PREVENTING DECAY OF THE INTERFACE BETWEEN ELECTRICALLY CONDUCTIVE ADHESIVES AND METAL PADS USING GRAPHENE BASED BARRIERS

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ABSTRACT

Electrically conductive adhesives (ECAs) seem to be a promising substitute to traditional metal-based solders, because of they being environmentally friendly materials requiring much lower processing temperatures, and offering a much finer pitch. However, a critical problem related to the use of ECAs is that the contact resistance to the metal pad tends to increase significantly during aging tests due to galvanic corrosion, particularly in 85°C/85% relative humidity (RH) atmospheres. In this respect the reported impermeability of graphene, a property prohibiting most molecules including water vapor from penetrating the film, has made graphene a major candidate as an anti-corrosion barrier material. The use of graphene as an anti-corrosion barrier material on steel and other metals has already been reported in literature. In this paper, the use of graphene-based barriers[12] between the ECA and the copper pads on a printed circuit board for alleviating the galvanic corrosion problem is reported.

A PCB test board was designed for monitoring the effects of introducing the graphene-based barrier on the contact resistance between ECA and copper while exposing the board to a 500 hour aging test in 85℃/85% RH. For samples without graphene-based barriers it was found that the contact resistance increased rapidly during the first 200 hours of the aging test, while the contact resistance for samples with the graphene-based barriers remained stable. For these samples with graphene-based barriers, the contact resistance showed a much smaller decay during the aging test than for those samples without graphene-based barriers. These findings indicate that graphene-based barriers could be a solution for improving the reliability of electrically conductive adhesives, especially in harsh 85°C/85% RH environment conditions.

INTRODUCTION

An electrically conductive adhesive is an adhesive material with good electrically conductive properties. It consists of a conductive filler, an epoxy resin, a diluent, a curing agent, and some other additives. The choice of resin controls the adhesive bonding strength, while the electrical conductivity depends on the choice of conductive filler, and the viscosity depends on the choice of diluent. The curing agent cannot only improve the bonding strength of the adhesive, but it can also condense the matrix resin and enable additional contact to the conductive filler which in our case consists of silver flakes in order to create more conductive paths.

Compared to solders which have been widely used as interconnect materials in electronic assemblies for surface mount applications, electrically conductive adhesives have many advantages; they are more environmentally friendly, they require much lower processing temperatures and they offer the possibility of a much finer pitch[1]- [3]. Therefore, it is a promising material for substituting traditional solders. However, one critical problem associated with electrically conductive adhesives is that the contact resistance between the adhesive and a non-noble metal surface tends to increase significantly during aging, particularly in high temperature atmospheres with high relative humidity (85°C/85% RH), due to galvanic corrosion[4]-[6]. Graphene is a 2D material of only one atom layer thickness consisting of sp2 bonded carbon atoms arranged in a honeycomb lattice with extreme properties such as high thermal conductivity, high optical absorptivity, and high mechanical strength. Graphene is widely used in detectors, super-capacitors, batteries, and other electronic devices based on the aforementioned properties[7]. Berry et al.[8] reported on the impermeability of graphene - a property that prohibits most molecules from penetrating. Guo et al.[9] reported that because of its impermeability graphene can be used as a barrier membrane for environmentally hazardous agents. Kirkland et al.[10] reported that graphene can be used as anti-corrosion coatings alleviating galvanic corrosion.

Due to these properties of graphene[10]-[12], we have studied the effects of introducing graphene-based barrier films between the electrically conductive adhesive and the non-noble metal pad to see if the use of such barriers could alleviate the galvanic corrosion problem deteriorating the contact resistances. A series of test samples were designed and carefully prepared to verify whether graphene-based film barriers can enhance the reliability of electrically conductive adhesives, especially in harsh 85°C/85% RH atmospheres.

EXPERIMENTS

A test device for measuring the contact resistances between electrically conductive adhesives and non-noble metals was designed as shown in Fig 1. The device consists of a set of copper wires separated by 1 mm gaps on a printed circuit board. The equivalent electrical circuit and a cross-sectional view of the test structure are shown in figures 2 and 3, respectively. First, the device must be cleaned by diluted hydrochloric acid, and dried at room temperature. Second, a graphene-based solution was dispensed across the gaps as anti-corrosion barriers while the test structure is placed on a heating platform at about 30 to 40°C. After the water was evaporated, graphene was dispensed again; this step was repeated several times. In a third step, the electronic conductive adhesive was applied on top of the graphene barriers covering the gaps between the copper wires, thereby connecting the metal wire segments on the printed circuit board. In parallel, identical PC boards were prepared without any graphene-based barriers; actually three samples of each test structure were prepared. After curing, the copper wires are contacted at the end pads so that the contact resistances could be conveniently monitored during the experiment. The top view of a complete test structure is shown in Fig. 4.

To evaluate the reliability of the graphene-based barriers and their anti-corrosion properties, the test structures prepared as described in the previous section was placed in a climate chamber where the temperature and humidity could be carefully controlled for aging test. Before starting the aging test, the sum of the contact resistances of each sample was noted using an ohmmeter, and during the aging test variations of the contact resistances were monitored periodically.

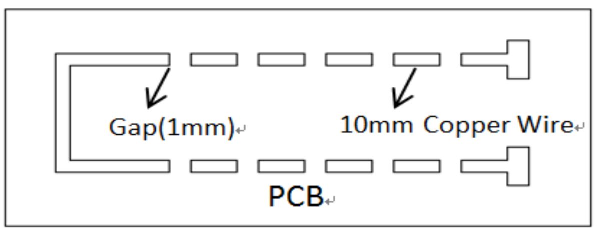

Figure 1: Contact resistance PCB test structure.

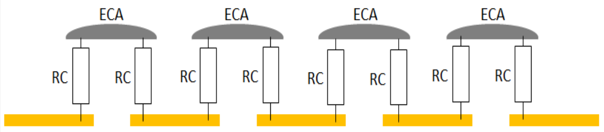

Figure 2: Equivalent electrical circuit of series contact resistances.

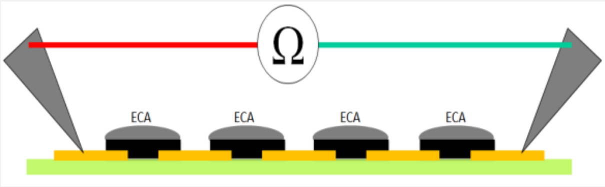

Figure 3: Cross sectional view.

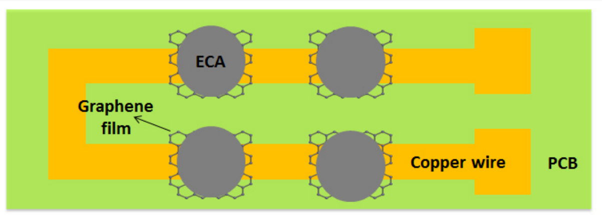

Figure 4: Top view of complete PCB test structure.

RESULTS AND DISCUSSION

After introducing the graphene-based barriers between the electrically conductive adhesive and the copper pads, and after conducting the aging test at 85ºC in 85% relative humidity for 500 hours the following results were obtained. For the samples without graphene-based barriers the contact resistance between the electrically conductive adhesives and the copper wires increased rapidly during the first 200 hours of aging, while the contact resistance for samples with graphene-based barriers remained stable, as shown in the left-hand graph of Fig. 5. This implied that graphene-based membrane actually worked as expected as a protective barrier against any galvanic corrosion. It is well known that galvanic corrosion takes place when two metals of different electrochemical potentials are in contact in the presence of water, especially when one or more of the metals is a non-noble metal. Due to the impermeability of graphene, the mechanisms behind corrosion - ($Cu \rightarrow Cu^{2+} + 2e$) for anodic copper and the cathodic reaction $2H_2O + O_2 + 4e \rightarrow 4OH^-$ - were reduced. During corrosion copper hydroxide is formed, and easily broken down into copper oxide with very low electrical conductivity. As shown by the graphs of Fig. 5, samples without graphene-based barriers matches this corrosion mechanism very well; it further demonstrated that the corrosion current density was reduced after applying graphene film barriers.

According to variations in contact resistance between the electrically conductive adhesives and the non-noble metal wiring, the contact resistance shifts during 500 hours of aging in 85°C/85% relative humidity are shown in the right-hand graph of Fig 5. As can be concluded from these graphs, samples with graphene film barriers showed a considerably smaller shift in the contact resistance values than those without any graphene-based barriers. The results indicate that graphene-based barriers can be used to improve the reliability of electrically conductive adhesives, especially under 85ºC/85%RH conditions.

CONCLUSION

In this study, the reliability of graphene-based barrier films was investigated when used as protective membranes for anti-corrosion by conducting 500 hours of aging tests under 85°C/85% RH conditions. Our results indicate that stable contact resistances without any aging effects were obtained by using graphene-based barrier films between the electrically conductive adhesives and the non-noble copper wiring on a printed circuit board. In other words, our results from this systematic study strongly suggests that graphene-based barrier films can considerably improve the reliability of electrically conductive adhesives when used in electronic packaging.

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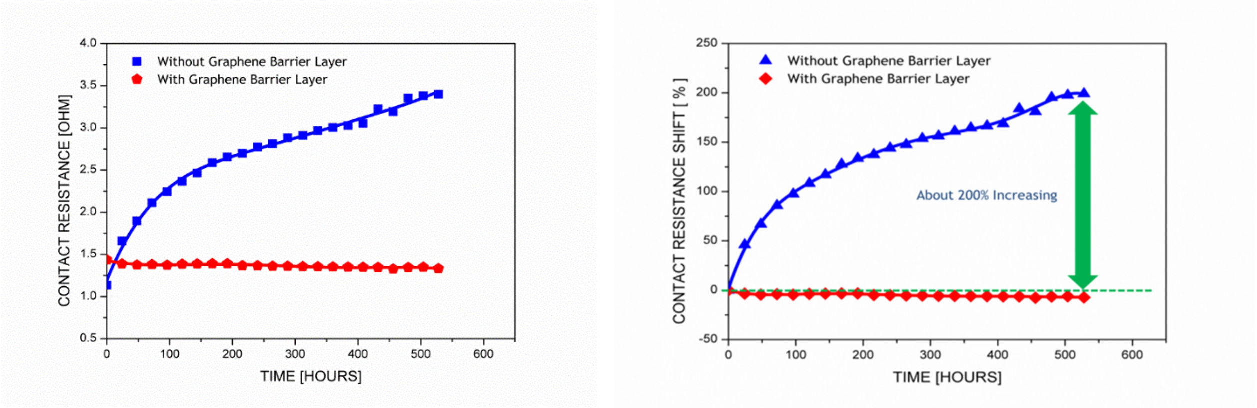

Figure 5: Aging test results: Contact resistance vs. time (left-hand graph), and the contact resistance shift vs. time (right-hand graph).

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