Silver Pastes with Excellent Thermal Conductivity

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Abstract*—Thermally conductive adhesives (TCAs) have been widely used in electronic packaging industry, such as for chip packages in smart phones and high-power LED lightings, as they combine the workability of polymer resins with the high thermal conductivity of fillers[1-4]. The polymer resins endow adequate adhesion strength and provide sufficient mechanical robustness. The thermally conductive fillers mainly determine the capacity of heat dissipation; and the filler can be carbon nanotube, graphene, aluminum nitride, and metal, etc. Among the metallic filler materials, silver is regarded as a competitive TCA filler because of the superior thermal conductivity (~400 W·m^{-1}·k^{-1}) and resistance to oxidization. The interfacial resistance can be dramatically reduced when sintering behavior is occurred. Yet, it is still a great challenge to fabricate silver-based TCA samples at low temperature with a relatively high thermal conductivity since it is hard to sinter at a moderate temperature. In this work, a simple surface treatment of silver micro-flakes is applied. Laser flash apparatus results show that the out-of-plane thermal conductivity of 85 wt% TCAs achieve 22 W·m^{-1}·k^{-1} when cured at 190 °C. The out-of-plane thermal conductivity of the TCA sample is ideal for applications in high-power thermal interface materials. It is notable that the surface treatment only simply includes two steps: hydrazine hydrate treatment and iodination treatment. A careful study on the influence factors such as surface treatment, curing temperature was conducted. The excellent heat conducting behavior renders the TCA with a good deal of future applications in high-power electron packaging.

***Keywords*—silver micro-particles; hierarchical structures; low-temperature sintering; electronic devices**

I. INTRODUCTION

Heat dissipation ability for chip modules is crucial to performance characteristics of most electronic devices. With the trend of high density integration, miniaturization of chips and the emergence of various applications such as high performance portable electronics and solid state lightings, heat dissipation has become an urgent problem. Without efficient thermal dissipation, thermal failure occurs to the chips, and the life-time and reliability of electronic devices would decrease substantially.

Thermal interface materials basically include three types: solder, thermally conductive adhesives (TCAs) and phase change materials. With the requirement of lead-free packaging, thermally conductive adhesives have aroused tremendous attention. Thermally conductive pastes are based on polymers, the fillers of thermally conductive adhesives include metal (copper, nickel [5], silver [6], etc.), carbon based materials (carbon nanotube [7], carbon fiber [8], etc.), and ceramic fillers (boron nitride [9], aluminum oxide [10], etc.). Among these materials, silver has drawn broad attentions [11-18]. Silver microparticles and nanoparticles can be sintered at relatively low temperature compared to carbon and ceramics, and the phonon scattering is weak. Besides, silver has the highest thermal conductivity among all metals, and is resistant to oxidation.

In this work, silver micro-flakes were modified with a simple surface treatment. The first step was hydrazine solution treatment; and the second step was iodine solution treatment. Besides, a post-curing process was also beneficial for increasing the thermal conductivity of the thermally conductive adhesives. Regardless of the orientation of silver micro-flakes and the shear force during slurry mixing, out-of-plane thermal conductivity can achieve 22 W· m^{-1}·k^{-1}.

II. EXPERIMENTAL

A. Surface Treatment

Silver micro-flakes were dispersed in alcohol and washed by hydrazine solution (85wt%). After vigorously stirring, the suspension was then washed by alcohol to remove the residual hydrazine hydrate. Simultaneously, 2.5‰ iodine-alcohol solution was added to silver-ethanol solution by peristaltic pump at the speed of 10 rpm. The pre-treated silver micro flakes were dried in a thermostatic vacuum drier at 60 centigrade.

B. Preparations of Thermally Conductive Adhesives

The mass ratio of epoxy and methyl tetrahydrophthalic anhydride (MTHPA) was calculated according to the epoxy equivalent weight (EEW) of the bisphenol A epoxy and the hydrogen equivalent weight HEW of the MTHPA. A planetary rotary mixer (Hasai. Co., Shenzhen, China) was used to mix the epoxy and MTHPA adequately. Then a small amount of catalyst was added. After that, silver micro-flakes were dispersed into the resin, and the slurry was mixed with the planetary rotary mixer at 1800 rpm for 15 minutes. The as-prepared silver pastes were cured at 150 °C for 1 h, and then 190 °C for 0.5 h.

C. Thermal Property Measurements

The out-of-plane thermal conductivity of the TCAs (1cm×1cm×0.1cm) was evaluated by Netzsch Laser Flash Apparatus (LFA). The thermal diffusivity (D) was obtained through LFA measurement, and the thermal conductivity was calculated by the as-follow formulas, where a represents the ratio of silver micro-flakes, the numerical values of C_{silver} and C_{epoxy} are 0.24 J· g^{-1}·K^{-1} and 1.2 J· g^{-1}·K^{-1}, respectively. ρ represents the density of TCAs.

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$$\lambda = D \times \rho \times C_p \quad (1)$$

$$\rho = \rho_{air} \times m_{air} / (m_{air} - m_{water}) \quad (2)$$

$$C_p = a \times C_{silver} + (1-a) \times C_{epoxy} \quad (3)$$

III. RESULTS AND DISCUSSIONS

A. The Influence of Surface Treatment on Silver Micro-flakes

As depicted in Fig.1, with the hydrazine and iodine treatments, nano-islands of Ag@AgI nanostructures appear on the surface of silver micro-flakes [8]. SEM images suggest that these nano-islands are distributed on the surface of silver micro-flakes homogeneously. After mixing the epoxy and silver micro-flakes, the silver paste sample with 85 wt% of silver was injected into a square-shape mold. When cured at 150 °C for 1 h and then 190 °C for 0.5 h, the TCA samples were obtained. LFA measurements indicated that the out-of-plane heat conductivity coefficient of surface treatment TCA sample achieved as high as 12.17 mm^2/s, the calculated thermal conductivity was 22.10 $W \cdot m^{-1} \cdot k^{-1}$. With regard to the TCA sample without surface treatment, the heat conductivity coefficient under the same curing condition was merely 0.874 mm^2/s, and the calculated thermal conductivity was 1.581 $W \cdot m^{-1} \cdot k^{-1}$.

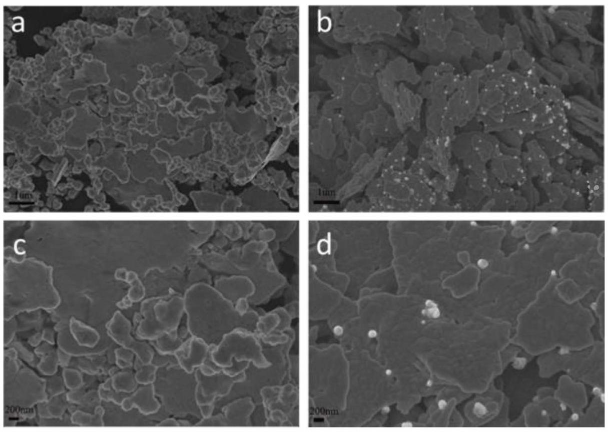

Fig. 1 (a), (c) SEM images of bare silver micro-flakes (b), (d) SEM images of surface treatment micro-flakes

Fig. 2 TCA samples without silver micro-flakes (left) and with silver micro-flakes (right)

B. The Influence of Silver Filler Loading on Thermally Conductive Adhesives

Silver filler loading has a remarkable influence on the thermally conductive behavior of the TCAs. Five different concentrations of silver micro-flakes with and without surface treatment are used to investigate the influence of silver filler loading on TCA samples. To reduce measurement errors, each point of the chart in Fig 3 is the average value of the experimental data.

With increased silver filler loading, the capacity of heat transmission enhances accordingly. As shown in Fig 2, thermal conductivity of TCAs using bare silver micro flakes as fillers increases from 0.342 $W \cdot m^{-1} \cdot k^{-1}$ to 1.581 $W \cdot m^{-1} \cdot k^{-1}$, corresponding with the increased silver loadings from 60wt% to 88wt%. As compared, thermal conductivity of TCAs filled with surface treatment silver micro-flakes increases from 1.129 $W \cdot m^{-1} \cdot k^{-1}$ to 26.6 $W \cdot m^{-1} \cdot k^{-1}$, corresponding with the range of the silver loading from 60wt% to 88wt%. The chart in Fig. 2 demonstrates that the thermal conductivity of TCAs with surface treatment silver fillers boosts compared to those without surface treatment. Meanwhile, as the filler loading increases, the viscosity of silver pastes increases accordingly.

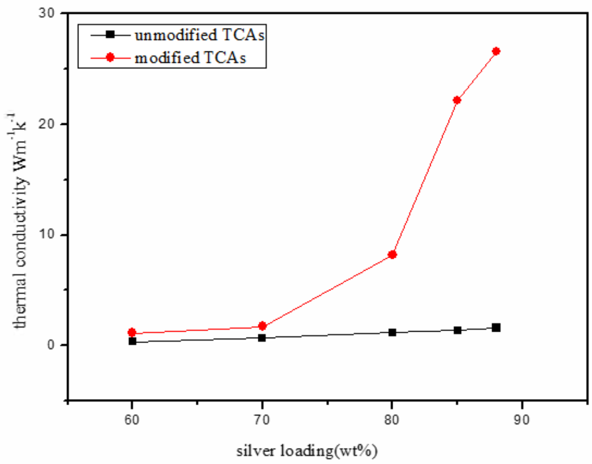

Fig. 3 Thermal conductivity of TCA samples with different silver filler loading

C. The Influence of Curing Temperature on Thermally Conductive Adhesives

Curing condition can significantly influence on the thermal conductivity of the TCAs. As shown in Fig. 4, when increasing the curing temperature, sintering behavior between silver micro-flakes becomes stronger. At a relatively low curing temperature (below 130 °C), small micro-flakes began to sinter, when increasing the curing temperature, sintering behavior became more significant. When cured at 190 °C, silver micro-flakes became closely connected and three-dimensional conductive network was well constructed.

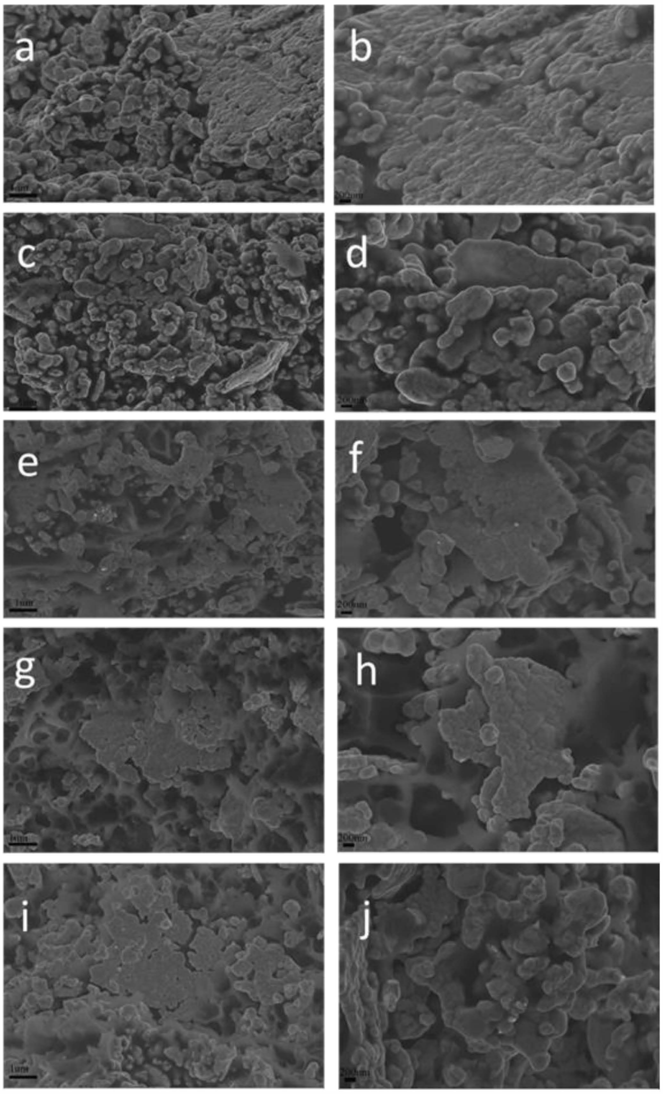

Fig. 4 SEM images of cured 85wt% TCAs with various curing temperature, 110 ℃ (a, b),130 ℃ (c, d),150 ℃ (e, f),170 ℃ (g, h),190 ℃ (i, k)

D The Influence of Silver Loading on Shear Force

An important index to evaluate the mechanical property of TCAs is the binding strength between the chip and the substrate. Typically, shear force test is applied to evaluate the shear force between the chip and the substrate. As shown in Fig 6, with the increase of silver loading, the mass fraction of epoxy resin decreases, followed by the decrease of shear force. The shear force decreased significantly when the silver loading increased from 80wt% to 88wt%. When the silver loading was 85wt%, the shear force was 15 MPa, and the substrate and the chip were firmly contacted. However, when the silver loading increased to 88 wt%, the shear force was below 5 MPa, which means that it can't act as a good thermal interface material.

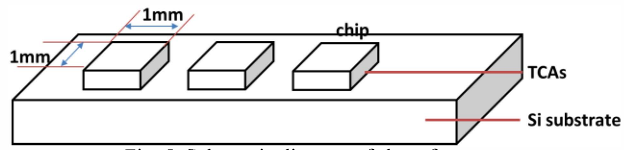

Fig. 5. Schematic diagram of shear force test

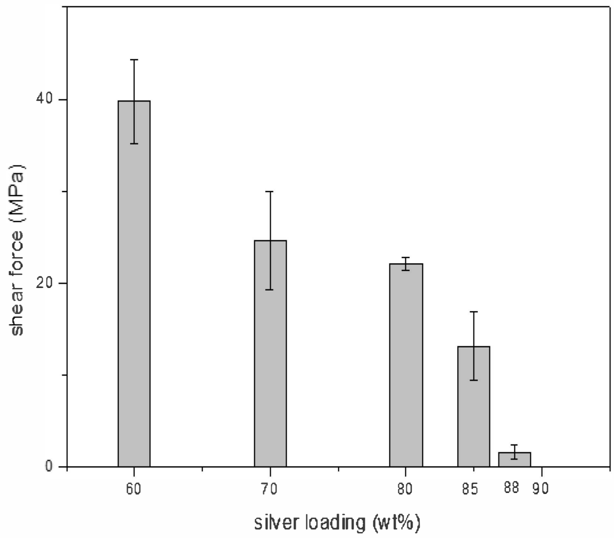

Fig. 6 Shear force test with different silver loading

IV. CONCLUSIONS

In summary, we combined the hydrazine and iodine treatments to modify the commercial silver micro-flakes, and used them to prepare TCAs with epoxy resin binder. After surface treatments, small nano-islands appear on the surface of silver micro-flakes; besides, thermal conductivity of TCAs has a significant increase. The thermal conductivity of 85wt% TCAs was 22 $W \cdot m^{-1} \cdot k^{-1}$, nearly 14 times higher than TCAs without surface treatments. The binding strength of modified 85wt% TCAs was 15 Mpa, the TCAs has a good capacity of heat transmission as well as binding power. These TCAs can act as excellent thermal interface material for high-power electrical packaging.

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