

The post-curing technology for conductivity improvement of low-viscosity electrically conductive adhesives

Andrzej Moscicki^a, Tadeusz Sobierajski^a, Tomasz Falat^b, Jan Felba^b

^a AMEPOX Microelectronics
ul. Jaracza 6, 90-268 Lodz, Poland

^b Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology
ul. Grabiszynska 97, 53-439 Wroclaw, Poland

Tomasz.Falat@pwr.wroc.pl

Keywords: adhesive joint, conductivity, ink-jet printing, post-curing technology

Abstract

Polymer electronics plays more and more important role nowadays, especially in flexible electronics. The progress is also reflected in packaging materials and technologies. 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 ink-jet printing technology seems to be very promising for bumps making in Flip-Chip type interconnections. Unfortunately, the technology is only in its infancy. It needs adhesives with very low viscosity, while such formulations have too low filler content to be conductive.

In the paper, the post-curing technologies which may improve the adhesives conductivity are presented.

Introduction

In electronic industry the isotropic conductive adhesives are becoming more useful comparing to solder in SMT assembly. Basic advantages of solder replacement with electrically conductive adhesives are as follows: lower joining temperatures, lack of lead and other toxic metals in adhesive formulations, less manufacturing process steps (use of flux and subsequent cleaning after assembly is not necessary).[1]

Electrically conductive adhesives consist of the polymer base material and conductive filler. Silver is the most commonly used conductive filler. Its concentration in isotropic conductive adhesives is usually sufficiently greater than the percolation threshold to guarantee low resistance with allowance for manufacturing tolerances.

With large development of ink-jet printer in the last ten years, a lot of non-printing applications emerge for this technology. As printing techniques are used in the electronic industry (screen printing for example), ink-jet appears as a very interesting technology because of his non-contact process (for three-dimensional printing), and because of the potential high resolution and high printing speed [2].

Unfortunately, the high concentration of filler in conductive adhesives causes increasing of the viscosity. The ink-jet printing technology needs adhesives with very low viscosity, therefore there is wanted technique which can improve the adhesives conductivity with low filler concentration.

The former our tests with adhesive formulation of epoxy resin and *K-1631P* Ag filler shows that the size of particles observed on surface is increasing during the post-curing process (Figure 1). The figure 1 shows the SEM images of the same formulation before and after 2h and 10h in 180°C post-curing process. All pictures was done with the same magnification.

This effect is very interesting and can be useful for conductivity improvement of low-viscosity electrically conductive adhesives by post-curing process and we decided to check it.

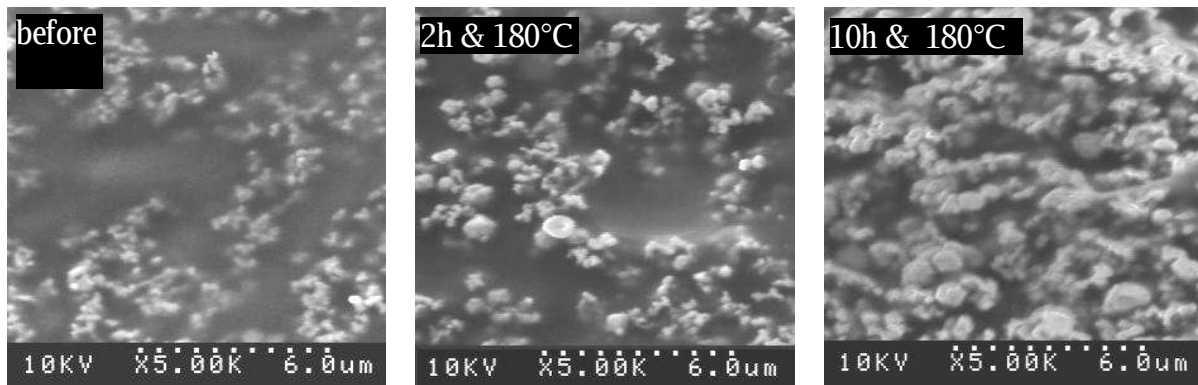


Figure 1. SEM images of surface of epoxy resin with K-1631P Ag filler formulation before and after 2h and 10h in 180°C post-curing process.

Materials

To study the influence of the post-curing technology on the conductivity improvement of the low-viscosity electrically conductive adhesives the formulation with AX10C 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 semiflake (Figure 2) with the average particle size of 3-6 µm.

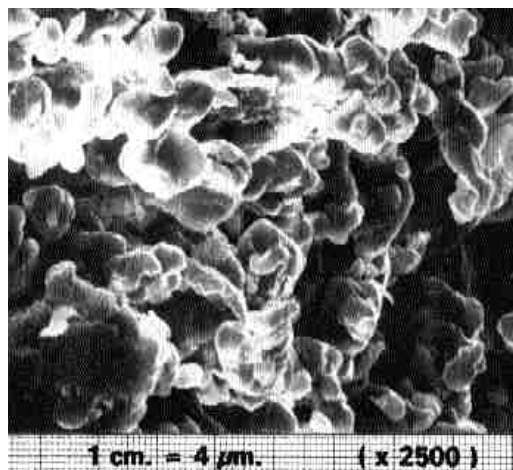


Figure 2. SEM image of AX10C silver powder and flakes

As the base material the same epoxy resin as in former tests was used. It was two component resin with the viscosity of 1000 mPas (+/- 100) at 25°C, and specific gravity of 1.13 g/cm³, 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. These formulation was applied in five samples. The filler and formulation has been prepared by AMEPOX *Microelectronics*.

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 was 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 3).

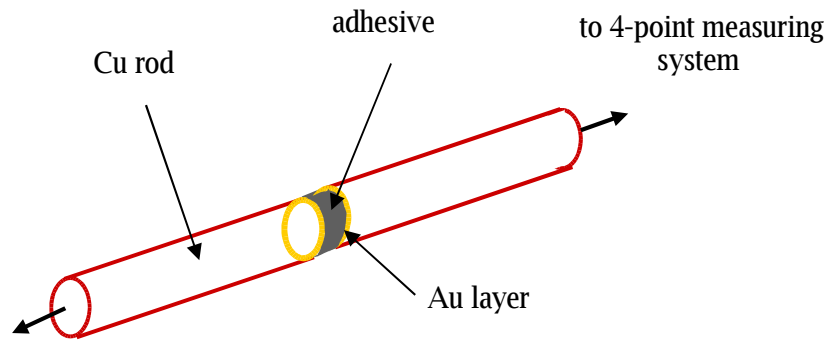


Figure 3. Four-point probe configurations

In order to estimate the resistance of adhesive, both rods were put into the teflon template and joined by adhesive layer. Adhesive layers had a controlled thickness of 1 mm as well as surface area ($4\pi \text{ mm}^2$). 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 $1^\circ\text{C}/\text{min}$ temperature gradient, then 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.

Joint resistance

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

- 1) 0.5h & 180°C – two samples
- 2) 2h & 180°C – three samples

Results of measurements are gathered in **Table 1**

Table 1. Results of measurements

Sample number	Resistance [Ω]		
	after curing ($25^\circ\text{C} - 120^\circ\text{C}$: $1^\circ\text{C}/\text{min}$; 15 min/ 120°C)	after post-curing process (30 min/ 180°C)	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

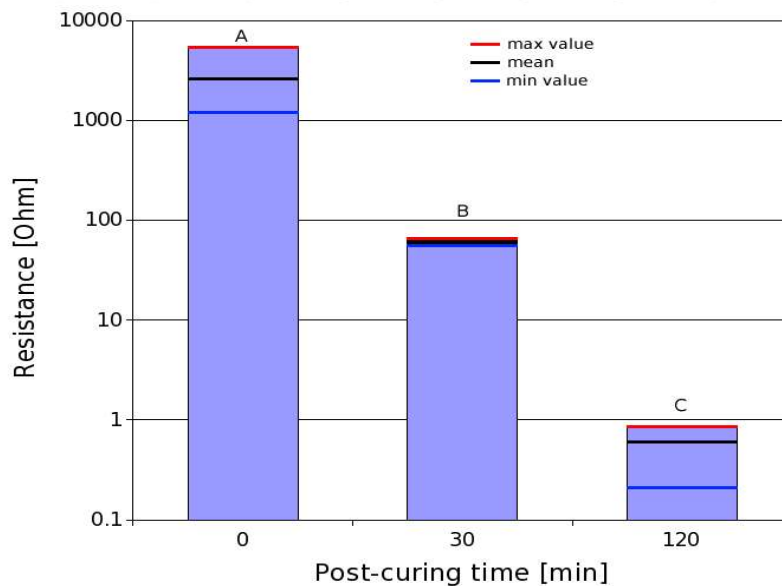


Figure 4. The adhesive joint resistances vs. post-curing processes time

Figure 4 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 in 180°C post-curing process (samples 1, 2) and C – after 120 minutes in 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 phenomenons:

- cure shrinkage of epoxy resin
- increasing the size of particles (Figure 1)

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 imposible, therefore in longer (120 min) post-curing process the increasing of the particles size is more probable.

Conclusions

The resistance 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 26% to keep low-viscosity of adhesive. It has been demonstrate that the post-curing process permits to increase the conductive of adhesive joints significantly.

References

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