

ABSTRACT

EAKER, COLLIN BRITTAIN. Surface Characterization and Manipulation of Eutectic Gallium Indium in Aqueous Media. (Under the direction of Michael D. Dickey).

The purpose of this thesis is to better understand and control the interfacial properties of eutectic gallium indium (EGaIn) in aqueous media and under applied potential. EGaIn is a liquid metal alloy at room temperature. This characteristic of EGaIn, along with the spontaneous formation of a passivating oxide layer at its surface, allows EGaIn to be used in microfluidic devices. This compatibility with microfluidics could have an enormous impact on the growing field of flexible electronics, which relies on conductive materials that can withstand repeated strain and deformation.

Understanding the wetting characteristics is an important part of predicting how a material acts on the micro-scale. The surface tension of a material plays an increasingly large role in the behavior of liquids as the length scale shrinks. Measuring the surface tension of EGaIn is challenging due to the presence of the oxide skin and the large surface tension of the metal in the absence of the skin. As a consequence, the values in the literature span a wide range of values. Chapter 2 explains the challenges of measuring the surface tension and describes two separate techniques used to measure the surface tension of EGaIn without the skin.

Chapter 3 describes a new phenomenon that occurs when an oxidative potential is applied to EGaIn in a conductive solution. This effect causes the EGaIn to spread out in the solution, maximizing its surface area against the forces of surface tension and the physical stabilization of the oxide layer. Various capillary and electrochemical methods proved that electrocapillarity – the change in surface tension of a material due to a change in surface charge density - is not the cause of the spreading. The spreading is instead believed to be

caused by a reduction in the capacitive energy at the interface between the EGaIn and the conductive solution, both separated by the dielectric oxide layer. The spreading is compared to a well-characterized system in the literature – electrowetting-on-dielectric – and a mathematical model describes the characteristics of the spreading. At reducing potentials, electrocapillarity lowers the surface tension of the metal and can be utilized to produce EGaIn microspheres at a faster rate than has been reported previously.

Finally, Chapter 4 describes how aqueous media affect EGaIn, and details a method by which it can be protected from any undesirable effects caused by exposure to aqueous solutions.

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Surface Characterization and Manipulation of Eutectic Gallium Indium in Aqueous Media

by
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BIOGRAPHY

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Chapter 1

Overview

The goal of this thesis is to study and manipulate the surface properties of eutectic gallium indium (EGaIn), a metal alloy that remains liquid at room temperature, in different aqueous media. We describe the various techniques used to measure and characterize these properties, and discuss how they can be utilized in various applications.

Chapter 1 describes EGaIn including the unique mechanical, chemical, and electrical properties that have been utilized to create a variety of functional devices, particularly in the field of flexible electronics. We provide a review of the properties of EGaIn and how they compare to other low melting point metals. In particular, we discuss the surface properties that allow EGaIn to be molded into non-spherical shapes and remain stable.

Chapter 2 introduces the concept of surface tension, and the various methods by which it is measured. We discuss why many of these methods are unsuitable for EGaIn, the techniques that we use to measure the surface tension of EGaIn without its surface oxide layer, and compare our results to various other studies in the scientific literature.

Chapter 3 focuses on the effect of oxidative spreading in EGaIn. We utilized this oxidation to create a capacitive spreading of the EGaIn in electrochemical solutions. We describe how this spreading occurs with and without the application of an oxidative electrical potential. This chapter will also describe the electrochemical techniques used to prove that the spreading effect is not caused by electrocapillarity, as previously reported in the literature.

We present our hypothesis for the cause of the spreading and describe a mathematical model that we have developed based on a similar system. Furthermore, we discuss various potential applications for the spreading. Finally, we report on a new technique based on electrocapillarity to make microspheres from EGaIn.

Chapter 4 discusses how EGaIn reacts when exposed to various aqueous media. We will quantify how EGaIn dissolves into various solutions, and how these solutions affect the EGaIn surface and oxide layer. In this chapter, we will also introduce a new method by which the EGaIn surface can be protected from the effects caused by these solutions.

Introduction

Eutectic gallium indium (EGaIn) is a metal alloy comprised of approximately 75% gallium and 25% indium by weight. EGaIn has a melting point of 15.5°C, making it a liquid at room temperature.¹ The low viscosity, high electrical conductivity, and formation of a stabilizing oxide layer, or “oxide skin”, on the surface make EGaIn a promising material for use in a variety of applications. In this study, we attempt to quantify the physical properties of the EGaIn surface and to understand its unique chemical and electrochemical characteristics. Of particular interest is the behavior of EGaIn at the micro-scale, where an understanding of these properties can lead to control of the material in novel, flexible devices.

Gallium is a metal used primarily in electronic materials (e.g. LEDs², FETs³, and solar cells^{4,5}) as a semiconductor, primarily in the form of gallium arsenide (GaAs)⁶ and gallium nitride (GaN).^{7,8} Gallium has a melting point of 30°C⁹, but it has been known to supercool to

35°C beyond its melting point.¹⁰ In the liquid form, gallium is a shiny silver in color and resembles mercury. Much like aluminum¹¹ and silicon¹², gallium will form a passivating amorphous oxide layer at the surface when exposed to ambient oxygen.⁹ This oxide layer is thin (0.5 – 1 nm in thickness)¹⁰ and will not grow thicker over time without the application of an oxidative electrochemical potential.¹³ This oxide skin provides gallium with unique properties. It allows the gallium to be supercooled by removing nucleation sites for the crystalline gallium phase.¹⁴ Unlike most liquid metals, the oxide skin allows the gallium to be deformed into any shape without beading back up into its equilibrium position. Although its melting point is low, gallium still remains solid at room temperature. However, gallium can be combined with various metals (e.g. indium and tin) that will depress the melting point and make the resulting alloys liquid at room temperature. This study will focus primarily on EGaln, a binary alloy of 75 wt% gallium and 25 wt% indium¹⁵, which was chosen to ensure the metal stays in the liquid phase during the room temperature studies. Despite the presence of indium, the ‘skin’ is composed primarily of oxides of gallium and therefore the conclusions should apply to other alloys based on gallium.

Mercury is one of the most commonly used liquid metals, with unique properties that allow it to be utilized in a variety of fields. Historically, mercury has been used to create thermometers, barometers, and as electrodes in voltammetric experiments.^{16,17} More recently mercury has seen a rise in its use at the micro-scale, taking part in the creation of micropumps¹⁸, valves¹⁹, and optical switches.²⁰ However, mercury has two principal

disadvantages in comparison to EGaIn. Mercury is highly toxic, and exposure can take place through inhalation of its vapor or adsorption of organic forms of mercury through the skin.²¹

The primary disadvantage, however, is the fact that it does not form the oxide skin. The high surface tension of mercury (486 mN/m) and the lack of the stabilizing oxide layer cause mercury to bead up into a sphere so that it can minimize its surface area.²² EGaIn, however, will retain its shape when deformed, because the mechanical strength of the oxide skin will prevent it from returning to its equilibrium shape. This oxide skin can be removed easily, by electrochemical reduction in solution or by application of acidic ($\text{pH} < 3$) or basic ($\text{pH} > 10$) solutions.²³

Most of the electronic devices used today are built from rigid materials, such as copper, aluminum and silicon. Recent research has focused on flexible electronic devices. Flexible electronics allow for an array of applications that are not possible with conventional electronics, such as flexible sensors²⁴, displays^{25,26}, and photovoltaics.²⁷ One of the challenges of flexible electronics is finding materials that can withstand large strain and repeated deformations while still providing electrical characteristics that similar to that of bulk materials.²⁸ This can be accomplished by strategic deposition of thin conductive films or by incorporation of conductive liquids into flexible polymeric materials like polydimethylsiloxane (PDMS).²⁹ Most conductive liquids, though, are based on aqueous solutions. These solutions are not suitable for use in flexible electronics because they have a high vapor pressure, low conductivity relative to metals, and are subject to electrolysis.

Another class of conductive liquids, ionic liquids, has no vapor pressure but also has low relative conductivity and is subject to electrochemical breakdown at higher voltages.³⁰ Liquid gallium can be used with flexible electronics, but its melting point is above room temperature. Although mercury has a high enough conductivity for flexible electronics, its intrinsic surface properties prevent it from remaining stable in micro-channels. Though it can also be injected into micro-channels, the high surface-to-volume ratio of the channels, coupled with the high surface tension of the mercury, causes the mercury to spontaneously retract from the channels when the pressure is removed.¹

EGaIn has an electrical conductivity of 3.4×10^4 S/cm (about an order of magnitude lower than copper)³¹, and a viscosity of 1.99×10^{-3} Pa·s, (approximately twice that of water).³² It can be injected continuously into micro-channels and will remain stable even when no pressure is being applied. This stability is provided by the oxide skin; the pressure necessary to inject the EGaIn into the channel is governed only by the strength of the skin (critical surface yield stress ≈ 500 mN/m)¹, the surface tension of the EGaIn (which will be quantified in Chapter 2) and the size of the channel. The oxide skin can also be removed at the end of the channel, allowing EGaIn to cleanly retract from the channel. By utilizing this property of EGaIn in conjunction with soft lithography techniques³³, a variety of flexible electronic devices have been developed. Some examples of these devices include pressure responsive antennas³⁴, memory resistors³⁵, transparent and flexible pressure sensors³⁶, micro-electrodes³⁷, and stretchable conductive fibers.

Approach

The surface tension is one of the governing properties that determine the characteristics of the EGaIn in micro-channels. The pressure required to inject EGaIn into these channels scales linearly with the surface tension of the liquid. In order to determine the surface tension of EGaIn, it is necessary to remove the oxide skin. We use two different methods - drop-shape analysis and the drop weight method – to determine the surface tension of EGaIn without the oxide skin.

We discovered that EGaIn spreads out to maximize its surface area in an oxidative solution or when an electrochemical oxidative potential is applied. We will utilize electrochemical techniques to determine the cause of the spreading, and will attempt to apply this spreading phenomenon to microfluidic systems. Electrocapillarity causes a change in the surface tension of a material with an applied potential. We take advantage of this decrease of surface tension to create microspheres of EGaIn using microfluidics at a rate faster than has been reported previously. Finally, we apply various analytical techniques (atomic absorption spectroscopy, contact angle measurements) to determine the effect of aqueous solutions on EGaIn and attempt to find various ways that we can stabilize EGaIn against these effects.

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Chapter 2: Surface Tension of Eutectic Gallium Indium

Introduction

In order to use EGaIn in microfluidic systems, it is necessary to understand the physical properties that affect its behavior on sub-mm length scales. For EGaIn, this includes two surface characteristics that determine its behavior on the microscale: the mechanical strength of the oxide skin¹ and surface tension. This chapter will focus specifically on the surface tension. We define surface tension, explain why it is important to characterize the surface tension of EGaIn, and describe some of the methods by which surface tension is measured. We also detail how the surface tension of liquid metals, including EGaIn, has been measured in the scientific literature, and why the measurement is complicated by the oxide layer. Finally, we discuss how we measured the surface tension, and how our results for the surface tension of EGaIn in acid compare to those reported previously.

Surface Tension

Surface tension (or surface energy) describes the free energy change necessary to increase the surface area of a medium, and is measured in force per unit length (N/m) or energy per unit area (J/m²). The surface tension depends on the cohesive intermolecular forces of the substance; water, for instance, has a higher surface tension in air (72.8 mN/m) than cyclohexane (25 mN/m), because of hydrogen bonding. In general, higher boiling points correspond to higher surface tension values. The surface tension can also be affected by the

addition of molecules into solution called surfactants. These are typically amphiphilic molecules that decrease the interfacial tension between two dissimilar fluids. Surface tension will also decrease as the temperature increases.²

One of the consequences of working with micrometer scale systems is the huge increase in the surface area-to-volume ratio of the fluid. At small scales, surface tension can have a profound influence on the system; therefore, understanding the surface tension and wetting properties is crucial to predicting and manipulating the behavior of materials in micro-channels. The pressure inside of a material at a curved interface can be described by the Young-Laplace Equation, Equation 1.^{3,4}

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1)$$

In Equation 1, ΔP is the pressure difference across the interface, γ is the surface tension, and R_1 and R_2 are the radii of curvature. The implication of the Young-Laplace equation is that the pressure necessary to inject materials into micro-channels will increase linearly as the radius of the micro-channels decreases. It also implies that liquids with higher surface tensions will require larger applied pressures to go into the channels. This is important for high surface tension materials, such as liquid metals. Mercury, with a surface tension of approximately 486 mN/m, will not remain stable in microfluidic systems and will instead flow out of the channel and bead up into a spherical shape to minimize its surface area.² EGaIn, on the other hand, can remain stable when the forcing pressure is removed because of

the stability that the oxide skin provides in the channel.

A variety of methods have been utilized for measuring the surface tension of different liquids. With the Wilhelmy plate method, the force necessary to withdraw a rigid plate from a liquid determines the surface tension.⁵ Similarly, the Du Noüy ring method involves lifting a ring out of the liquid and measuring the force necessary to break contact with the surface.⁶ The capillary rise method uses a capillary tube and allows for an equilibrium to occur between the forces of gravity and capillarity. The surface tension can then be ascertained from the height change and contact angle between the liquid and the capillary tube.⁷ While all of these methods are useful for certain materials, they have limited applicability to EGaIn. While the oxide skin is advantageous in allowing the EGaIn to remain stable in micro-channels, it also makes determining the surface tension of EGaIn difficult. In addition to providing a physical resistance, the oxide layer also prevents EGaIn from taking an equilibrium shape that could be used to measure the surface tension. Previous attempts have been made to characterize the surface tension of gallium and its alloys.⁸ While some of these methods did not take the oxide skin into account when making the measurements⁹, others found various ways to remove it^{10,11} or prevent it from forming.¹² These involved performing the experiments in acidic solutions or in an atmosphere with a low enough oxygen concentration to avoid oxidation. Many of these reports utilized the drop-shape analysis, which will be described in detail.

We used a combination of two different techniques to determine the surface tension of EGaIn: drop-shape analysis and the drop-weight method. The drop-shape analysis method is a quick, simple, and automated way to measure the interfacial tension between two fluids. Drop-shape analysis can be applied to two different systems: a drop of fluid hanging from a needle (pendant drop) or a drop sitting on a substrate (sessile).¹³ Figure 1 shows examples of these two drops in a 1M HCl solution.

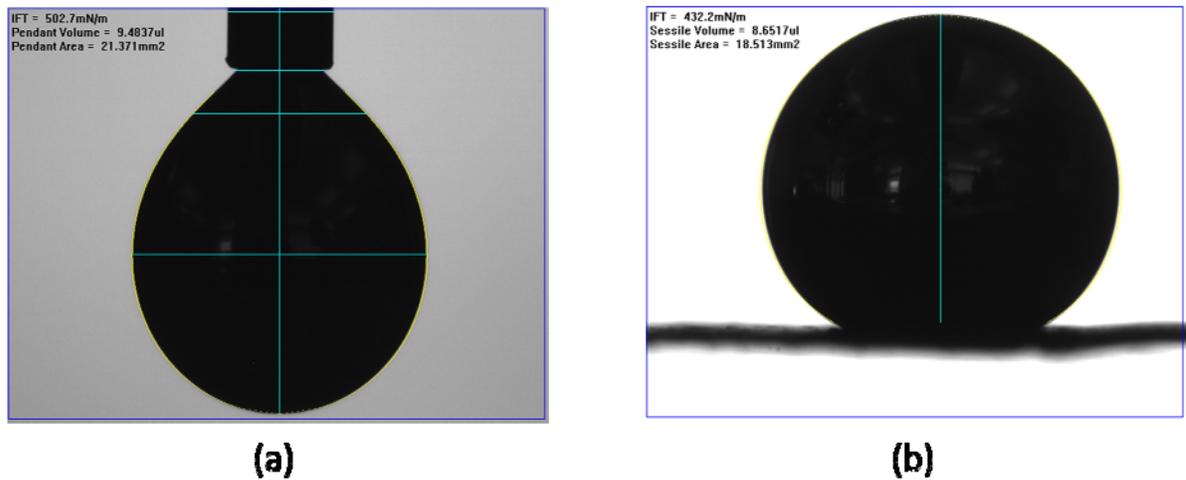


Figure 1: (a) Pendant drop and (b) Sessile drop for drop-shape analysis

The shape of the drops in Figure 1 represents a balance between gravitational forces and surface tension. Drop-shape analysis works by fitting the Laplace-Young Equation to the geometry of the drop. This equation, however, has no analytical solution. In this case, an iterative method is used to find a numerical solution to the Bashforth-Adams equation.¹⁴ Drop-shape analysis relies on two assumptions that must be satisfied in order to get an accurate measurement of the interfacial tension: the drop must be axisymmetric and distorted

by gravity. While the first condition is easy to meet for most liquids, it is more difficult for EGaIn. When the oxide skin is present, EGaIn will conform to any shape, so the drop cannot be assumed to be axisymmetric. The drop shape is a byproduct of the force balance between gravity and surface tension. If the drop is too small, the surface tension force will dominate and the drop will remain spherical. This method requires that the drop is large enough to be shaped by gravity as well as surface tension. For EGaIn, we estimate that the capillary length – the height necessary for gravity to shape the drop – is approximately 3 mm.

Although the drop-shape analysis is a simple and effective technique, problems arose with the EGaIn system. The roll-off angle of EGaIn was too small to use the sessile drop method to measure the surface tension. Consequently, rough surfaces or concave wells had to be utilized to stabilize the droplets. It is apparent in Figure 1 that the substrate is not smooth; this experimental configuration introduces uncertainty into the measurements. The pendant drop also required that the system be at equilibrium. When a pendant drop of EGaIn forms, it either pulls back into the needle by the large surface tension forces or it grows and drops down due to the forces of gravity. In spite of this, we were able to get a close approximation of the EGaIn surface tension by the pendant drop method by using it in conjunction with the drop-weight method. When a liquid is forced through the needle at low flow rates, the growing pendant drop on the end experiences both surface tension and gravitational forces. At the instant before it drops from the needle, these forces are assumed to be in equilibrium. Tate's Law is then used to correlate the two forces, as shown in Equation 2.¹⁵

In this equation, m is the mass of the drop at the instant before it falls, g is the acceleration due to gravity, and r is the capillary radius. In many drop weight experiments, the mass of the drop is measured by a mass balance after it has fallen off of the needle. However, this does not represent the true mass of the drop before it detaches, as seen in Figure 2.

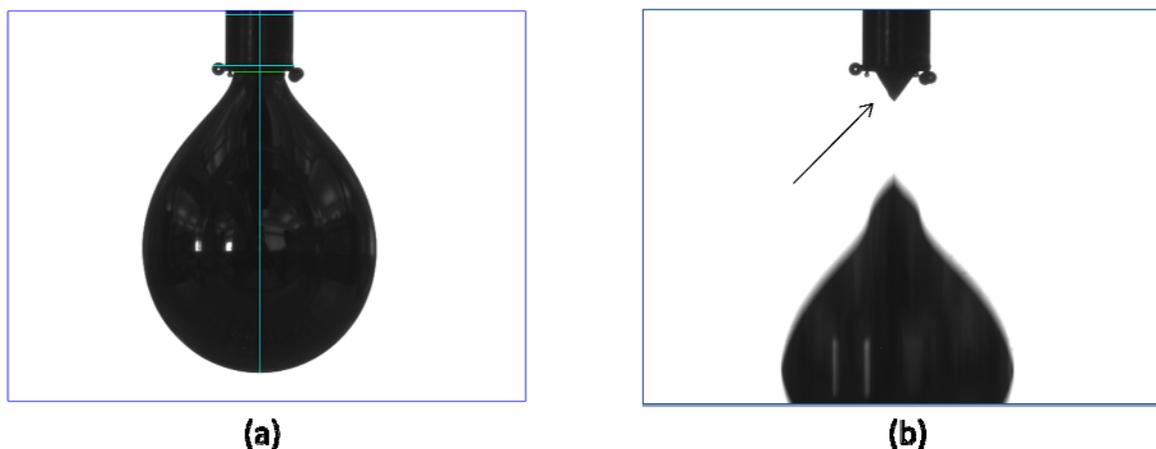


Figure 2: (a) Drop immediately before it falls. (b) Falling drop with residual liquid on tip of the dispensing needle.

When a balance measures the drop weight, a correction factor accounts for the smaller size of the drop that falls off of the needle.¹⁶ However, in our experiments, we did not measure the mass directly, but we calculated it from the volume of the drop before it fell and from the known density of EGaIn. We also took the buoyancy force into account from the density of the immersion fluid. This method of measuring the drop weight eliminated the need for any correction factors and allowed us to use Tate's Law directly to calculate the surface tension.

Experimental

A First Ten Angstroms FTA1000 goniometer made all the measurements required to calculate surface tension. We first used de-ionized water in air to calibrate the device, with a flow rate of 1 $\mu\text{L/s}$ in air. Video taken at a rate of 68.3 frames per second measured the volume of the drop the instant before it fell off of the needle. The software associated with the goniometer calculated the pendant drop surface tension and the last 10 data points before the drop fell were taken and averaged for each run. For the de-ionized water, we used a stainless steel syringe with a capillary diameter of 0.635 mm. We then used EGaIn in 1M HCl in order to remove the oxide skin. For the EGaIn system, a polytetrafluoroethylene (PTFE) needle, with a capillary diameter of 0.84 mm, was used to avoid surface corrosion in the acid. The flow rate was 0.25 $\mu\text{L/s}$ for the EGaIn.

Results

The surface tension of water with the pendant drop method was determined to be 73.74 ± 1.75 mN/m, in comparison to the literature value of 72.8 mN/m. Vibrations in the system were the cause of error in this experiment as our goniometer was not placed on an anti-vibration plate, and some shaking was seen in the droplet. The drop weight method was less accurate, with an average drop size of 17.2 μL and a surface tension value of 84.48 ± 0.52 mN/m.

The surface tension of EGaIn was determined to be 522.55 ± 0.28 mN/m from the pendant drop method, and 424.80 ± 0.49 mN/m from the drop weight method. Although others have previously quantified the surface tension of EGaIn, the experimental conditions of these studies make direct comparison of the results difficult. One study found the EGaIn surface tension to be 90 mN/m using similar equipment, but this was taken in de-oxygenated silicone oil⁹. Two previous studies found the surface tension to be approximately 440 mN/m in HCl; one of these studies was performed by pendant drop at elevated temperature (50°C)¹⁰, and another used the drop-weight method without accounting for correction factors in their equation.¹¹ In our experiments with de-ionized water, the drop-weight method was the less accurate of the two measurement techniques.

Conclusions

The presence of the oxide skin makes determining the surface tension of gallium alloys difficult. Using drop-shape analysis and the drop-weight method, we measured the surface tension of EGaIn in a solution of 1M HCl. We also measured the surface tension of water in air to within 2% of the accepted literature value to establish confidence in our techniques. We found that the surface tension of EGaIn was 522.55 ± 0.28 mN/m from the pendant drop method, and 424.80 ± 0.49 mN/m from the drop weight method. However, more work is necessary to understand the variation between the two different methods used so that the surface tension of EGaIn can be more accurately quantified. These methods may be useful to

characterize the EGaIn in a more broad range of environments including different concentrations of acid that etch the oxide skin, basic solutions, surfactants, and different temperatures. Understanding the surface tension of EGaIn under these conditions will help to understand the behavior of EGaIn at the microscale.

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Chapter 3: Capacitive spreading due to electrochemically induced oxidation of eutectic gallium indium

Introduction

This chapter describes the discovery and elucidates the mechanism of spreading of EGaIn resulting from the application of oxidative potentials to the liquid metal in electrolytic solutions. When an oxidative potential is applied to a drop of the liquid metal in solution, the drop spreads out dramatically and increase its surface area. This spreading requires overcoming the high surface tension of the metal, which acts to minimize its surface area, and the mechanical stability provided by the thin oxide layer that coats the metal. Although this spreading has been used previously in order to make a high contrast light valve, the spreading was attributed to electrocapillarity.¹ We have used electrochemical techniques to prove that electrocapillarity is not the cause of the spreading phenomenon. Instead, the spreading is believed to be caused by a capacitive effect, with the oxide skin acting as a very thin dielectric layer between the EGaIn and the surrounding solution. The energetic penalty associated with increasing interfacial energy is offset by the decrease in capacitive energy accomplished by spreading. We used an analogous system – electrowetting-on-dielectric – to mathematically characterize and model the spreading based upon our capacitance hypothesis. We note, however, that EGaIn does not spread at all using conventional electrowetting-on-dielectric, which makes the spreading described in this chapter even more remarkable. We utilized this spreading effect to form high aspect ratio fibers composed of liquid metal and to

electrochemically induce the liquid metal to fill micro-channels and, under certain conditions, to remain stable inside the channels. In addition, we used the electrocapillary effect to create microspheres of EGaIn.

Chemical Spreading

This section describes some unexpected results that we observed in aqueous solutions: placing a drop of EGaIn in a $\text{KAu}(\text{CN})_2$ gold plating solution (Technic Inc.) caused unusual spreading to occur; that is, it spread into a flat, disc shape. Gold has a higher standard reduction potential in solution, which means that gold/gallium form a redox couple. The gold ions reduce and precipitate out of solution while oxidizing the gallium.² The spreading in the $\text{KAu}(\text{CN})_2$ solution occurred gradually over the course of an hour. Figure 1 shows an example of a drop of EGaIn that was left in the solution for several days.

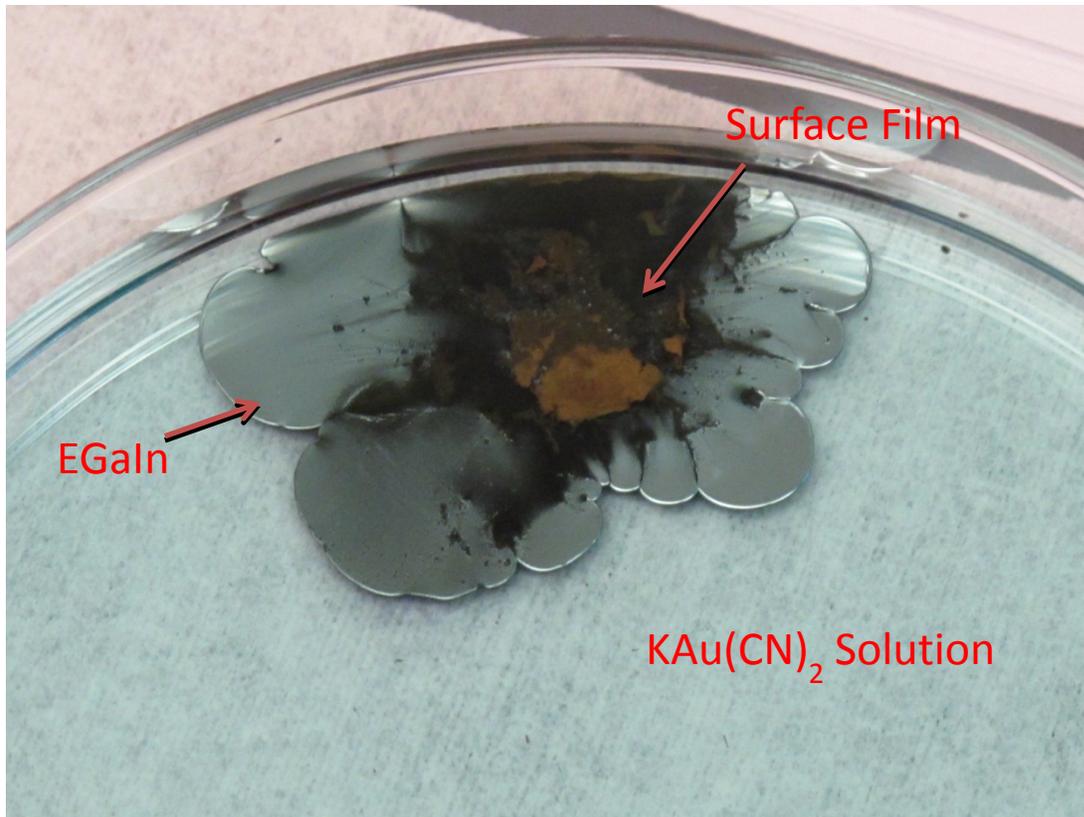


Figure 1: EGaIn spreading in $\text{KAu}(\text{CN})_2$ solution. The container is 10 cm in diameter.

Based on the color, there appeared to be two different regions on the surface of the EGaIn. One area was a shiny silver color, while another had a dark film on the surface. We used Energy Dispersive Spectroscopy (EDS) to characterize the chemical difference between the surface film and the silver portions of the EGaIn. EDS results revealed that the silver portions were gallium and indium with trace amounts of oxygen. The surface film was comprised of approximately 20 wt% oxygen, indicating that the oxide skin had grown thicker in these areas. Additionally, clusters of gold were found on the surface film. These results suggest that the oxide skin is present in the shiny areas.

In addition to using the gold plating solution, we tried other metal salts to test if spreading would occur. For example, we used CuCl_2 , which is used as a catalyst³ and as an etchant for printed circuit boards.⁴ Copper also has a higher standard reduction potential than EGaIn, which means that the copper should deposit onto the surface of the oxidizing EGaIn surface. A 1M solution of the CuCl_2 caused spreading to occur in a matter of seconds. We report these observations here to provide the motivation to study the oxidative spreading described in this chapter. We also include it in this chapter because it demonstrates some unexpected behavior of the mechanical stability of EGaIn in aqueous salt environments. Finally, the oxidation of the metal via redox chemistry (c.f., Figure 1) causes spreading in a manner that is similar to the spreading induced by applying an oxidative potential, which is consistent with our interpretation of the importance of oxidation for spreading.

EGaIn Spreading

When an electrode applies an oxidative potential to a drop of EGaIn in a conductive aqueous solution relative to a counter-electrode in the solution, the drop flattens out against the substrate that supports the drop, as seen in Figure 2. In this example, a stainless steel syringe serves as the anode, and a copper wire as the cathode in a 1M NaOH solution. Notably, a thread of EGaIn provides an electrical connection between the spread droplet and the anode. When this thread breaks, the EGaIn beads back up into its equilibrium shape due to etching of the oxide layer.

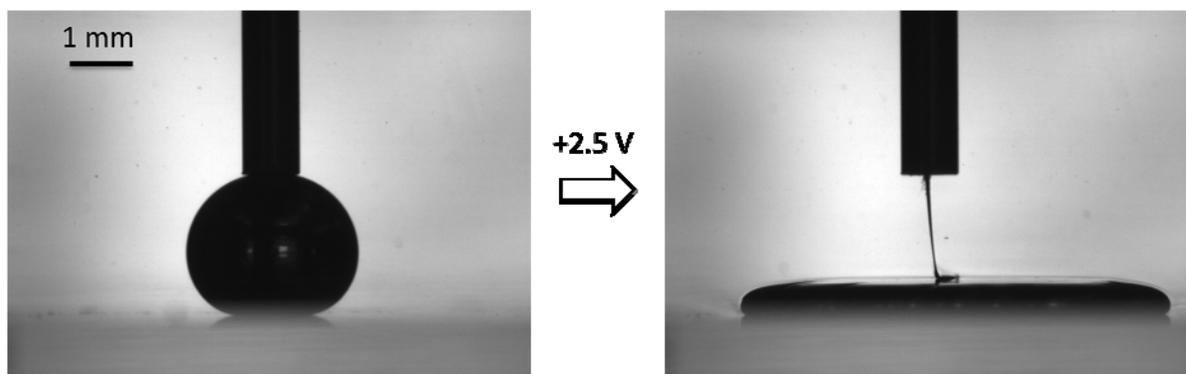


Figure 2: An EGaln drop in a 1M NaOH solution assumes a spherical shape (left) due to the large surface tension of the metal. Upon application of a 2.5 volt oxidative bias (right), the droplet spreads. Images taken with FTA1000 goniometer.

One of the most unusual aspects of the spreading is that it does not occur with the application of a reductive potential and the contact angle does not change during spreading. Reductive potentials remove the oxide skin and cause the EGaln to bead up into a sphere. To understand the cause of the spreading, we first tested the surface and solution conditions that allowed the spreading to occur. Based on our observations, and the scientific literature, we established three possible causes for the spreading phenomenon: oxidative stresses, electrocapillarity, and capacitance. In the oxidative stress scenario, we hypothesized that large oxidative potentials could drive ions through the skin (so called “anodization”, which is used to increase the thickness of oxide on aluminum and other metals) and cause the oxide volume to increase. In this case, the oxide can either get thicker or can expand laterally and create shear stresses on the surface. This hypothesis came from the fact that only oxidative potentials allowed the spreading to occur. Electrocapillarity is the reduction of surface tension due to a change in the charge density on the surface and has been used

previously to get mercury to spread, albeit not as dramatically as that shown in Figure 2. We sought to determine if this was sufficient to cause the spreading on the surface. With the capacitance model, we theorized that the oxide layer serves as a thin dielectric that separates charges in the solution from charges in the metal. EGaIn could spread to maximize surface area and thereby lower capacitive energy. We tested a variety of different parameters to determine their effect on the spreading. It should be noted that the purpose of these tests was not to quantify the spreading, but rather to determine conditions where the spreading does or does not occur at 5 volts. We first tested the characteristics of the solutions in which we could get EGaIn to spread. The pH value did not affect the spreading, as the EGaIn flattened out in solutions of 1N HCl and 1N NaOH. At these extreme pH values, the EGaIn beads back up to its equilibrium spherical shape when the oxidative potentials cease to be applied. This result is expected since gallium oxide is amphoteric and both strong acid ($\text{pH} < 3$) and base ($\text{pH} > 10$) remove the skin. When the pH is closer to neutral values, as in aqueous salt solutions, the metal also spreads, but maintains its shape when the potential is removed, due to the presence of an oxidized skin.⁵ From both visual inspection and physical perturbation, we found the skin to be present in all spreading experiments. We also considered the type and size of anions. Spreading occurred with every salt solution we tried, including sodium fluoride, sodium chloride, HCl, and NaOH at concentrations of 0.01M, 0.1M, and 1M. We observed spreading in PY₁₄TFSI, an ionic liquid. To determine if the anions needed to penetrate the oxide for spreading to occur, we used two solutions with comparatively larger anions compared to the simple salts: sodium dodecyl sulfate (SDS), a surfactant with a

sulfate group attached to a 12-carbon chain; and poly-acrylic acid (PAA) an acrylic acid polymer with negative charges along the molecule. Spreading occurred in both solutions, though the spreading was limited in SDS because of its low solubility in water. The spreading in polyelectrolyte (PAA) suggests that oxidative stress may not be the primary factor driving the spreading process. Although spreading occurred regardless of ion type, solutions with lower concentrations required higher voltages for spreading. For instance, in NaOH, 1M solutions required 2-2.5 volts, 0.1M solutions required approximately 4 volts, and 0.01M solutions required 10+ volts.

The temperature of the solution played a role in the spreading, but only in acidic or basic solutions. We tested EGaIn drops in three different solutions: 1M HCl, 1M NaOH, and 1M NaF at 70°C. In HCl and NaOH, the spreading did not occur at any potential. In the 1M NaF, the spreading effect was not diminished at all by the change in temperature. The difference between these experiments was the presence of the oxide skin; in acid and base, the oxide skin was not present on the surface, because the elevated temperatures accelerated the rate of dissolution of the oxide into solution before it could form on the surface. In the NaF solution, the solubility of the oxide skin was not drastically increased, so the spreading was not hindered. This indicated that the oxide skin was a necessity for spreading to take place.

In addition to determining the role that the solution played on the spreading, we also sought to find out if the substrate on which the drop was sitting was a requisite for spreading. We speculated that the positively charged EGaIn droplet might be attracted to negative charges

on the surface. We found that the spreading was substrate agnostic, with spreading taking place on hydrophilic borosilicate glass and on hydrophobic polytetrafluoroethylene (PTFE), or Teflon.⁶ We also observed spreading on two positively charged substrates. In one case, spreading occurred on glass treated with an ammonium-terminated methoxysilane, designed to adhere to the surface with a permanent positive charge.⁷ In a separate experiment, the substrate itself was used as an electrode; a glass slide coated by atomic layer deposition with a 50 nm tungsten film served as an electrode (W is one of the few metals that does not alloy with gallium). An EGaIn drop placed on the slide, inside of a reservoir of 1N NaOH, spread when applying a positive potential to the tungsten. In this experiment, the W and the EGaIn are presumably at the same potential, although the experiment is somewhat complicated by the existence of an oxide layer on the W. Regardless, these observations – coupled with the fact that the contact angle of the EGaIn did not change with spreading – indicated that the spreading was not a result of conventional wetting phenomena.

Though an oxidative voltage was necessary to cause the spreading in all cases, there were several pieces of evidence to indicate that mechanical stresses caused by the oxidation itself did not play a role in the spreading. In fact, most evidence indicates that the thickening oxide skin was a hindrance to the spreading phenomenon. When the EGaIn drops were on a substrate in the 1M NaOH, the spreading continued as the voltage increased. In 0.1M NaOH, where the oxide skin could not be removed as quickly, a point was reached at which the a film developed on the EGaIn and the surface appeared rough. After this point, no further spreading occurred, as shown in Figure 3.

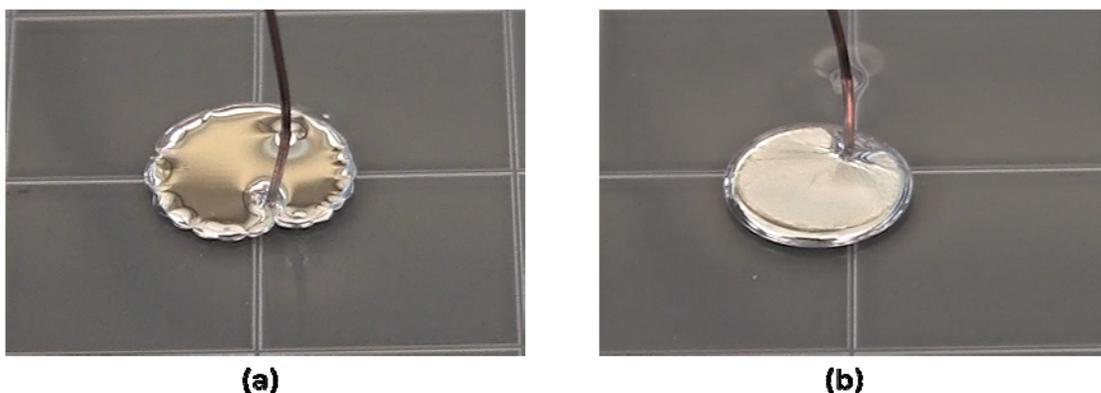


Figure 3: EGaln spreading at 4 volts in (a) 1M NaOH and (b) 0.1M NaOH. A reflection image of the copper electrode off of the EGaln surface is apparent in (a), while a rough oxide layer covers the EGaln in (b).

When it was determined that the oxide skin itself was not physically causing the spreading, but was necessary for spreading to occur, we sought similar systems in the literature to explain the spreading behavior.

Electrocapillarity

First described in 1875 with mercury, electrocapillarity describes the reduction in the surface tension of a fluid caused by a change in charge density on the surface.⁸ One of the most well-known examples of the electrocapillary effect is the “mercury beating heart”, in which a drop of mercury can be made to oscillate in solution by a competing redox reactions occurring at the surface that cause the drop to oscillate between a state of high and low surface tension.⁹ This change in charge density can also be brought on by the application of either an oxidative or a reductive potential to the metal, thereby allowing this voltage change to alter the shape of the drop based on the corresponding surface tension. When surface tension is plotted

against applied potential, the result is an electrocapillary curve. The apex of the electrocapillary curve represents the highest possible surface tension of the fluid. The potential at which this occurs is called the point of zero charge, and it is this lack of charge at the metal/solution interface that causes the high surface tension. The Gibbs-Lippmann equation predicts that from this point, any potential change – positive or negative – will cause a parabolic reduction in the surface tension.¹⁰ Previous studies have measured the electrocapillary curve of pure liquid gallium at different pH values and with a variety of cations and anions.¹¹ It was determined that the point of zero charge for pure gallium is approximately -1 volt vs. the Normal Calomel Electrode (NCE), with this potential corresponding to the re-orientation of water dipoles in the solution.¹²

We utilized a chronoamperometric method to develop an electrocapillary curve for EGaIn. Chronoamperometry is an electrochemical technique that steps a working electrode up or down to an oxidative or reductive potential. A potentiostat holds the voltage of the working electrode constant relative to a reference electrode and measures the current response of the system over time. In our case, the working electrode was the droplet of EGaIn that emerged from a polymer tubing while pumping the metal. This experiment is similar to a classic electroanalytical technique known as voltammetry at a dropping mercury electrode, or polarography. This method involves feeding a mercury drop through a small capillary until its weight can no longer be supported by surface tension and the drop falls off of the capillary. The mercury drop serves as an electrode with a variable surface area for electrochemical reactions.¹³ Although galinstan, a gallium alloy comprised of 67.5 wt%

gallium, 22.5 wt% indium, and 10% tin, has found use in electrochemical experiments¹⁴, gallium is typically avoided in electrochemistry because of its tendency to form a surface oxide.¹⁵ The presence of the oxide skin interferes with current measurement, making mercury the preferred electrode material among liquid metals.

In order to determine the surface tension through this chronoamperometry method, we used a technique similar to polarography to measure the time it took for each individual drop to fall from the capillary. By setting a constant flow rate, we could use Equation 1, a rearranged version of Tate's Law (introduced in Chapter 2), to estimate the total surface tension at each individual potential:

$$\gamma = \frac{\rho \dot{Q} t_d g}{2\pi r} \quad (1)$$

In this equation \dot{Q} represents the volumetric flow rate of EGaIn and t_d represents the average lifetime of a drop before it falls due to gravity. The chronoamperogram provided a measure of the drop time. As the surface area of the drop grew with time, the current increased as well¹⁶. Once the drop fell off of the capillary tube, there was an abrupt decrease in the current, as shown in Figure 4.

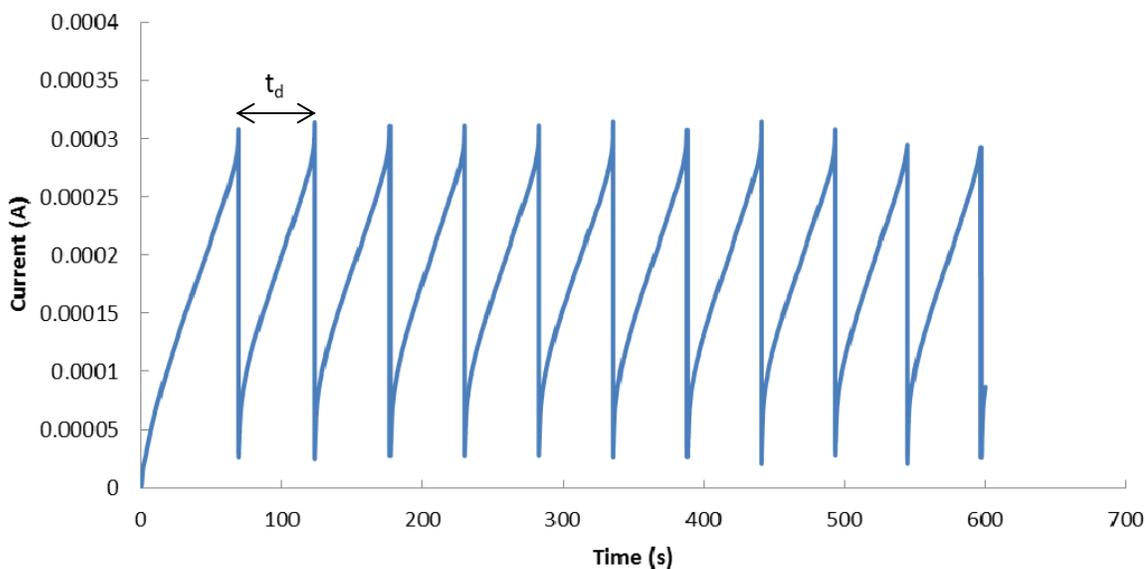


Figure 4: Chronoamperogram at -1 volt vs. Ag/AgCl, in 10 mM NaOH solution. The difference in time between two sequential events corresponds to the drop time (t_d) of the EGaIn at that potential, and each of these drop times were taken and averaged.

An electrochemical cell used EGaIn as the working electrode, a platinum wire acting as the counter-electrode, Ag/AgCl as the reference electrode, and 10 mM NaOH as the solution. At higher concentrations of 1M NaOH, the EGaIn began forming “wires” at the oxidative potentials, preventing the drop times from being measured accurately. The solution was purged with nitrogen for 1 h before experiments began, and nitrogen flowed continually through the cell to prevent dissolved oxygen from reacting with the EGaIn drops. Visual inspection confirmed that no oxide layer formed on the drops without an applied bias (although the oxide skin is very thin and likely undetectable by the naked eye, the interface becomes less ‘liquid-like’ in the presence of the skin). We used a flow rate of 1 mL/hr for

each run, and varied the applied potential from -2 to 2 volts vs. Ag/AgCl, in increments of 0.2 volts. The inner diameter of the capillary tubing was 0.51 mm. Each run lasted for 10-15 minutes, with data being gathered every .05 seconds.

Electrocapillarity Results

Figure 5 is the electrocapillary curve.

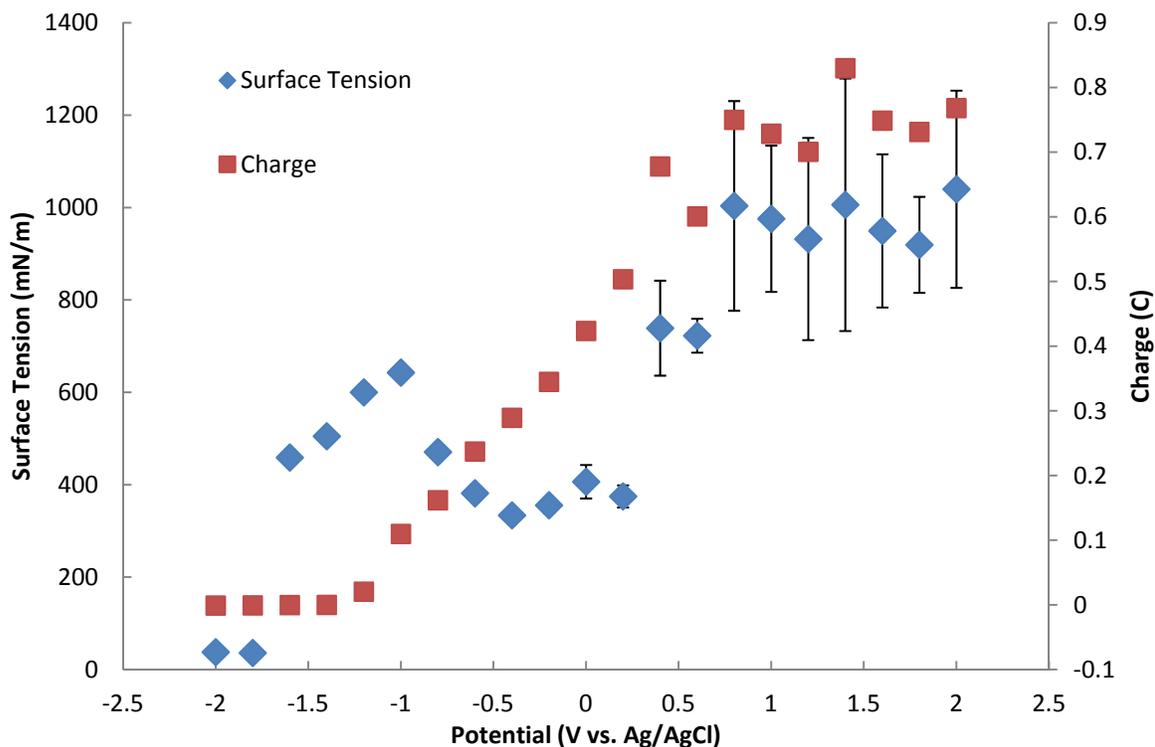


Figure 5: Electrocapillary curve for EGaIn in 10 mM NaOH solution.

The total charge that passed through the EGaIn drops on each experiment was calculated by integrating the current over the lifetime of each drop using a trapezoidal approximation.

These data show the surface tension of EGaIn at its smallest value (≈ 40 mN/m) at the most negative potentials, when no oxide skin is being formed and the drop has a large negative charge density on the surface. As the potential is pushed to more positive values, the surface tension begins to rise and the drops falling from the capillary tube get larger. At approximately -1 volt vs. Ag/AgCl, the drop achieves a maximum surface tension and begins to decline at more positive voltages. The calculated charge values confirm that the potential of zero charge is between -1 and -1.2 volts, indicating that the electrocapillary curve is in close agreement with the literature values.

Instead of continuing to decrease to a smaller surface tension, the curve flattens out at approximately -0.4 volts and ultimately began to increase, leveling off to a near constant value at around 1 volt. This value is the potential at which oxidation began to occur in the system. The oxidation is implied by the current-time data, where the rising current begins to fluctuate instead of producing a smooth curve. This fluctuation becomes more pronounced at more oxidative potentials, as shown in Figure 6.

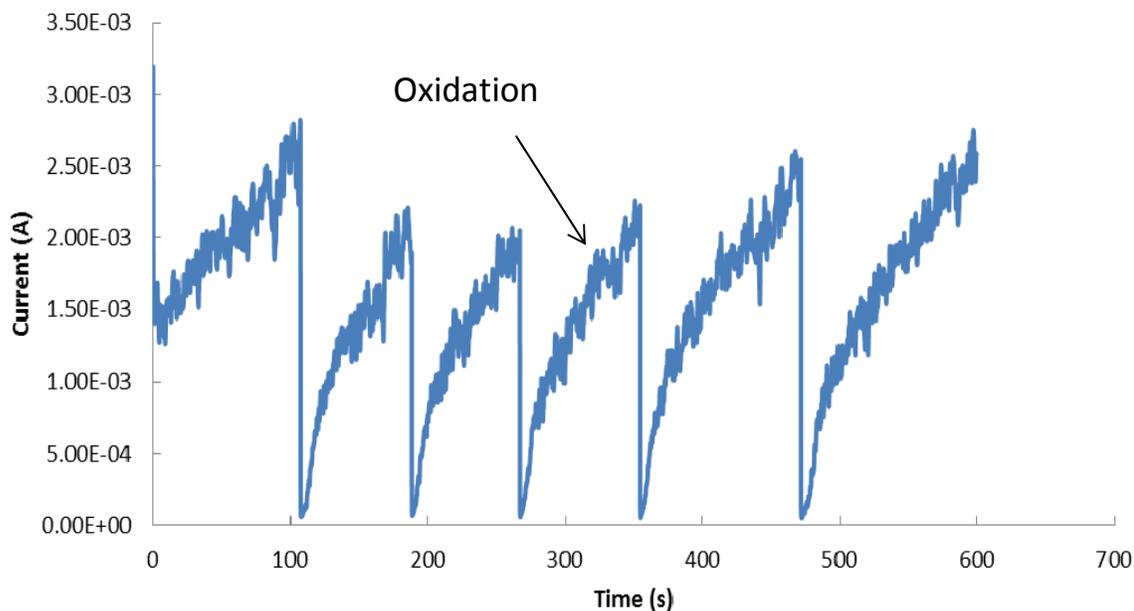


Figure 6: Current versus time of extruded droplets at 1 volt vs. Ag/AgCl. The noise in the data is believed to be due to effects arising from the oxide skin.

These fluctuations occur because the drop continually breaks the oxide skin as it is growing, and areas of newly exposed EGaIn are then oxidized as they make contact with the solution. As these areas are oxidized, spikes can be seen in the current. The oxide skin provides mechanical stabilization to the drops, allowing them to grow to a mass larger than would be allowed by surface tension forces alone. This makes the determination of the surface tension at these potentials impossible, as discussed in Chapter 2. The data correspondingly get noisier, as seen in the error bars in Figure 6.

The electrocapillary curve shows clearly that the spreading effect on the oxide skin is not due to a decrease in the surface tension caused by electrocapillarity. The lowest surface tensions

are seen at the most reductive potentials, where we observe no spreading behavior (later in this chapter, we show that the lowered surface tension can be used to produce microdroplets). At oxidative potentials, the oxide skin gives physical support to the EGaIn, provided the solution concentration and voltage are below a certain value. These results – along with the oxide stabilization of the skin – strongly indicated the spreading was a result of capacitance.

Electrowetting-on-dielectric

Electrocapillarity offers a simple method to change the interfacial tension of liquids and thereby change the contact angle on a substrate. Aqueous liquids, however, undergo electrolysis at potentials exceeding a few hundred millivolts. This obstacle may be overcome by placing a thin dielectric layer between the aqueous solution and the conducting electrode.¹⁷ This technique is called electrowetting-on-dielectric (EWOD) and Figure 7 depicts the general setup for EWOD.

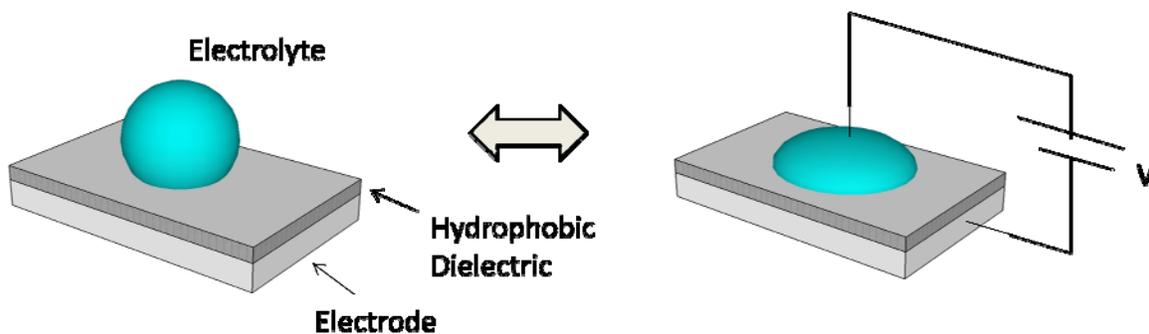


Figure 7: Conventional electrowetting-on-dielectric with an aqueous solution in air

In this setup, the dielectric layer sits between a conductive liquid and a solid electrode. The conductive liquid resides in a non-conductive fluid that can be either a vapor or a liquid. Applying a voltage between the conductive liquid and the electrode creates a charge difference on the surface causes the liquid to increase its surface area against the substrate and the contact angle to decrease. Upon removal of the voltage, surface tension forces cause the liquid to bead back up into its equilibrium shape. When working with an aqueous solution, the dielectric layer is typically coated with a hydrophobic layer to increase the difference in contact angle between the two switching states.¹⁸

EWOD has been applied to a wide variety of different systems. It has been used to transport liquids across closed surfaces¹⁹ and through micro-channels.²⁰ This micro-pumping by electrowetting shows great promise for lab-on-a-chip applications, as there are no moving parts and much higher velocities can be achieved than with other electrical transport methods²¹. Electrowetting has been successfully utilized in a number of display technologies: aqueous solutions have been used as focal lenses²²; dark oils have been used as light switches²³; and colored oils have been used to create color displays.²⁴ It has also been successfully demonstrated in a number of different liquid metal systems. Contact angle switching via electrowetting has been applied to both liquid mercury^{25,26} and to galinstan.²⁷ However, in spite of its myriad applications, EWOD remains impractical for use with EGaIn. The system is governed by the electrowetting equation, Equation 2:

$$\cos(\theta) = \cos(\theta_Y) - \frac{\epsilon\epsilon_0 V^2}{2d\gamma_{LV}} \quad (2)$$

In Equation 2, θ is the contact angle, θ_Y is the contact angle without an applied bias, ϵ is the dielectric constant, ϵ_0 is the permittivity of free space, V is the voltage, d is the dielectric layer thickness, and γ_{LV} is the surface tension between the liquid and vapor phase.²⁸ The second term on the right-hand side of the electrowetting equation represents a balance between the capacitance per unit area and the surface tension of the liquid. This means that lower surface tension liquids require lower voltages to change contact angles and that larger voltages result in smaller contact angles. It also means that the thickness of the dielectric layer should be reduced as much as possible to decrease the voltage necessary to induce spreading. However, the dielectric thickness represents a trade-off: if the dielectric layer is too thin, then it will be susceptible to dielectric breakdown at larger voltages; if it is too thick, then the required voltages will go up. Because of this limitation, most dielectric layers are on the order of hundreds of nanometers to microns thick and the voltages used to induce spreading are on the order of tens to hundreds of volts (in contrast, the spreading in Figure 2 requires a few volts). Figure 8 shows a plot of the theoretical values for the contact angle change of EGaIn in an idealized system. For comparison, the theoretical contact angle change of an aqueous solution is also shown. Because the surface tension of EGaIn is 1-2 orders of magnitude higher than that of most aqueous solutions used in EWOD, there is minimal change in contact angle even at large voltages.

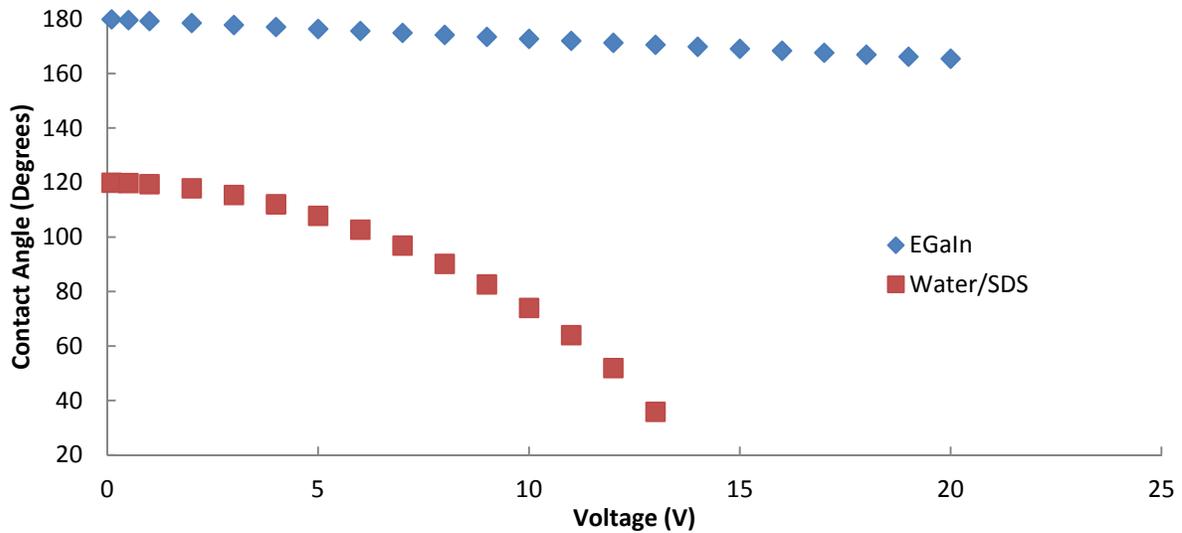


Figure 8: Prediction of the contact angle as a function of voltage using the electrowetting equation. EGaIn in air and water/1 wt% SDS in dodecane on a 300 nm Parylene C substrate.

Though the water solution will actually reach a saturation contact angle²⁹, even in an idealized system, 20 volts will only allow for a contact angle change of 15° with the EGaIn. In reality, however, several factors will prevent this change from taking place. The oxide skin on the EGaIn provides mechanical stability, and cannot be present when the voltage is applied. Although acidic or basic solutions can remove the skin, they can also conduct charge and would interfere with EGaIn spreading by their increased affinity for the oppositely charged surface. In order to stop the oxide skin from forming, the experiment must be performed in an atmosphere with oxygen concentrations below 1 ppm, which is impractical for most systems.

Though EWOD is not a practical system for EGaIn, we use the equations upon which it is

based to model the oxidative capacitance system. In this case, the dielectric layer is not between the liquid and the substrate, but the liquid metal and the conductive solution in which it sits. The oxide layer itself, with a thickness of approximately 1 nm, acts as the dielectric between the two.³⁰ When the EGaIn spreads out, the oxide layer can act as a “self-healing” dielectric.³¹ EWOD is based on the Gibbs free energy equation for the system, Equation 3:

$$G = \sum \gamma_i A_i - \frac{\epsilon \epsilon_0 V^2}{2d\gamma_{LV}} A_{LV} \quad (3)$$

In this equation, G is the Gibbs free energy, γ_i represents the surface tension at each interface and A_i represents the surface area at those interfaces. For the EGaIn drop on a substrate, Equation 3 becomes Equation 4:

$$G = \gamma_{SL} A_{SL} + \gamma_{LV} A_{LV} - \frac{\epsilon \epsilon_0 V^2}{2d\gamma_{LV}} A_{LV} \quad (4)$$

When the EGaIn flattens out across the surface, as in Figure 1, the area between the EGaIn-substrate surface area and EGaIn-liquid surface area is assumed to be equal because the geometry resembles a disk. Differentiating Equation 4 with respect to the area yields Equation 5:

$$\frac{dG}{dA} = \gamma_{SL} + \gamma_{LV} - \frac{\epsilon \epsilon_0 V^2}{2d\gamma_{LV}} \quad (5)$$

This equation implies that, as long as the capacitive energy is greater than the surface tension forces, the drop will continue spreading. Although this equation relies on several first order assumptions (equivalent surface areas, that the oxide thickness is not increasing with time or voltage), the order of magnitude analysis has thus far agreed with experimental evidence. Assuming a dielectric constant of 10 for gallium oxide³², a thickness of 1 nm, and a potential of 2.5 volts, the capacitance energy is approximately 280 mJ/m², a value that is on the same order of magnitude as the EGaIn surface tension (≈ 500 mJ/m²). Further studies are in progress to confirm the validity of the model.

Applications

In addition to flattening out on a substrate, oxidative potentials produce interesting behavior in other systems involving EGaIn. Sufficient flow rates through a capillary tube will allow the EGaIn to stretch out into “wires”, as opposed to beading into drops that fall off of the end of the capillary. Figure 9 highlights this phenomenon. Notably, reversing the bias to reductive potentials caused the droplets to decrease in size by several orders of magnitude. This observation is consistent with reductive potentials lowering the surface tension and underscores that the formation of fibers cannot be explained by electrocapillarity.

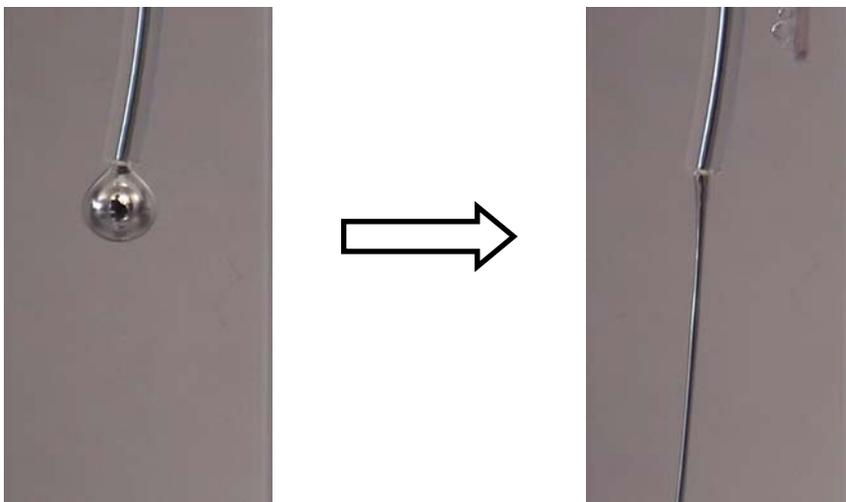


Figure 9: EGaIn pumped out of a polymer tube of 0.51 mm inner diameter at a flow rate of 20 mL/hr. The surrounding solution is 1M NaOH, with an applied bias of 5 volts.

One of the more promising results of the oxidative phenomenon comes from the behavior in micro-channels. EGaIn has been shown to have a variety of uses in micro-channels^{33,34}, and selectively filling and emptying these channels with an applied electrical bias is an improvement on the current methods of filling the channels with mechanical pressure. In order to do this, we connected an EGaIn reservoir to an electrolyte solution through a capillary tube. Applying an oxidative potential to the EGaIn caused the metal to fill the channel within seconds. Surprisingly, the meniscus of the EGaIn was concave down (Figure 10), indicating that the capillary pressure due to the curvature of metal interface opposed the direction of flow.³⁵ While the EGaIn will retract from the channel in basic or acidic solutions, neutral pH solutions allowed the EGaIn to remain in the channels once it flows. Figure 9 shows a micro-channel being filled with EGaIn in direct opposition to gravitational and

interfacial forces.

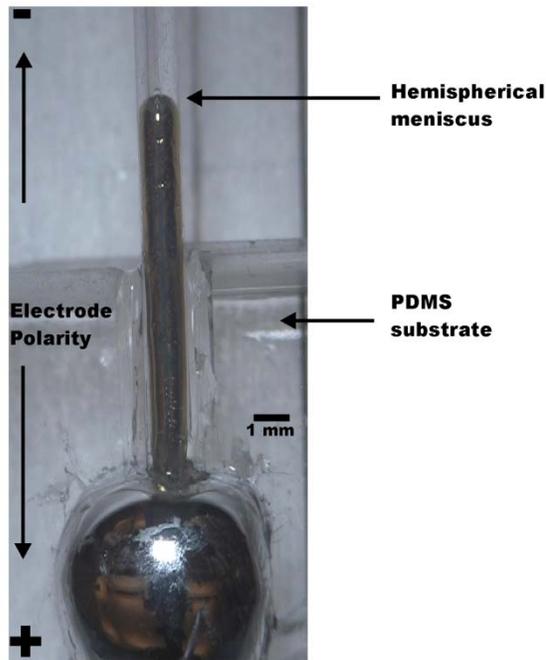


Figure 10: EGaln entering the channel due to oxidative bias. The solution is 1M NaF, with a potential of 22 volts. Image courtesy of M. Rashed Khan.

EGaln Microspheres

One potentially useful property of EGaln is its ability to form stable, monodisperse microspheres. These microspheres have the potential to be used in a wide array of devices, from self-healing circuits³⁶ to energy-harvesting systems.³⁷ Previous studies have created uniform, spherical, stable droplets of EGaln with a diameter of less than 30 μm .³⁸ However, the maximum flow rate for these drops was 1 mL/hr, and the droplet diameter was limited to the size of the micro-channels used in the experiments. In order to overcome these

limitations, we used the previously mentioned electrocapillary effect to create the EGaIn microspheres. When applying reductive potentials to EGaIn flowing out of a capillary, the size of the drops decreases due to a reduction in the surface tension. This means that gravity will pull the drop off of the capillary at a smaller volume than it would be in the absence of applied potential.^{39,40}

We injected the EGaIn at a constant rate of 20 mL/hr through a 100 μm wide x 600 μm tall PDMS channel. The end of the channel was placed downward into a variety of solutions. We used 1M NaF, oleic acid, 1 wt% PVA, and various mixtures of these solutions. The largest obstacle in creating stable microspheres was finding a solution that was both electrically conductive and that adequately stabilized the smallest drops. We varied the voltage from -1 through -50 volts with a copper counter-electrode in solution, with the larger voltages giving smaller microdroplets. The smallest stable drops were approximately 250 μm in diameter, as seen in Figure 11. These were made in a 50 wt% mixture of the PVA solution and 50 wt% mixture of oleic acid. Although smaller drops than these were seen, they merged too quickly to be measured. We suspect that smaller droplets may be possible by using a flow focusing orifice to constrict the droplets.

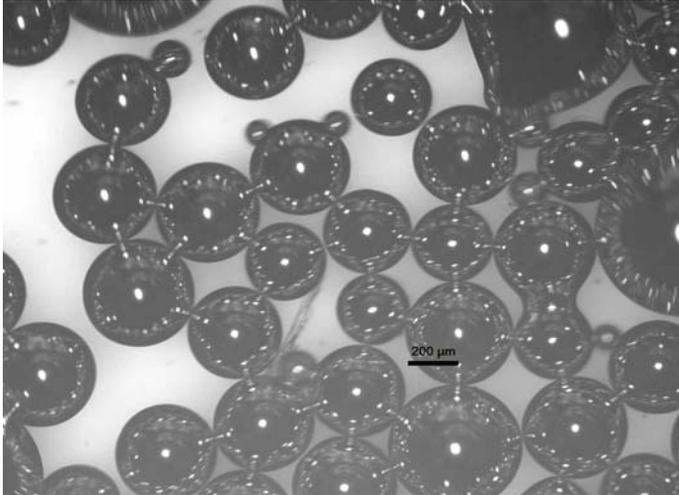


Figure 11: EGaIn microspheres from electrocapillarity

In order to create more stable drops, further studies will have to be performed to find a solution that is both electrically conductive but allows enough stability to prevent the drops from merging together.

Conclusions

By applying electrochemical techniques to the oxidative spreading of EGaIn, we have proven that the maximization of surface area of the metal is caused by a decrease in capacitive energy and not by the electrocapillary effect. Though they are similar in principal, this spreading provides several advantages over electrowetting-on-dielectric systems. It does not require a surface with a dielectric layer, uses voltages that are several orders of magnitude lower, and is not subject to dielectric breakdown. This effect is useful for getting the metal to flow into channels, to spread the metal and to form stable microfibers. Further studies will be needed to verify the details of this capacitive model; they will also be necessary to

understand the mechanism behind the behavior of EGaIn in microfluidic systems under oxidative conditions. Although electrocapillarity was not the cause of the spreading, it has proven useful as a means by which microspheres can be made at a faster rate than previously reported.

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Chapter 4: Characteristics of the oxide skin on EGaIn in aqueous media

Introduction

The goal of this chapter is to describe some preliminary results that suggest methods for altering the behavior of the metal/metal-oxide system in aqueous solutions. The surface of EGaIn alters its behavior and characteristics depending on the characteristics of the solution in which it is immersed. For example, acidic ($\text{pH} < 3$) or basic ($\text{pH} > 10$) solutions remove the oxide layer, which causes the EGaIn to bead up into a spherical equilibrium shape. In contrast, pH neutral aqueous solutions cause the skin to grow over time, which alters the mechanical and electrical properties of the liquid-skin composite.

This chapter describes the behavior of the metal in aqueous solutions and provides some preliminary results that suggest methods to stabilize and destabilize the metal. We first quantified the dissolution of the oxide skin when the EGaIn was placed in acidic or basic aqueous solutions, and when a voltage was applied to EGaIn in these solutions. We also utilized surface modification to increase the hydrophobicity of the metal and thereby stabilize it against the effects caused by prolonged exposure to aqueous media (i.e., to prevent etching of the skin by either acid or base, to stabilize micro-droplets against coalescence, and to slow down any deleterious effects of water).

EGaIn in Aqueous Media

The oxide that forms on EGaIn is an amphoteric substance that is unstable in aqueous solution when the pH is less than 3 or greater than 10.¹ Previous rheological studies have shown that the mechanical properties of the oxide skin decrease with more acidic conditions and eventually completely disappear at a pH of approximately 1.² We speculated that the removal of the skin by acid competes with the formation of the skin by oxidation and should therefore depend on whether oxygen is present or not. Thus, we performed a series of experiments in which we used atomic absorption spectroscopy to quantify the amount of dissolved gallium (and indium) in solution as a function of the chemical environment. Previous studies in the literature have quantified the dissolution of pure solid gallium in aqueous solutions, using de-ionized water and various concentrations of NaCl. These studies found that higher concentrations of NaCl caused greater dissolution over time; X-ray Photoelectron Spectroscopy (XPS) analysis also revealed that gallium oxide (Ga_2O_3) and gallium oxide monohydroxide ($\text{GaO}(\text{OH})$) formed on the surface in the presence of water.³ Our studies focus more on the importance of oxygen, acid, and other oxidative driving forces (i.e., electrochemical oxidation such as that used in Chapter 3 and redox couples). To test the behavior of EGaIn in solution, we left 100 μL drops of EGaIn in 5 mL of 1M HCl and de-ionized water in sealed vials for variable time periods and then analyzed the solutions by atomic absorption spectroscopy. This analysis allowed us to quantify the concentration of gallium and indium that dissolved into solution. Table I summarizes these results.

Table I: Atomic absorption spectroscopy results for solutions exposed to EGaIn for various time periods

Time	Solution	Ga. Conc. (mg/L)	In. Conc. (mg/L)
1 minute	1M HCl	.81	< 0.02
	DI Water	.44	< 0.02
2 Weeks	1M HCl	227	0.33
	DI Water	1.5	< .02
4 Weeks	1M HCl	628	0.075
	DI Water	2.9	< 0.02

These results suggest that the amount of dissolved gallium increases with time. It also shows the presence of acid significantly increases the dissolution of the oxidized gallium. These results suggest that the skin, which is composed of oxides of gallium forms continually and dissolves slowly into the solution; this dissolution is accelerated by the acid. The indium concentration generally remained 3 orders of magnitude lower than the gallium concentration, and was undetectable in de-ionized water.

During the spreading experiments (Chapter 3) in concentrated acid and base, we noticed that the oxide skin was never readily visible, although it had to be present due to the stabilization of structures that would be forbidden by surface tension (c.f., Figure 1 in Chapter 3). This observation suggested that the oxide skin dissolved into solution at a rate similar to the rate it

formed. To test this hypothesis, we tested whether oxidative bias increased the dissolution of gallium into solution. We applied a 10 volt oxidative potential for 1 minute to a 100 μ L drops of EGaIn in 5 mL of 1M HCl and 1M NaOH, and tested the solution with atomic absorption spectroscopy. Table II summarizes these results. Although a slight color change could be seen on the EGaIn surface when the oxidative bias was applied, the surface roughness of an oxide layer was not visually apparent.

Table II: Atomic absorption spectroscopy results for samples exposed to an oxidative bias

Solution	Ga. Conc. (mg/L)	In. Conc. (mg/L)
1M HCl	413	25
1M NaOH	372	1.98

These data indicate that both the gallium and indium can dissolve into solution at higher rates when the oxidation is driven electrochemically. Furthermore, electrochemical oxidation causes much higher concentrations of indium in solution than those without bias (Table I).

EGaIn Stabilization

Rheological tests show that in de-ionized water, the modulus of the oxide skin of EGaIn decreases by an order of magnitude likely due to the chemical transformation of the oxide to a monohydroxide or Ga_2O .³ When placed in aqueous media at near-neutral pH for extended

periods of time, EGaIn began to develop a black crust on the outside (consistent with Ga_2O). This crust represents a potential problem for using EGaIn as a conductor or soft micro-electrodes⁴ in aqueous media (for example, those used in biological systems). We sought to modify the surface to limit the contact between the EGaIn surface and the water. This goal has the additional benefit of improving the stability of the metal oxide skin in acid and base.

We first considered creating a gold film from the $\text{KAu}(\text{CN})_2$ solution, and then applying a thiol monolayer to increase the hydrophobicity of the surface^{5,6}. However, we determined that the gold was only distributed in small clusters on the EGaIn surface and it also caused the metal to change shape (Chapter 3).

Oleic acid was used initially as the immersion media in EWOD testing, but we found, to our surprise, that the oxide skin on EGaIn that had been exposed to oleic acid could not be etched away by acid or base. Oleic acid is a molecule that contains a carboxylic acid group connected to a 17-carbon chain. When placed in a 1M HCl solution, EGaIn functionalized with oleic acid retained its non-spherical shape upon repeated shaking. In contrast, pristine EGaIn beads up into a sphere immediately upon exposure to strong acid, as shown in Figure 1.



(a)



(b)

Figure 1: EGaIn exposed to 1M HCl when (a) untreated and (b) treated with oleic acid.

The EGaIn coated with oleic acid would eventually bead up to its equilibrium shape, but this process took several days. We initially believed that the carboxylic group on the molecule may have been chemically reacting with the gallium to form a monolayer with a carbon tail. In order to test this hypothesis, we purged a solution of oleic acid with N_2 for one hour. We have previously shown that purging de-ionized water with N_2 will prevent the oxide skin from forming; that is, the oxidative potential of EGaIn is not strong enough to drive the reduction of water and therefore no oxidation of the surface occurs. We injected fresh EGaIn into the de-oxygenated oleic acid to see if any the surface modification occurred. The surface did not visually appear to develop any skin, and the EGaIn retained its spherical shape when perturbed. These results suggest that no chemical reaction takes place on the surface of the metal and that the interaction of the oleic acid with EGaIn must be occurring on the oxide skin.

We utilized several methods to test how well the oleic acid protected the surface from further oxidation due to water exposure. We smeared EGaIn onto three glass slides: one was left untreated as a control; one was treated with a 1 wt% polyvinyl alcohol (PVA) solution, a solution that had previously been used to stabilize EGaIn droplets; and one was treated with oleic acid. These slides were placed into an incubator (i.e., a humid environment), kept at 37°C and 100% humidity, and left for 4 weeks. Figure 2 illustrates that no black crust was visible on the EGaIn that had been treated with oleic acid compared to the untreated and PVA-treated samples.

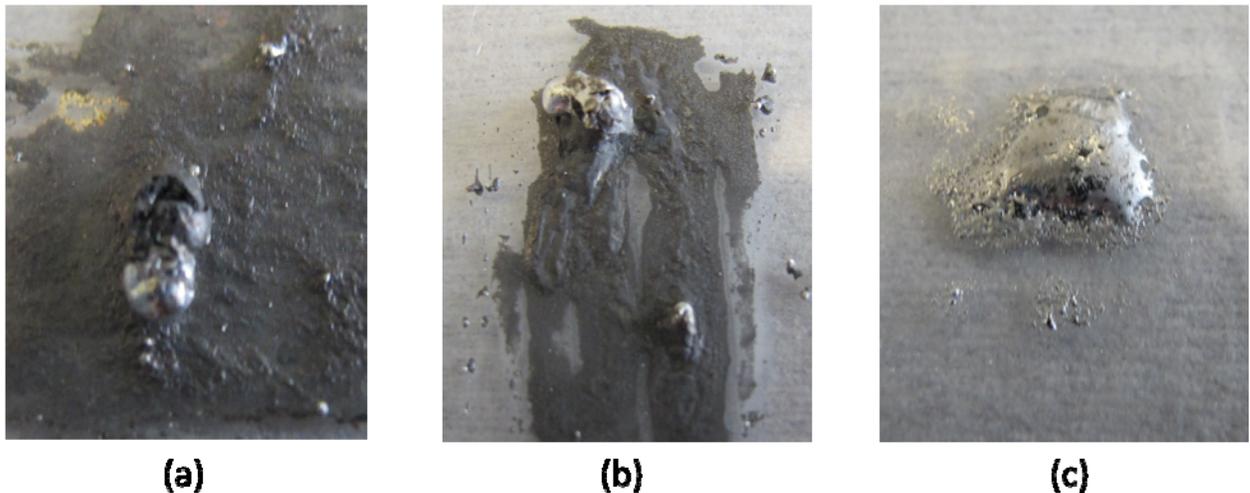


Figure 2: EGaIn left in an incubator for 4 weeks. (a) Untreated, (b) PVA treated, (c) Oleic Acid treated. Samples courtesy of Nicholas Hallfors.

To characterize the hydrophobicity of the oleic acid coating, we performed contact angle measurements. When a drop of liquid is placed on a flat surface, it will develop an equilibrium with the substrate. This equilibrium depends on the composition of the substrate,

and is described by Equation 1.⁷

$$\gamma_{SV} = \gamma_{LV} \cos(\theta) + \gamma_{SL} \quad (1)$$

In Equation 1, γ_{SV} is the surface energy between the substrate and vapor phase, γ_{LV} is the surface tension of the liquid, γ_{SL} is the surface energy between the substrate and the liquid phase, and θ is the contact angle. When the liquid phase is an aqueous solution and the vapor phase is air, larger contact angles mean that the surface is more hydrophobic.⁸ Long chains of carbon molecules can be hydrophobic on surfaces, and are often applied to glass slides by silanization.⁹

We created the substrates by applying a thin film of EGaIn to a glass substrate by way of a glass slide, in a technique similar to doctor blading.¹⁰ Although this can lead to non-uniformities, EGaIn cannot be applied evenly by spin-coating because of the unique rheological behavior. The contact angle of de-ionized water on an untreated EGaIn film was 4.85° (Figure 3), indicating that the native oxide skin forms a very hydrophilic surface. This result, however, is at odds with the literature values that place the contact angle of water on a uniform amorphous Ga₂O₃ film at 70° - 80°.¹¹

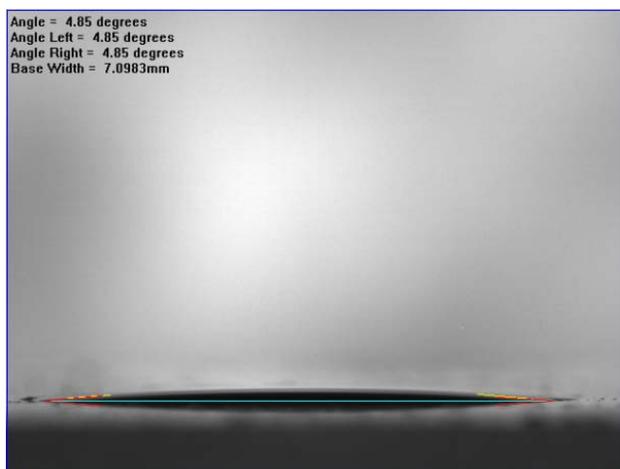


Figure 3: Contact angle of de-ionized water on EGaIn film.

After applying 3 mL of oleic acid to the surface and wiping off the excess, the average contact angle increased to $85.1^\circ \pm 9.7^\circ$, with a hysteresis of 3.2° . As a result of wiping off excess solution, the surface became rougher, as shown in Figure 4. The resulting physical heterogeneity could have affected the contact angle measurements, but nevertheless, the contact angle increases significantly after treating the surface with oleic acid.

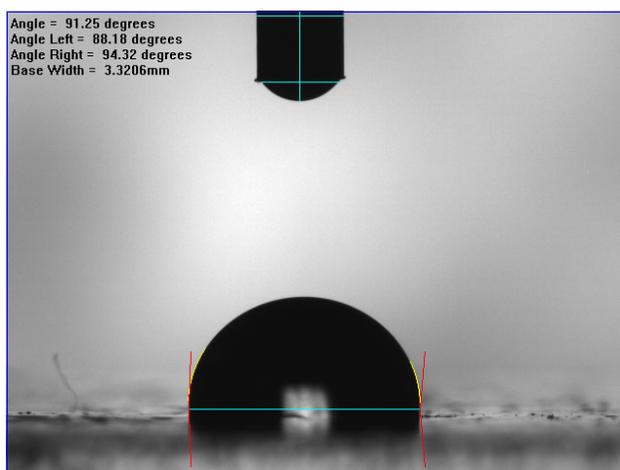


Figure 4: Contact angle of water on EGaIn film treated with oleic acid.

We hypothesized that the carboxylic acids were bonding to the oxide layer. We repeated the

coating procedure with perfluorooctanoic acid (PFA), which is a molecule comprised of a carboxylic group attached to a fluorinated 8-carbon chain. Surface fluorine groups tend to be very hydrophobic, with fluoropolymers often being used in EWOD experiments^{12,13}. We applied a 20 mM solution of PFA to an EGaIn film on a glass slide and measured the contact angle of DI water to be $63.7^\circ \pm 0.3^\circ$, with a hysteresis of 2.2° . This surface was also subject to roughness, as shown in Figure 5. We expected the PFA treated metal to have a contact angle greater than or equal to that of the oleic acid treatment. We suspect that residual PFA may be lowering the surface tension of the water by acting as a surfactant.

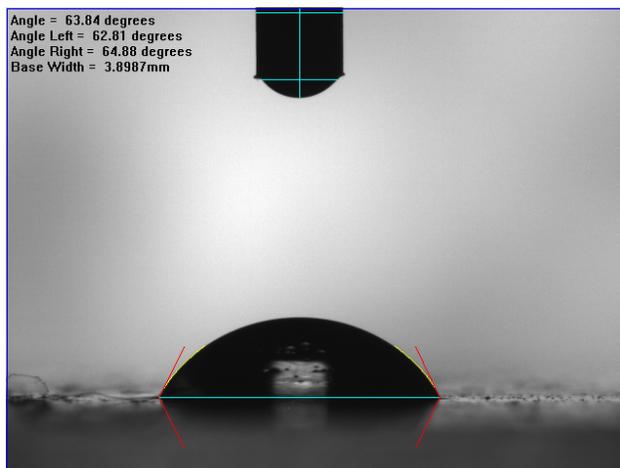


Figure 5: Contact angle of water on EGaIn film treated with PFA.

Although the preliminary results for these materials are promising in the sense the contact angle can be dramatically changed relative to an untreated surface, further studies are needed to more accurately characterize the surface. XPS analysis, which can detect the fluorine groups from the PFA on the surface, is underway.

Conclusions

Although many of the experiments presented in this chapter are only preliminary, we have demonstrated that we can use the chemical and electrochemical properties of EGaIn to alter its behavior on the micro-scale. We have quantified the dissolution of the EGaIn oxide skin in acidic and basic solutions, and under electrochemical oxidation. We have also shown that the skin can be modified to become more hydrophobic, which helps stabilize the oxide against the effects of acid, base, and water. Future work includes additional characterization (e.g., XPS, contact angle measurements) of the surface after application of these materials.

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