Ultrasonics - Sonochemistry 41 (2018) 375–381

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Ultra-low temperature sintering of Cu@Ag core-shell nanoparticle paste by ultrasonic in air for high-temperature power device packaging

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A R T I C L E I N F O

Keywords:
Cu@Ag nanoparticles
Ultrasonic-assisted sintering
Microstructure
Shear strength

A B S T R A C T

Sintering of low-cost Cu nanoparticles (NPs) for interconnection of chips to substrate at low temperature and in atmosphere conditions is difficult because they are prone to oxidation, but dramatically required in semiconductor industry. In the present work, we successfully synthesized Cu@Ag NPs paste, and they were successfully applied for joining Cu/Cu@Ag NPs paste/Cu firstly in air by the ultrasonic-assisted sintering (UAS) at a temperature of as low as 160 °C. Their sintered microstructures featuring with dense and crystallized cells are completely different from the traditional thermo-compression sintering (TCS). The optimized shear strength of the joints reached to 54.27 MPa, exhibiting one order of magnitude higher than TCS at the same temperature (180 °C) under the UAS. This ultra-low sintering temperature and high performance of the sintered joints were ascribed to ultrasonic effects. The ultrasonic vibrations have distinct effects on the metallurgical reactions of the joints, resulting in the contact and growth of Cu core and the stripping and connection of Ag shell, which contributes to the high shear strength. Thus, the UAS of Cu@Ag NPs paste has a great potential to be applied for high-temperature power device packaging.

1. Introduction

With the development of integrated circuits and semiconductor technology, the chip packaging tends to be miniaturization, high integration, high power density and excellent electrical-mechanical performances [1] with harsh working environments, such as high temperature, large current and humid ambient, leading many challenges for the chip interconnection [2]. At the same time, as the emerging of the third generation wide bandgap semiconductors, such as SiC and GaN, the working temperature of the chips may exceed 300 °C in long-time operation [3]. Therefore, the study of novel interconnection materials and packaging methods is crucial to take full advantage of the brilliant properties of the wide bandgap semiconductors in high power devices.

Presently, the main solutions for the above interconnection are high temperature lead-free solder, nanoparticles (NPs) sintering and transient-liquid-phase (TLP) bonding [3–7]. However, the high temperature lead-free solder has some drawbacks such as high soldering temperature (Zn-based solder) [8], poor processing performance and expensive (Au-based solder) [9], and high brittleness (Bi-based solder) [10], danger to cause damage of chips and degrade the reliabilities of joints. Those factors extremely limit the application of high temperature lead-free solders. In TLP bonding process, a low-melting-point (or eutectic phase formed after diffusion) interlayer is used to react with high-melting-point substrates to produce joints consisted of high-remelting-point full intermetallic compounds (IMCs), which can be processed at relatively low temperature [11–13]. However, it often requires a long processing time to obtain full IMCs, which may lead to extra thermal stress degrading severely the reliability of the joints [6,11,14]. It is not economical in the practical mass production. With the development of nanotechnology, the metals can be synthesized in nanosize with high surface activity and low melting point due to the size effect. Nanoparticles sintering becomes a new choice for high temperature packaging, such as Ag or Cu NPs sintering, because the sintering temperature is lower but the sintered structures have good performances with high remelting temperature [15]. Though the Ag nanoparticle paste has been exhaustively investigated and practically applied, its wide application has been extremely limited because of severe migration and high cost [16]. Cu nanoparticle paste may be a better alternative material due to its better performances than Ag nanoparticle paste but with lower cost. However, the storage and sintering process of Cu nanoparticle paste are more challenged because of the poor oxidation resistance of nano-sized Cu in air [17]. One of the most desirable ways is to combine the merits of Cu nanoparticle paste and Ag nanoparticle paste. Thus, a paste

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http://dx.doi.org/10.1016/j.ultsonch.2017.10.003
Received 16 June 2017; Received in revised form 15 September 2017; Accepted 3 October 2017
Available online 04 October 2017
1350-4177/

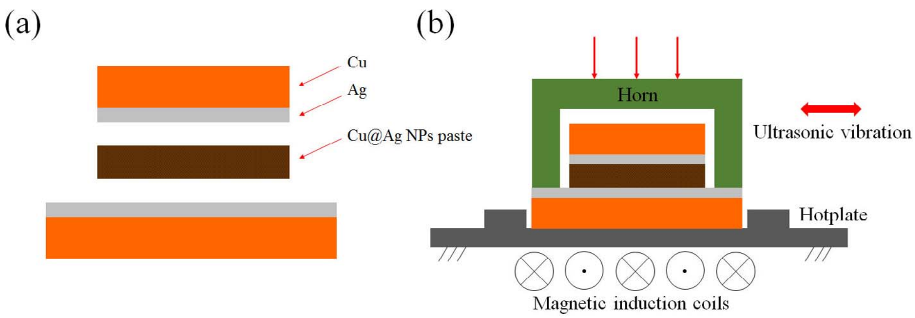

Fig. 1. (a) Schematic of the sintering sandwich structure of Cu/Cu@Ag NPs paste/Cu, and (b) the ultrasonic-assisted sintering (UAS) principle.

prepared by compositing Cu NPs with Ag NPs was utilized in Cu-Cu bonding. Unfortunately, it also needs a protective atmosphere during sintering at a high temperature [18]. To remedy these drawbacks, a Cu-Ag core-shell (Cu@Ag) NPs paste has been proposed for printing electronics because of its anti-oxidation, anti-migration and lower cost features [19]. It is noticed that nanoparticles sintering needs a high pressure, a long time, a relatively high temperature and/or all above to date. For example, Tian et al. sintered a Cu/Cu@Ag NPs paste/Cu sandwich at 250 °C for 20 min with a pressure of 5 MPa to reach shear strength of 26.5 MPa [20]. The sintering conditions, such as temperature, time, and pressure, also have to be degraded so as to satisfy the actual demands.

Recently, ultrasonic-assisted soldering has been proved able to braze dissimilar alloys at low temperature within a very short time and high reliable joints were achieved [21–23]. In our previous works, a full Cu_6Sn_5/Cu_3Sn IMCs joint, and a nearly sole Ni_3Sn_4 IMCs joint through ultrasonic-assisted TLP (U-TLP) were successfully obtained within a very short time [24,25]. Obviously, ultrasonic vibration played an important role during the IMCs joint formation. Spontaneously, ultrasonic-assisted sintering (UAS) of Cu@Ag NPs paste could be a good candidate method for high temperature device packaging so as to decrease the sintering conditions, which will be much helpful for preventing the heat damage on the chips, and to enhance the sintering degree to fabricate dense structures by depressing voids and accelerating crystallization. Thereby, the purposes of this paper are to obtain reliable joints of Cu/Cu@Ag NPs paste/Cu at a low temperature within a very short time by the UAS method and to analyze the mechanism of ultrasonic effects on the morphology and properties of the sintered joints.

2. Experimental procedures

2.1. Materials

Copper sulfate pentahydrate, sodium hypophosphite, ethylene glycol, trisodium citrate dehydrate and ethyl alcohol were purchased from Damao Reagent Co. Polyvinylpyrrolidone (PVP) was obtained from Aladdin Reagent Co. Silver sulfate was purchased from Sinopharm Chemical Reagent Co. Ltd. Deionized water was supplied in the washing stage. All chemical reagents were of analytical grade and without any subsequently treatment.

2.2. Preparation of nanoparticle pastes

Cu NPs were prepared similar to Yan's method [17]. Briefly, a mixture of 10 g PVP and 10 g sodium hypophosphite was dissolved in 160 mL of ethylene glycol that had been heated to 80 °C in the atmosphere. Next, 10 g copper sulfate pentahydrate was added to 40 mL of ethylene glycol, which had also been heated to 80 °C, and then, the second hot ethylene glycol solution was quickly added to the first solution under vigorous magnetic stirring. After holding for 20 min of the chemical reaction, the hot reaction solution was naturally cooled to ambient temperature. After that, the final solution was washed by ethyl alcohol and deionized water via centrifugation for at least 3 times. Then the product was collected ready for further use.

A mixture of 0.64 g trisodium citrate dehydrate and 1 g as-prepared Cu NPs was dissolved in 100 mL deionized water with magnetic stirring. When the 0.5 g silver sulfate was dissolved into 250 mL deionized water completely, it was added dropwise into Cu NPs solution with appropriately magnetic stirring. The reaction was continued for 90 min. After the reaction, the Cu@Ag NPs were obtained using centrifugation, and then washed with ethyl alcohol and deionized water. Nanoparticle pastes were prepared by mixing 80 wt% Cu@Ag NPs, 15 wt% ethyl alcohol and 5 wt% deionized water through ultrasonic dispersion for 3 min.

2.3. Sintering and bonding process

Schematics for the sandwich Cu/Cu@Ag NPs paste/Cu interconnection system and the UAS principle are shown in Fig. 1a and b, respectively. The Cu discs with diameters of 10 mm and 5 mm, respectively, deposited with 2 μm thick Ag as fake chips, were used to fabricate the joint. The thickness of Ag layer has a little difference because of the Ag layer was polished before sintering process to obtain clean surface, which has no influence on the results in this work. The sandwich samples were preheated at 100 °C for 30 s before heated to the sintering temperature to evaporate the moisture and other organics. The ultrasonic parameters of ultrasonic frequency, time and power were fixed as 35 kHz, 10 s and 230 W, respectively. The sintering temperature was set at 150 °C, 160 °C, and 180 °C, respectively. The ultrasonic pressure was set as 0.2 MPa in order to guarantee good contact between the ultrasonic horn and the samples to realize exceeding ultrasonic effect. To determine the overall temperature profile of the interconnecting system during the UAS process, a thermocouple was placed into the internal of the Cu@Ag NPs paste, and connected it to a thermoelectric-signal collector and a data recording system. To discover the effects of ultrasonic on the properties of joints, the thermo-compression sintering (TCS) of the same sandwich structures was also carried out with the applied pressure of 5 MPa and the same temperature as UAS, and the sintering time was set as 20 min.

2.4. Characterization

The morphologies of the Cu@Ag NPs and the microstructures of the joints were observed by Scanning Electron Microscope (SEM, Hitachi S-4700) equipped with an Energy Dispersive X-ray Spectrometer (EDS) detector. In order to further prove that the Cu NPs have been completely coated by Ag, the Cu@Ag NPs were analyzed by X-ray diffraction (XRD, Rigaku D/max-2500PC, Cu Kα), and the as-prepared Cu NPs and Cu@Ag NPs were stored for serial of days at ambient temperature to investigate the antioxidation of Cu@Ag NPs. To evaluate the mechanical property of the joints, the shear strength tests were carried out at a constant displacement speed of 0.2 mm/s and 5 samples for each condition were tested.