New Nano Size Filled TIM Material With High Thermally Conductive Properties

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Abstract

One of the largest problems connected with actual electronic and microelectronics systems is removing of heat generated by them, particularly through the power elements. The most so far widespread technical solutions in the range of high thermally conductive layers (Thermal Interface Materials - TIM), are compositions on the base of organic adhesives including as a fillers the particle of silver in the powder or flake shapes with the reason that it is material with very high thermal conductivity (ov. 420 W/mK). The compositions of this type are mostly thermally curing or sintering. Unfortunately this solution contain organic resins, what give the big limits the final value of the thermal conductive coefficient in the large degree, and also limits the maximum range of applying materials.

Introduction

All electronic devices generate heat, and this heat must be dissipated to guarantee reliability and prevent untimely failures. This is the main problem which is dedicated extremely wide applications as commercial electronics, computers, phones, automotive electronics, aircrafts, aerospace – almost all sectors of industry. This shows the importance of the problem we discuss.

The most popular up to now, thermally interface materials (TIM) contain some kind of polymer base matrix with different types of fillers as silver powder, copper, alumina powder and other. Such a materials were used by decades, but current technical challenges in the range of the maximization packing of the electronic circuits place a lot of higher technological requirements. One with the best known material which is used as a TIM is formulation similar to ECA contains epoxy resin filled with silver powder or flake, sometimes with nano size silver additive. Unfortunately, polymer component is the highest barrier for achieve acceptable thermally conductive value for modern electronic applications.

Nano Size Silver as Filler for TIM Material

The effect of the lowering melting temperature for nano size Ag was described by M.A. Asoro and all [1]. They found that for Ag nanoparticles the sintering temperature in some case decreases below 200°C. According to they results similar graph like for gold should to be for silver also (Fig.1.)[2]. Another challenge is that use of the nanoparticles prevents of the surface oxidation and sulfidation of the particles themselves, as well as the agglomeration and aggregation will be avoided. All those properties are connected with existing of protection layers on the nanoparticles surface [3]. These materials should stop the unwanted pre-sintering, agglomeration, aggregation and also chemical change of the particles. Like shown on Fig.2 the articles are coated by surface agent. The surfactant should be stable up to the processing temperature and possible mostly removed by used temperature. The removal of the surfactant from the surface at higher temperatures starts the sintering process. Partially the surfactant organic remains in the pores of the sintered joint.

Fig.1. The theoretical values for melting process of nanogold.

Fig.2. Sintering mechanism of coated silver nanoparticles.
There are several methods of nano Ag powder producing. They can be briefly described as:

- chemical reaction process
- thermal decomposition process
- metal dissipation in plasma process
- laser ablation process
- electrochemical process
- vapor condensation process
- and others.

Only methods that provide singular nanoparticles separated from others can be used for production of nanosilver particles as filler for described TIM application. From all, we choose the chemical reaction process, because this will give selection about protection layer possibility without changing silver powder structure. From several types of protective layers we decide to choose as below:

- nanosilver with carboxylate coating (nAg1),
- nanosilver with amine type coating (nAg2),
- nanosilver with polymer coating (nAg3).

SEM pictures all those nAg fillers are presented below (Fig.3).

Fig.3. SEM pictures of nanosilver with different protective layers.

Also particles size distribution all selected nAg has been done with result as on (Fig.4).

Fig.4. Distribution of nanosilver particles by Malvern Zetasizer.

Additional condition is that use the nano size silver as a TIM material require that the protection layer should be removed as low as possible before sintering process. For obtaining this information the next analysis has been done, about influence of thermal energy supplied to nanosilver as a function of percentage coating weight lost. Fig.5 presents the dependency of silver nanoparticles layers vs. temperature (150 °C and 230 °C) and time of sintering.
Fig. 5. The removing of protective coating at 150°C and 230°C as a function of time.

All tests we did, gave very important information, that nAg3 (with polymer type coating) has the most uniform and stable formulation properties, and quite low percentage of protection layer.

After all tests, we choose nanosilver nAg 3 type for next work with formulation of TIM materials.

TIM Materials With Nanosilver

For checking the usability of nanosilver particles as a filler to new TIM materials, we have prepared several different samples for tests and three of them was chosen for further analysis:

1. Sample as paste with very high loading silver nanoparticles – contains 95% b.w of silver filler and 5% b.w of epoxy resin
2. High loading formula with mix silver nano and micro silver flake (in the ratio 50/50) – contains 95% b.w of total silver fillers and 5% b.w of epoxy resin
3. High loading formula with mix silver nano and micro silver flake (in the ratio 60/40) – contains 95% b.w of silver fillers and 5% b.w of epoxy resin

First of all we did a measurement of the physical parameters (viscosity, specific gravity and resistivity) prepared samples. The viscosity test was made by BROOKFIELD viscometer in 250 C, with spindle speed of 10 rpm. The resistivity test was made by four probe methods [4]. Test results of studies have been presented in Table 1.

Table 1. The physical parameters of the prepared composites: viscosity, specific gravity, resistivity

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity [mPas]</td>
<td>23,5</td>
<td>123</td>
<td>120</td>
</tr>
<tr>
<td>Specific gravity [g/cm³]</td>
<td>2,2</td>
<td>2,2</td>
<td>2,2</td>
</tr>
<tr>
<td>Resistivity [Ωcm]</td>
<td>ab. 7x10⁻⁶</td>
<td>3,5x10⁻⁵</td>
<td>4x10⁻⁵</td>
</tr>
</tbody>
</table>

Thermal Characterization

The thermal characterization was done with a thermal test stand, which uses an altered steady state method which is based upon the standard ASTM D5470[5].

The method uses two reference bodies with known thermal conductivity and dimensions to determine the heat current by means of the temperature gradient $\Delta T$, along the thermal path from a heater (thermal test chip) to a thermal sink (water cooler) under a specific pressure, as shown in Fig. 6.

Thus it is possible to measure the effective thermal resistance $R_{th}$ of the device under test (DUT), which is located between the reference bodies, by the known relation:

$$R_{th \text{eff}} = \frac{\Delta T}{Q}$$

Furthermore with this it is possible to determine the related effective thermal conductivity $\lambda$ by taking account of the dimensions of the specimen:

$$\lambda_{\text{eff}} = \frac{d_{\text{eff}}}{R_{th \text{eff}} \cdot A}$$

where $d$ is the effective thickness and $A$ the surface of the device under test.

In all measurements is a liquid metal as thermal interface material (TIM) used to reduce the interface resistance between the DUT and there reference material and to maintain the measurement condition constant and comparable.

The thermal conductivity of the DUT itself can be determined by the following equation:

$$\lambda_{\text{DUT}} = \frac{d_{\text{DUT}}}{A \left(R_{th \text{eff}} - R_{\text{th.interface}}\right)}$$

when the thermal interface resistance (two times liquid metal) was determined previously.

Result and Conclusions

To examine the influence of the particle size in different silver sinter mixtures a sandwich sample structure of bare silicon and the desired silver sinter mixture was used (see Fig. 7).
For these it is necessary to first determine the exact thermal resistance and conductivity of the used reference material (bare silicon), which proved to be approximated 147 Wm$^{-1}$K$^{-1}$. Altogether three mixtures have been examined. Every mixture was sintered for an hour at the same condition at a temperature of 200°C and a pressure of 10 MPa. For all measurements the same conditions have been applied:

- Pressure: 500 kPa
- Heater temperature: 100°C
- Heat sink temperature: 15°C
- Reference body material: Copper

The results of the measurements are depicted in the following table (Table 2).

Table 2. Result of thermal conductivity TIM samples with nano silver particles.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity [W/mK]</td>
<td>175 ±23%</td>
<td>63 ±21%</td>
<td>120 ±22%</td>
</tr>
</tbody>
</table>

The big difference with results of thermal conductivity connected with samples 1 and 2 was related with packaging of silver fillers inside TIM formulations (Fig.8).

As it can be seen on diagram (Fig.9), the highest thermal conductivity is achieved by sample “1” (95% nAg) with about 175 Wm$^{-1}$K$^{-1}$. The conductivity of samples “2 and 3” is lower, which reason is connected with structure problems like empty spaces inside material between flake and nano size silvers or other defects in the samples. To provide a clear statement on this the structure has to be examined in future also.

Acknowledgments

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References: