PROPERTIES OF MODIFIED ELECTRICALLY CONDUCTIVE ADHESIVES

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Abstract

Electrically conductive adhesives - ECAs is one of the options, how to make lead-free environmental interconnections in electrical engineering. This work deals with electrical properties of electrically conductive adhesives. The work first describes the characteristics and composition of isotropic conductive adhesives - ICA and then the possibility of modifications that improve its mechanical and electrical parameters. The aim of this work is the measurement of electrical resistance and nonlinearity of connections created with isotropic conductive adhesives and compare changes in these variables after adjusting adhesives by adding silver nitrate and its subsequent annealing.

Keywords: electrically conductive adhesives, isotropic conductive adhesives, mechanical and electrical parameters, nonlinearity

INTRODUCTION

Electrically conductive adhesives function on the principle of adding conductive particles to a non-conducting adhesive matrix. With these adhesives, we can even achieve anisotropic conductivity, which is an enormous advantage compared to solder. These anisotropic conductive adhesives - ACAs are primarily used during the assembly of LCD display integrated circuits. Another type of conductive adhesive is isotropically conductive adhesive - ICA. This adhesive conducts current through all directions, similar to solder. ICAs contain a large amount of conductive particles with a series-parallel connection. The conductivity of these adhesives is worse due to insulation layers between particles. Therefore, they are mainly used for surface assemblies (SMT) and conductive component assemblies (THT). [1]

Isotropic conductive adhesives (ICAs) are, apart from unleaded soldering, another alternative to conductive joining in the electronics field. [2] They consist of two fundamental components - binding components - binders and conductive components - fillers. The binding component is epoxide resin, the hardener of which is usually cycloaliphatic amine. After hardening, conventional care is applied (infrared, ultraviolet, convection) and the hardening period usually ranges between several minutes to 2 hours. The fillers are 5 – 15 µm electrically conductive particles, which are equally dispersed in the adhesive. The isotropic conductive adhesive conducts identically in all directions if the particles are mutually in contact and their concentration exceeds the percolation threshold. The most frequently used material for these particles is silver, which also has excellent thermal conductivity. Conductive filler can achieve a low resistivity of about $10^{-4} \, \Omega\cdot cm$, compared to typical adhesives with a resistivity of $10^{14} \, \Omega\cdot cm$ and solder $10^{6} \, \Omega\cdot cm$.

Since isotropic conductive adhesives fall behind solder in mechanical properties and conductivity, we try to minimize these differences by way of modification:

- improving mechanical properties

A simple method of overcoming the disadvantage in mechanical solidity is adding a small amount (1-3%) of microcarbon fibers, thanks to which we can break down mechanical forces within the circuit more effectively.[3] So far, we have proved the mechanical force was improved by 40%.
• improving properties using nanoparticles

The majority of common isotropic conductive adhesives use silver flakes as filler and is hardened at temperatures ranging between 120-150°C. [4] Conventional filler must be added in a sufficient quantity (around 60 - 80%), to achieve direct physical contact between filler particles. The properties of nanoparticles are completely different. As we can see, using carbon nanotubes or indium-stannum oxide (ITO - 90% In$_2$O$_3$ + 10%SnO$_2$), the percolation threshold was reduced to the lowest value 2%! By using smaller amount of filler, this permits the formation of solid and transparent conductive materials.

• improving electrical conductivity via annealing

Based on experiment, we saw that additional annealing significantly reduces adhesive resistivity. [5] Typical electrically conductive adhesives with silver flakes supplemented with nanoparticles were used during the experiment. Samples were hardened at 150°C for a period of 60 minutes and were then annealed for 10, 30, 60 minutes at 180°C and 60 minutes at 200°C.(Fig. 1.) The resistivity dropped intensively after annealing 10min/180°C. This implies only a short period is needed for sintering. The conductivity did not improve after annealing for 60 minutes at 200°C.

![Fig. 1 Resistivity for various annealing processes](image)

EXPERIMENTAL PART

2.1 Preparing symplex

Determining the change in electrical properties during the modification of two types of adhesives produced by Amepox Microelectronics: ECO SOLDER AX 20 and ECO SOLDER AX 70MN. Both adhesives are typical adhesives with an epoxide matrix and silver flakes. They differ in the conductive filler concentration, viscosity and resistivity. The manufacturer provides the following values [6]:

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Values of silver, viscosity and resistivity provided by the manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AX 20</td>
</tr>
<tr>
<td>Content of silver ( %)</td>
<td>75 ± 1 %</td>
</tr>
<tr>
<td>Viscosity</td>
<td>650 – 750 000 cps</td>
</tr>
<tr>
<td>Resistivity</td>
<td>3,0 – 3,5.10$^{-6}$ Ωm</td>
</tr>
</tbody>
</table>

AgNO$_3$ or butylglycidylether solvent was added to these adhesives. The following combinations were achieved: AX 20(70)-0 clean AX 20 (AX 70MN)

AX 20(70)-1 AX 20 (AX 70MN) + AgNO$_3$

AX 20(70)-2 AX 20 (AX 70MN)+ solvent

AX 20(70)-3 AX 20 (AX 70MN)+ solvent + AgNO$_3$

Quantity of individual components added:

AgNO$_3$ : 0.2% weight of adhesive
Butylglycidylether: about 0.015 ml/g adhesive

AX 20-2 and AX 20-3 samples were used after 44 hours of mixing, which could have had an impact on the results from measuring.

Each sample was used on average for two printed circuits, each for seven SMD (surface mount device) resistors. The samples were then hardened at 150°C for 30 minutes in a convection kiln with a flat heat profile, there electrical resistance was measured via the four-point method on an LCR meter and non-linearity was checked. The samples were then annealed at 200°C for 20 minutes and measured once again. With the annealing process we wanted to achieve the sintering of silver particles and verify the impact on the electrical quality of the circuit.

### 2.2 Measuring resistance via the four-point method

The measurement was performed on an Agilent LCR meter via the four-point method, which is suitable for measuring smaller resistances. (Fig. 2.)

SMD resistors with a theoretical zero resistance (about 15 mΩ) were used during the mounting, supply contacts had a resistance to the circuit of about 3 mΩ, however, their impact was eliminated by using the four-point method.

![Diagram - measuring resistance via the four-point method](image)

**Fig. 2** Diagram - measuring resistance via the four-point method

### 2.3 Measuring non-linearity

Non-linearity in the circuit is an undesirable effect, for it deviates the slope of the volt-amp curve of the circuit, which may then have a partially rectifying behavior. [7] Non-linearity is therefore a significant circuit quality index and depends on the amount of defects in the circuit.

Non-linearity on the measured sample is demonstrated during the harmonic analysis. Two harmonic signals with different frequencies ($f_1$ and $f_2$) are conducted onto the sample and we then see intermodulating signals via the spectral analyzer. (Fig. 3.)

![Diagram for measuring non-linearity](image)

**Fig. 3** Diagram for measuring non-linearity

### MEASURING RESULTS

Two circuits, each with seven resistors, were mounted for each adhesive sample. Non-linear voltage values do not provide much information. In our case, we only compare its deterioration or improvement after the adhesive modification.

The resulting averages of measured values for both adhesives are shown in **Tables 2, 3, 4 and 5.**
The graphs depict the dependencies how individual quantities change after specific chemical modifications and after annealing.

**Fig. 4** Dependance of ECO SOLDER AX 20 adhesive resistivity by way of modification

**Fig. 5** Dependance of ECO SOLDER AX 20 adhesive non-linearity by way of modification

**Table 2** Measured resistances in mΩ for the modified adhesive AX 20

<table>
<thead>
<tr>
<th>Composition</th>
<th>AX 20-0</th>
<th>AX 20-1</th>
<th>AX 20-2</th>
<th>AX 20-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (mΩ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>post hardening</td>
<td>111</td>
<td>108</td>
<td>83</td>
<td>555</td>
</tr>
<tr>
<td>post annealing</td>
<td>91</td>
<td>92</td>
<td>74</td>
<td>430</td>
</tr>
</tbody>
</table>

**Table 3** Measured non-linearity in µV for the modified adhesive AX 20

<table>
<thead>
<tr>
<th>Composition</th>
<th>AX 20-0</th>
<th>AX 20-1</th>
<th>AX 20-2</th>
<th>AX 20-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (µV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>post hardening</td>
<td>17.5</td>
<td>9.6</td>
<td>3</td>
<td>10380</td>
</tr>
<tr>
<td>post annealing</td>
<td>9</td>
<td>6.8</td>
<td>1.6</td>
<td>4570</td>
</tr>
</tbody>
</table>

**Fig. 6** Dependance of ECO SOLDER AX 70MN adhesive resistivity by way of modification

**Fig. 7** Dependance of ECO SOLDER AX 70MN adhesive non-linearity by way of modification
Table 4 Measured resistances in mΩ for the modified adhesive AX 70MN

<table>
<thead>
<tr>
<th>Composition</th>
<th>AX 70-0</th>
<th>AX 70-1</th>
<th>AX 70-2</th>
<th>AX 70-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (mΩ)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>post hardening</td>
<td>71</td>
<td>64</td>
<td>73</td>
<td>77</td>
</tr>
<tr>
<td>post annealing</td>
<td>80</td>
<td>61</td>
<td>73</td>
<td>76</td>
</tr>
</tbody>
</table>

Table 5 Measured non-linearity in µV for the modified adhesive AX 70MN

<table>
<thead>
<tr>
<th>Composition</th>
<th>AX 70-0</th>
<th>AX 70-1</th>
<th>AX 70-2</th>
<th>AX 70-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (µV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>post hardening</td>
<td>5</td>
<td>3.2</td>
<td>2</td>
<td>3.6</td>
</tr>
<tr>
<td>post annealing</td>
<td>8.9</td>
<td>7.2</td>
<td>2.2</td>
<td>5.8</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Adding AgNO$_3$ improved the conductivity of the circuit as well as its quality for both adhesives. However, the resistance dropped by only several mΩ (see Table 2 and 4).

Adhesive AX 20 was, upon adding solvent, or solvent and AgNO$_3$, was left in the cooling equipment and used only after 44 hours. AX 70MN was used immediately after mixing. This time delay between mixing and utilization had a significant impact on the circuit properties. Table 2 and 4 show that for AX 20, the solvent slightly reduced the electrical resistance of the circuit, however, in circuit with nitrate, it caused the degradation of adhesive, making it unusable for practice with these properties. As expected, upon adding solvent to adhesive AX 70 MN, its conductivity became slightly worse and the addition of nitrate it even worse. On the contrary, non-linearity improved. We believe the solvent has a positive effect on the overall circuit homogeneity.

The properties of both adhesives were very different for annealing, as can be seen on the graphs. We anticipated annealing would lead to the sintering of silver particles, and therefore the improvement of their mutual contact, to the removal of some non-homogeneity and therefore reduce resistance and non-linearity. Both measured quantities did in fact significantly improve for adhesive AX 20, see Fig. 4. and 5. The result was completely different for adhesive AX 70MN. The resistance of the circuit did not change excessively, however non-linearity became noticeably worse, see Fig. 6. and 7.

ACKNOWLEDGEMENTS

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LITERATURE

[1.] www.thomsit.cz
[6.] www.amepox-mc.com