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Thermal Ageing of Electrically Conductive Micro/Nano Adhesives

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Abstract—**Electrical as well as mechanical properties of electrically conductive adhesives can be modified by addition of different types of nanoparticles. It has been investigated if changes of the resistance of adhesive joints caused by thermal ageing will differ in dependence on the type of nanoparticles added into adhesives. It has been found that adhesive joints formed of adhesives modified such the way have the same dependence of the resistance on the conditions of thermal ageing. That means, that nanoparticles added into adhesive in concentration up to 2,5 % b. w. does not cause changes of an ageing mechanism of adhesive matrix.**

Keywords-micro/nano adhesives; thermal ageing

I. Introduction

After prohibition of the use of lead in electronics assembly two new types of environmentally friendly materials have been developed: electrically conductive adhesives and lead-free solders. It is possible to meet with soldering as well as adhesive joining in electronics assembly now. Adhesive joints have mostly lower quality than soldered ones. Even though adhesives are more expensive than lead-free solders, there are areas of electronics assembly, where they cannot be substituted. These areas are assembly of temperature sensitive components, assembly of components on temperature sensitive substrates and assembly of integrated circuits having fine pitch or ultra fine pitch packages [1].

Adhesive assembly of fine pitch or ultra fine pitch packages is carried out using adhesives with anisotropic electrical conductivity [2]. These adhesives make current conduction in direction of axis “z” only possible. Therefore they are also named “z” adhesives. Assembly of fine pitch or ultra fine pitch packages is carried out using an adhesive foil, which is located under integrated circuit. Advantage of this type of montage, in comparison with the soldering, is very low probability that conductive bridges will be created between neihgbouring leads. Soldering of packages of these types is difficult just with the respect to high probability of bridging [3].

Electrical properties of adhesive joints, such as the resistance, noise and nonlinearity of a current vs. voltage characteristic, are worst in comparison with soldered joints and limit their use in some applications. Therefore great effort is paid to improve conductivity of adhesives and to decrease nonlinearity and noise of adhesive joints. The use of very high concentration of electrically conductive particles in adhesive (for exampled 95 % b.w.) is not possible, because, starting from some concentration, the higher is concentration, the worst are mechanical properties of adhesive. This critical concentration depends on the type of adhesive and on the type of filler particles. Following ways of improvement of electrical parameters of electrically conductive adhesives are used the most often:

- Addition of conductive nanoparticles into electrically conductive adhesive of a standard type, that means into adhesive filled with conductive microparticles. The concentration of nanoparticles must be low to avoid decline of mechanical properties of adhesive joints. Nanoparticles create conductive bridges between microparticles. It is assumed that density of a conductive net in adhesive increases and electrical resistivity decreases.

  It is necessary to note that it has been observed decrease of electrical conductivity of adhesive after addition of conductive nanoparticles into adhesive very often. The reason is that the number of contacts between particles increases after addition of nanoparticles. Because contact resistances are a significant part of the total joint resistance, increase of number of contacts in the conductive net can outbalance resistance decrease caused by bridges created of nanoparticles and conductivity of adhesive decreases. Nanoparticles have different shapes. It is possible to meet balls, grains, flakes, wires or tubes. Materials of nanoparticles are silver, gold, nickel or copper, nanotubes are mostly of carbon [4], [5], [6].

- Addition of proper chemicals (e.g. silver nitrate) into adhesive with the goal to create, during adhesive curing, conductive nanoparticles as a product of temperature dissociation of these chemicals. Function of these nanoparticles is the same like function of nanoparticles added into adhesive directly.

- High-pitched stirring of adhesive before application. It has been found that proper stirring can significantly decrease resistivity of adhesive. The reason is elimination of surface film of ions covering conductive particles. After elimination of this film quality of contacts between adhesive increases and the contact resistance decreases.

It has also been found that addition of some types of nanoparticles into electrically conductive adhesive can improve adhesive adhesion to some types of surfaces.

Nanoparticles of alumina or silicon dioxide are used for improvement of heat conductivity of adhesives. These particles are added in low concentrations to cause low decrease of electrical conductivity of adhesive only.

Concentration of nanoparticles added into electrically conductive adhesives is limited. Addition increases viscosity of adhesive and makes conditions for its successful application, e.g. for stencil printing, worse. Therefore concentrations of nanoparticles added into electrically conductive adhesives filled with conductive microparticles are between 0,5 % to 2,5 % b.w.

The goal of the work has been to find if addition of different types of conductive nanoparticles into electrically conductive adhesives with isotropic electrical conductivity influences value of electrical conductivity during thermal ageing of adhesives.

II. Experimental Procedures and Results

A. Electrically Conductive Adhesives

Two types of ICAs based on epoxy matrix filled with silver flakes have been used for experiments. Parameters of adhesives have been as follows:

- Formulation A: One-epoxy base resin, silver concentration 75 % b.w., curing schedule 150 °C/10 min, electrical resistivity 3.10^{-4} Ωcm, application technology: screen printing, stencile printing, dispensing.

- Formulation B: One-epoxy phenolic hybride base resin, silver concentration 70 % b.w., curing schedule 180 °C/10 min, 200 °C/4 min, electrical resistivity 2.10^{-4} Ωcm. application technology: screen printing, stencile printing, dispensing.

B. Nanoparticles Added into Adhesives

Following types of nanoparticles have been added into electrically conductive adhesives:

- Multi-walled carbon nanotubes with the diameter of 20 nm. Concentration has been 0,3 % b.w.

- Silver balls (grains) with the diameter of 40 nm. Concentration has been 2,5 % b.w.

- Colloid silver. Concentration has been 2,5 % b.w.

C. Forming of Adhesive Joints

Adhesive joints have been created by assembly of resistors with the “zero” resistance – jumpers on test boards. The boards have been manufactured of FR4 covered with 35 µm copper foil. No special surface finish of pads has been used. The pads have been cleaned using abrasive set M3.

Adhesives have been applied by dispensing, semi-automatic pick and place machine SMT M01A has been used for assembly of jumpers. Jumpers have been of the type 1206 with Pd surface finish.

Seven jumpers have been mounted on one test PCB. Layout has made three-terminal and four-terminal measurement possible.

D. Temperature Ageing of Samples

Temperature ageing of samples has been carried out in a climatic chamber WTB Binder. The ageing temperature has been 125 °C, the ageing time has been 1342 hours. Ageing has been carried out at ambient atmosphere.

E. Measurement of Resistance of Adhesive Joints

The resistance of adhesive joints has been in the range of 70 to 120 mΩ. The measurements have been carried out using a four-terminal probe.

A Precision LCR meter HP 4284A has been used for the resistance measurement. The measuring frequency has been 1 kHz.

Every presented value has been found as a result of mathematical processing of 35 measured values.

F. Mathematical Processing of Experimental Results

Results have been statistically processed using SW QC Expert [7]. First outliers have been found using a Grubb’s test and deleted from the data files, and then mean and median have been calculated. These variables have been investigated with the goal to show how presentation of different types of statistical variables can distort perception about the course of a parameter under examination. It has been also studied how courses of variables can differ if measured data are not mathematically processed by a proper way and outliers are not deleted before calculation of basic statistics – mean and median [8].

It is necessary to be aware that results of measurements are random samples. Distribution of measured values is significant for possible mathematical processing of results. For example, mean calculated as an arithmetical average can be found this way for normally distributed data only.

Rightness of measured values has to be verified with the repetition of measurements. The higher is number of repetition, the higher is probability of a right measured result.

G. Experimental results

Experimental results expressed for different types of mathematical variables are presented in Fig. 1 to Fig. 5.

Influence of different types of nanoparticles added into adhesives on the course of the joint resistance in dependence on the time of temperature ageing is presented in Fig. 1 and 2 for formulation A and in Fig. 3 and Fig 4 for formulation B. Figures 5 and 6 compare graphs found for mean and median of the joint resistance for cases when outliers are not deleted, resp. are deleted. It is shown that deleting of outliers can change results of the measurement significantly. Therefore this step should be involved in every processing of measured values.

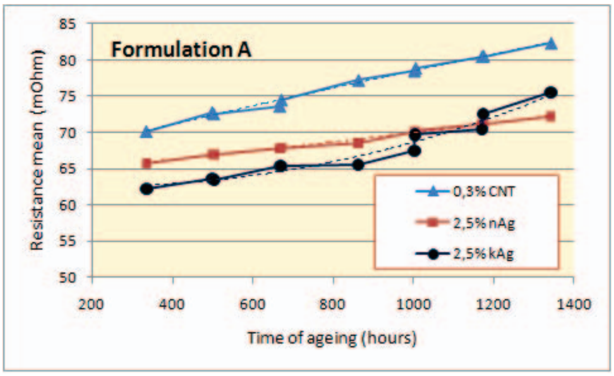

Figure 1. Resistance of adhesive joints formed of formulation A added with CNT, silver nanoparticles (nAg) and colloidal silver (kAg). Means of measured values are presented after deleting of outliers. Trends are plotted by a dashed line

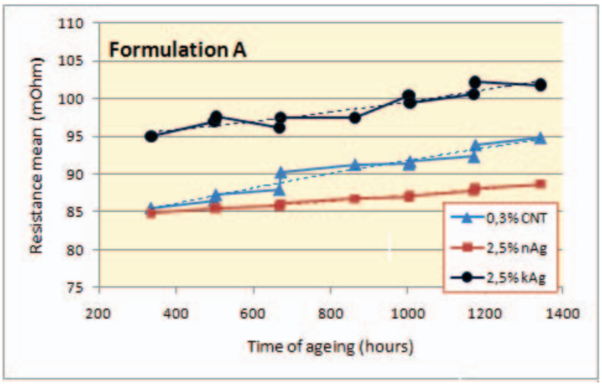

Figure 2. Resistance of adhesive joints formed of formulation A added with CNT, silver nanoparticles (nAg) and colloidal silver (kAg). Medians of measured values are presented after deleting of outliers. Trends are plotted by a dashed line

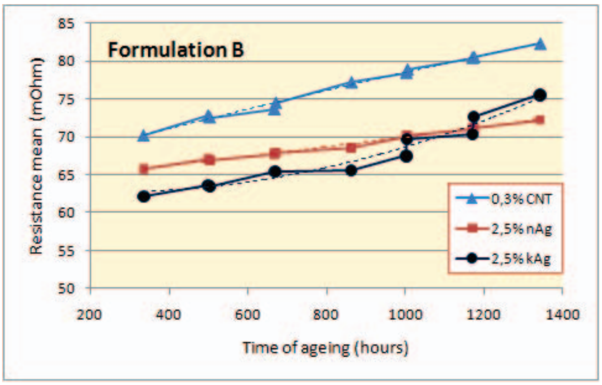

Figure 3. Resistance of adhesive joints formed of formulation B added with CNT, silver nanoparticles (nAg) and colloidal silver (kAg). Means of measured values are presented after deleting of outliers. Trends are plotted by a dashed line

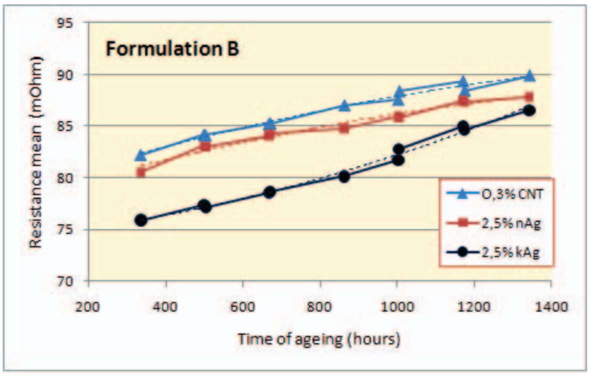

Figure 4. Resistance of adhesive joints formed of formulation B added with CNT, silver nanoparticles (nAg) and colloidal silver (kAg). Medians of measured values are presented after deleting of outliers. Trends are plotted by a dashed line

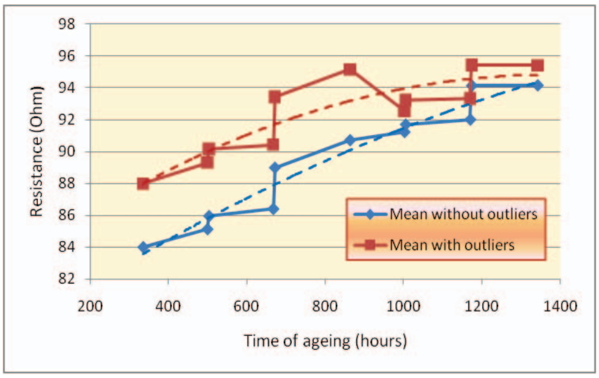

Figure 5. Mean after and before deleting of outliers. Trends are plotted by a dashed line.

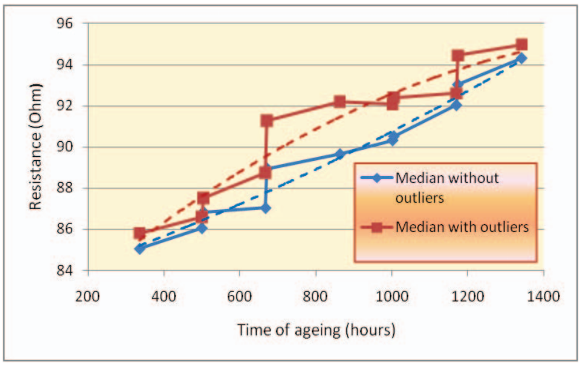

Figure 6. Median after and before deleting of outliers. Trends are plotted by a dashed line.

Standard deviation of measured values has been also examined. It has been found that the standard deviation is acceptable. The variation coefficient defined by the equation $V = s/m$, has been lower than 10 % (s… standard deviation, m… mean).

III. Discussion of Results

It has been found that addition of conductive nanoparticles into electrically conductive adhesive has weak influence only on the course of the adhesive joint resistance in thermal ageing.

Adhesives under test have been filled with silver flakes. The total resistance between two flakes can be described using the equation:

$$R_{TOT} = R_{F1} + R_{F2} + R_{CF1F2} \tag{1}$$

Where R_{TOT} … the total resistance of two connected flakes, R_{F1} … the resistance of the flake no. 1, R_{F2} … the resistance of the flake no. 2, R_{CF1F2} … the contact resistance between flakes.

If conductive nanoparticles are added into electrically conductive adhesive with the goal to improve electrical conductivity of adhesive, it is assumed that the nanoparticles will create conductive bridges between microparticles. If such a bridge between two flakes is formed of two nanoparticles, the electrical resistance of a bridge can be approximately written as:

$$R_{TOTB} = R_{CF1N1} + R_{N1} + R_{CN1N2} + R_{N2} + R_{CF2N2} \tag{2}$$

Where R_{TOTB} … the total resistance of the bridge formed of two nanoparticles, R_{CF1N1} … the resistance of a contact between the flake no. 1 and the nanoparticle no. 1, R_{N1} … the resistance of the nanoparticle no. 1, R_{CN1N2} … the resistance of a contact between nanoparticle no. 1 and no. 2, R_{N2} … the resistance of the nanoparticle no. 2, R_{CF2N2} … the resistance of a contact between the nanoparticle no. 2 and the flake no. 2.

The total resistance R_{FBTOT} of two flakes, which are connected mutually and in parallel by a bridge formed of two nanoparticles can be written as follows:

$$R_{FBTOT} = R_{F1} + R_{F2} + \frac{R_{CF1F2} . R_{TOTB}}{R_{CF1F2} + R_{TOTB}} \tag{3}$$

The change of the resistivity of adhesive after addition of nanoparticles depends on the types of nanoparticles, on their contcentration and material, on homogeneity of their spreading in adhesive and on many other parameters. If nanoballs or nanograins are used, the resistivity of adhesive increases, because these particles do not form bridges between micropartilcles only, but they separate microparticles as well. This way number of contacts increases and resistivity of adhesive increases, too. If nanowires or nanotubes are added into adhesive, resistivity of adhesive decreases usually, because they connect more flakes together.

Results, which have been found, have confirmed assumption that addition of conductive nanoparticles will not influence the course of the adhesive joints resistance changes caused by temperature ageing. The reason is that addition of nanoparticles does not change properties of matrix of electrically conductive adhesive. Due to the fact that resistivity changes depends strongly on properties of resin and these properties are not changed by addition of nanoparticles, there is no reason for some dramatic changes of thermal endurance of modified adhesives in comparison with adhesives without modification.

IV. Conclusions

Two types of electrically conductive adhesives with isotropic electrical conductivity have been tested. Adhesives have been of epoxy type filled with Ag flakes and modified with addition of carbon nanotubes, silver nanoballs and colloid silver in small concentrations. It has been examined if addition of nanoparticles changes course of the adhesive joints resistance during temperature ageing. The ageing temperature has been 125 ^{o}C. No significant changes have been found.

Adhesives have been of an epoxy type. They have been filled with silver flakes; dimensions of flakes have been 15 to 35 μm, concentration 70 to 75 % b.w .

It has been also found that it is necessary to delete outliers at first for correct presentation of measured data. When outliers are not deleted, the course can be markedly different. It is also important to use a proper statistical variable for data presentation. The courses can significantly differ in accordance on the statistical variable, which is presented.

V. Acknowledgement

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