength when using Cu NPs may be attributed to improved atomic matching between copper and copper than between copper and silver. TEM analysis of the joints demonstrated that no clear interface between the Cu NPs and the Cu substrate could be detected, whereas interfaces between Ag NPs and Cu substrate can be observed.^{8,17}

Typical fracture surfaces of joints bonded using Cu-Ag mixed NPs (molar ratio 1:1) at different temperatures are shown in Fig. 7. Different fracture microstructures are formed when bonding at different temperatures. At bonding temperature of 120°C, the isolated Cu-Ag mixed NPs are still encapsulated by polymers. No sintering and fracture trace are detected, and this leads to low bonding strength. When the bonding temperature is increased to 160°C, more Cu grains are observed, which can be attributed to evaporation of organic component. In this case, most of the Cu-Ag mixed NPs are agglomerated together and the corresponding shear strength is increased. At bonding temperature of 180°C, the fracture trace appears, and this results in significant improvement of joint strength. As the temperature is increased to 200°C and 240°C, obvious dimple microstructures are observed at the fracture surface, illustrating that the bonding material has some ductile characteristics at these temperatures.²⁵ The fracture of the joint at the Cu wire instead of at the joint area shows that robust joints have been fabricated.

To evaluate the bondability of Cu-Ag mixed NPs with different Cu contents, Cu-Ag mixed NPs with different molar fractions (Cu/Ag molar ratio: Cu, Cu4/Ag1, Cu1/Ag1, Cu1/Ag4, and Ag) were prepared. The shear test results showed that the bondability improves with increasing Cu content in the Cu-Ag mixed NPs. Stronger joint is formed on increasing the content of Cu NPs in the Cu-Ag mixed NPs. Joints fabricated using different Cu-Ag mixed NPs exhibited different fracture surfaces, as shown in Fig. 8. The toughness fracture features of the shear fracture surface increased as the content of Cu NPs in the Cu-Ag mixed NPs increases. It should be noted that, when using pure Ag NPs as the bonding material, the fracture of the joint occurs on the surface between the sintered Ag structure and Cu substrate. This result indicates that the interface binding strength between the sintered Ag layer and Cu substrate is lower than that between the sintered Cu layer and Cu substrate. These experimental results confirm that higher content of Cu is beneficial for improvement of joint strength when bonding to Cu substrate.

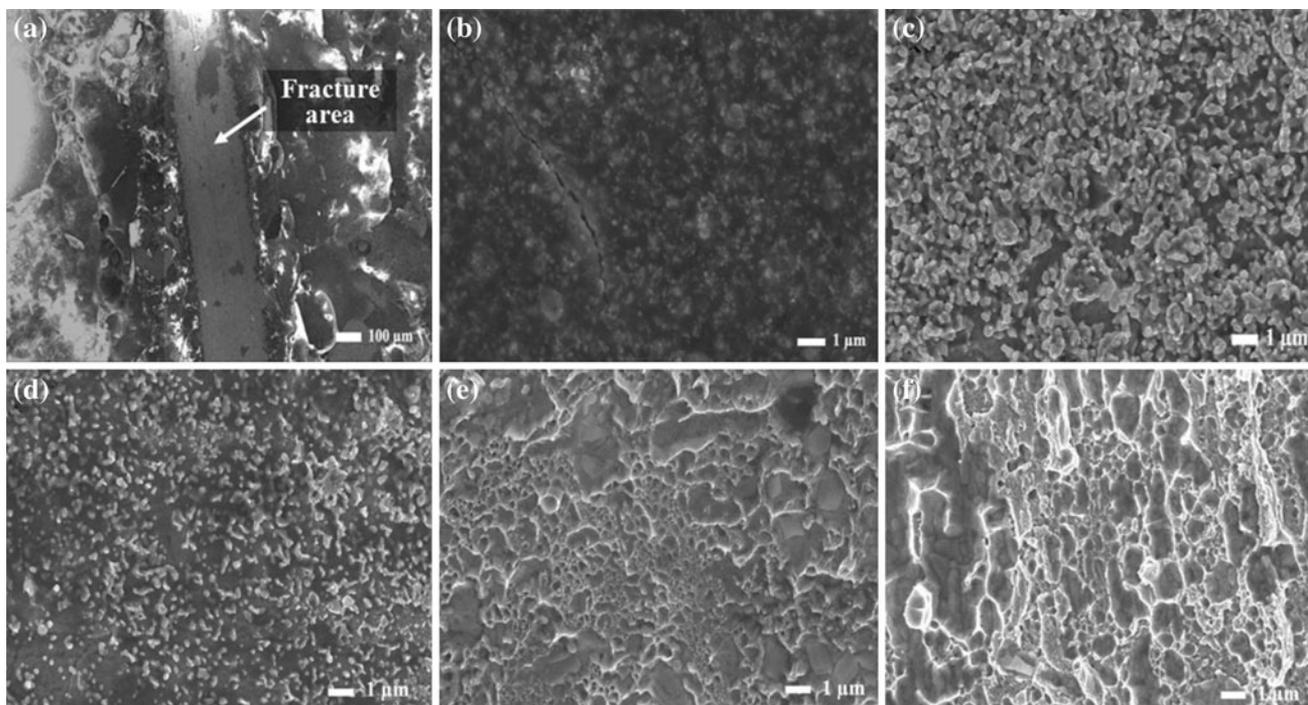


Fig. 7. SEM images of fracture surface of joints using Cu-Ag mixed NPs at different bonding temperatures: (a) low magnification, (b) 120°C, (c) 160°C, (d) 180°C, (e) 200°C, (f) 240°C.

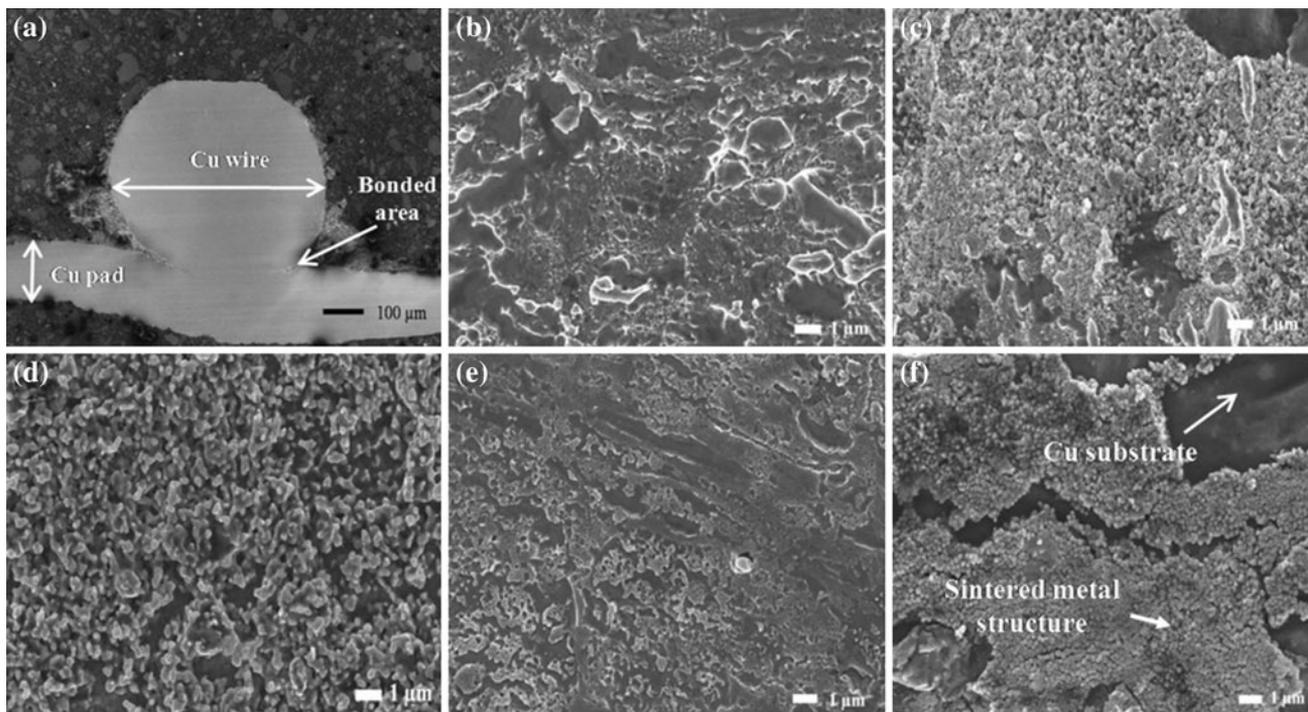


Fig. 8. Representative SEM images of fracture surface of joints using Cu-Ag mixed (different Cu/Ag molar ratio) (a) typical cross-section of the joint, (b) Cu, (c) Cu₄/Ag₁, (d) Cu₁/Ag₁, (e) Cu₁/Ag₄, (f) Ag.

CONCLUSIONS

We have proposed a simple method to prepare polymer-protected Cu-Ag mixed NPs. The polymer

coated on both the Cu and Ag NPs can protect them from oxidation when heated in air below 280°C. Based on this, a low-temperature bonding method

with Cu-Ag mixed NPs at ambient atmosphere has been developed. Strong joints are fabricated at low temperature of 160°C. Since these Cu-Ag mixed NPs show advantages including low cost, low process temperature, and good resistance to electrical migration, they have potential for application in the electronics packaging industry.

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