Abstract

Isotropic conductive adhesives (ICAs) with lower bonding temperature, higher resolution and environmental friendly have been used extensively in packaging process. In order to improve the electrical and thermal conductive properties of ICAs, two kinds of bimodal high temperature stable ICAs with matrix SHT6 and fillers with composition of macro silver flakes and boron nitride nanoparticles or macro silver flakes and silicon carbide nanoparticles were studied. In these two kinds of adhesives, the silver flakes were 75wt%, and the contents of nanoparticles were 0wt%, 0.5wt%, 1.5wt%, 2.5wt%, 3wt%, 5wt% in weight. All the samples were cured at 150°C for 1 hour. SEM images and EDS results show the nanoparticles disperse randomly in the ICA. The electrical resistivity of these ICAs depends on the contents of silver flakes and is hardly affected by BN nanoparticles and SiC nanoparticles. The thermal conductivity of these ICAs increases firstly with the weight increase of the BN nanoparticles and SiC nanoparticles. And then it decreases when the content of the nanoparticles beyond a certain point.

Keywords: isotropic conductive adhesives (ICAs); thermal conductivity; electrical resistivity

1. Introduction

The electronic industry has gained a rapid growth in various sectors such as the computer, telecommunications, automotive and consumer sectors. Some of the key drivers for this growth depend on the capabilities of the interconnect materials, such as electrical conductivity, thermal conductivity, reliability and so on. Silver-filled thermoset polymers were first patented as isotropic conductive adhesives (ICAs) in the 1950s [1]. Since then, conductive adhesives have been used more and more extensively for surface mount and chip interconnection because of their better properties, such as strongly heat-resistance, highly adaptability for high density packing, environment protection and so on, than Sn/Pb solders [2–5]. However, fundamental understanding of conductive adhesives lagged far behind some commercial requirements.

Isotropic conductive adhesives generally consist of polymeric resins (such as epoxies, diluents, coupling agent, curing agent, and other macromolecule modifiers) and conductive fillers. The conductive fillers are always silver flakes because of its good electrical conductivity and also well electrical conductivity of its oxide [3]. Furthermore, silver wires, nickel particles, tin particles and other metals and alloys are also used as the fillers to improve the properties or cut down the production cost [6–9]. In order to improve thermal and electrical properties of isotropic conductive adhesive, two new kinds of bimodal high temperature stable ICAs with new matrix named SHT6 and conductive fillers which were macro silver flakes and boron nitride (BN) nanoparticles or macro silver flakes and silicon carbon (SiC) nanoparticles were studied in this paper. In addition, the
influence of contents of nanoparticles on electrical resistivity and thermal conductivity was also investigated.

2. The adhesives preparation

A new kind of polymeric matrix named SHT6 was selected as the binder matrix for all the electrically and thermally isotropic conductive adhesives study in this paper. The matrix consisted of epoxy resin, silane coupling agent, reactive diluents, imidazole as curing agent. It mixed up at a prescribed weight ratio to give a homogeneous solution of the polymer matrix. One kind of nanoparticles (BN or SiC) was introduced into ICA formulations while keeping the macro silver flakes content the same. The diameters of these nanoparticles are under 100nm and that of silver flakes are 1~10\(\mu\)m. Then the ICAs were mixed in a solder cream mixer (MIX500D SLOPE) for 20min and cured at 150\(^\circ\)C in an oven (DHG-9023A, Instrument Co. Ltd. Qingxin) for 1 hour.

Boron nitride or silicon carbide was introduced into the adhesive respectively with a total silver loading of 75wt% by weight. The detailed formulation information of these isotropic conductive adhesives is listed in Table 1. Eleven different components of the ICA were prepared, in which the contents of the nanoparticles (ether BN or SiC) were 0wt%, 0.5wt%, 1.5wt%, 2.5wt%, 3wt%, 5wt% in weight.

<table>
<thead>
<tr>
<th>Items (wt%)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
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<td>Matrix</td>
<td>25</td>
<td>24.5</td>
<td>23.5</td>
<td>22.5</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>Silver flake</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>BN Or SiC Nanoparticles</td>
<td>0</td>
<td>0.5</td>
<td>1.5</td>
<td>2.5</td>
<td>3</td>
<td>5</td>
</tr>
</tbody>
</table>

3. Morphology of the adhesives

SEM images (fig 1a) show the morphology of the bimodal ICAs with silver flakes and silicon carbide nanoparticles. EDS results of A point (fig 1b) shows obvious peak of element C, O, and Ag, which illustrates this is the Ag flake. They tightly integrate in the ICA. And peak of Si appears in the EDS pattern of particle B (fig 1c), which illuminates its the SiC nanoparticle. They distribute randomly in the ICA. Some of them contact with silver flakes or other silicon carbide nanoparticles and some of them separate in the matrix.

4. Electrical resistivity of the adhesives

Four-point probe method was used to measure the bulk resistivity in the investigation of the electrical properties of the ICAs. And all the measurements of ICAs were done after curing. In the four-point probe measurement, the electric current (I) was constant and the voltage (U), the wide of the ICA sample (w), the length between the two points of the voltage under measurement (l) and the thickness of the cured ICA was measured separately. The resistivity (R) was obtained from the following equation:

\[
R = \frac{U \times w \times h}{I \times l}
\]
Fig. 2. Electrical resistivity vs. the contents of SiC or BN nanoparticles in ICAs with a total silver loading of 75wt% by weight.

Fig. 2 shows the electrical resistivity characteristics with the contents of nanoparticles in adhesives ranging from 0% to 5%. It can be seen from the curves that the electrical conductivity is hardly affected by the content of nanoparticles for samples with BN nanoparticles from 0% to 5% by weight in this study. The bulk resistivity of the adhesives with SiC nanoparticles subjects to the same laws when the content of SiC nanoparticles ranges from 0% to 3% and it is a little higher than that of the adhesive with BN nanoparticles with the same weight ratio of nanoparticles. However, the electrical resistivity increases much suddenly for the samples when the weight ratio of SiC nanoparticles rises to 5%. The resistivity of the adhesive is increased by one order of magnitude.

5. Thermal conductivity of the adhesives

The thermal conductivity of the ICA samples was measured by laser flash method. The sample was a wafer with a thickness of 1.2mm and diameter of 10.2mm. The laser thermal conductive detector was used to measure the thermal diffusivity ($\alpha$) and the Dynamic Stability Control (DSC) was used to measure the specific heat capability ($C_p$) of the ICA samples. And then, the thermal conductivity ($\lambda$) was calculated by following formulation:

$$\lambda = C_p \times \alpha \times \rho$$

Fig. 3 and Fig. 4 shows the characteristics of the thermal conductivity of the ICAs with the increase of nanoparticles content and temperature. The thermal conductivity of these ICAs increases firstly and then decreases when the content of the nanoparticles beyond a certain point.

The thermal conductivity of the adhesive with nanoparticles increase with the increase of weight ratio of nanoparticles when the nanoparticle is in the low ratio (boron nitride nanoparticle is lower than 2wt%, silicon carbide nanoparticle is lower than 3wt%) because of the high thermal conductivity of boron nitride and silicon carbide. Further addition of nanoparticles does not have any significant effect on the thermal conductivity probably due to increased clustering during the sample preparation. It can be seen from Fig. 3 the thermal conductivity in 100°C of the adhesive is lower than it in the 150°C and 200°C of the same adhesive. According to Inoue et al [10~12], this is due to the fact that the physical annealing effect in terms of decreasing inter-particle resistance can be induced during heating process of the resistivity measurement even if the ICA specimens are fully-cured. The curing temperature in this study is 150°C. With the test temperature became higher, the adhesives actually underwent an annealing process. The thermal conductivity increases with the rising of testing temperature. Fig 3 and fig 4 show the thermal conductivity of adhesive with SiC nanoparticles increases much more than it of adhesive with BN nanoparticles.
Fig.4. Thermal conductivity vs. content of SiC nanoparticles in ICAs with a total silver loading of 75wt% by weight

6. Conclusion

The electrical and thermal properties of the ICAs containing nanoparticles previous to heat were investigated experimentally in this paper. The contents of nanoparticles have no obvious influence on the electrical resistivity of adhesive with BN nanoparticles, while the electrical resistivity increases rapidly with the content ranging from 3% to 5% for the adhesives with SiC nanoparticle.

The thermal conductivity of the adhesives with nanoparticles increases with the rise of weight ratio of nanoparticles when the contents below a certain weight ratio. However, it decreases when the weight ratio exceed the point. The thermal conductivity is increasing with increasing testing temperature due to the annealing during the testing. In addition, the thermal conductivity of adhesives with SiC nanoparticles is higher than that with BN nanoparticles.

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References

