Thin Films of Liquid Metal (GaIn) by Electrophoretic Deposition of Nanoparticles

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ABSTRACT

This work discusses a novel method to deposit thin films of a liquid metal, eutectic gallium-indium (EGaIn), on a copper substrate through electrophoretic deposition (EPD). The EPD procedure involves the application of an electric field in the range of 200-250 V/cm to an isopropyl alcohol solution containing a charging salt (0.108 M $MgSO_4$), and EGaIn nanoparticles (0.03 g/L). These experimental conditions were found to form a conductive liquid metal layer approximately 10-20 μm thick with a naturally forming solid oxide skin on EGaIn, adding enhanced mechanical stability and self-healing characteristics to the liquid film. Optical profilometer analysis of the thin films revealed a rough surface morphology as a result of the oxide layer. Film thickness and mass were found to be strongly connected to EGaIn concentration in solution, charging salt concentration, environmental temperature, and EPD duration. Specifically, film thickness was directly correlated to EGaIn concentration and EPD duration. This work has implications in flexible electronics and other circuitry as a novel self-healing and conductive agent to repair damaged electrical circuits.

I. Introduction

In the last few decades, flexible electronics, with their lightweight, portable, bendable, and compressible properties [1] have risen to prominence through their use in flexible displays, antenna rays, photovoltaics, transistors, radio-frequency identification RFID tags, and biomedical devices [2]. However, as a consequence of the increased mobility they offer, circuits in flexible electronics undergo increased stress and strain through bending, twisting, and compressing of repeated use. Over time, repeated bending, twisting, and stretching produces mechanical failure in the circuits in the form of microcracks [1], consequently increasing the electrical resistance. As these cracks propagate through the circuit, they eventually complete degrade the device leaving it damaged beyond repair. The goal of this work is to create a conductive thin film to effectively fill in and coat electronic circuits to repair and prevent possible damage resulting from microcrack formation and propagation.

Another area of interest in the past few years has been liquid metals. Specifically, gallium based liquid metals such as eutectic gallium (EGaIn, 75% Ga 25% In by weight) for their low toxicity, low melting point (~15.5 °C), high viscosity, high surface tension, and electrical conductivity (~29.4 x 10^{-6} Ω-cm) [3]. EGaIn's most prominent feature however, is its ability to spontaneously form a thin solid oxide skin when exposed to molecular oxygen. This oxide layer provides enhanced mechanical stability to films providing structural support, allowing even droplets to be stacked on top of each other and maintain shape under pressure.
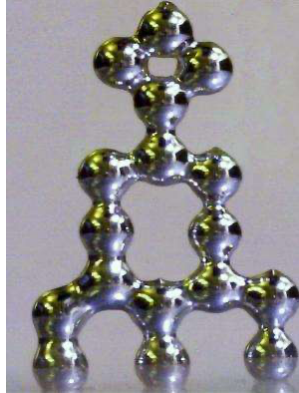
Fig 1. Stacked EGaIn Droplets[4]

Additionally, the oxide layer provides self-healing characteristics which arise from the oxide layer's ability to immediately reform when ruptured. The use of liquid metals such as EGaIn to create conductive thin films to overlay circuitry in flexible electronics has potential applications to create self-healing circuits resistant to microcrack formation and propagation. The proposed mechanism behind the self-healing capabilities of liquid metal coated circuits arise from the liquid metals ability to flow in microcracks as they form. Electrical conductivity of the circuit improves as the liquid metal fills in microcracks, improving device efficiency and functionality, effectively re-healing the circuit.

Several methods have been explored for EGaIn thin film generation including atomized spraying[2]. Unfortunately, despite atomized spraying's ease of use and reproducibility, highly selective patterns and intricate patterns can be difficult to produce. Electrophoretic deposition (EPD), on the other hand, has not been investigated despite being known for its ability to create thin films that are industrially scalable, extremely selective, and safe[5]. While the complete and specific mechanics of the EPD process are not completely understood, the general and accepted mechanism of electrophoretic deposition is simple to both use and understand. [7]

The EPD process involves the application of an electric potential across a colloidal solution of charged nanoparticles. The first step of the EPD process is to create the nanoparticle solution.

Once the nanoparticle solution is created, a charging salt is added to solution. The ions that then form from the dissociation of the charging salt in solution, bind to the nanoparticles in a solution giving them a partial charge [Fig 2].

Fig 2. Charging Salt ions bind to nanoparticle [Varanasi et. al unpublished]

The second step after the production of a nanoparticle solution, is the application of an electric potential across two electrodes in solution. Upon the application of an electric field, the partially charged particles migrate through solution and deposit onto the oppositely charged electrode [Fig 3].
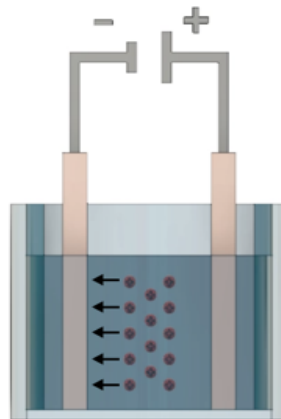

Fig 3. Schematic of Electrophoretic Deposition Method [Varanasi et. al unpublished]

While the procedure is rather straightforward, there exist multiple theories explaining the correlations and causations of each variable in electrophoretic deposition. Two of which include the Hawmaker and Avgustnik models which correlate particle deposition to electric field strength, electrophoretic mobility, surface area of the electrode, and particle concentration in solution.[8][9] Across literature, the accepted variables that influence deposition are particle size, solvent characteristics, suspension stability, deposition time, voltage, concentration of particles, and substrate characteristics.[7] The hypothesis of this experiment is that electrophoretic deposition can be applied to room temperature liquid metals, specifically EGaIn, to create thin films via the systematic variation and optimization of the variables listed above. Additionally, we hypothesize that these thin films will be able to provide self-healing characteristics to electronic circuitry by filling in microcracks and restoring conductivity.

II. EXPERIMENTAL METHODS

2.1 Alternative Deposition Methods

To create a basis of comparison for the thin films generated via electrophoretic deposition, two alternative deposition methods were attempted. These methods, despite not being used in standard industry practice, were designed to for simplicity and cost/time efficiency.

2.1.1 Physical Deposition

The first method tested, hereby referred to as physical deposition, involved the application of liquid metal to a substrate via a syringe. EGaIn was placed in a 3 mL syringe and deposited onto the copper substrate in an attempt to create a liquid metal thin film.

2.1.2 Dry Deposition

The second method tested, referred to as dry deposition involves the application of a liquid metal nanoparticle solution to a substrate. As the solvent from the nanoparticle solution evaporates, the nanoparticles deposit onto the surface of the substrate. The nanoparticle solution was synthesized via QSonica Sonicator with 40 amplitude, 5 seconds on, 2 seconds off, for a total runtime of 10 minutes and poured over a copper plate at room temperature.

2.2 Electrophoretic Deposition Procedure

2.2.1 Nanoparticle Solution Synthesis

The first step of EGaIn electrophoretic deposition is to create a liquid metal nanoparticle solution. Before the production of a nanoparticle solution, it is essential to identify the solvent, charging salt, and particle characteristics. For the solvent, as described by Powers et. al, the dielectric constant of an ideal EPD solvent must fall in the range of 12-25. Additionally, low solvent viscosities were found to correlate to increased deposition.[11] Based on these values, Isopropyl alcohol was chosen as the solvent vehicle for the electrophoretic deposition system due to its low viscosity (2.0439 cP) and its dielectric constant (19.92).[7] Additionally, as found by Heaves et. al, particle size in solution is suggested to be in the range of 1–20 μm.[10] As for the charging salt identity, an ideal charging salt contains ions with high polarizing power. Magnesium salts are commonly used in electrophoretic deposition for their high solubility and strong polarizing power.[2]

With these factors in mind, the nanoparticle solution was synthesized by sonicating 300 μL of commercially available EGaIn with 0.13 grams of $MgSO_4$, a

common charging salt, in 10 mL of isopropyl alcohol in an ice bath using a QSonica Sonicator with 40 amplitude, 5 seconds on, 2 seconds off, for a total runtime of 10 minutes. These values were optimized via a procedure of trial and error to find the conditions for electrophoretic deposition.

2.2.2. Electrophoretic Deposition

After the nanoparticle solution is created and stabilized in an ice bath around 4 °C, electrophoretic deposition was conducted in the solution. An electric potential of 100 V was applied by a high voltage power source (Trek model 609E-6 High Voltage Amplifier, Agilent 33330A 30MHz function and Arbitrary Waveform Generator Agilent 34405A 5.5 Digit) between two copper electrodes with an electrode separation of 0.5 centimeters for 30 minutes creating an electric field with a magnitude of 200 V/cm.

2.2.3 Deposit Treatment

After the optimized EPD process, a dark sticky non-conductive deposit of EGaIn nanoparticles coated with an oxide layer was observed which will be referred to as wet deposition in this work [Fig 4]. The wet deposition is expected to contain co-deposited magnesium compounds from the $MgSO_4$ charging salt in the EPD process [2]. This paste like deposit was treated with dilute aqueous hydrochloric acid during which the wet deposition was observed to form liquid metal droplets [Fig 5]. The hydrochloric acid serves the dual purpose of removing the oxide layer surrounding the nanoparticles allowing them to coagulate as well as removing co-deposited magnesium compounds [5]. After sufficient

time and removal of the hydrochloric acid, the wet deposition formed a uniform, conductive, biphasic, liquid metal thin film as the droplets coagulate into one discrete film.

Fig. 4 Wet Deposition
[Varanasi et. al unpublished]

Fig. 5 Acid Addition
[Varanasi et. al unpublished]

Fig. 6 Liquid Metal Thin Film
[Varanasi et. al unpublished]

III. RESULTS AND DISCUSSION

3.1 Comparison to Alternative Deposition Methods

3.1.1 Physical Deposition

While simplistic, Physical Deposition [Fig 7] is extremely easy to implement, providing high specificity, and low production costs. However, despite these benefits, the thin films produced are discontinuous, uneven, and highly labor intensive. Rather than consisting of a single discrete thin film, the liquid metal thin films produced were uneven and better characterized by large droplets scattered across the surface of the substrate. This method left large portions of the substrate uncovered; however, the deposit strongly adhered to the surface of the substrate remaining over extended periods of time.

Fig 7. Physical Deposition Results [Varanasi et. al unpublished]

Despite these positives, liquid metal thin film generation via physical deposition is not a viable or industrially scalable method to suit the defined purposes.

3.1.2 Dry Deposition

Dry deposition [Fig 8] produces even thin films, at a low cost and with low labor intensity; however, this method offers little to no specificity regarding placement of the deposit. While the deposit did extend over the substrate, there are portions of the substrate with significantly less deposition than others. Additionally, post-acid treatment, dry deposition was found to not return to its original liquid form. The deposit formed could be easily scratched off and formed cracks within itself. Therefore, despite its positives, dry deposition is not a viable method of liquid metal thin film generation.

Fig 8. Dry Deposition Results [Varanasi et. al unpublished]

Electrophoretic deposition, unlike physical deposition and dry deposition, provides an industrially scalable, specific, uniform and labor efficient method of liquid metal deposition.

3.2 Experimental Difficulties

Experimental difficulties in this work included non-uniform coatings, incomplete adhesion, lack of metal deposition, and deposition efficiency. These difficulties were overcome through a systematic process of altering deposition variables, of environmental temperature, EPD Duration, electric field strength, solvent identity, and nanoparticle concentration and adjusting experimental conditions.

3.3 Experimental Trials

Initial experiments were conducted without charging salt; however, it was found that the resulting deposit weakly adhered to the surface of the electrode. It was observed that the addition

of charging salt, MgSO$_4$, improved deposit adhesion, efficiency (estimated by deposit mass vs. initial EGaIn added), and uniformity. By varying MgSO$_4$ concentrations while keeping other variables constant, it was found that at 0.13g of charging salt for 10 mL isopropyl alcohol maximized deposit adhesion, efficiency, and uniformity. Before acid treatment, the wet deposition formed can be easily removed via mechanical means; however, after acid treatment, the liquid metal can properly adhere to the copper substrate without interference from the oxide and magnesium compounds. After approximately 30 minutes, EPD is no longer efficient as most nanoparticles have either been deposited or have settled out of solution. Additionally, it was observed that running EPD in an ice bath at approximately 4 °C increased deposition efficiency. We hypothesize that this increase in deposition efficiency is a result of increased stability of the solution since with increased stability, more nanoparticles remain suspended in solution and are available for deposition. It was also found that the applied electric field strength, EPD duration, and initial EGaIn concentration in the nanoparticle solution strongly influenced the EPD deposit thickness and mass.

3.3 Surface Morphology

Upon the creation of the liquid metal thin film, surface morphology characterization was conducted using an optical profilometer (Filmetrics Profilm3D). It was determined that the average thickness of the deposit was around 11.46 μm [Fig 9] with a step height between 10-20 μm [Fig 10].
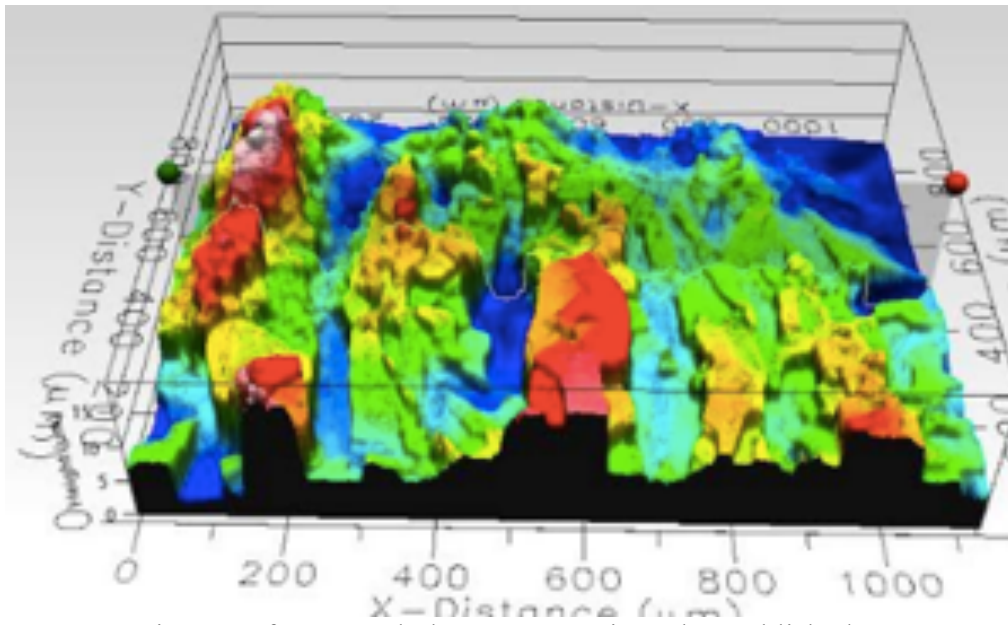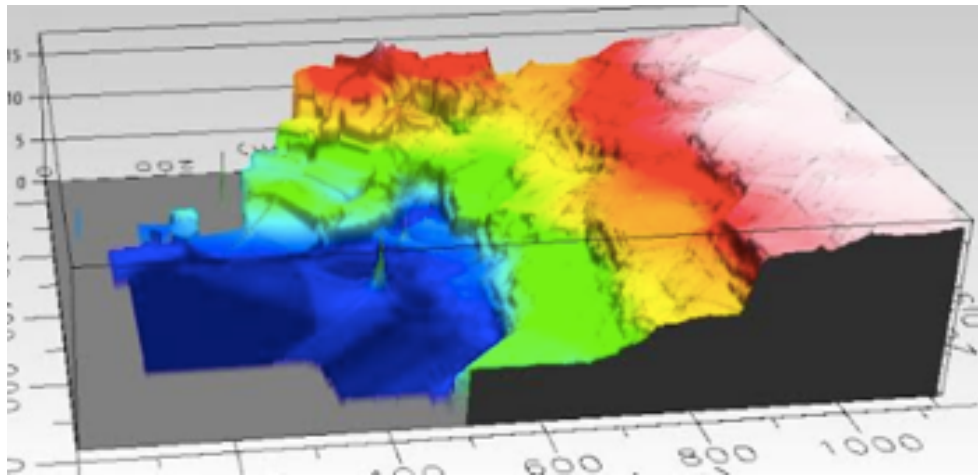
Fig 9. Surface Morphology [Varanasi et. al unpublished]

Fig 10. Step Height [Varanasi et. al unpublished]

IV. CONCLUSION

It is demonstrated that it is possible to create a conductive liquid metal thin film of eutectic gallium indium via electrophoretic deposition (EPD). Conductivity testing after the formation of a liquid metal thin film was found to be nearly identical to the conductivity pre-deposition,

demonstrating the thin films conductive properties. EPD was found to create more efficient and effective liquid metal thin films than alternative methods including physical deposition and dry deposition. Film thickness is directly correlated to EPD duration, electric field strength, and EGaIn nanoparticle concentration in the solution. Further work includes stress-conductivity testing, EPD rate testing, and EPD characterization. Stress-conductivity testing entails the measurements of conductivity of a circuit over time as the circuit undergoes stress from bending and stretching to characterize and quantify the benefits of liquid metal thin films on flexible circuits. EPD rate experiments are essential to understand the rate of electrophoretic deposition of liquid metal nanoparticles and to understand under which conditions and parameters rate is optimized. EGaIn EPD characterization entails quantifying the impact of variables on the thin film thickness and mass and understanding how each parameter can be refined to produce desired thin films.

V. ACKNOWLEDGMENTS

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