Advanced Interconnect Materials for Ink-jet Printing by Low Temperature Sintering

Rongwei Zhang and C. P. Wong
School of Materials Science and Engineering, Georgia Institute of Technology,
771 Ferst Drive, Atlanta, GA, 30332, USA
Phone: 404-894-8391, fax: 404-894-9140, email: cp.wong@mse.gatech.edu

Abstract

In this study, we reported the development of a novel highly electrically conductive adhesive (ECA) that can be used in ink-jet printing and have the function of adhesive by a single step of low temperature sintering/curing. With the introduction of silver nanoparticles into the formulation, the electrical resistivity of the resulting ECAs is about 10^{-5} ohm·cm after sintering at 180 ^{o}C or using a typical lead-free reflow profile (sintering/curing time: several minutes), which is compatible with industrial processis and favorable for the industrial applications. As is known, the strong adhesion of epoxy may enable the resulting ECA to be printed on various kinds of substrates, especially on flexible organic substrates, which is very promising for microelectronic applications. Moreover, the effects of time, temperature and the acid on the electrical resistivity of the ECA have been investigated, providing an in-depth understanding of the enhanced electrical properties. Finally, the contact resistance of the ECA on Cu surface can be stabilized for more than 1500 hrs. Thus the newly developed ECA can be ink-jettable, be compatible with industrial processes, has very low electrical resistivity by low temperature sintering/curing and could provide a strong adhesion to various substrates. The superior material properties of the formulated ECA combined with ink-jet printing technology will be very promising for a wide range of industrial applications in electronic industry.

Keywords conductive adhesive, ink-jet printing, low temperature sintering, interconnect, silver nanoparticles

Introduction

As microelectronics are continuously driven toward smaller, higher density, and lower cost, ink-jet printing technology has attracted extensive interests, due to its significant advantages over other technologies such as photolithography. The advantages of ink-jet printing are cost-effectiveness, direct printing, no tooling, non-contact processing, real-time production of coating materials by digital design, much less waste of precious materials, the ability to produce fine pattern, environmental friendliness and so on. [1-4] These unique advantages address the needs for next-generation microelectronic packaging and allow the technology to be widely used in many fields ranging from integrated circuits, transistors, organic light-emitting diodes, sensors, biotechnology to solar cells. Although a wide variety of materials can be ink-jettable, the technology presents demanding requirements for the material properties such as rheological properties, surface energy, environmental stability, adhesion to substrate and achievement of desired properties such as very low electrical resistivity on the substrate. Therefore, the development of ink-jettable materials is crucial for the application of ink-jet printing technology. Currently, most ink-jettable materials such as commercially available electrically conductive inks and Ag pastes do not offer an adhesive function on various kinds of substrates.

To the best of our knowledge, only one research group reported the formulation of ink-jettable conductive adhesives by two-step curing. [5] In the first step, UV curing has been applied, which required an oxygen-free environment. As the authors reported, UV curing of the highly filled conductive adhesive is challenging as parts of matrix only receive very little UV radiation via reflection from other particles. In the second curing step, 180 ^{o}C and a pressure of 2 MPa were used and then the materials were post cured at an elevated temperature (e.g., 130 ^{o}C for 30 mins). The electrical resistivity of the conductive adhesive is 6×10^{-4} ohm·cm. Electrically conductive adhesives (ECAs), as promising lead-free interconnect materials, offer the advantages of mild processing conditions, environmental friendliness, fewer processing steps, lower stress on the substrates, fine-pitch capability and so on. These advantages enable ECAs to be widely used in the electronic industry. Compared with eutectic Sn/Pb solders, the main disadvantages of polymer-based electrically conductive adhesives are the low electrical conductivity and poor reliability under reliability tests such as 85 ^{o}C and 85% relative humidity (RH) and thermal cycling test, which considerably limit their applications in electronic packagings. In order to enhance the electrical properties of ECAs, various approaches have been reported such as replacing the lubricant with aldehyde [6] and short-chain diacids, [7] increasing the cure shrinkage of polymer binders and thus more intimate contacts between conductive fillers, introducing Ag nanowires [8, 9] and Ag nanoparticles into the ECAs. Low temperature sintering of metal nanoparticles presents a promising approach to increase the electrical conductivity of interconnect.

Metal nanoparticles have received significant attention due to their unique characteristics such as enhanced reactivity of surface atoms, depression of melting point, catalyst, biological, electrical and optical properties. In particular, it is well-known that the melting point of metal nanoparticles can be dramatically reduced by decreasing the size of the material due to the tremendous increase in surface energy. Taking advantaging of this property, sintering of conductive inks at a low temperature has been widely achieved to produce conductive patterns in microelectronics. [2, 3, 10-13] The critical temperature at which the sintering of metal nanoparticles begins depends on the particle size, organic surfactants/contaminants on the nanoparticle surfaces, pressure, atmospheric gas. [14] Although the sintering can start at a low temperature slightly higher than 100 ^{o}C, higher temperature (more than 300 ^{o}C) was typically needed to achieve very low resistivity. [2]

Our previous work has demonstrated the formulation of highly electrically conductive adhesives by low temperature sintering. [15-17] Generally, the overall electrical resistance of the conductive adhesives is the sum of the resistance of fillers, the contact resistance between fillers and the contact resistance between fillers and pads. Through sintering, the contact resistance among conductive fillers can be effectively reduced resulting in the low resistivity of the materials and low resistance of the joint (Figure 1). In this study, we report the development of a novel highly electrically conductive adhesive (ECA) that can be used for ink-jet printing and have a function of adhesive by a single step of low temperature sintering/curing. The effects of sintering time, temperature and the acid on the electrical resistivity of the ECAs have been investigated, providing an in-depth understanding of the enhanced electrical properties.

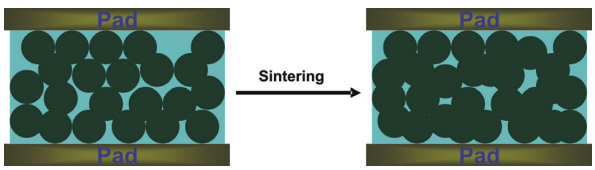


Figure 1 Schematic representation of the elimination of interface among conductive fillers in ECAs by sintering process.

Experimental

The epoxy resin and hardener used were diglycidyl ether of bisphenol F (DGEBF, Resolution Performance Products) and hexahydro-4-methylphthalic anhydride (HMPA, Lindau Chemicals), respectively. The catalyst was 1-cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN, Shikoku Chemicals Corp.) Silver nanoparticles were synthesized by the combustion chemical vapor condensation method. [17] All the chemicals were used as received.

Silver nanoparticles and silver flakes were incorporated into the mixture of the epoxy resin and HMPA. The optimal ratio of silver nanoparticles and silver flakes was 4:6 and a diacid was used as the surfactant to prevent the agglomeration. The mixture was sonicated for more than 1 hr to obtain a good dispersion of silver nanoparticles in the epoxy resin. Then the catalyst was added into the formulations and continued to sonicate for another 30 minutes. After sonication, the formulated paste was thermally cured at different temperatures or using a typical lead-free profile to produce ECAs.

The resistivity of the ECAs was calculated from the bulk resistance of the specimen with specific dimensions. Two strips of a Kapton tape (Du Pont) were applied onto a pre-cleaned glass slide. The formulated paste was printed on the glass slide. After thermal cure, the bulk resistance (R) of this ECA strip was measured as well as the size of the specimen. The bulk resistivity, ρ, was calculated using Equation 1:

$$\rho = \frac{t \times w}{l} \times R \qquad (1)$$

where l, w, t are the length, width and thickness of the sample, respectively.

The formulated paste was dispensed onto the test vehicles for the measurement of contact resistance and then was used for reliability test. [17]

The morphology of the polymer composites was studied by field emission scanning electron microscopy (SEM, JEOL 1530).

Results and Discussion

Figure 2 shows the effect of an acid on the electrical resistivity of the ECA with 80 wt% Ag flakes and Ag nanoparticles (6:4) cured at 150 ^{o}C and anneal at 180 for 1 hr. Compared with the resistivity of the ECA with 80 wt% Ag flakes (10^{-4} ohm·cm), the incorporation of silver nanoparticles into the ECA will lead to more than one order of magnitude higher electrical resistivity since incorporation of nanoparticles will increase the number of contacts and decrease the contact area among filler particles. After annealed at 180 ^{o}C for 1 hr, the contact resistance between filler particles can be significantly reduced due to the sintering among particles, which effectively eliminates the interfaces among silver nanoparticles and between silver particles and silver flakes. [15, 17] The sintering process has been described by the grain boundary diffusion model. [18, 19] It is believed that the grain boundary diffusion is dominant in the initial stage of sintering due to it is lower activation energy than that for lattice diffusion. [20, 21] Although bulk silver has a high melting temperature (961.8 ^{o}C), the reason that annealing could reduce the resistance by two orders of magnitude is due to the fact that sintering temperature can be considerably lowered due to thermodynamic size effect. [17]

More interestingly, much lower electrical resistivity was achieved with an additional acid than that of without acid after annealing. Figure 3 shows the change of morphologies of ECAs before and after the sintering. After sintering, the growth of particle size was observed (Figures 3 (b) and (d)). The absence of an acid results in the aggregation of silver nanoparticles in the ECA. During sintering, surface diffusions driven by the reduction of interfacial energy occur among silver nanoparticles and lead to larger aggregates, as seen from Figure 3 (b). Once the large aggregates form, it makes further sintering of these large aggregates more difficult at the same temperature since more energy is required for sintering of large particles. As a result, separate aggregates forms and there is no obvious necking between large aggregates. When an acid was employed, sintering seems to occur during the curing of the ECA at 150 ^{o}C. Acids can chelate to silver surface and prevent self-cohesion of silver nanoparticles and the formation of aggregates. With the presence of an acid, silver nanoparticles were well dispersed into the polymer matrix. During the curing/sintering, the acid will debond from the surface of silver nanoparticles at 145 ^{o}C as measured from DSC [15] and then the sintering occurred. Due to the good dispersion of silver nanoparticles in the polymer matrix, no obvious large aggregates were observed during curing/sintering. Instead, the inter-particle necking forms and thus it results in the formation of a continuous conductive network within the polymer matrix, significantly contributing to the low resistivity. Therefore, factors such as the physical

property (melting point etc) of an acid, the interaction between an acid and the metal filler and debonding temperature will strongly affect the sintering process and consequently leads to different electrical properties of the resulting ECAs. In the following study, the acid was used.

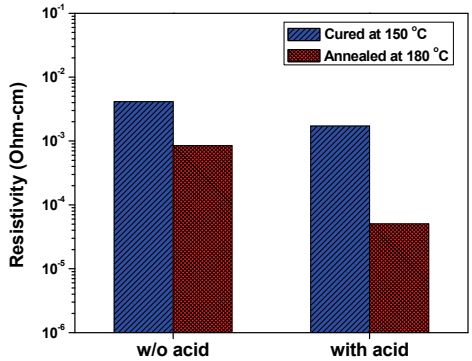
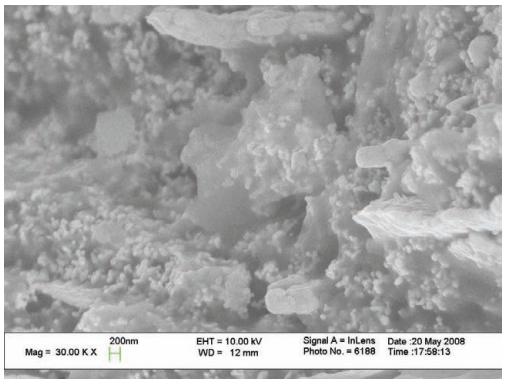
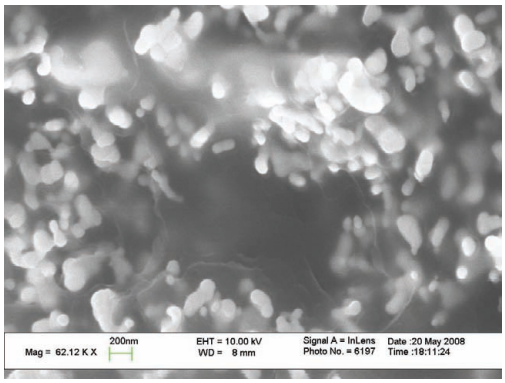


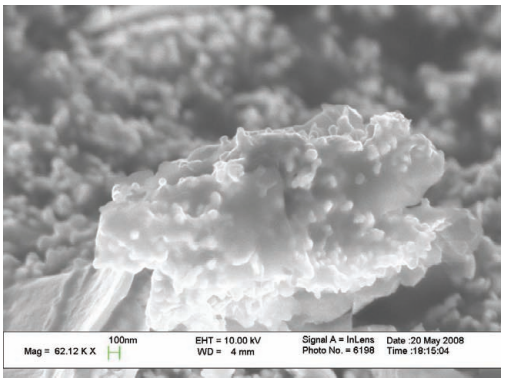
Figure 2 Effect of the acid on the electrical resistivity of ECAs.



(a)



(b)



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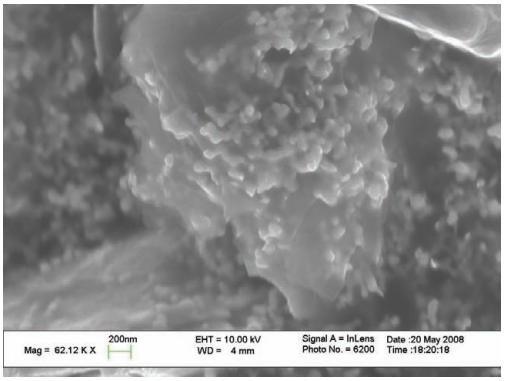

(d)

Figure 3 SEM micrographs of the cross-section of ECAs (a) cured at 150 °C, without an acid, (b) annealed at 180 °C, without an acid, (c) cured at 150 °C, with an acid, (d) annealed at 180 °C, with an acid.

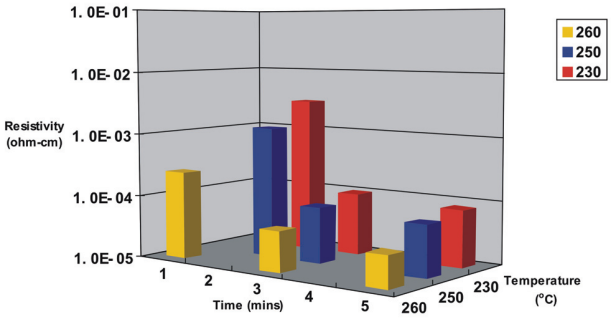

Figure 4 Effect of time and temperature on the resistivity of ECAs.

In order to fabricate ECAs in a more fast way, the simultaneous curing and sintering in one step have been investigated to facilitate practical applications. The effects of time and temperature on the electrical resistivity of the ECAs were showed in Figure 4. It has been found that the ECAs were either cured/sintered at 230 °C and 250 °C for 2 mins or cured/sintered at 260 °C for 1 min have high resistivities. As the temperature and time increase, the curing/sintering will be more complete and thus results in a much lower resistivity.

Moreover, Figure 5 shows the effect of the filler loading on the resistivity of ECAs using a typical lead free profile (sintering/curing time: several minutes). Importantly, the resistivity of the ECA with 80 wt% Ag filler is about 10^{-5} ohm·cm. The fast sintering/curing of ECAs will greatly facilitates their real applications in the field of microelectronics.

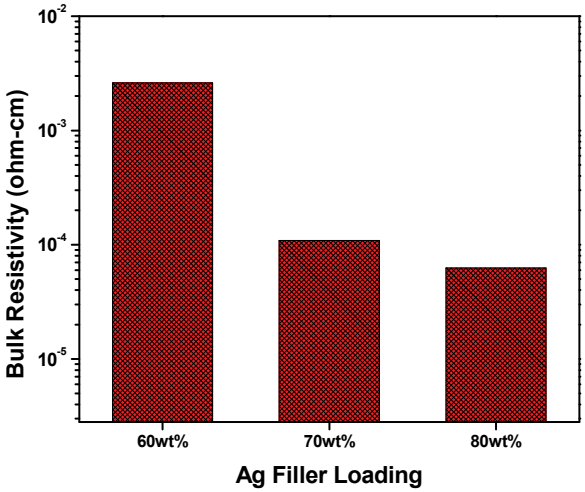

Figure 5 Bulk resistivity of ECAs with 60 wt%, 70 wt% and 80 wt% of Ag loading cured by a typical lead-free reflow profile.

Due to its low cost and low dielectric constant, copper is the most interesting metal for microelectronics. However, the most challenging problem is the easy oxidation of copper. Figure 6 shows the contact resistance of the ECA with acid on Cu surface under 85°C and 85% relative humidity (RH). The contact resistance is about 0.1 ohm and can be stabilized for more than 1500 hrs under 85°C and 85%RH. High reliability of the ECAs will further enable them to be used in the real applications.

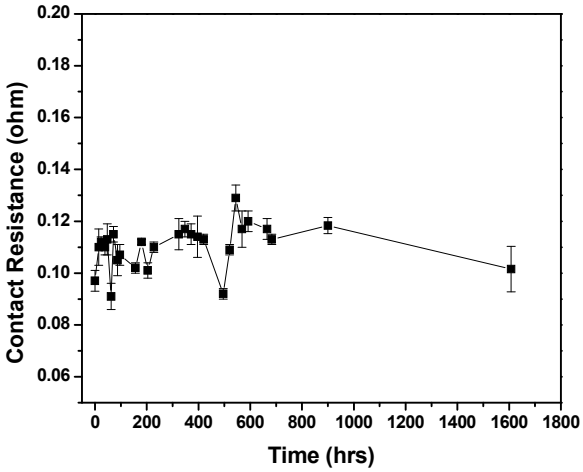

Figure 6 Contact resistances of ECA with an acid on Cu surface.

Conclusions

With introduction of silver nanoparticles, ECAs with low electrical resistivity have been successfully fabricated by low temperature sintering/curing. The key factors such as effect of acid, sintering time and temperature on the electrical were investigated by morphology studies. With acid, the good dispersion of Ag nanoparticles in the polymer matrix facilitates the sintering among conductive fillers and thus formation of conductive network in the polymer matrix. In addition, the low resistivity of ECAs can be achieved by using a typical lead free reflow profile, which is very convenient for industrial applications. The resulting ECA shows very a stable contact resistance on Cu surface. The superior electrical properties of ECAs with excellent reliability combined with ink-jet technology are very promising for high-performance interconnect applications.

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