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Preparation of nanoparticle and nanowire mixed pastes and their low temperature sintering

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ABSTRACT

A new mixed nano paste consisting of silver nanoparticles, silver nanowires and copper nanoparticles has been proposed as the active material in an alternative joining approach for interconnection in electronic packaging. The mixed nano paste was optimized by adding different contents of copper nanoparticles into silver nanoparticle and nanowire pastes. Compared with the common silver nanoparticle paste, the electrochemical migration time of this mixed nano paste increased with greater addition of copper nanoparticles. Silver nanowires were also found to decrease the resistance of this mixed nano paste effectively due to their continuity. Although higher additions of copper nanoparticles into the mixed nano paste could facilitate the desired result of anti-electrochemical migration, they also decrease the shear strength of the sintered joints using the mixed pastes. In order to balance anti-electrochemical migration and sintering properties of the mixed nano pastes, when 10% copper nanoparticles were added to the mixed silver nanoparticle and nanowire pastes, the average shear strength of sintered joints at 250–350 °C was above 25 MPa. Based on the comprehensive properties, the mixed silver nanoparticle nanowire with 10% copper nanoparticle pastes were determined to be a better paste for sintered connections in electrical packaging.

1. Introduction

There is an ongoing search for reliable and environmentally friendly interconnect materials in the microelectronics packaging industry [1]. Bonding by sintering of metallic nanoparticles (NP) is one of the low temperature joining technologies, which is a promising alternative for lead-free electronic packaging technology [2,3]. There have been many studies exploring metallic nanoparticle pastes for use in low temperature sintering, including Ag [4,5], Cu [6,7] and Ag oxide paste [8,9]. Among these nano pastes, Ag NP paste is receiving considerable attention due to the low sintering temperature, high melting point, good mechanical reliability and high thermal and electrical conductivity [10,11].

In order to improve the functional properties of metallic nano pastes, there are some investigations about mixed Ag and Cu NPs for low temperature joining. This is because of the following advantages: (i) Decreasing the sintering temperature, e.g., Yan et al. [12] reported that using the polymer-protected mixed Cu–Ag NPs, strong joints could be obtained at a low temperature of 160 °C. (ii) Improving ion migration resistance. Electrochemical migration (ECM) occurs between two oppositely biased and closely spaced electrodes with an aqueous electrolyte, and causes short-circuit failure of electronic devices due to dendrite growth [13]. The trend towards miniaturization and concurrent reduction in the pitch and spacing of conductors in electronic packages will increase the risk of ECM failure [14]. Sintered Ag NP paste shows very low resistance to ECM due to its anodic solubility [15]. Y. Morisada et al. [16] reported that a mixed Cu–Ag NP paste with 46.5 mass % Ag and 53.5 mass % Cu had four times higher ionic migration resistance

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compared with the Ag nanoparticles. (iii) Decreasing cost. Resource scarcity and cost of silver are serious problems for electronic packaging applications. Compared with Ag NP paste, Ag–Cu NP paste could greatly reduce the cost. (iv) Improving thermal properties. Mixed Ag–Cu paste have relatively desirable thermal conductivity, coefficient of thermal expansion and performance index. Tan et al. [17] reported the thermal conductivity and coefficient of thermal expansion of sintered mixed Ag–Cu nano paste had a declining trend with increased Cu content.

Although ECM is an important factor that affects the reliability of electronic packaging, detailed phenomena and mechanisms of ECM of mixed Ag–Cu nano paste have not yet been reported. In this study, the mixed nano pastes including Ag NPs, Ag nanowires (NWs) and Cu NPs were researched, especially as to the electrochemical migration and sintering characteristics. The resistance to electrochemical migration of the mixed nano paste was measured by the water drop (WD) test, and the ECM process and mechanism were discussed in detail. The sintering properties of the mixed nano pastes were evaluated by the shear strength and fracture characteristics of sintered joints. These mixed nano pastes provide a novel possibility for sintering and interconnection in the microelectronics industry.

2. Material and methods

2.1. Synthesis of Ag NPs, Cu NPs and Ag NWs

Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) and sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) were purchased from Xilong Chemical Co., Ltd of P. R. China. Silver nitrate ($AgNO_3$) and ethylene glycol (EG) were purchased from Beijing Chemical Works of P. R. China. Polyvinylpyrrolidone (PVP, K-30) was purchased from Sinopharm Chemical Co., Ltd of P. R. China. Chemicals and reagents were all analytical grade and used without any purification. Ag NWs were synthesized using the polyol method from the literature [18,19]. In this study, 0.3 mg PVP was added to 30 mL of EG in a round-bottom flask (equipped with a condenser, thermocontroller and magnetic stirring bar) and heated to 170 °C. After 6 min, 265.4 mg $AgNO_3$ and 30 mL of EG solution were added dropwise to the hot solution. The reaction was kept for 30 min at 170 °C until all $AgNO_3$ had been completely reduced [4]. The Cu NPs and Ag NPs were synthesized in ambient atmosphere by the polyol method [20]. To remove the residue of PVP and EG, the nanostructures were washed with deionized (DI) water and centrifuged at 4000 rpm for 30 min. The purified solvent was extracted from the centrifuge pipes using a pipette leaving behind the highly concentrated Cu NP, Ag NP and Ag NW pastes.

2.2. Preparation of the mixed nano pastes

0%, 10% and 20% molar fractions of Cu NP paste were mixed with Ag NP paste by stirring and labeled as Ag NP, Ag NP + 10 Cu NP, Ag NP + 20 Cu NP, respectively. In order to study reinforcement of the properties of sintered joints, the mixed Ag NP, Ag NW and Cu NP pastes were also prepared. The Ag NP + Ag NW pastes was prepared by mixing of Ag NP and NW pastes in the molar ratio of 4:1. Then 0%, 10% and 20% molar fractions of Cu NPs paste were added to the mixed Ag NP + Ag NW pastes. The pastes were fully stirred and labeled as Ag NP + Ag NW, Ag NP + Ag NW + 10 Cu NP and Ag NP + Ag NW + 20 Cu NP.

2.3. Sintering process using mixed nano pastes

Ni/Ag-plated Cu discs were produced in the laboratory and used as dummy chips. The 2–3 μm of Ni layer was first electroplated on each Cu disc (diameter 10 mm), and then a 5 μm Ag layer was electroplated on the Ni-plated Cu disk. Prior to sintering, the Ni/Ag-plated Cu discs were ultrasonically cleaned in acetone for 10 min. The mixed nano pastes were coated on the surfaces of discs then dried at 85 °C to remove any low boiling point components. A small disc (diameter 6 mm) was placed on top of each big disc (diameter 10 mm) when enough pastes had been gathered. The sintering process was conducted in air at 250 °C under pressures of 2–5 MPa for 5 min. The shear strength of joints was measured using the thermal-mechanical simulator Gleeble 1500D with a displacement speed of 5 mm/min at room temperature.

2.4. Characterizations

The morphology and microstructure of mixed nano pastes were examined by field-emission scanning electron microscopy (SEM) (Zeiss EVO MA 10, Germany). Elemental composition of mixed pastes was determined by energy dispersive x-ray spectroscopy (EDS) (Oxford INCA 200, England). The structure and phases of mixed pastes were identified by X-ray diffraction (XRD) (Rigaku D/max-2500, Japan) at room temperature. The thermal properties of mixed nano pastes were characterized by a combination of thermogravimetry (TG) and differential scanning calorimetry (DSC) (Netzsch, Germany). The temperature ranged from 50 to 600 °C in air and the heating rate was 10 °C/min. In DSC, the heat flow to the sample as a function of time was measured, and the total enthalpy of reaction could be obtained by integration of the heat flow over the entire exothermic peak.

The mixed nano pastes were sintered in a furnace at 250 °C for 30 min. The electrical conductivity of mixed nano pastes was measured by a four-probe method. The ECM of mixed nano pastes was measured by the WD test [21,22]. Fig. 1 shows the ECM pattern and a sample for WD testing. A drop of distilled water (about 0.3 mL) was placed between the direct-patterned mixed nano paste electrodes and a 5 V bias voltage was applied. Resistance of the path between stripes of mixed nano pastes after sintering was measured by a picoammeter, and the change of resistance as a function of time was recorded. Failure of the material by ECM was considered to have occurred when the leakage current reached 1 mA, and this time was defined as ECM time [23]. Dendrite formation was visually inspected under a 3D-microscope. After the WD test, the dendrites were identified by SEM and EDS.

3. Results and discussion

3.1. Characteristics of NPs and NWs

The Ag NPs, Ag NWs and Cu NPs were synthesized by polyol method, and the morphologies are shown in Fig. 2. Most of Ag NPs were spherical and the size of the NPs was about 50–100 nm. The length of Ag NWs was 8–20 μm and the average diameter was

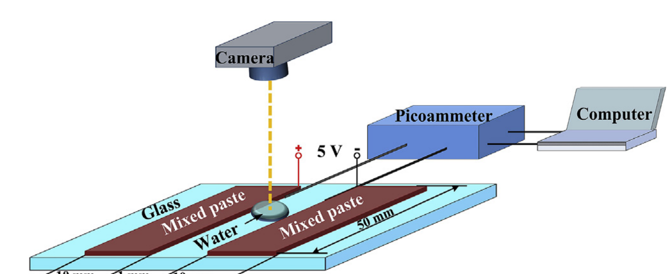

Fig. 1. Schematic of the ECM pattern design for water drop testing.