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Featured Letter

Cu-Cu bonding enhancement at low temperature by using carboxylic acid surface-modified Cu nanoparticles

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ABSTRACT

The carboxylic acid (formic acid and oxalic acid) surface-modification was applied on Cu nanoparticles (NPs) to remove surface oxidation. The synthesized Cu NPs were soaked in the mixture of carboxylic acid and dehydrated ethanol for surface-modification. The reliable Cu-Cu bonding joints using formic acid and oxalic acid surface-modified Cu NPs were achieved at 250 °C, and the shear strengths were improved to 20.2 MPa and 32.4 MPa, respectively. The bonded Cu NPs layer exhibited obvious sintering necks and ductile characteristics. The experimental results demonstrated that low temperature bonding using carboxylic acid surface-modified Cu NPs had the potential to fulfill the requirements of three-dimensional (3D) integration.

1. Introduction

The three dimensional integrated circuit (3D-IC) achieves high density integration, small form factor, low power consumption, and cost-effectiveness, which is considered as a promising method to break through the limitations of Moore's law [1–3]. Additionally, Cu-Cu bonding is one of key technologies for 3D integration to provide electrical and thermal interconnects and mechanical supports. Currently, nanoscopic diffusion bonding using Ag nanoparticles (NPs) is widely applied in Cu-Cu bonding owing to their thermal stability and high electrical conductivity [4]. However, the high cost and low electro-migration resistance of Ag NPs limit their practical applications.

Cu-Cu bonding by sintering Cu NPs becomes a promising solution due to their excellent electrical conductivity, high migration resistance, and low cost [5,6]. However, the spontaneous oxidation of Cu NPs significantly reduces the electrical conductivity and increases the bonding temperature. Although the polymer protective layer coated on the surface of Cu NPs, such as polyvinylpyrrolidone (PVP) [7], cetyltrimethyl ammonium bromide (CTAB) [8], and polyethylene glycol (PEG) [9], is utilized to prevent the oxidation of Cu NPs, surface oxides still exist as a passivation layer, which results in bonding temperature higher 300 °C. The reductive atmosphere (hydrogen and formic acid vapor) is adopted to further reduce the oxidation [10–12]. However, the sandwich bonding structure (Cu-NPs-Cu) hinders the sufficient contact between Cu NPs and the reductive atmosphere. Furthermore, the danger of hydrogen explosion still exists in the bonding process, and formic acid vapor is prone to corrode the bonding chamber.

In order to solve these problems, we proposed Cu-Cu bonding enhancement at low temperature by using carboxylic acid (formic acid and oxalic acid) surface-modified Cu NPs. The synthesized Cu NPs were soaked in the mixture of carboxylic acid and dehydrated ethanol for surface-modification. The reliable Cu-Cu bonding joints using carboxylic acid surface-modified Cu NPs were achieved at 250 °C.

2. Materials and methods

The Cu NPs were synthesized by water phase reduction method at room temperature. Firstly, copper acetate monohydrate (2.0 g), PVP (6.0 g), and CTAB (0.45 g) were dissolved in deionized water (50 mL) by magnetic stirrer. The pH value of the solution was adjusted to 10.0 by ammonia water. Then, 8.0 mL hydrazine hydrate (85%) was rapidly poured into the solution with continuous stirring for 10 min. The synthesized Cu NPs were subsided by centrifugation. Finally, the washing process with dehydrated ethanol was performed to remove impurities for three times.

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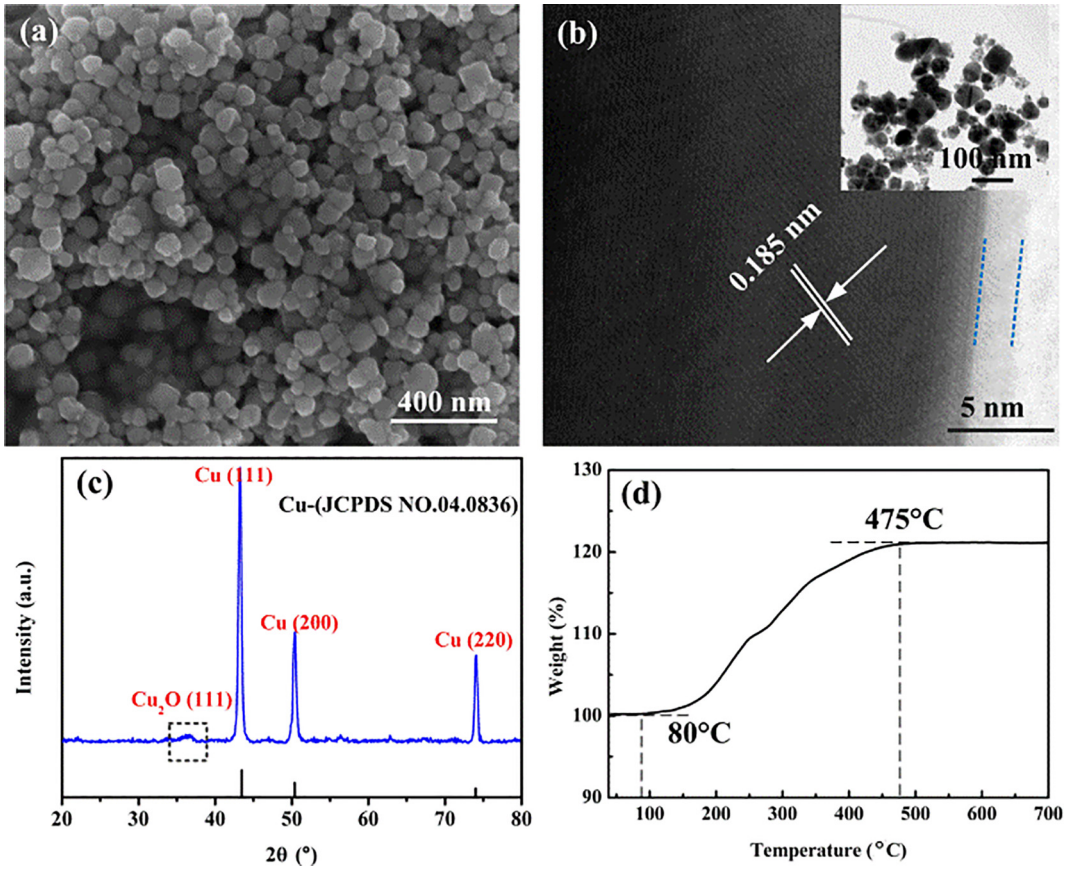

Fig. 1. (a) SEM image, (b) HR-TEM image, (c) XRD pattern, and (d) TG curve of Cu NPs.

Carboxylic acids including formic acid and oxalic acid were used in this work. For formic acid surface-modification, the washed Cu NPs were soaked in the mixture of formic acid (3 wt%) and dehydrated ethanol (97 wt%) for surface-modification. Then the surface-modified Cu NPs were separated by centrifugation after being soaked for 10 min, and washed by dehydrated ethanol to remove copper ions. Finally, these Cu NPs were collected by vacuum drying at 40 °C for 60 min. Cu NP paste was prepared by mixing the Cu NPs (65 wt%), dehydrated ethanol (32 wt%), and formic acid (3 wt%) at 2000 rpm for 10 min through vacuum mixer. The effect of formic acid in the Cu NP paste was to prevent the re-oxidation of the surface-modified Cu NPs. Subsequently, the Cu NP paste was uniformly printed on a Cu substrate, and another substrate was mounted on the printed Cu NP layer. Under the bonding pressure of 10 MPa and the protection of Ar-H_2 (5% H_2) gas mixture, Cu-Cu bonding experiments was performed at 250 °C for 60 min. The oxalic acid surface-modification and bonding processes were same as the formic acid process.

The morphological features of Cu NPs were investigated by scanning electron microscope (SEM) and transmission electron microscope (TEM). The sintered Cu NPs film, the bonding interface, and cross sections of Cu-Cu bonding joints were analyzed by scanning electron microscope (SEM). The thermal analysis and crystal structures of Cu NPs were carried out by using thermal-gravimetric analyzer (TG) and high-resolution X-ray diffractometer (XRD).

3. Results and discussion

Fig. 1(a) shows the SEM micrograph of the synthesized Cu NPs. It is clearly that the Cu NPs have good dispersibility without hard agglomeration. The Cu NPs have quasi-sphere shapes with the average diameter of 60 nm. Fig. 1(b) displays the HR-TEM image of Cu NPs with lattice fringes of 0.185 nm, corresponding to the (1 1 1) plane of face centered cubic structures of copper crystal. In addition, an amorphous organic shell with the average thickness of 2 nm is clearly observed, which restrains the oxidation and agglomeration of Cu NPs. Fig. 1(c) presents the XRD pattern of Cu NPs. Three diffraction peaks of Cu NPs are detected at 43.23°, 50.39°, and 74.05°, which represent the (1 1 1), (2 0 0), and (2 2 0) planes of Cu crystal. In addition, a tiny shoulder peak indexed as the (1 1 1) diffraction of Cu_2O appeared, associated with slight oxidation. These characteristic peaks conform the formation of face-centered cubic (FCC) copper phase with little oxides. Fig. 1 (d) shows the TG curve of Cu NPs in the air. The weight gain of about 21% is induced by the oxidation of Cu NPs, and the Cu NPs begin to thermally oxidize at 80 °C and higher. Therefore, the protection atmosphere is essential to avoid further oxidation of Cu NPs.

The XRD and SEM analysis were performed to evaluate the effect of carboxylic acid surface-modification on the removal of surface oxides, as shown in Fig. 2. As the synthesized Cu NPs are directly sintered at 250 °C, the weak Cu_2O diffraction peak at 37.22° is still detected, which indicates that the H_2 in the protection atmosphere is not capable of reducing the copper oxides at 250 °C. However, it is interesting that the Cu_2O diffraction peaks completely disappear after surface-modification, and the surface melting phenomenon and neck growth of Cu NPs are observed. These results clearly confirm that the surface oxides of Cu NPs are effectively removed by carboxylic acid surface-modification.

Fig. 3 presents the shear strength and cross-sectional SEM images of Cu-Cu joints at 250 °C. When the Cu NPs are directly