Ag Nanowire and Nanoplate Composite Paste for Low Temperature Bonding

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Nanopastes based on noble metals for low temperature bonding are currently of great interest. We have developed Ag nanowire and nanoplate composite paste. Copper-copper joining has been achieved using solid state sintering of nanopastes. We show that an enhanced bonding strength can be achieved by integrating Ag nanoplates into Ag nanowire pastes. Ag nanowire and nanoplate composite pastes are capable of being a low-temperature interconnect material potentially for interconnection in lead-free microcircuits, flexible electronic packaging and sensing applications. [doi:10.2320/matertrans.M201414]

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1. Introduction

Last decades have witnessed a growing demand of lead-free solders mainly for the concern of environmental and health issues. One of the emergent applications is for flexible electronics packaging.[1-5] Nevertheless, soldering temperature of conventional Sn based lead-free solders is more than 200°C, making it challenging to mount electric elements on heat-sensitive organic substrates such as polymer and paper.[5-8]

It is therefore essential to develop low temperature bonding process without damage of these flexible substrates. One possible solution is to use metallic nanomaterials and take the advantage of nanosintering.[9] In a nanosintering process, nanomaterials are sintered together through diffusion. The driving force of diffusion in nanosintering arises from a high surface energy. The significant decrease of the sintering temperature is a result of diffusion enhancement at the nanoscale because of a low activation energy and a high specific surface energy. The nanosintering can be dramatically speed up by the size effect, the shape effect and/or the surface melting.[9-12] For example, intensive studies focus on using Ag, Cu and Au nanoparticle pastes with typical sintering temperatures ranges from 150°C to 300°C, which are lower than the melting point of the corresponding bulk materials due to the size effect.[9-12,15] Although pressure is required to facilitate the bonding processing, these studies display the feasibility of using nanopaste for electronic packaging and flexible electronic interconnections. Recent studies focus on the shape effect, for instance, the interconnecting between one dimensional nano materials such as nanowires and nanotubes.[16-19] One attractive study is using Ag nanowire pastes for pressure-less bonding. The thinning of organic coating on Ag nanowire surface and “in-situ cleaning effect” further enables sintering at room temperature.[12] However, the maximum bonding strength of Ag nanowire paste is around 9 MPa, which is relatively lower than nanoparticle pastes.[12] This can probably be due to the tendency of nanowires to form reticular structures to a lesser extent than nanoparticles.[19] Ongoing efforts focus on further improving the bonding strength using composite materials, similar to a ferroconcrete structure material while having a low processing temperature and a low bonding process pressure.[19] The incorporation of nanowires and nanoparticles results in a densified structure after sintering, enhanced fracture resistance and bonding strength.[19] Although a maximum bonding strength of 16.8 MPa has been achieved at 200°C, it is still relatively low (3 MPa at 60°C) with a processing temperature below 100°C.[19] Obviously, a further improvement of bonding strength is desired.

Ag nanoplate is a thin plate single crystal material with stacking faults in the middle plane.[20] Vast studies have been focused on Ag nanoplates for a variety of applications, such as the biochemical sensing, optics, surface-enhanced Raman spectroscopy, etc.[20-23] However, few have examined the behaviors of adding Ag nanoplates to Ag nanowire paste as a systemic reinforcement additive for bonding. In this work, we presented Ag nanoplate and nanowire composite paste (designated as Ag NPL/NW paste) for low temperature bonding. The shape-induced nanosintering of nanoplates and nanowire was remarkably higher than both nanoparticle and nanoplate pastes. The experiments showed the bonding strength of Ag NPL/NW paste was 2–3 times stronger than Ag nanoparticle and nanowire composite paste (designated as Ag NP/NW paste) at a temperature below 100°C. The nanosintering between Ag nanowire and nanoplate has been investigated. The resistivity of Ag NPL/NW paste after sintering was investigated. The cracks perpendicular to the fracture surfaces were discussed.

2. Experimental Procedure

Ag nanoplates were synthesized by a modified hydrothermal method.[24] In a typical synthesis, 170 mg of AgNO3 (Fisher Scientific International) and 3.36 g of polyvinyl-pyrrolidone (PVP) (Mw ≈ 1,300,000, Fisher Scientific Inter-
were mixed in 10 mL deionized water and then autoclaved in a stainless steel with a Teflon liner of 23 mL capacity at 120°C for 21 h. Ag nanowires were synthesized by a wet chemical method following Ref. 3. After synthesis, the as-prepared Ag nanoplate and nanowire were washed and condensed via a centrifugal concentration process separately. The sediments were collected and dispersed in ultrapure water (electrical resistivity approximately 18 MΩ/cm). Finally, the Ag NP/NW paste was prepared by add Ag nanowire paste into Ag nanoplate paste with a mass ratio (Ag nanowire:Ag nanoplate) of 3 : 7.

The bonding strength was measured via a similar method as Ref. 12). Period to bonding, the copper wires are prepressed with acetone and hydrochloric acid. Then, the Ag NPL/NW paste was drop cast to the joint of two copper wires through a needle. After that, the samples were dried naturally at room-temperature (24°C) or post heated from 80°C to 160°C in air for 1 h. The morphology of Ag NPL/NW paste was observed using a dual beam FIB/SEM instrument (Zeiss Auriga Crossbeam FIB/SEM) before and after post heating.

3. Results and Discussion

Figure 1 shows the morphology of as-prepared Ag nanowires and Ag nanoplates after centrifuging. As shown in Fig. 1(a), the Ag nanowires had a pentagonal shape with 5~20 µm in length and 40~80 nm in diameter. The Ag nanoplates were 100~250 nm in diameter and 12~20 nm in thickness as shown in Fig. 1(b). Figure 1(c) displays the Ag NPL/NW paste. The Ag nanowires do not aggregate and are uniformly dispersed in the Ag nanoplates. The concentration of the paste is 20 mass% (6 mass% Ag nanowires and 14 mass% Ag nanoplates).

Figure 2(a) illustrates the schematic diagram of copper wire joining using Ag NPL/NW paste as mentioned in the Experimental Section. After drop casting, Ag NPL/NW paste forms a ferroconcrete structure as shown in Fig. 2(b). SEM images in Fig. 2(c) and (d) show the top view and cross-sectional view of nanocomposite paste. Interestingly, different from the isotropy of Ag NP/NW paste,19) this Ag NPL/NW paste shows an anisotropic stacked structure, in which Ag nanoplates act as matrix while Ag nanowires being uniform dispersed in Ag nanoplates serving as fillers.

To investigate the sintering behaviors of this nanocomposite paste, the copper wire joints were thermally sintered from room temperature (24°C, marked as RT) to 160°C for 1 h using a hotplate. The morphology of the sintered Ag NPL/NW paste is shown in Fig. 3. The metallic interconnections occurred between Ag nanowires/Ag nanowire and Ag nanoplates/Ag nanoplates. The Ag nanowires show the end-to-end and manners at room temperature as shown in Fig. 3(a), (c). These zig-zag Ag nanowires probably obtained from two mechanisms, either crystal growth or nanojoining. Firstly, previously studies illustrates that V-shaped Ag nanowires form due to twinned crystal plane induced growth and crystal lattice match induced fusion during synthesis process.25,26) Nevertheless, only very few V-shaped Ag nanowires was observed in our as-prepared Ag nanowire paste. Secondly, it has been shown that washing may remove the organic surface result in a reactive surface, which readily allows Ag atoms to diffuse. Thus, Ag
nanowires can even sinter at room temperature.\textsuperscript{12) Surface selective activation lead to self-oriented nanojoining of Ag nanowires in end-to-end (shown in Fig. 3(b)) joining manners.\textsuperscript{27) In addition, the side-to-side joining manner of Ag nanowires has also been observed in previous study.\textsuperscript{12)} Notably, the sintering between Ag nanoplates and Ag nanowires has also been observed in an edge-to-side manner as shown in Fig. 3(b)\textsuperscript{(d)}. The sintering between Ag nanowire/nanoplate at room temperature is probable because the thickness of Ag nanoplates is 5–20 nm, which is only \(\approx 10\%–20\%\) of the Ag nanoparticles reported in Peng et al.\textsuperscript{14,19} This dimensional decrease enhances the Ag atom diffusion between Ag nanoplate edges and Ag nanowire sides and further enables sintering. The sintered Ag nanoplates and nanoplates lead to the neck growth and direct metallic bonding. The Ag nanoplates can be parallel to Ag nanowires (shown in Fig. 3(b)) or perpendicular to Ag nanowires (shown in Fig. 3(d)). The increase in temperature further facilitates the solid state sintering and result in larger neck size\textsuperscript{9) as shown in Fig. 3(e), (f).

The bonding strength of Ag NPL/NW pastes as a function of bonding temperature is presented in Fig. 4 (solid lines). The bonding strength is 12 MPa at room temperature, 2 times higher than Ag nanowire pastes. This high bonding strength can be attributed to the sintering of Ag nanoplate/nanowire and Ag nanowire/nanowire, ferroconcrete structure of Ag NPL/NW paste, high density of the paste and adhesion from PVP. As the bonding temperature increases, the difference between the bonding strength of Ag NPL/NW paste and Ag NP/NW paste dramatically decreases. The bonding strength of Ag NPL/NW approximately stabilized at around 16.5 MPa at 100°C without a processing pressure, which is significant stronger than those in reported results investigating bonding with other paste materials such as Cu nanoparticles (<1 MPa) or Ag nanoparticles (2–4 MPa) processed with 5 MPa pressure.\textsuperscript{9,14,28) The increase of bonding strength associated with the decrease of resistivity reveals the effect of sintering to this high bonding strength. The dashed line in Fig. 4 presents the resistivity of Ag NPL/NW paste as function of preceding temperatures. The rapid decrease of resistivity from room temperature to 80°C mainly arises from the further sintering between Ag nanoplate/nanowire and Ag nanowire/nanowire as we mentioned. This nano-sintering leads to the increase of contact points and neck sizes, which reduces resistance of nanojoints. However, only a slight decrease of resistivity was observed with further increasing temperature to 160°C. Meanwhile, the bonding strength shows an increase from room temperature to 80°C, and also unchanged from 80°C to 160°C. Thus, the sintering of Ag nanopaste contributes to enhance the bonding strength. Based on the experiment, an optimized preceding temperature of 80°C can be achieved with a bonding strength of 16.2 MPa and a resistivity of 5.3 m\(\Omega\)m. This low bonding temperature with high bonding strength and low resistivity displays a great advantage using Ag NPL/NW for flexible organic electronics packaging and interconnection.\textsuperscript{3,4}

The formation of ferroconcrete structure is also responsible for the high bonding strength. Figure 5 shows SEM images of cracks produced perpendicular to the fracture surfaces. The regions reveal the role of the nanowire in the fracture of the bonding material because the primary crack cannot be readily characterized after failure.\textsuperscript{19) Crack propagation is suppressed by bridging of the nanowires as shown in Fig. 5(a), (b) in a similar way to Ag NP/NW paste bonding at 150°C. The defects and plastic deformations were observed as shown in Fig. 5(b), revealing that the bonding between Ag nanowires and Ag nanoplates reduced the failure by a “pulling-out” procedure of the nanowires.\textsuperscript{19) After “pulling-out” of Ag nanowires, the final failure occurred in Ag nanowire, with
plastic deformations at the failure of Ag nanowires as show in Fig. 5(c). Again, these plastic deformations confirm the contribution of sintering to the high bonding strength. This failure mechanism is also found from 80°C to 160°C as shown in Fig. 5(d)-5(f). This mitigated failure mechanism of Ag NPL/NW enhances the damage tolerance of joints in electronics packaging.

4. Conclusion

Ag nanowire and nanoplate composite paste was developed in this study. The bonding strengths of 12 MPa at room temperature and 16.5 MPa at 100°C have achieved with Copper-copper joining. We show that an enhanced bonding strength can be realized via reinforcement of Ag nanoplates in Ag nanowire paste. Ag nanowire and nanoplate composite pastes are capable of being a close room temperature bonding material potentially for interconnection in lead-free microcircuits with thermal sensitive substrates, flexible electronic packaging and sensing applications.

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