Ročník 2011 electroscope Číslo VI

Study on the Effect of Addition of Spherical Silver Nanoparticles into Electrically Conductive Adhesives

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Abstract:
Electrical resistance and nonlinearity of current vs. voltage characteristic of joints formed of electrically conductive adhesives modified with addition of spherical silver nanoparticles are investigated. The resistance of adhesive joints is measured using a four point method, the nonlinearity of the current vs. voltage charactristic using a modulation technique. Measurement of nonlinearity using powering of joints with the very pure sinusoidal current is discussed, too. The samples are prepared by adhesive assembly of jumpers (resistors with the "zero" resistance) of the type 1206 on a test board of FR4 covered with a copper foil with the thickness of 40 μm. Contact leads of jumpers have surface finish proper for adhesive assembly. No special surface finish of pads is used. Adhesive is applied by dispensing, jumpers are placed using a semi-automatic pick and place machine. The results of the measurement show that addition of spherical silver nanoparticles into standard adhesive does not improve neither electrical conductivity of adhesive, nor nonlinearity of a current vs. voltage characteristic of adhesive joints. The reason is increase of number of contacts in conductive net in adhesive caused by added nanoparticles.

Anotace:
Jsou zkoumány odpor a nelinearitavoltampérové charakteristiky spojů vytvářených elektricky vodivými lepidly modifikovanými doplněním kulových stříbrných nanočástic. Odpor adhezních spojů je měřen čtyřbodovou metodou, nelinearitavoltampérové charakteristiky modulační technikou. Je také diskutováno měření nelinearity s použitím napájení spojů ze zdroje velmi čistého sinusového proudu. Vzorky byly připraveny adhezní montáží odporů s „nulovou“ hodnotou typu 1206 na testovací desku plošného spoje z izolantu FR4 s měděnou fólií o tloušťce 40 μm. Kontakty odporů byly povrchově upraveny pro adhezní montáž. Nebyla použita žádná speciální úprava připojovacích plošek na plošném spoji. Lepidlo byla aplikováno dispenzí, osazení bylo provedeno pomocí poloautomatického osazovacího stroje. Výsledky měření ukázaly, že doplňování kulových nanočástic do elektricky vodivého lepidla nezlepší ani elektrickou vodivost lepidla, ani nelinearitu voltampérové charakteristiky spojů. Důvodem je vzrůst počtu kontaktů ve vodivé síti lepidla způsobený doplněnými nanočásticemi.

INTRODUCTION

Electrically conductive adhesives (ECA) are materials used for conductive joining in electronics besides soldering [1]. ECA are composed of two components: of insulating matrix into which electrically conductive particles of filler are mixed. These particles are mostly metal flakes with dimensions from 10 to 30 microns for adhesives with isotropic electrical conductivity. The most frequently used material of flakes is silver. The concentration of filler in adhesive is between 60 to 80 % b.w. Therefore the price of ECA is comparable with the price of silver on the market. Other metals, such as gold, palladium or nickel are also used.
Epoxy, silicon or polyamide resin is used as an insulating matrix. The most frequently used resin is epoxy. Silicon or polyamide resins are used for applications appointed for harder climatic conditions [2], [3].
With respect to the price of electrically conductive adhesives and with respect to the fact that contemporary electronics is mostly focused at fabrication of low cost products, adhesive assembly is limited for special applications only. It is used for assembly of heat sensitive components, which could be damaged with the soldering temperature and for assembly of comonents with fine pitch or ultra-fine pitch packages, where soldering causes bridging of neighbor component leads.
Electrical and mechanical properties of ECA are worst in comparison with properties of lead free solders.
Especially the resistance of adhesive joints, nonlinearity of these joints and their noise are higher than the same parameters of soldered joints and can limit the use of adhesive assembly for some applications [4]. Therefore different ways are tested for improvement of these properties. The use of different types of nanoparticles as filler [5], [6], [7] or addition of nanoparticles into standard adhesive [8], [9] were tested with different results. Different types of surface finishes of filler particles are under investigation as well [10], [11], [12], [13], [14].

The paper shows results of a study of the resistance and nonlinearity [15] of adhesive joints formed of adhesive filled with micro-particles into which a small amount of spherical nanoparticles is mixed. The method of the measurement of joint resistances as well as the measurement of nonlinearity of adhesive joints is also presented.

EXPERIMENTAL

Samples Preparation

Electrically conductive adhesive used for experiment is of an epoxy type (bis-phenol epoxy). Electrical conductivity of adhesives is isotropic. Epoxy matrix is filled with silver flakes in concentration of 75 % b.w.

Three types of spherical nanoparticles are used for modification of adhesives. Diameter of nanoparticles is 6 – 8 nm, 3 – 55 nm and 80 – 100 nm. Concentration of nanoparticles is 1 %, 3 % and 5 % b.w.

Adhesive joints are formed by assembly of jumpers of the type 1206 on a test board. Adhesive is applied by dispensing. Jumpers with surface finish for adhesive joining are used. Jumpers are resistors, which should have the “zero” resistance. The measured resistance of jumpers is 14 mΩ. The test board is of FR4 plated with copper foil of the thickness 40 μm. The layout makes the four point measurement possible. No special surface finish is used for the pads. The test board with assembled resistors is shown in Fig. 1, the dimensions of the layout in Fig. 2 and the structure of an adhesive joint in Fig. 3.

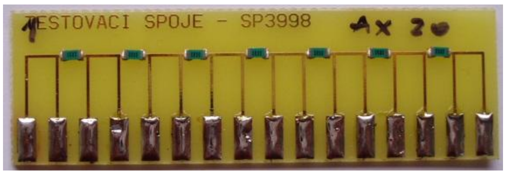

Fig. 1: Test board with assembled jumpers

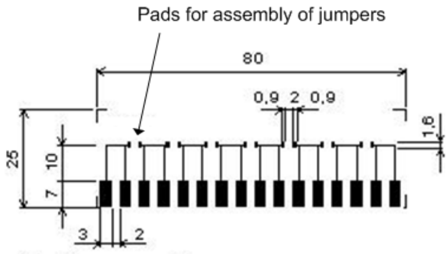

Fig. 2: Layout of the test board

Measurement

The resistance of adhesive joints is measured using the four point probe (see Fig. 4). Five measuring tips are used for the measurement. They are labeled 1 to 5 in Fig. 4. The first measurement is carried out in position Y of the switch S. If it will be assumed that the resistance between a measuring tip and a jumper lead (this resistance is in the range of 0,24 to 0,86 mΩ) is so small that it can be neglected in comparison with the resistance of the adhesive joint (the joint resistance is in the range of 10 to 45 mΩ), the measured voltage is:

$$U_{TIP5} = I(R_{JUMPER} + R_{JOINT}) \qquad (1)$$

The principle of the measurement of nonlinearity of adhesive joints is shown in Fig. 5.

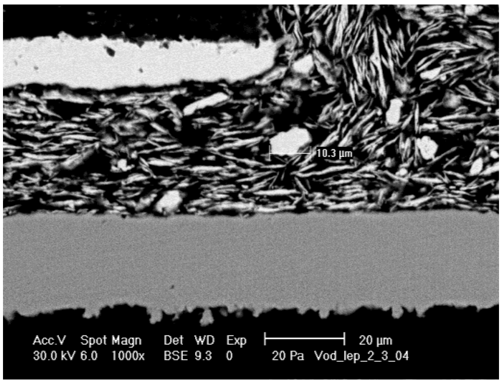

Fig. 3: Adhesive joint. There is a part of a body of a component in the left top corner, basic wide gray line is Cu. Silver flakes of electrically conductive adhesive are in the middle of the figure

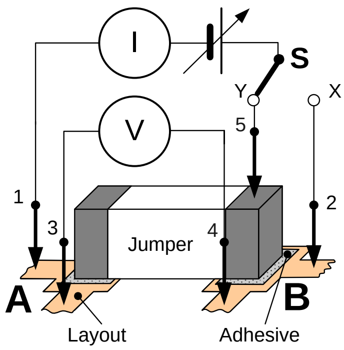

Fig. 4: Resistance measuring using four point method

If the switch S is switched in position X, the value of the measured voltage is:

$$U_{TIP2} = I(R_{JUMPER} + 2R_{JOINT}) \qquad (2)$$

The resistance of the adhesive joint is:

$$R_{JOINT} = \frac{U_{TIP2} - U_{TIP5}}{I} \qquad (3)$$

Nonlinearity of the current vs. voltage characteristic can be measured by two ways: using powering of a joint with a very pure sinusoidal current and

measuring of third harmonic of a periodical voltage, which occurs on the joint, or using a modulation technique. The principle of the modulation technique is as follows:
A nonlinear component is powered with two sinusoidal signals with frequency f1 and f2 (see Fig. 5). Nonlinearity causes origin of intermodulation periodical signals with the frequency:
.

$$f = nf_1 + mf_2 \quad (4)$$

If the third harmonic is examined, then sum of parameters n and m must be equal to 3. Following frequencies are used: f1 = 150 kHz, n = 2, f2 = 4,1062 MHz, m = 1, and f = 4,4062 MHz.
Because level of signal, which is measured, is in µV, the measuring system must be carefully screened and grounded. It is necessary to avoid to earth loops.

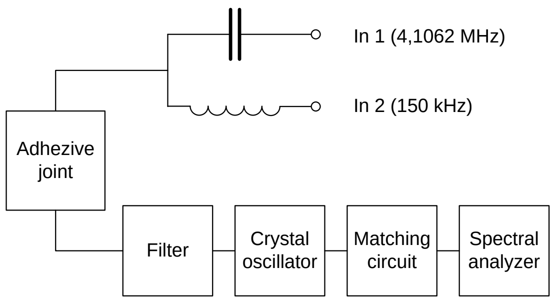

Fig. 5: Principle of measuring of joint nonlinearity using modulation technique

MEASURED RESULTS AND DISCUSSION

Measured results are shown in Fig. 6. Nine groups of samples are prepared and measured – for every concentration of nanoparticles and for every type of nanoparticles. Twenty eight values are measured for every combination.
Data are processed using mathematical smoothing. The simplest method of mathematical smoothing is used – two maximum and two minimum values of data measured for every combination nanoparticle type /concentration are deleted and average is calculated of 24 values.
It is shown that addition of nanoparticles does not improve electrical conductivity of adhesive joints. The reason is that nanoparticles do not create additional bridges between neighboring silver flakes of filler, but they locate between flakes and increase number of contacts in conductive net in adhesive.
Electrical conductivity of a balk is based on a phonon-electron interaction. The conductive mechanism in a contact is based on two mechanisms: on a constriction mechanism and on tunneling.

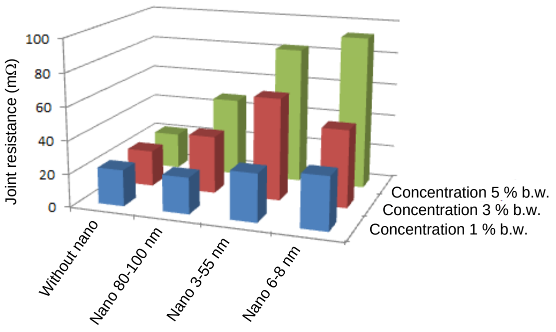

Fig. 6: Joint resistance for different concentrations and different types of added silver spherical nanoparticles

If flakes are used, the constriction mechanism can be neglected due to the higher number of contacts between flakes in comparison with the number of contacts between balls and to the higher contact ares of contacts.
The tunneling resistance is higher in comparison with the resistance of balk. The higher is number of contacts in the conductive net; the higher is the resistance of the adhesive joint. Addition of nanoparticles causes increase of number of contacts in adhesive, therefore the resistance of adhesive joints formed of ECAs modified with the conductive nanoparticles is higher.

CONCLUSIONS

The electrical resistance and nonlinearity of the current vs. voltage characteristic of adhesive joints formed of electrically conductive adhesive modified with spherical silver nanoparticles are investigated. It is found that addition of nanoparticles into adhesive does not improve its electrical properties. The reason is an increase of the number of tunneling contacts in conductive net in adhesive caused by nanoparticles.

ACKNOWLEDGMENTS

The author would like to thank Ministry education, youth and sports for the financial support (project "Diagnostics of Materials", no. MSM6840770021).

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