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Conductivity improvement of electrically conductive adhesives by thermal post-curing processes

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Abstract: Polymer electronics plays more and more important role nowadays, especially in flexible electronics. The progress is also reflected in packaging materials and technologies. In many applications metallic solders are replaced by electrically conductive adhesives based on polymer's matrix. Very high volume production also requires new methods of adhesive deposition. The novel techniques of adhesive applying in microelectronic packaging need adhesives with very low viscosity. The electrical conductivity of standard electrically conductive adhesives are obtained by dispersing high volume of filler (e.g. silver flakes) in the polymer matrix. Unfortunately, the high concentration of filler in adhesive causes increasing of its viscosity. Therefore the adhesives with low filler content may be used instead, but it is worth to indicate that the low filler concentration causes the low electrical conductivity. To overcome this problem the thermal post-curing processes which improve the electrical conductivity of low content adhesives may be used. In the paper such processes are presented. It was proved that because of this processes the electrical conductivity had been decreased over four times order of magnitude in comparison to the initial value (after curing).

Key words: electronic packaging, electrically conductive adhesive, conductivity, thermal processes

1. INTRODUCTION

The electronic components need to be electrically connected for power, ground and signal transmissions. The lead-containing solder alloys was in fact the only interconnect material in most areas of electronic packaging technologies in the past decades. The new legislations of European Union limiting the use of lead-containing electronics forces manufacturers to find new solutions. The efforts have been focused on two alternatives: lead-free solders and polymer-based electrically conductive adhesives.

Compared to the solder technology, electrically conductive adhesives offer numerous advantages, such as environmental friendliness (elimination of lead usage and flux cleaning), mild processing conditions, fewer processing steps (reducing processing cost), and especially, the fine pitch capability due to the availability of small-sized conductive fillers. Because of this, in electronic industry the isotropic conductive adhesives are becoming more useful comparing to solder in surface mount technology assembly, ball grid array package, chip scale package, and flip–chip technology [1]

The miniaturization, the real progress of microelectronic circuits, needs both packaging technologies with lower scaling parameters and new materials. The ink-jet technology meets short of miniaturization expectations. The technology appears as a very interesting because of its non-contact process (for three-dimensional printing), and because of the potential high resolution and high printing speed [2]. There are investigations [3, 4] which aim is to use electrically conductive adhesives for this technology. Unfortunately, until now there are no reports about commercial application of ink-jet processes with conductive adhesives.

Electrically conductive adhesives consist of the polymer base material and conductive filler (silver is the most commonly used conductive filler). The fillers provide the electrical properties and the polymer matrix provides the physical and mechanical properties of an adhesive. Electrical conductivity depends on metal loading concentration in polymer matrix. Figure 1 shows the form of the transition from high to low resistance as metal loading is progressively increased. Commercially obtainable isotropic conductive adhesive contain 70-80wt% silver flakes which is sufficiently grater than the percolation threshold to

guarantee low resistance with allowance for manufacturing tolerances. [5]. Such formulations cannot be applied by ink jets due to their high viscosity and relatively large silver particles.

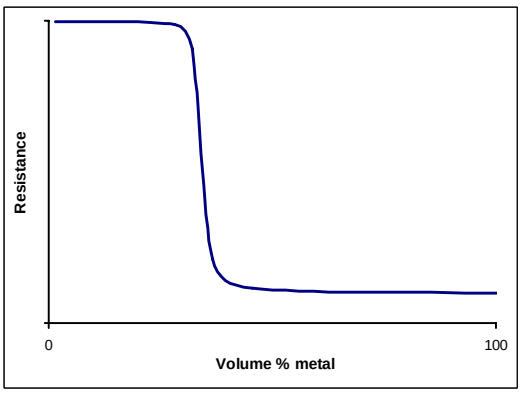

Fig. 1. Generalized percolation curve showing the abrupt drop in resistance at the percolation threshold

The ink-jet printing technology needs adhesives with very low viscosity which is only possible for filler contraction far below the percolation threshold. The idea of the work is to investigate the post-curing processes which change the electrically nonconductive structures (after printing and curing) for conductive one.

2. PRELIMINARY TEST

The preliminary tests with adhesive formulation of epoxy resin and Ag powder filler (without solvents) shows changes of the adhesive surface structure during the post-curing thermal process. The figure 2 presents the SEM images of the same formulation before and after 2h and 10h in 180°C sintering. All pictures were done with the same magnification. As it can be seen the size of particles observed on surface is increasing. It indicates the possibility of conductivity improvement of low-viscosity electrically conductive adhesives by post-curing process.

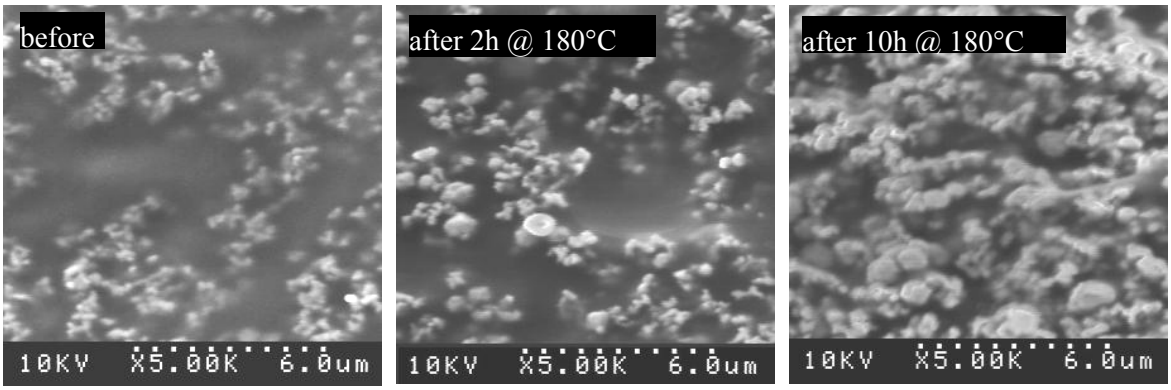

Fig. 2. SEM images of surface of epoxy resin with Ag powder filler formulation before and after 2h and 10h in 180°C post-curing process.

3. MATERIALS

To study the influence of the post-curing technology on the conductivity improvement of the electrically conductive adhesives the low-viscosity formulation with silver powder and flakes filler was used. This is specially prepared silver powder with extremely high value of tap density (5.8 – 6.5 g/cm3). Particles look like the mixture of very fine powder and semi flake (Figure 3) with the average particle size of 3-6 μm.

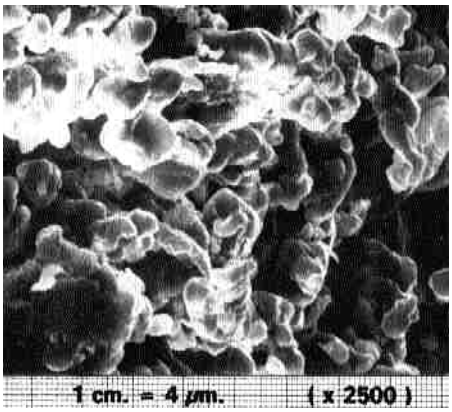

Fig. 3. SEM image of used silver powder and flakes as filler

As the base material the same epoxy resin as in preliminary tests was used. It was two component resin with the viscosity of 1000 m·Pa·s (+/- 100) at 25 °C, and specific gravity of 1.13 g/cm^3, epoxy equivalent – 202.

The volume content of filler in adhesive was 26 vol % (65.4 wt %). The volume content was achieved by weight proportion of components, taking into account the tap density of the filler and specific gravity of the resin. This formulation was applied in five samples. The filler and formulation has been prepared by AMEPOX Microelectronics.

4. SAMPLES AND TEST METHOD

Samples were prepared in the form of two copper rods with 4 mm diameter and 1 mm gap between them. The contact surfaces of rods were covered with gold layer to prevent copper against the oxidation. Testing samples had to enable contacts to free move due to the adhesive shrinkage (Figure 4).

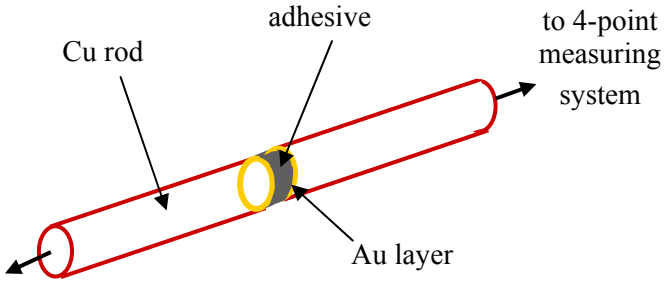

Fig. 4. Four-point probe configurations.

In order to estimate the resistance of adhesive, both rods were put into the PTFE (Teflon®) made template and joined by adhesive layer. Adhesive layers had a controlled thickness of 1 mm as well as surface area (4·π mm^2). The whole system (template with copper rods and adhesive) was placed into oven. Curing conditions of the adhesive were as follows: from 25 °C to 120 °C with 1 °C/min temperature gradient, and then additionally 15 min in 120 °C.

The DC resistances of the adhesive joints were measured with the use of a four-point (Kelvin) probe method. Current probes were located on the ends of rods, while the voltage probe separation was 10 mm for every test.

5. RESULTS

The resistance of the joints was measured after curing and then after post-curing processes. The two post-curing processes were done:

1. 0.5 h @ 180 °C – for two samples

2. 2 h @ 180 °C – for three samples

Results of measurements are gathered in Table 1

Tab. 1. Results of measurements

Sample number	Resistance [Ohm] after curing (25 °C – 120 °C @ 1 °C/min; 15 min @ 120°C)	Resistance [Ohm] after post-curing process (30 min @ 180°C)	Resistance [Ohm] after post-curing process (120 min @ 180°C)
1	1665.8	55.31	
2	1628,1	65.41	
3	5547.0		0.854
4	1198.6		0.210
5	2965.0		0.767

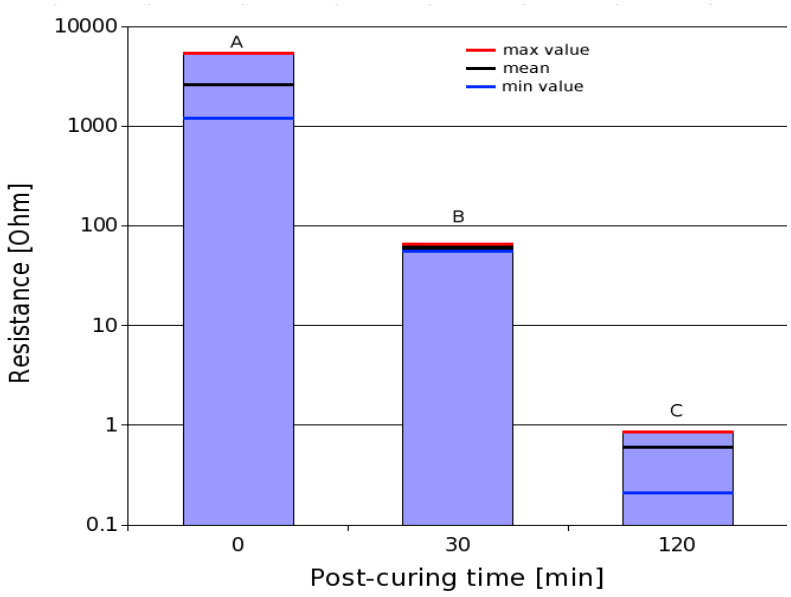

Fig. 5. The adhesive joint resistances vs. post-curing processes time

Figure 5 shows decreasing of the tested adhesive joint resistances after post-curing processes. The results was divided into three parts: A – before post-curing process (every samples) and B – after 30 minutes at 180°C post-curing process (samples 1, 2) and C – after 120 minutes at 180°C post-curing process (samples 3, 4, 5). On this figure the minimal and maximal measured resistances and mean values as well were indicated.

The results clearly exhibit how big influence on adhesive joints conductance has post-curing process. After two hours in 180 °C the joint resistance decreases about 5000 times and finally reaches value below 1 ohm.

The observed decreasing of resistance during the post-curing process is probably caused by more intimate contact between Ag particles due to the following phenomena:

1) cure shrinkage of epoxy resin

2) increasing the size of particles (Figure 2)

The cure shrinkage of the epoxy resin can be dominant phenomenon in shorter (30 min) post-curing process, but after that time the shrinkage is rather impossible, therefore in longer (120 min) post-curing process the increasing of the particles size is more probable. The increasing of the particles can be caused by the silver recrystallization. In general, the recrystallization begin when the temperature exceed so-called recrystallization threshold T_r. The following equation (1) expresses an experimentally estimated value of T_r [6, 7]

$$T_r \approx 0.4 \cdot T_m \quad [K] \qquad (1)$$

where: T_m is melting point temperature [K].

The value of T_r strongly depends on purity of material and for extremely pure metals recrystallization can be observed even at 0.2 of melting point temperature.

The applied post-curing temperature in presented paper was: 180 °C (453.15 K). It is about 37% of silver melting point temperature (1234.93 K) and it is possible that increasing size of particles was due to recrystallization effect, but it is not checked yet and should be verified.

6. CONCLUSIONS

The resistances of joints made of the low-viscosity electrically conductive adhesives were measured. Adhesive were formulated on the base of epoxy resin with Ag filler. The volume content of filler in adhesive was fixed on 26vol% to keep low-viscosity of adhesive. It has been demonstrate that the post-curing process permits to increase the conductive of adhesive joints significantly.

7. ACKNOWLEDGMENTS

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