Improvement of the Thermal Conductivity by Surface Iodination

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***Abstract* — With the increasing demand of high power density electronics, heat dissipation becomes an urgent problem. In order to address this problem, we introduce a surface modification method for silver that are employed as fillers to prepare the thermal conductive adhesive (TCA). After simple iodine pre-treatment, there exist some nano-sized small structures on the surface of fillers. Compared to the control sample, the TCA with modified fillers exhibits a superior thermal conductivity. The conductivity increases accordingly to the increase of curing temperature. This facile filler modification method may efficiently improve the performance of the TCAs and find broader applications in high density packages.**

Keywords — thermal conductive adhesive; thermal conductivity; surface iodination

I. Introduction

With the increasing packaging density and power density of electronic devices, heat dissipation becomes one of the most urgent and complicated problems since the accumulated heat often induces thermal fatigue and chemical reactions, which shortens the service life of the devices [1, 2]. Thermally conductive adhesives (TCAs) are the good candidates for solving such a problem.

Generally, a TCA consists of fillers which act as the media for heat dissipation, and the binder are used to adhere the fillers together and provide adequate mechanical strength. Due to a variety of advantages including the high thermal conductivity (427 $Wm^{-1}K^{-1}$) and chemical stability, silver is usually selected as the fillers for both electrically and thermally conductive adhesives. Compared to other conventional thermal conductive materials, such as carbon and ceramic, silver fillers are prone to percolate in the resin dispersant with a low contact resistance, which is favorable in both electrical and thermal conductance applications. This is primarily ascribed to the free electrons which can transfer heat much more efficiently than phonons. In addition, silver has a relatively weak lattice scatting at the boundary of the crystals, allowing the efficient transfer of phonon. Such advantages promote silver considerable prospective in thermal management applications.

Technically, there exist two common ways to increase the conductivity of silver adhesive. One is to increase the concentration of the fillers. The increased filler content can help build up more percolation channels so as to improve the thermal conductance. Yet it may increase the viscosity of the paste and cause dispensing and printing problems. The other one is to sinter the fillers at higher temperatures. Even though the melting point of silver is about 962 ^{o}C, the nano-sized silver surface features and particles can be sintered at rather low temperatures [3]. The sintering of silver substantially decreases the contact resistance of the fillers, in which way reduces the scatting of electrons and phonons. However, the sintering of metal nanoparticles usually involves a high temperature (>200°C) curing process [4, 5], which may be harmful to many temperature sensitive electronic components. In some cases, nanoparticles are involved to reduce the melting point, yet increasing the viscosity of the adhesive simultaneously.

To overcome this dilemma, in present work, we introduce a facile method to enhance the thermal conductivity of TCA by a simple surface modification method. The method involves a simple iodine treatment of the micron-sized fillers prior to the dispensing of the fillers in the resin, which is based on our previous work regarding the electrical conductivity of adhesives [6, 7]. In the following paragraphs, we systematically investigate the performance of the TCAs based surface modified conductive fillers, including the morphology of fillers and the thermal conductivity of TCA in the case of various filler concentrations, curing temperatures.

II. Experimental procedure

Silver particles were purchased from Chengdu Banknote Printing Complex, China (SF-01C). Bisphenol – A epoxy resin (Epon 828) and methyltetrahydrophthalic anhydride (MTHPA) were obtained from Shell and Nanya. Initially, we dispersed the silver particles in ethanol. Then iodine – ethanol solution was added dropwise to modify the surface of silver particles. The ratio of silver to iodine was maintained 500 : 1 by weight. The solution was kept stirring for 1 hour at ambient temperature. The resin binder was prepared by mixing the

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epoxy resin and MTHPA harder according to the equal epoxide equivalent weight (EEW) of the epoxy resin and the hydroxyl equivalent weight (HEW) of the hardener. A small amount of catalyst was added to the resin dispersant to accelerate crosslinking. The TCA samples were made by mixing the silver fillers and the resin dispersant in a planetary rotary mixer with 1500 rpm for 16 minutes. The control samples using bare silver particles were also prepared for comparison.

Netzsch Laser Flash Apparatus (LFA) 447 NanoFlash was used in this work to measure the electrical conductivity of the cured TCA under through-plane mode. Prior to the measurement, the TCA was cured as small cylinders with diameter of 12.7 mm and height of 3.0 mm. Under this macroscopic scale, the cylinders are assumed to be isotropic and homogeneous in conductivity, where the thermal percolation effects in the fillers-resin system had been averaged out. During the measurement procedures, a good transient signal match from the LFA instrument has been achieved (error under 10 %). The thermal diffusivity (D) obtained was used to calculate the thermal conductivity (λ) by $\lambda = D \times \rho \times C_p$, where ρ and C_p are the density and thermal capacitance of the adhesive. The average λ for each TCA cylinder is thus obtained. Any difference in λ among test samples will be solely due to the surface treatment of the silver fillers.

The morphology of the silver particles was investigated using a Hitach S-4800 field emission scanning electron microscope (FE-SEM). The differential scanning calorimetry (DSC) curves were recorded by a Netzsch 447 F3 thermogravimetry in nitrogen.

III. RESULT AND DISCUSSION

The silver particles were immersed in ethanol and a small amount of iodine-ethanol solution was added dropwise, as depicted in Fig. 1. The scanning electron microscopy (SEM) images of the particles are shown in Fig. 2. As shown in these SEM images, the fillers present an isotropic shape and the grain size distribution is of 1 ~ 2 microns. Compared to the smooth surface of the bare silver, the iodine modified silver shows many small isolated islands with the size below 100 nm are distributed on the surface. It is still not clear to identify the exact structure of these small islands. It appears after the iodine treatment, which is suggested to play an important role on the conductivity enhancement. The SEM images of the cross-section of the TCA samples show a random distribution of the fillers in the resin dispersant, indicating the isotropic property of the prepared samples.

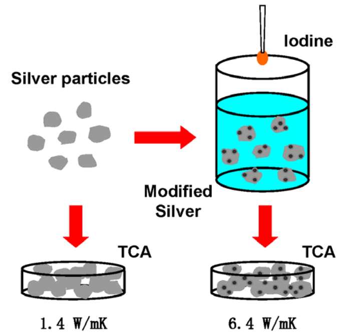

Fig. 1 Surface modification of silver fillers

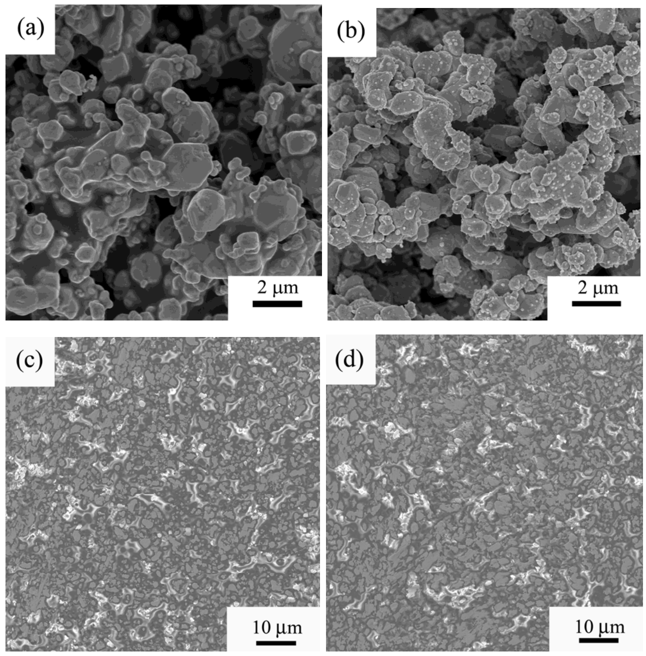

Fig. 2 SEM images of the silver particles and the cross-section of the TCAs (a: bare silver particles b: surface modified silver particles c: TCA with bare silver particles, d: TCA with surface modified silver particles)

The silver particles are mixed with a proper amount of epoxy resin and form a paste. After curing the paste, the TCA samples are examined. The thermal conductivity of the TCAs with bare silver and iodine modified silver particles are presented in Fig. 3. Four concentrations of silver content were used to investigate the thermal conductivities of the TCA samples. The thermal conductivity of TCA increases with the increase of silver concentration, and the increasing trend becomes faster as well. The thermal conductivity for the control sample is increased from 0.6 $Wm^{-1}K^{-1}$ to 1.4 $Wm^{-1}K^{-1}$ when filler concentration is raised from 60 wt% to 80 wt%. Meanwhile, the sample with modified fillers shows a dramatically increased conductivity from 1.2 $Wm^{-1}K^{-1}$ to 6.4 $Wm^{-1}K^{-1}$ at the same filler concentration. In other words, the surface modification of fillers not only enhances the thermal conductivity, but also enhances more rapidly than the control sample. In the previous works, we have demonstrated that the nano-island on the surface of silver particles had a positive effect on the electrical conductivity of the adhesive. Since the thermal energy can be transported by means of electrons, it is then expected that this enhanced electrical conductivity simultaneously reinforces the thermal transfer, as a result, enhancing the thermal conductivity.

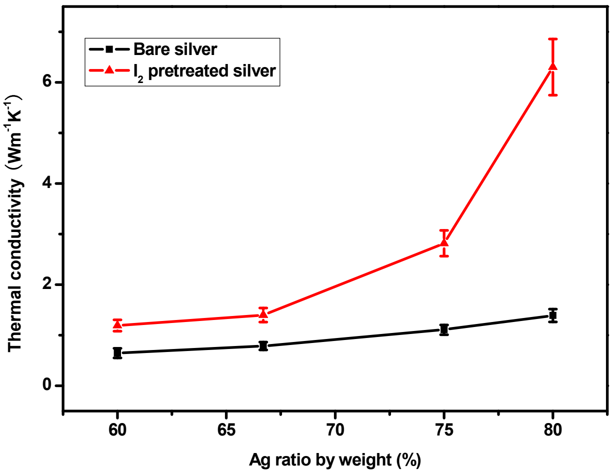

Fig. 3 Thermal conductivity of the TCA with various silver concentrations (Curing condition: 150 °C for 15 minutes)

This enhanced thermal transfer character is strongly relative to the nano-structure of the surface of fillers, whereas the DSC result in Fig. 4 does not show any noticeable phase transition. A small peak at 80 °C for the sample is due to the evaporation of ethanol. No other significant heat flux is detected. It's reasonable to believe that no sinter process for silver fillers happens below 300 °C. Therefore, the enhancement of thermal conductivity does not result from the particle sintering.

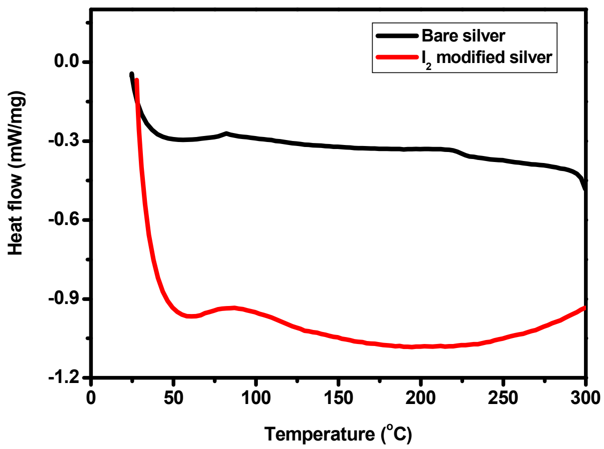

Fig. 4 DSC curves of the silver particles

In order to give a full image of the ability of thermal conductivity enhancement based on this surface modification method, , we measured the thermal conductivity of the samples under various curing temperatures. As can be seen in Fig. 5, the control samples with 80 wt% silver fillers do not show any significant change when the curing temperatures varies from 110 to 190 °C. The thermal conductivity is maintained at around 1.4 ~ 1.5 $Wm^{-1}K^{-1}$. On the other hand, the samples with surface modified silver shows a linear increase of thermal conductivity along with the increase of curing temperature. The conductivity is enhanced from 5.4 $Wm^{-1}K^{-1}$ to 7.3 $Wm^{-1}K^{-1}$, corresponding to the curing temperature carrying from 110 to 190 °C. This result suggests that a higher curing temperature is beneficial to the improvement of thermal conductivity, when the silver particles undergo the iodination treatment beforehand.

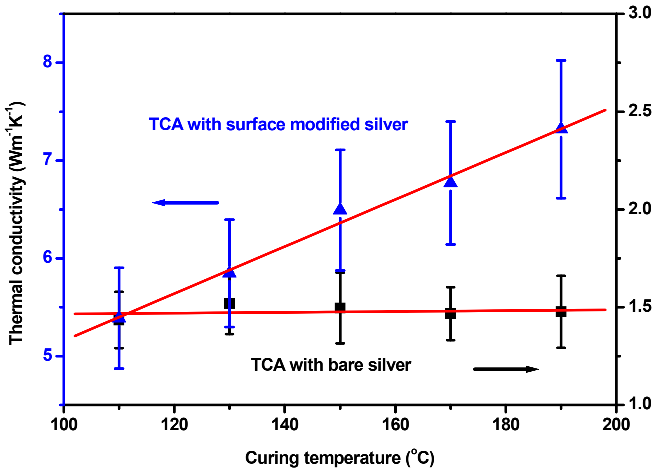

Fig. 5 Thermal conductivity of TCA with at 80 wt% filler concentration in various curing temperatures (the curing duration for 110 °C is 2 hours and the others are 30 minutes; Blue: TCA with modified silver fillers, Black: TCA with bare silver fillers)

Our previous work had shown that the iodine treatment for the silver fillers can substantially change the surface property of the silver fillers and thus significantly reduce the contact resistance among the fillers. Therefore the transportation of both electrons and phonons on boundary of fillers can be boosted up. Moreover, we note that a higher curing temperature seems beneficial to the reduction of contact electrical resistance since the thermal conductivity of the samples is enhanced accordingly.

IV. CONCLUDING REMARKS

With a simple surface modification of silver fillers, the thermal conductivity of the TCA is enhanced from 1.3 to 6.4 $Wm^{-1}K^{-1}$, which is about 500% of enhancement. It is by far the highest ever reported value in science community for an isotropy TCA with the silver content of 80 wt% without any high temperature sintering process. Based on a solution based treatment for an ordinary micron-sized silver powders, the contact resistant between fillers may be reduced. Therefore, the barrier that prevents the electron and phonon transportation is reduced, so as to enhance the thermal conductivity. This method is simple and low cost, thus suitable to mass manufacture. We envisage broad applications of this technique in the packaging for heat radiating at high density integrated electronic devices.

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