<u>Formation of Self Assembled Monolayers on Various Surfaces and Their Thermostability</u>

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Introduction

Manufacturing industries depend heavily on tin-lead, a common eutectic alloy. However, due to recent government legislation and concerns about the toxicity of lead, researchers are investigating possible substitutes, but finding an alternate for a metal as useful as lead is a formidable challenge. The current replacements for lead solders are highly inefficient in the manufacture of circuit boards because of their high processing temperatures.

Dr. C.P. Wong's group has investigated the benefits of an electrically conductive adhesive (ECA), an organic polymer doped with metal particles, as an alternative to tin-lead solder for circuit board production. These adhesives would require lower processing temperature than the lead-free metal solders. Despite this promising characteristic, ECAs cannot compete with metal solders that have the high electrical current capability due to the differences in the interfaces between the metal solder/bond pad and ECAs/metal bond pad.

A possible solution to this problem is the introduction of a self-assembled monolayer (SAM) on the interface between the metal particles and the ECAs/ metal bond pad. These molecules adhere to the metal surface and form covalent bonds allowing electrons to flow, therefore reducing electrical resistance and allowing a high current flow.

An important consideration when examining the advantages of SAM compounds pertains to the adherence capabilities of SAM compounds to specific metal surfaces. In order to test these compounds, various metal surfaces are immersed into SAM solutions. During this process, the SAM compounds dissolved in the solvent are highly mobile and move to the metal surface and form a uniform coating on the surface. The treatment period and the concentration of the solution are important parameters when determining the coating quality (uniformity, planarity and consistent tilt angle of the coating layers). In addition, the thermal stability of the SAM coating will be a critical issue to practically use because the SAM coating will be used to improve the interface between ICA joints, which exert a high temperature process for fabrication.

This experiment analyzes the preliminary adherence and thermostability of various SAM molecules onto different metal surfaces, Au, Cu, Sn, and SnPb surfaces.

Samples Preparation

Three different self-assembled monolayers were employed, diphenyl dithiol sulfide (MPS), octadecanethiol (ODT) and mercpatoacetic acid (MAA). Their chemical structures are shown in Figure 1.

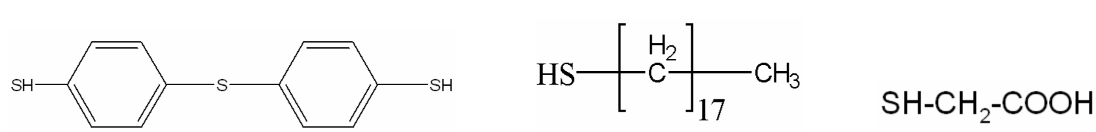


Figure 1. Chemical Structures of Self-Assembled Monolayers Used in this Study (MPS, ODT and MAA, respectively).

The Au and Cu substrates were sputtered on glass and wafer plates, and the tin and tin-lead surfaces were prepared on FR-4 board. All the surfaces were rinsed in isopropyl alcohol and allowed to dry under the hood. They were then treated by UV/ozone at 0.75 L/min for 3 minutes, placed into the SAM solution, and allowed to incubate for 30 minutes, 2 hours, 6 hours, and 24 hours under a controlled nitrogen environment. The SAM solutions were prepared at 0.1, 1, 10 mM by dissolving the SAM in ethanol. Ten grams of solution were used for each surface treated with ODT or MPS; fifteen grams of solution were used for the surfaced treated with MAA.

After the treatment time the surfaces were removed from the solution and rinsed with ethanol in order to remove excess un-adhered SAM molecules. The surfaces were then dried of excess solvent with argon.

Measurement tools and techniques used

The contact angle of deionized (DI) water was tested using a goniometer (Figure 2). The contact angle was determined by measuring the angle (θ) between the linear line on the water surface and the base line as shown in Figure 3. The thermal effect on the SAM compound was studied. The contact angle of water drops was measured after heat-treatment at 100C and 150C after testing for 30 minutes, 1 hour, and 2 hours time.

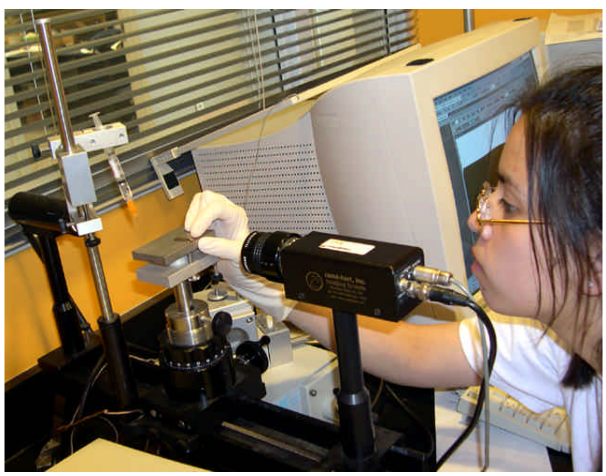


Figure 2. Goniometer for Measuring Contact Angle.

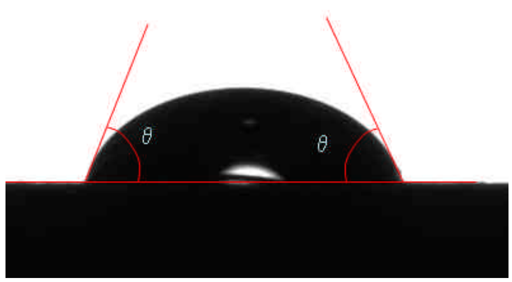
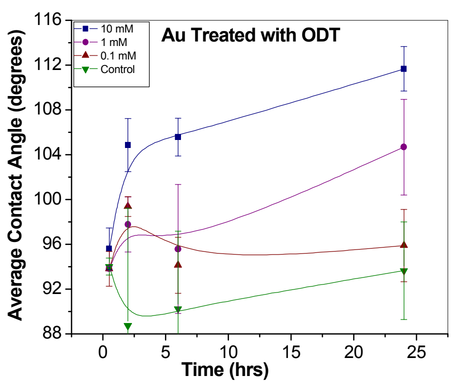


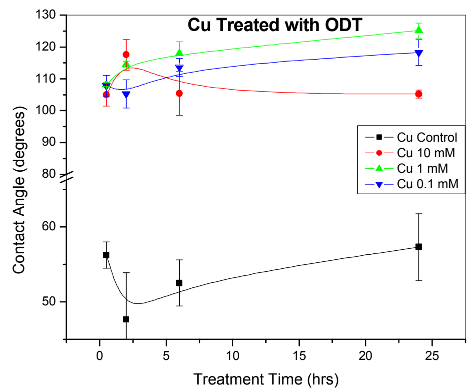
Figure 3. An example of a water drop image in the goniometer to measure contact angle on a SnPb surface.

Data

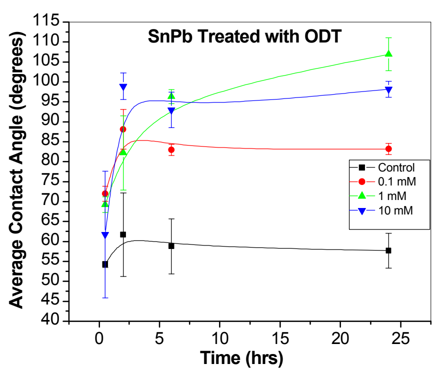
Contact Angles of ODT on Au, Cu, and SnPb



(a)



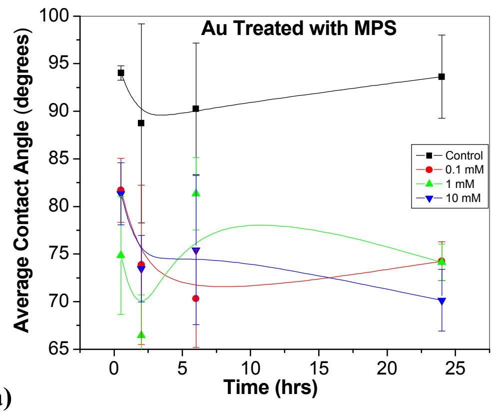
(b)



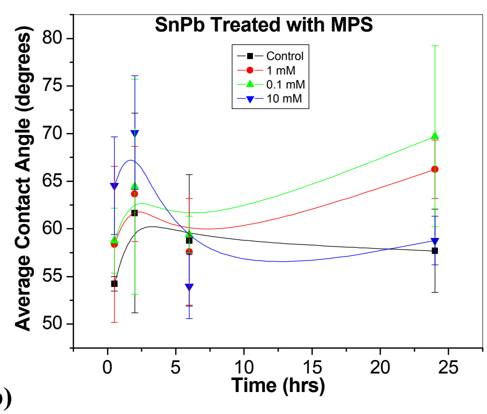
(c)

Figure 4. Contact angle values of DI water on a Au (a), Cu (b) and PbSn (c) surfaces as a function of treatment time with difference concentrations (0.1, 1 and 10 mM) of octadecanethiol.

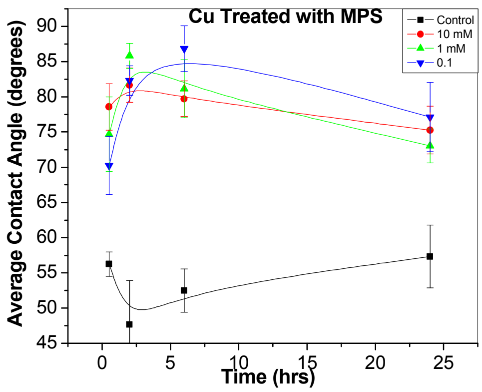
Contact Angles of MPS on Au, Cu, and SnPb



(a)



(b)



(c)

Figure 5. Contact angle values of DI water on a Au (a), PbSn (b) and Cu (c) surfaces as a function of treatment time with difference concentrations (0.1, 1 and 10 mM) of MPS.

Contact Angles of MAA on Au, Cu, Sn, and SnPb

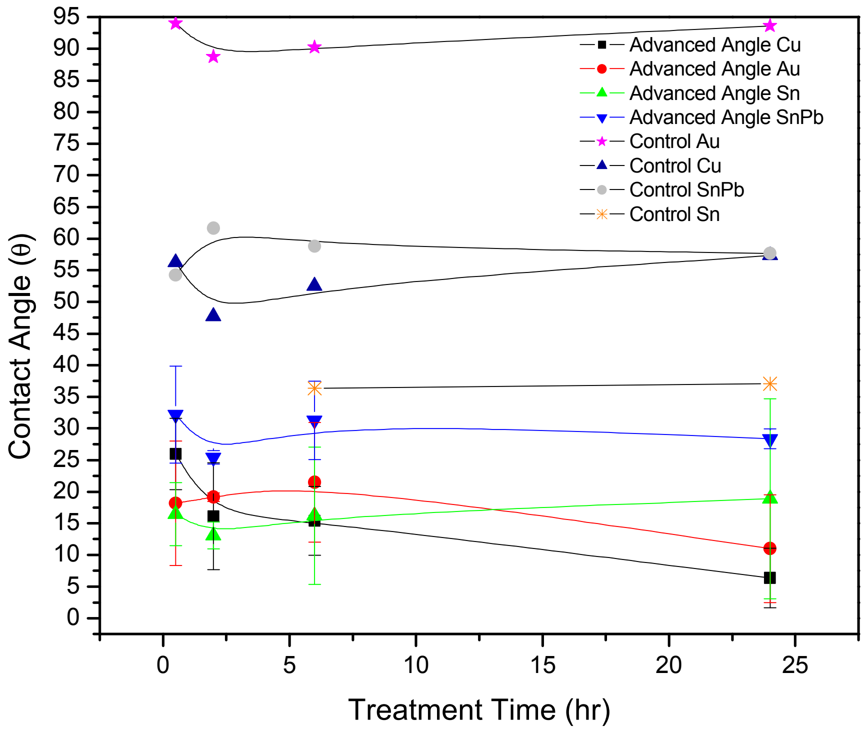
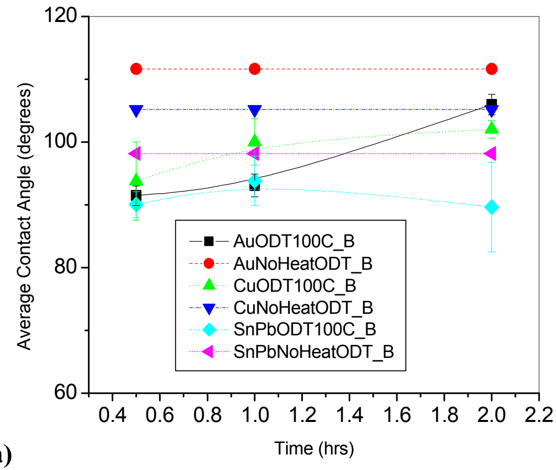
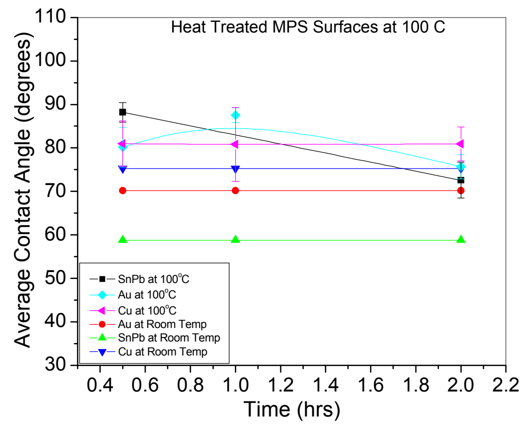


Figure 6. Demonstrates that MAA coats well. In addition, gold and copper increase in hydrophilicity with time.

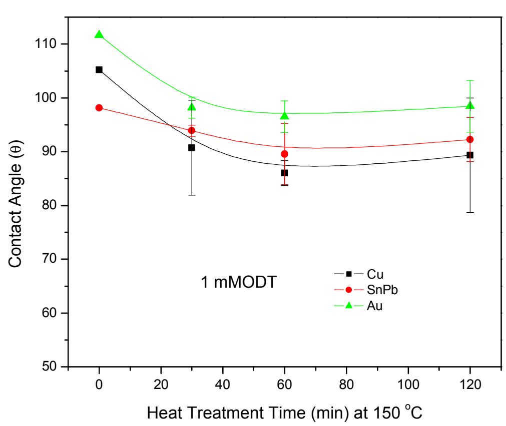
Contact Angles of Heat Treated Surfaces Coated with ODT, MPS and MMA at 100°C and 150°C



(a)



(b)



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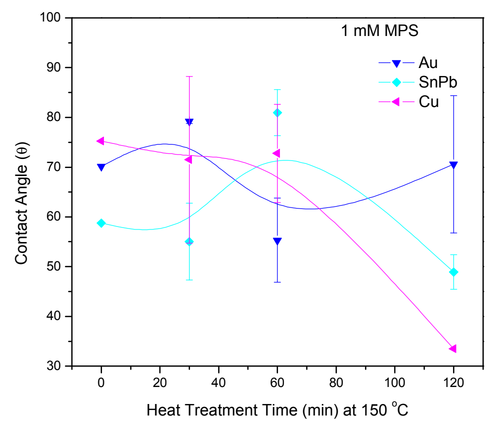
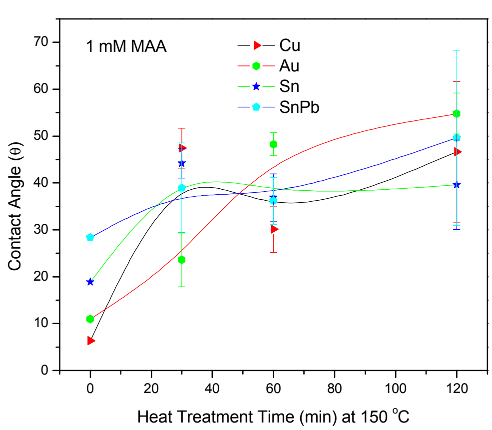


(d)



(e)

Figures 9-13. Contact angle values of DI water on various surfaces as a function of treatment time at 100°C [(a) and (b)] and 150°C [(c), (d) and (e)].

Data Analysis

Formation of SAM on Various Surfaces

The contact angles increased dramatically on ODT-coated metals, suggesting that ODT, a hydrophobic material, coats well. The contact angles of the gold surfaces increased greatly; therefore, gold surfaces coat well over long periods of time when exposed to larger concentrations of ODT, unlike those of copper. The angles increased by more than half almost immediately, and the different concentrations of ODT did not appear to create significant changes in contact angles. ODT adheres to copper quickly. The angles of the tin-lead surfaces also plateaued early, around two hours. Indeed, ODT adheres to metal surfaces evenly.

The same cannot be said for MPS. MPS is a hydrophilic material. The angles on the gold surfaces display this characteristic well; contact angles are significantly lower. However, SnPb surfaces seem relatively unaffected by the MPS, and the contact angles of copper increase dramatically at first. This phenomenon may be attributed to the structure of MPS and its different modes of alignment.

MAA, a hydrophilic material, had more definite results. The angles on the gold plated surfaces especially decreased dramatically. MAA adhered to tin and tin-lead surfaces quickly, as evidenced by the plateaus in the graphs. The angles of the gold and copper surfaces, however, continued to decrease long after the other two lines plateaued, so length of time spent in the concentration is important for these metals.

Thermal Stability of SAM

The contact angles of all metals concerned remained relatively the same when coated with ODT and heat-treated at 100°C; however, when heat-treated at 150 °C, the angles decreased slightly, suggesting that the coating of ODT sustained degradation at 150 °C. Although this degradation was slight, it implies that at a higher temperature or over a longer time period, ODT coats may be deteriorated enough to cause problems. Tin-lead surfaces heat-treated at 100°C and copper surfaces heat-treated at 150°C, both coated with MPS, showed a slight decrease in contact angle measurement, but because of the varied results from testing mentioned earlier, these results may or may not be reliable. The other angles at 100°C and 150°C, however, remained relatively the same, suggesting that MPS is thermally stable.

The angles of the metal surfaces heat-treated at 150°C showed increases. These increases show that MAA wears off slowly after exposed to extreme temperatures.

Conclusion

Goniometer testing demonstrates that SAM molecules readily adhere to metal surfaces. Because copper treated with ODT seems to be the most hydrophobic coating, it can be concluded that ODT adheres to copper the best while gold is the best metal for MAA. MPS gave mixed results perhaps because it could align in various arrangements upon the metal surfaces due to the three sulfurs in its structure. The level of SAM adherence plateaued for tin and tin-lead after 6 hours, but gold and copper showed continuing adherence up to 24 hours.

The samples hold promise when they were tested for thermostability. Nevertheless, all coatings sustained degradtion, however slight. Overall, the material that proved the strongest was ODT.

Acknowledgments

Thanks to every kind soul in Dr. C.P. Wong's group who looked kindly and not irritably (as far as I know) down upon this poor, unenlightened intern.

Special thanks go to Dr. C.P. Wong; Jack Moon for taking time out of his day to explain the entire scientific world to me even though he didn't have to; Ted Chang, a college student who I worked with; Haiying Li, for help with other projects; and Michelle Wong for her immense help, emotional support, and refusal to allow me to do anything in the lab until I was safely clothed.