Electrical Properties of ACA Joints Assisted by Conjugated Molecular Wires

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Abstract

Anisotropic conductive adhesives (ACAs) have been considered as one of promising interconnect materials for next generation high performance devices. However, high joint resistance and low current carrying capability of ACA joints have been a bottleneck to deploy ACAs in high power devices. In this study, we introduced conjugated dithiols into ACA formulations to construct the molecular wire junction between conductive fillers and metal pads to facilitate the electron transport through the joint. With introduction of molecular wires, the electrical conductivity and current carrying capability were significantly improved. The factors that lead to the improved electrical properties were discussed.

Keywords anisotropic conductive adhesive, molecular wire, electrical property, contact resistance

Introduction

As microelectronics are driven toward smaller, higher density, light weight, environment-friendly and lower cost solutions, anisotropic conductive adhesives/films (ACAs/ACFs) are becoming popular as one of promising candidates for lead-free interconnection, due to their technical advantages such as fine pitch capability (<40 μm pitch), low temperature processing ability, low cost and environmentally friendly materials and process, etc. [1-3] These numerous advantages of ECAs over the conventional solder technology allow the wide applications of ECAs in the fields of liquid crystal display (LCD) and smart cards where low temperature interconnects are needed. [4] A cross-section of the joint formed by anisotropic conductive adhesive (ACA) between the integrated circuit (IC) and substrate is shown in Figure 1.

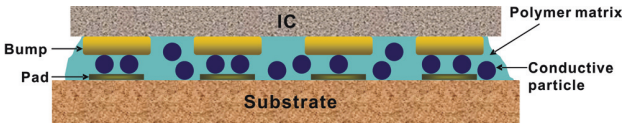

Figure 1 Schematic representation of a cross-section of an ACA junction.

In ACA joints, the unidirectional electrical conductivity is achieved through the conductive particles trapped between ICs and substrates when the ACA is fully cured under pressure and heat. Electrical contact resistance of the ACA joint has been extensively studied experimentally [5, 6] and through theoretical calculation. [7-9] Due to the restricted contact area and poor interfacial bondings of the ACAs and metal pads compared to the metallurgical joint of the metal solders, the ACA joint has lower electrical conductivity, conductivity fatigue in reliability tests, poor current carrying capability and poor impact strength. [10, 11] Moreover, during the ACA joint assembly, an ultrathin of residue polymer layer trapped between conductive particles and contact pads acts as a potential barrier that hinders flow of electrons, leading to high joint resistance (tunneling resistance). [5, 7, 9, 12, 13] Consequently, these issues will significantly restrict wide applications of ACAs in the fields of high power devices, such as microprocessors. Therefore, the interfacial design between the conductive particles and IC/substrate pads may play a key role in the overall performance of ACA joints.

In recent years, electron transport in metal-molecule(s)-metal junctions has attracted much attention since fundamental understanding of the electronic transport properties of such a system will facilitate the development of molecular electronics. [14] The main goal was to understand the effect of molecular structures and their bonding/contacts with electrodes on how electrical current transports through a metal-molecule(s)-metal junction. Dadosh et al. investigated the effect of the backbone of the molecules on the electrical conduction. [15] It has been found that both the oxygen in (4-mercaptophenyl)-ether and the methylene groups in 1,4-benzenedimethanethiol suppress the electrical conduction relative to 4,4'-biphenyldithiol, a fully conjugated molecule. Kushmerick et al. reported the effect of bond-lengths on the conductance of molecular wires experimentally and theoretically. [16] Another factor that controls the electron transport through the joint is the nature of the contact, i.e., either physisorption or chemisorption. Sun et al. reported the density functional theory calculations of the influence of the molecular terminal group. [17] Wang et al. also studied the influence of terminal group and surface structure on the I-V curves of alkanethiol monolayers on Au (111) and found that tunneling currents through the investigated monolayers of the molecules depend remarkably on terminal groups. [18] Moreover, the conductance of the junction could be strongly affected by the adsorption site, packing density and tilt angle of the modified monolayer ECA molecule. The strength of interaction between a gold tip of scanning tunneling microscope and the terminal groups of the molecules could also affect the conductance. [19] Compared with the gold-amine contact, gold-sulfur (thiol group) binding has higher electronic conductance. Various metals and functional groups have been studied as an alternative for Au-S binding. [19] Hence, the molecules are likely to tune the electrical properties of the junction.

Previously, we have explored the crucial factors that govern the enhanced electrical properties of the ACA joint with the study on the characteristics of molecular wires, interaction between Ag particles and molecular wires, molecular orientation on Ag particles and their thermal stability. [20] In this study, with introduction of conjugated

molecular wires into the ACA formulations, we investigated the effect of these molecular wires on the electrical properties of ACA joints. By investigation of surface alignment of biphenyl dithiol (BPD) on Ag and Au surfaces with contact angle measurement and surface enhanced Raman spectrometry (SERS), we investigated the electrical properties of ACA joints with Ag particles and Au-coated polymer particles as conductive fillers. The key factors that contribute to the improved electrical conductivity and high current carrying capability were discussed. The resulting ACAs with better electrical conductivity, higher current-carrying capability and enhanced thermal stability will enable their applications in fine pitch and high performance interconnects in microelectronics.

Experimental

Surface Characterization of Molecular Wires on Gold-coated Si Wafer and Silver Particles

The gold (Au)-coated Si wafers with titanium adhesion layer was prepared by e-beam deposition. In order to study the surface alignment of biphenyldithiol (BPD) on gold (Au) surface, Au-coated Si wafers were cleaned with UV & ozone (Samco, Model UV-1) for 5 minutes and then immersed in the dithiol solution under nitrogen for 24 hrs. After the treatment, the Au surface was rinsed with solvent that used to dissolve the excess unadhered dithiol molecules. The contact angles of deionized (DI) water on the surface were obtained by a goniometer (Rame-Hart Co., Netcong, NJ).

For the coating of silver particles, the silver particles were dispersed in the solution of BPD and then sonicated, which was incubated under nitrogen for 24 hrs. After treatment, Ag particles coated with BPD were centrifuged and the supernatant was removed. Then Ag particles coated with BPD were re-dispersed with solvent. The cycle was repeated for 4 times to remove the unadhered molecules. Finally, Ag particles coated with BPD were dried under vacuum for Raman measurements. Raman spectra of molecular wire-coated Ag particles were obtained using Bruker Optics FT-Raman (Equinox 55) with near infrared (NIR) lasers (λ=1064 nm).

Electrical Properties of ACA Joints

For characterizing the electrical properties of submicron-sized Ag particle filled ACAs, filler particles were added in a polymeric resins, in which bisphenol-F type epoxy, anhydride and imidazole were used as epoxy, hardener and catalyst, respectively. Conjugated molecules were incorporated into the above mixtures. The electrical contact resistance of the ACA joints (contact area: 150×150 μm^2) was measured by a four-point probe method. [11] The applied current was varied by a power supplier (HP model 6553A, HP Hewlett Packard, Palo Alto, CA) and the voltage of the interconnect joints was measured with a Keithley 2000 multimeter (Cleveland, Ohio).

Results and Discussion

Surface Adsorption of BPD on Gold and Silver

Self-assembly of conjugated thiol compounds onto gold or other metal surfaces to form a well-ordered and densely packed organic layer is very attractive for their broad applications in molecule electronics. [14] For the practical use of these ordered layers, it is quite important to understand their surface alignments since the different surface alignments will affect the way in which electrical transport will be established between these molecules and metal electrodes, and thus results in different electrical performances. Figure 2 shows the contact angle values of DI H_2O droplets on Au surfaces with and without BPD treatment. The contact angle of the Au surface decreases after the treatment with BPD. For conjugated dithiols, the lower contact angle may results from the exposed hydrophilic terminal thiol group (-SH). Therefore, BPD forms monothiolates with Au substrate while the other thiol group is available for further binding.

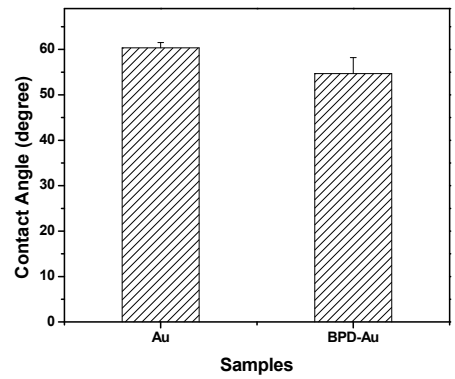

Figure 2 Contact angle measurements of DI H_2O droplets on Au-coated Si wafer surfaces

It has been well known that the adsorption characteristics of dithiols strongly depend on the processing conditions including the type of substrate and solvent, the concentration and the duration of self-assembly. [24-26] Joo et al. reported that 1,4-benzenedithiol chemisorbed dissociatively on both gold and silver surfaces by surface-enhanced Raman scattering study. [26] But these dithiols were adsorbed on Au by forming one single Au-S and the other thiol moiety is pendent. However, dithiol molecules were absorbed on silver with a flat orientation by forming two Ag-S bonds. The reason that dithiols showed different absorption behavior on gold and silver has not been clearly understood yet. Figure 3 shows (a) Raman spectrum of BPD, (b) BPD treated Ag particles and (c) Ag particles treated with BPD and baked at 260 ^oC for 10 minutes. The bands at 913 and 2,553 cm^{-1} in Figure 3 (a), assigned to the C-S-H bending and the S-H stretching vibrations, respectively, were completely absent in the BPD treated Ag particles (Figure 3 (b)). These indicate that BPD absorbs on the Ag particles as dithiolate and thus lies flat on the silver particle surface [26]. After treatment at 260 ^oC for 10 minutes, all the bands in Figure 3 (b) are present (Figure 3 (c)). This indicates that BPD has high thermal stability on a Ag particle surface. In summary, BPD lies tilted on a Au surface with a pendent thiol group and it lies flat on a Ag particle surface by forming two Ag-S bonds.

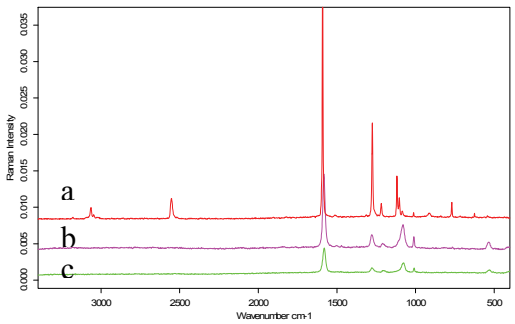

Figure 3 Raman spectra of (a) BPD, (b) BPD treated Ag particles and (c) BPD-treated Ag particles baked at 260 ^{o}C for 10 minutes.

Electrical Properties of ACA joints

The total resistance of a physical contact is composed of constriction resistance and tunneling resistance. Constriction resistance occurs as the electrical current must squeeze through the small contact area to cross the interface. Tunneling resistance is due to the intermediate layer between conductive particles and metal surfaces. The total resistance therefore can be written as [27]:

$$R = R_c + R_t = (\frac{\rho_1}{4a} + \frac{\rho_2}{4a}) + \frac{\sigma}{\pi a^2} \quad (1)$$

where R_c is the constriction resistance, R_t is the tunnel resistance, ρ_1 and ρ_2 are the bulk electrical resistivity of the two contacting bodies, a is the radius of contact area, and σ is the tunnel resistivity of the interface. Tunnel resistivity is a function of the film thickness s, the work function Φ for electron emission from metal into film (electron-injection barrier), and the relative permittivity ε_r of the film material. It can be expressed as [28]:

$$\sigma = \sigma(s, \Phi, \varepsilon_r) = \frac{10^{-22}}{2} \frac{A^2}{1 + AB} e^{AB} \Omega cm^2 \quad (2)$$

$$A = 7.32 \times 10^5 (s - \frac{7.2}{\Phi})$$

$$B = 1.265 \times 10^{-6} \sqrt{\Phi - \frac{10}{s\varepsilon_r}}$$

The total resistance of ACA joints consists of constriction resistance, tunneling resistance and bulk resistance. Bulk resistance is the intrinsic resistance of the conductive filler and may be neglected in comparison with constriction resistance and tunneling resistance. [8] Therefore, based on above equations, the contact resistance is dependent on mechanical property of the filler, processing pressure, epoxy material properties and so on. In ACA joints, experiments and computational models clearly indicated that an ultrathin film is present between conductive particles and metal surfaces [5, 7, 9, 12, 13], which causes considerable contact resistance at the interface. This thin film may be consisted of resin and possibly oxide (except all Au cases) and hydrocarbon contaminants on conductive particles. In order to remove the possible oxide layers and hydrocarbon contaminants and more importantly to construct conjugated molecular wire junctions between conductive fillers and metal surfaces, BPD was in-situ added into the formulation. Electrical conduction through metal-molecule-metal junction depends primarily on the characteristics of the molecule used, such as conjugated or saturated, the length of the molecules and interaction strength of the molecules with the metallic contacts. In particular, two benzene rings in BPD offer delocalized states which will be beneficial for the electron transport. The thiol groups will allow for the good contact with metal electrodes (gold and silver) since the thiol group has strong affinity to gold and silver.

It was found that BPD could lie flat on the silver particle surface, but this may not be good for electron transport. Therefore, BPD was directly incorporated into the formulation. As a result, it could be possible that BPD may bind to both the Au substrate and Ag particles to form molecular wire junctions. Compared with Ag particles, it may be easier to form molecular wire junction for Au-coated polymer particles since BPD lies tilted on the particle surface. Figures 4 and 5 show the effect of BPD on the electrical properties of ACA joint using Ag particles as conducting fillers. In both cases, the electrical resistance was decreased and current carrying capability was improved. The current carrying capability in this study was defined as the maximum current below which the I-V relationship remains linear. It has been extensively reported that the metal work function could be tuned by self-assembled monolayers (SAMs). [29-31] Depending on the molecular structures and the interaction between the molecules and metal electrodes, the work function of SAM-coated metals can be varied significantly. Theoretical studies indicated that the self-assembled monolayer of BPD on a Au surface will reduce the work function of the metal by 1.02 eV. [31] Based on Equation 2, the reduced work function will lead to the decrease in the tunneling barrier (tunnel resistivity) and thus decrease in the tunneling resistance. Therefore, the total resistance is decreased by the construction of molecular wires in between conductive particles and metal pads. In Figures 4 and 5, the initial ohmic contact followed by nonlinear behavior of the joint could be due to either resistive heating or rupture of insulating film at the contact. [12] Compared Figure 4 with Figure 5, it can be concluded that the increase in the current carrying capability is more pronounced for ACA joints based on Au-coated polymer particles than that of ACA joint based on Ag particles. It is believed that the formation of a molecular wire junction resulting from the tilted surface alignment of BPD on a Au surface contributes to the electron transport through the joint and thus less heat was generated during the current flow through the joint as a low resistance contact material should enhance thermal transport.

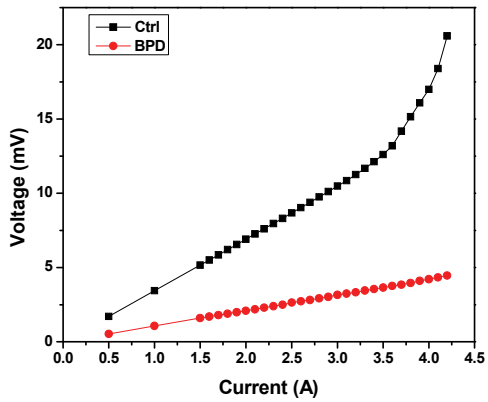

Figure 4 I-V curve of ACA joint using Ag particles as filler, (b) corresponding I-R curves

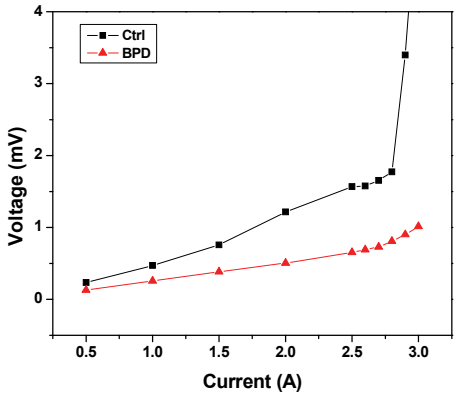

Figure 5 I-V curve of ACA joint using Au-coated polymer particles as filler.

Conclusions

With the introduction of molecular wires in between conductive fillers and metal pads, the electrical properties of ACA joints using both silver particles and Au-coated polymer particles have been significantly improved. The factors that lead to the decrease in contact resistance and higher current carrying capability were discussed in detail. With the improved electrical properties, ACA joints will have promising applications in high-performance fine pitch interconnect of microelectronics.

Acknowledgments

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