

Effect of Heat, Water and Chloride Ions on the Silver-Filled Epoxy on Bare Copper Interface in As-Bonded Semiconductor Die

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Abstract— Silver-filled epoxy die attach material is the state-of-the-art in attaching the die containing the integrated circuit on a carrier for semiconductor devices requiring high thermal dissipation. Herein, we show that the moisture and chloride ions do not significantly affect the adhesive joint integrity, comprising of bare copper substrate and Ag-filled epoxy glue, in systems that are already bonded. However, the bare copper substrate manifests varying degrees of corrosion. The oxide layer growth is evident in the cross-sectional scanning electron microscopy (SEM) images. The observed effect of these surface treatments on the adhesive joint is rationalized by the strength of the epoxy/oxide interaction.

Keywords— Ag-filled glue, corrosion, moisture, chloride, epoxy.

I. INTRODUCTION

Conductive adhesives (CA) are composites of polymer resin and conductive fillers [1]. The conductive fillers provide the composite with electrical conductivity through contact among the conductive particles. With increasing filler concentrations, the electrical properties of CA transform it from an insulator to a conductor [2].

Both thermoplastic and thermoset resins can be used as matrix material. Polyimide is the main thermoplastic resin used with an attractive advantage of 'reworkability', *e.g.* it can easily be repaired. A major drawback of the use of thermoplastic, however, is the degradation of adhesion at high temperature. Another drawback of polyimide-based conductive adhesive is that they generally contain solvents. During heating, voids are formed when the solvent evaporates. Most of CA are based on thermosetting resins; epoxy resins are the most commonly used formulations because they possess superior balanced properties. Silicones, cyanate esters, and cyanoacrylates are also employed in CA formulations [3-4].

Bonding semiconductor dies onto metal substrates through CAs is the state-of-the-art packaging process in the semiconductor and electronics industries for devices requiring high thermal dissipation. Due to the high electrical conductivity and lower cost of bare copper frames, the industry is shifting towards bonding dies directly to bare copper. The susceptibility of Cu towards corrosion, induced by the presence of moisture and oxygen in the environment, and accelerated by the presence of ionic contaminants such as sulfides and chlorides present due to handling, limit the full application of this emerging process technology [5-7].

Herein, we show that die bonded onto bare copper using Ag-filled epoxy CA exhibit resistance to moisture- and chloride-induced corrosion. The bare Cu substrate, however, shows progressive surface corrosion, and growth of the copper oxide layer.

II. EXPERIMENTAL DETAILS

Semiconductor dies are bonded on bare copper frames using a commercial Ag-filled epoxy-based CA, via optimized bonding parameters, established using standard design of experiment (DOE). Deionized water was used for all solution preparations. A 1000 ppm chloride standard solution (as NaCl) was purchased from ThermoFischer Scientific and used as the stock solution as received. 10 ppm and 100 ppm solution were prepared from the 1000 ppm standard solution. The water and neutral saline solution of varying chloride concentration were introduced separately using an atomizer, positioned parallel to the vertically oriented bonded units that are 50 cm away. The units were air dried before putting inside the oven for 24 h at a temperature of 175 °C. A second set of samples was baked for 24 h at 175 °C prior to surface treatment with water and neutral saline solution, followed by another 24 h at 175 °C. Output responses such as die shear (DS), bondline thickness (BLT), voids and fillet height were measured. Surface imaging to assess the presence of corrosion was done using Olympus SZ61. Scanning electron microscopy (SEM) was performed on cross-sectioned samples to check the integrity of the CA/Cu adhesive joint interface using Hitachi S4800 SEM.

III. RESULTS AND DISCUSSION

The integrity of the adhesion interface formed by the Ag-filled epoxy glue and the bare copper substrate is assessed through a series of surface and thermal treatments. Water and saline solution are used to simulate worst condition because moisture induces corrosion while the chloride ions in saline solution accelerate corrosion [5-7]. Fig. 1 shows the optical images of the sample treatment at time zero, after thermal treatment, and after surface treatment followed by thermal treatment. The exposed copper surfaces manifest clear signs of corrosion, *i.e.* they are variably colored. The different colors are indication of the different oxidation products and varying thickness of the oxide layers [8]. The results indicate that the thermal treatment alone induces corrosion, arising from the reaction of the exposed copper surface with the water and oxygen molecules present in the environment. Direct

exposition to moisture in the form of water mist from the atomizer followed by the thermal treatment promotes corrosion since there is a direct source of water, which reacts with the copper surface to form an oxide layer.

Moreover, the presence of 10 and 100 ppm saline solution accelerated the corrosion kinetics resulting in more pronounced oxidation. The degree of corrosion is more severe in the system exposed to the higher concentration of Cl^- . This observation is consistent with the mechanism of chloride-catalyzed corrosion in copper surfaces [6-7].

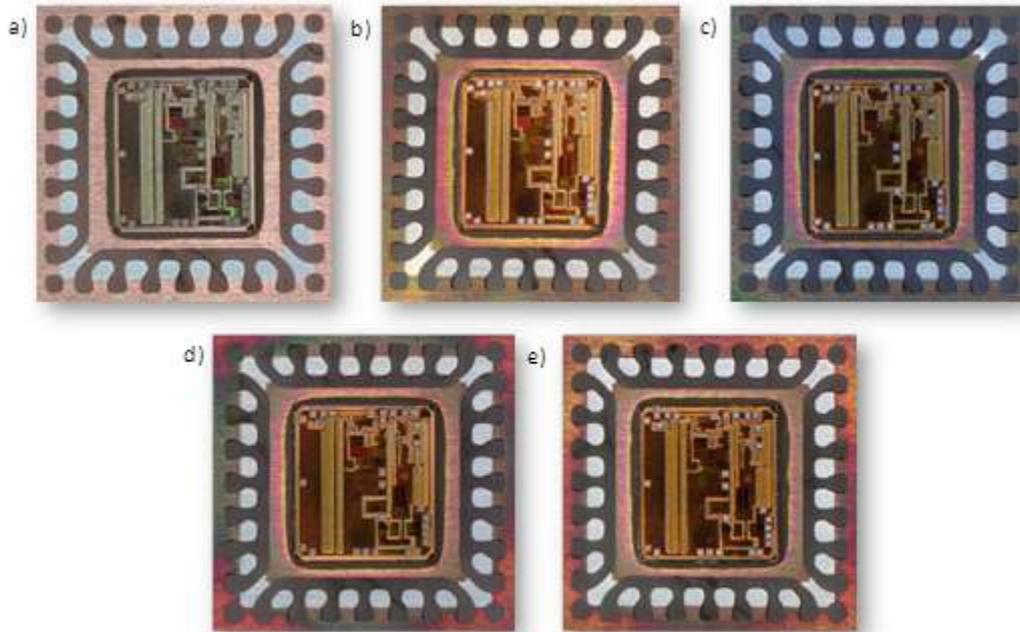


Fig. 1. Optical images of samples at a) time zero, b) after 24 h at 175 °C, and after exposure to c) water, d) 10 ppm Cl^- , and e) 100 ppm Cl^- solution followed by thermal treatment for 24 h at 175 °C.

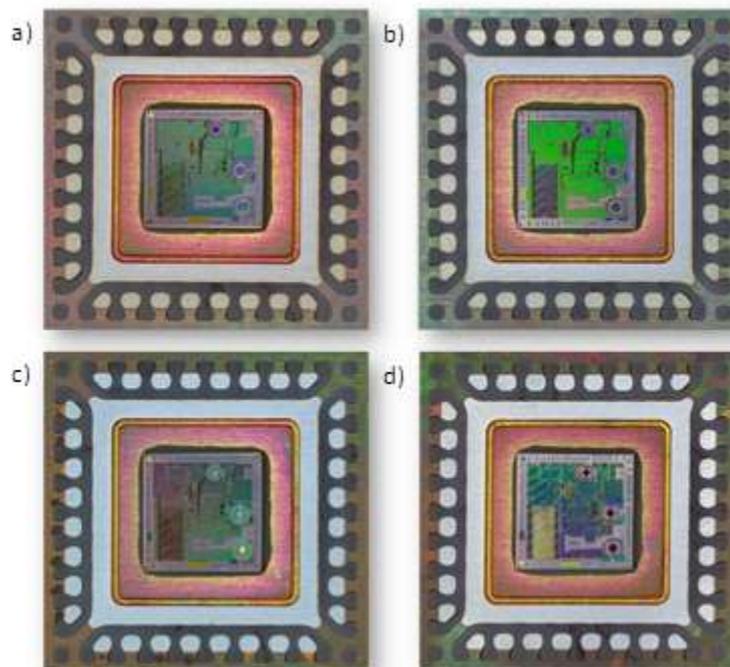


Fig. 2. Optical images of samples pre-baked for 24 h at 175 °C followed by another 24 h at 175 °C. Prebaked samples are subjected to a) no treatment, b) water, c) 10 ppm Cl^- , and d) 100 ppm Cl^- solution before the second bake step.

To better understand the effect of the surface and thermal treatment on the interfacial integrity of the adhesive joint, die shear test (DST) was performed. The results show that the surface and thermal treatments enhance the strength of the adhesion as manifested by the stronger force necessary so shear the die away from the copper substrate (Fig. 3). Interestingly, the higher values occur despite the visible signs of corrosion. We speculate that the effect of corrosion is exhibited solely by the copper surface, wherein the polymer adhesion of the epoxy matrix is enhanced due to the preferential interaction with the growing oxide layer thickness [9-10]. To validate the effect of the surface treatment on the oxide layer, we analyzed another set of samples wherein the oxide layer was induced by a pre-bake step at 175 °C for 24 h. The pre-grown oxide layer was then treated with water and chloride solution. DST results (Fig. 4) show a decrease in the required shear force indicating a deterioration of the adhesion of the epoxy on the copper surface. However, the results suggest an invariance with respect to the surface treatment, indicating that the degree of oxidation has gone beyond the acceptable limit that gives positive effect to the adhesion.

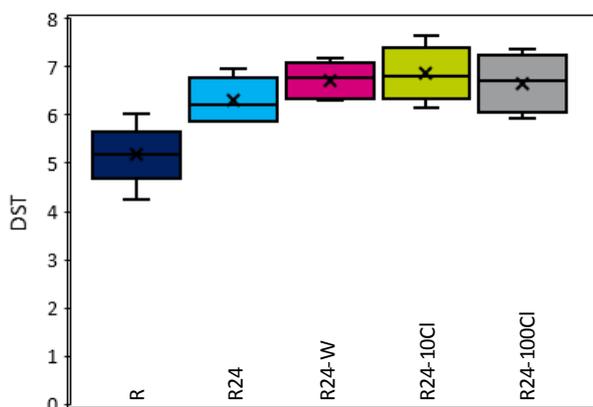


Fig. 3. DST results for samples at time zero (R), after 24 h at 175 °C (R24), and after surface treatment [water (R24-W); 10 ppm Cl⁻ (R24-10Cl); and 100 ppm Cl⁻ (R24-100Cl)] followed by thermal treatment at 24 h at 175 °C.

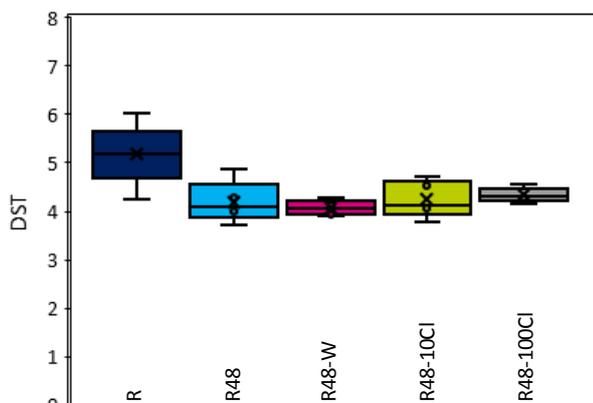


Fig. 4. DST results for samples pre-baked for 24 h at 175 °C followed by another 24 h at 175 °C. Prebaked samples are subjected to no treatment (R48), water (R48-W), 10 ppm Cl⁻ (R48-10Cl), and 100 ppm Cl⁻ (R48-100Cl) solution before the second bake step.

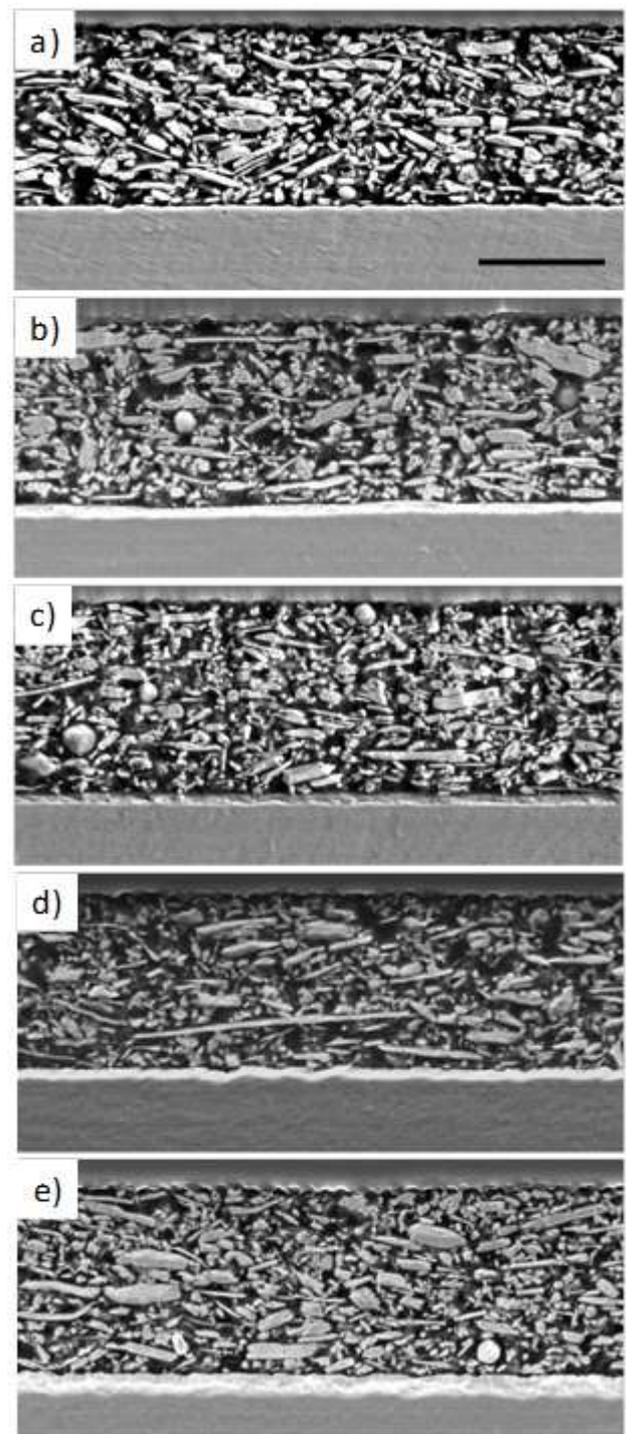


Fig. 5. SEM micrographs of samples at a) time zero, b) after 24 h at 175 °C, and after exposure to c) water, d) 10 ppm Cl⁻, and e) 100 ppm Cl⁻ solution followed by thermal treatment for 24 h at 175 °C. Scale bar = 2 μm.

SEM analysis was performed to check the effect of the surface and thermal treatment on the morphology of the interface. Fig. 5 confirms that the effect of the treatment is primarily manifested by the Cu surface; growth of the oxide layer is evident. Results also show that the thickness of the oxide layer follows the trend of 100 ppm Cl⁻ > 10 ppm Cl⁻ > H₂O ≈ heat. The effect of the surface treatment on the pre-

grown oxide layer exhibit a different trend; $H_2O > 100 \text{ ppm } Cl^- > 10 \text{ ppm } Cl^- > \text{heat}$ (Fig. 6). It is interesting to note that the corrosion of the oxide layer is more severe in the presence of water. This behavior can be associated with water being a direct starting material for corrosion as opposed to the Cl^- ion acting as a catalyst. It is possible that even in the presence of a catalyst, the reaction is retarded due to the limited availability of the reactant (H_2O). Nevertheless, the degree of oxidation is still more severe in the presence of higher concentration of Cl^- ions in the surface pretreatment.

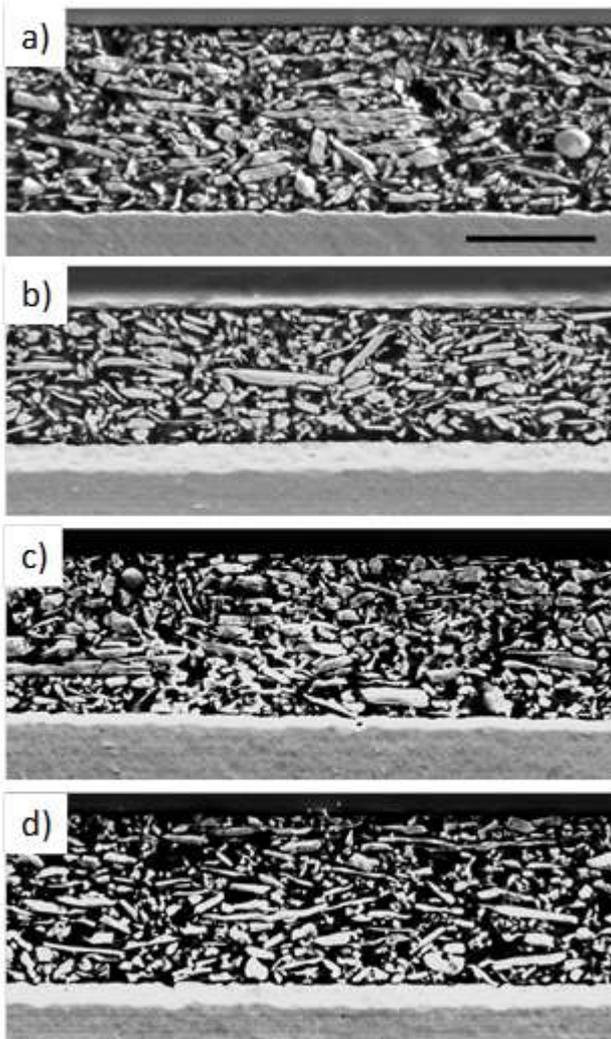


Fig. 6. SEM micrographs of samples pre-baked for 24 h at 175 °C followed by another 24 h at 175 °C. Prebaked samples are subjected to a) no treatment, b) water, c) 10 ppm Cl^- , and d) 100 ppm Cl^- solution before the second bake step.

IV. CONCLUSION

The effect of heat, water and chloride ions on the adhesive joint integrity in as-bonded semiconductor die on bare copper substrate by Ag-filled epoxy glue is explored. The results clearly show that the oxidation of the bare copper is induced in the presence of these surface pretreatments. However, the adhesive joint integrity did not deteriorate due to the preferential interaction of the epoxy on the oxide layer. The interaction of these surface treatments on the pre-grown oxide layer manifested as the deterioration of the force needed to shear the die from the substrate indicate a weakening of the adhesion of the epoxy on the copper surface.

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