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Tuning surface texture of liquid metal particles by exploiting material metastability

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Tuning surface texture of liquid metal particles by exploiting material metastability

by

Joel Cutinho

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Materials Science and Engineering

Program of Study Committee:
Martin Thuo, Major Professor
Shan Jiang
Jaime Juarez

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this thesis. The Graduate College will ensure this thesis is globally accessible and will not permit alterations after a degree is conferred

Iowa State University

Ames, Iowa

2017

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I dedicate this work primarily to my family, who have taught me to believe in God, myself and follow my desires.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iv</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>v</td>
</tr>
<tr>
<td>CHAPTER 1. INTRODUCTION AND BACKGROUND</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 2. TUNABLE SURFACE TEXTURE AND MORPHOLOGY OF LIQUID METAL PARTICLES BY UTILIZING INTERFACIAL METASTABILITY VIA THERMAL TREATMENT</td>
<td>15</td>
</tr>
<tr>
<td>CHAPTER 3. BULK METASTABILITY AS A ROUTE TO ENGINEER HIGH ENERGY INTERFACES</td>
<td>33</td>
</tr>
<tr>
<td>CHAPTER 4. CONCLUSION</td>
<td>43</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>45</td>
</tr>
</tbody>
</table>
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ABSTRACT

Surface roughness, and associated changes in properties, often dictate how a material is utilized or manifests unprecedented capabilities to well-known materials. Most approaches to engineer surface texture are, however, predominantly based on additive and/or subtractive routes that are often either; i) inefficient (arduous, lengthy and expensive), or ii) inaccessible (due to a need for specialized equipment and skilled manpower). Understanding a materials interface structure at the sub-nanometer scale, and pairing this with its thermodynamic landscape, offers a new frugal approach to engineer its surface texture. Herein, we demonstrate thermal-driven evolution of surface morphology by exploiting inherent structural complexity, and metastability, of the ultra-thin passivating oxide on liquid metal particles. We achieve tunable surface texture via thermal-triggered oxidation of the liquid, whereby structural order on the surface was controlled through kinetics (reduction potentials of constituent elements) and stoichiometry, the latter being driven by interfacial phase-segregation upon oxidation. Release of the underlying phase-segregated components lead to inversion in the composition of the surface of these metal oxides, with concomitant growth in the thickness of the passivating layer. We divide our study in two parts viz; i) utilizing a thermodynamically stable core with a metastable shell, and ii) engineering liquid metal particles with metastable core and a metastable interface. For the former case, we obtained particles characterized by crumples, patches and multi-tiered roughness with increase in processing temperature and time. The overall structure of the particle evolves from a smooth sphere into a crumpled sphere and eventually a textured surface with increasing temperature while retaining the liquid core. At temperatures >1173 K, the liquid core is not observed but a hollow solid particle is formed with significant inter-particle sintering. For particles with metastable core
and metastable interfaces, we observed greater effects of thermal stress due to phase change. The particles undergo spinodal decomposition upon solidification while differences in thermal expansivities of the constituent elements led to dendritic growth, albeit after a specific trigger temperature.
CHAPTER 1
INTRODUCTION AND BACKGROUND

Over the past century, progress in science, engineering and technology have translated into desirable applications, which have benefitted humankind as well as made their lives comfortable. However, at the present hour, worries such as diminishing resources and an unstable economy have led researchers to practice frugality in research. Frugality is the judicious utilization of resources to achieve remarkable results. This is best manifested by Prakash and co-workers who utilized paper to fabricate a folding microscope and a music box, the latter to use as non-electricity microfluidic chip.\textsuperscript{1, 2}

Innovation in materials science and engineering has led to groundbreaking applications in multiple fields in the industry as well as academia. One aspect of materials science is manifested in surface science, which studies the development, properties, and applications of surfaces of material systems. An important part of this research focus on engineering surface texture and morphology. The importance of the same is observed by the change in surface energy, which alters surface properties. For example, the free energy of a droplet is viewed as a sum of the contributions from capillary energy and surface energy changes (Equation 1). This in turn shows droplet height dependence ($h_{xy}$) that translates to a dependence on the underlying surface texture.\textsuperscript{3} Thus, surface texture induced altered wetting has benefitted developments in corrosion prevention\textsuperscript{4}, antifouling\textsuperscript{5, 6}, and superhydrophobic surfaces.\textsuperscript{7, 8} A variation in surface texture also affects its absorption properties modifying the dynamics of catalysis\textsuperscript{9}, drug delivery\textsuperscript{10, 11}, and surface optics.\textsuperscript{12-14} Hence, the need to tune surface texture and morphology can be stemmed from the importance of the aforementioned phenomena. This section will focus on the importance of the same by illustrating examples from nature and highlighting synthetic effort in achieving the same. We will also provide
an insight into our approach of achieving this purpose by utilizing stable and metastable liquid metals and alloys.

\[ G_{[h(x,y)]} = \iint [E_{\text{capillary}} + \Delta E_{\text{surface}}] = \iint [\gamma \sqrt{1 + (\Delta h_{xy})^2} + (\gamma_{SL} - \gamma_{SV}) \, dx \, dy] \quad (1.1) \]

### 1.1 Role of Surface Texture and Morphology in Nature

Nature has mastered the use of surface and interface engineering, for an array of functions.\(^ {15-18}\) Engineering surface texture to tune hydrophobicity is widely observed leading to comparable results, albeit via different surface morphologies, for example in the lotus (Figure 1a) and the rice (Figure 1b) leaves.\(^ {19-21}\) Similarly, surface texture engineering can be used to create hydrophilic surfaces essential for water harvesting, for example in the desert lizard (Figure 1c), or homeostasis.\(^ {22}\) Differences in wetting controls interfacial concentration of molecular species, which in turn can translate to thermodynamic work. It therefore follows that, surface engineering can manifest mechanically as shown in the strength of the deep-sea sponge (Figure 1d), drag-reduction in sharks (Figure 1e), and surface-tension floatation in the water-strider (Figure 1f).\(^ {21,23}\)\(^ {24}\) Complexity in surface texture can lead to unique surface properties thus ensuring the survival of biological organisms in xeric environments. This can best be manifested in the bi-phobic surface of the desert Namib beetle (Figure 1g) which helps in recruiting water from fog and transporting it to its mouth, ice-phobic surface of the penguin feathers (Figure 1h) which helps in keeping them warm, and characteristic colors on the wings of butterflies (Figure 1i) which keeps them away from predators.\(^ {25-27}\)
Figure 1: Role of surface texture in biological functions. Each picture is outlined in the form of an SEM image depicting the surface texture and an inset of the biological organism. a) Micrometer scale protrusions on the lotus leaf, these protrusions further have nanoscale features on them leading to superhydrophobicity and self-cleaning properties. Retrieved with permission from Royal Society of Chemistry© 2016.20 b) Characteristic texture on a rice leaf causing superhydrophobicity. Retrieved with permission from Royal Society of Chemistry© 2012.21 c) Hydrophilic surface of the Texas horned lizard to trigger capillary-driven water transport. Retrieved with permission from The Royal Society© 2015.22 d) Colloidal texture of the deep-sea sponge composed of silica nanospheres to achieve mechanical robustness. Retrieved with permission from Journal of Materials Research© 2006.24 e) Riblet morphology on a shark’s dermal denticle leading to the shark skin effect. Retrieved with permission from Royal Society of Chemistry© 2012.21 f) Grooves on the legs of the water strider ensuring floatation. Retrieved with

1.2 Synthetic Efforts to Engineer Surface Texture and Morphology

In an effort to tune surface texture and morphology for a variety of applications, researchers have employed many different methods over the past decade. Most methods include either addition of chemical moieties on a substrate (additive), or removal of those moieties (subtractive), or a combination of both (hybrid). In addition to these, there are a few other methods such as self-assembly which have recently gained interest. We have classified these methods as physical, chemical, and other methods respectively.

1.2.1 Physical methods

Most additive physical methods include an array of deposition techniques such as Physical Vapor Deposition (PVD)28, 29, Chemical Vapor Deposition (CVD)30-34, and electrospray deposition35, for example as shown by the change in surface morphology of InN films with deposition temperature (Figure 2a-c)30. On the other hand, etching by ions or electrons encompass most of the subtractive methods as depicted by the morphological evolution on Ge films with etching time (Figure 2d-f)36. Hybrid methods employ a combination of additive and subtractive methods.37-39 Figure 2g-i best showcase the hybrid methodology of obtaining hydrophobic fluorocarbon films via simultaneous deposition and etching process.38
Figure 2: Summary of physical methods to fabricate characteristic surfaces. a-c) Effect of temperature on the morphology of InN films deposited by Chemical Vapor deposition (CVD). Retrieved with permission from Journal of Applied Physics© 2008.18 d-f) Morphological development on Ge films after etching with different ions. Retrieved with permission from IOPscience© 2009.36 g-i) Surface morphology induced hydrophobicity of fluorocarbon films fabricated via a hybrid etching and deposition process. Retrieved with permission from Journal of Electronic Materials© 2015.40

1.2.2 Chemical methods

In another approach, chemisorption, or interface reactivity can be used to engineer surface texture. Additive methods employ a chemical reaction with the surface or substrate of interest. This is best manifested by the surface reaction of silane with physiosorbed water to obtain bio inspired bi-phobic surfaces on paper.41 Figure 3a depict the pristine paper whereas Figure 3b-c
depict the formation of polymerized particles with reaction time leading to tunable hydrophobicity. Subtractive methods usually utilize chemical etching to obtain tunable pore size or morphology on the surface. This can be observed in Figure 3d-g where the silica core in mesoporous silica particles (m-SiO$_2$@c-SiO$_2$) is selectively etched using a suitable chemical etchant. Increasing etching time increases pore size, thus leading to tunable texture of the mesoporous silica shell. In addition, Figure 3h-j outlines an interesting hybrid approach to obtain super repellent metallic surfaces by etching and concomitant surface oxidation.

**Figure 3:** Summary of chemical methods to tune surface texture and morphology. a-c) Variation in surface morphology with reaction time of silane and physiosorbed water to obtain bio inspired bi-phobic surfaces on paper. Retrieved with permission from Royal Society of Chemistry© 2016. d-g) Change in pore size of mesoporous silica shell with etching time. Retrieved with permission from Wiley Online Library© 2011. h-j) Outline of super repellent surface morphology obtained...
on Copper films via a two-step etching and surface oxidation process. Retrieved with permission from Royal Society of Chemistry© 2016.20

1.2.3 Miscellaneous methods

Other methods usually utilize top down45-47, bottom up10,48,49 or interfacial methods50-53 to achieve characteristic surface microstructure for various applications. For example, photolithography can be employed to realize micro-nano nested structures for display technology (Figure 4a-d). Such a microstructure ensures maximum transmission of photons to increase display efficiency.54 On the other hand, self-assembly is used to fabricate colloidosomes of intricate morphology from different templates (Figure 4e-g).55 Interfacial methods can be used to synthesize microparticles of polymer blends by utilizing interfacial instabilities in solution as well as tune surface roughness by varying blend ratio (Figure 4h-k).50 Also, interfacial reactions such as polymerization can form polymer shells for encapsulation of small or large molecules.53 Figure 4l-4m manifest a crumpled morphology of polyurea encapsulated triphenylphosphine-g-polystyrene and tris(o-tolyl) phosphine-g-polystyrene respectively in their unswollen states. The addition of a suitable solvent diffuses through the polymer shell walls, and swells up the particle by dissolving the core leading to a uniform spherical morphology. Such particles find numerous applications in site-specific catalysis and drug delivery.50,52,53
Figure 4: Summary of other methods employed to achieve tunable surface texture and morphology. a) SEM image of micro-nano nested hexagonal arrays grown by UV nanoimprinting lithography. b) magnified image outlining a single sphere. c) Cross sectional SEM image of the microstructures, d) Confocal microscopy of the top view. Retrieved with permission from American Chemical Society© 2015. e-g) SEM images of Fe-based colloidosomes obtained by self-assembly of cubical templates. Retrieved with permission from American Chemical Society© 2013. h-k) Tunable roughness of blends of PEG-b-PLGA and PLGA by varying PEG-b-PLGA ratio from 0% to 100%. Retrieved with permission from American Chemical Society© 2017. l-m) SEM images of encapsulated unswollen triphenylphosphine-g-polystyrene and tris(o-
(9), (10) Confocal image of swollen triphenylphosphine-g-polystyrene capsule. Retrieved with permission from American Chemical Society© 2006.50

1.3 Liquid Metals Featuring Surface Oxides as a means to Engineer Surface Properties

1.3.1 Overview of surface oxides on metals and alloys

Metals and alloys are an important class of materials used for diverse applications. Most metals are characterized by a thin layer of native oxide, which changes morphology as well as surface properties making surface growth of oxides a feasible route to engineer texture.56 Despite having a gamut of methods to grow oxides57-63, thermal treatment still finds its way as a feasible and effective route to achieve the same.64-68

1.3.2 Current research on liquid metals and alloys

Although, most of the commercially available metals are solid at ambient temperature, many researchers have turned their attention to liquid metals and their alloys over the last decade due to their easy moldability, flow properties, modelling, and zero elastic modulus.69 Mercury, gallium, cesium, and rubidium are examples of metals that are liquid at or near room temperature, however, mercury is highly toxic because of its high vapor pressure whereas cesium and rubidium are extremely reactive leaving us with gallium and its alloys.69 Gallium is a p block element having a melting point of around 30°C. It forms alloys with many elements most notably eutectic gallium indium (EGaIn: Ga:In 75.5:24.5 wt%), which is a liquid at room temperature (15.5°C, Figure 5d).70, 71 Whereas EGaIn is an example of a thermodynamically stable liquid metal, undercooling can also be utilized to obtain liquid metals at room temperature (Figure 5f), an example being Field’s metal (In:Bi:Sn 51:32.5:16.5 wt%, 62°C).72 A characteristic property of these liquids is the formation of self-passivating thin oxide skins of one of the constituent elements.70-73 The presence
of this skin has caused problems as it sticks to many surfaces, and acts as a barrier preventing the driving force for desirable applications.\textsuperscript{69} Researchers have succeeded in employing different methods to process or pattern liquid metals\textsuperscript{72, 74-83}, and utilize the native oxide for applications such as stretchable electronics\textsuperscript{75, 84-90}, sensors\textsuperscript{91-93}, memory devices\textsuperscript{94}, antennas\textsuperscript{95-97}, molecular electronics,\textsuperscript{73, 98-104} drug delivery\textsuperscript{105, 106}, and liquid metal interconnects\textsuperscript{72, 75, 107, 108} (Figure 5 & Figure 6 respectively). Recently, Tevis \textit{et al.} manifested a simple approach of shearing liquid metals to fabricate core shell microparticles (SLICE, Figure 5c).\textsuperscript{81} Both EGaIn and Field’s metal microparticles were synthesized by utilizing shearing with concomitant oxidation. The EGaIn particles were characterized by a Ga$_2$O$_3$ shell (0.6 nm) attached to a bidentate acetate ligand. It was proposed that these particles could be utilized as catalysts, or as carriers for drug delivery. However, smooth surface texture of these particles limited the surface area requirements for such applications. A need for engineering surface roughness necessitated a thorough study of the surface of EGaIn. In 1983, Dumke \textit{et al.} studied the surface of EGaIn using ion sputtering and Auger spectroscopy measurements. They claimed that the oxide formed under ambient conditions was predominantly Ga$_2$O$_3$ (less than 10 monolayers), and the top most layer of the liquid was enriched in In (94%), with the next immediate layer being slightly enriched in the latter.\textsuperscript{109} Roughly after a decade and a half, Regan \textit{et al.} and Tostmann \textit{et al.} confirmed this result, but claimed that the thickness of the oxide was 0.5 nm, and the subsequent layers beneath the topmost In layer were of eutectic composition.\textsuperscript{110-112} Later, Chiechi \textit{et al.} conducted Auger spectroscopy experiments, and concluded that the native oxide is passivating; sputtering this layer under high vacuum conditions and exposing the same system in ambient atmosphere caused the oxide to grow back.\textsuperscript{67} This study was further expanded by Cademartiri and co-workers who concluded that the native layer was heterogeneous with the presence of gallium and indium sub-oxides (Ga$^{+1}$) in addition to Ga$_2$O$_3$.
Most recently, Sodhi et al. achieved further insight into this structure by performing Parallel Angle Resolved X-ray Photoelectron Spectroscopy (PARXPS). They summarized that the surface layer was 0.6 nm, and it included a Ga$_2$O$_3$ native layer followed by a sub-oxide gradient Ga$_{2-x}$In$_x$O$_3$ and finally segregated In monolayer. We believe that this self-passivating oxide skin is the key to engineer surface texture and morphology.

**Figure 5:** Schematic depicting the various methods employed to process and pattern liquid metals. a) Voltage controlled microfluidic flow focusing to synthesize EGaIn microdroplets. Retrieved with permission from Wiley Online Library© 2015. b) Sonication to synthesize EGaIn nanoparticles. Retrieved with permission from American Chemical Society© 2011. c) Modified shearing technique to produce EGaIn as well as undercooled Field’s metal microparticles. Retrieved with permission from American Chemical Society© 2014. d) Phase diagram of the
Ga-In system depicting the eutectic region below room temperature.\textsuperscript{114} e) General phase diagram emphasizing the kinetics of undercooling.\textsuperscript{115} f) Laser ablation to fabricate soft electronics. Retrieved with permission from Wiley Online Library\textcopyright 2014.\textsuperscript{77} g) Stencil lithography to fabricate soft matter circuits. Retrieved with permission from American Chemical Society\textcopyright 2013.\textsuperscript{79} h) Direct write off to pattern liquid metal LEDs.

**Figure 6:** Schematic depicting the applications of stable and metastable liquid metals in various fields. a) Molecular electronics. b) Liquid metal interconnects. Retrieved with permission from Wiley Online Library\textcopyright 2016.\textsuperscript{107} c) Stretchable electronics. Retrieved with permission from Wiley Online Library\textcopyright 2015.\textsuperscript{116} d) Functional LEDs. e) Pressure sensitive sensors. Retrieved with permission from American Chemical Society\textcopyright 2016.\textsuperscript{93} f) Memory devices. Retrieved with permission from Wiley Online Library\textcopyright 2011.\textsuperscript{94} g-h) Metastable undercooled liquid for healing
of damaged surfaces and heat free soldering. Retrieved with permission from Nature© 2016.\textsuperscript{72} i) Targeted drug delivery. Retrieved with permission from Nature© 2015.\textsuperscript{105}

Despite challenges in oxides, the self-passivating oxide layer in liquid metals offer a great entry point to engineering surface texture especially when coupled with bulk or interfacial metastability. To understand the role of surface metastability, bulk stability may also play a critical role in the overall response of the material. It is therefore important to evaluate temperature-dependent evolution of the oxide surface with either a stable liquid core or a metastable liquid core. EGaIn is one such system with a graded metastable oxide layer (as discussed above) but with a thermodynamically stable core. Ambient undercooled metal particles, however, will bear an analogous oxide shell but with a metastable liquid core. To fully delineate the mechanism of oxide-driven texture evolution, EGaIn and undercooled metal particles derived from the SLICE process are subjected to thermal treatments, and surface texture and composition are characterized to affirm the underlying mechanism. Figure 7 illustrates the possible routes of tuning surface texture and morphology via growth of surface oxides by utilizing high temperature. The favorable route to grow the oxide depends on diffusion of oxygen through the native layer, thermal expansivity of the metal, mechanical properties of the oxide layer, and kinetics of oxidation.
Figure 7: Scheme illustrating the possible mechanisms of surface oxide growth and texture tunability.
CHAPTER 2.

TUNABLE SURFACE TEXTURE AND MORPHOLOGY OF LIQUID METAL PARTICLES BY UTILIZING INTERFACIAL METASTABILITY VIA THERMAL TREATMENT

(Part of this work is submitted to Chem. Mater)

2.1 Introduction

Roughness induced texture on material surfaces are of considerable importance as they govern the local surface area and surface energy at the interface. A clear outcome of this is manifested in wetting properties where air pockets existing between a droplet and the textured surface stabilize the interface.\(^5\) This property has inspired researchers to fabricate superhydrophobic and self-cleaning surfaces (Figure 1a) for corrosion protection and antifouling.\(^7, 8, 117-119\) High surface area also facilitates the absorption of small molecules and particles, thus acting as a host aiding in processes such as catalysis and drug delivery (Figure 1b).\(^9, 10, 120\) Most methods to modify surface texture and morphology are either additive,\(^18, 33-35, 43, 121-124\) subtractive\(^36, 125-128\), or a combination of both.\(^129-131\) Additive methods employ the addition of moieties on target surfaces whereas subtractive methods achieve this goal by removal of material. In addition, top-down,\(^46, 63, 132, 133\) bottom-up\(^134, 135\), and interfacial methods\(^52, 53, 136\) are also utilized to obtain characteristic surface patterns, however, most approaches require complicated surface chemistry, stringent conditions, and arduous procedures.

A simple route to engineer surface texture is the growth of oxides on metal substrates. Although multiple methods are available to grow oxides, thermal treatment is still a straightforward and effective method to achieve the same.\(^65, 66, 68, 137, 138\) Thermal oxidation not
only provides characteristic texture but also renders texture tunability by varying temperature. Liquid metals are an important class of materials as they have beneficial properties such as easy moldability, flow properties, conductivity, and zero modulus of elasticity.\cite{139} Most notably eutectic gallium-indium (EGaIn: 75.5\% Ga, 24.5\% In w/w, mp ≈ 15.7°C) has been on the forefront of research over the past decade, and has found applications in soft/stretchable electronics,\cite{75, 85, 116, 140-144} functional microparticles,\cite{74, 78, 80-83, 145} molecular electronics\cite{98-104}, and functional devices.\cite{92, 144, 146, 147} EGaIn is characterized by a thin passivating film of Ga$_2$O$_3$. Initially considered an issue, we and other groups have employed various techniques to utilize the oxide layer to encapsulate EGaIn, and thus create functional liquid metal particles.\cite{74, 78, 80-83} Nonetheless, these particles are limited by surface area requirements of afore-mentioned applications due to smooth surface texture. A thorough understanding of the surface of EGaIn is paramount to envision surface engineering. Many groups have studied the surface of EGaIn by using spectroscopy, and have concluded that it consists of a very thin film of Ga$_2$O$_3$ followed by a monolayer of segregated In followed by the eutectic liquid.\cite{70, 71, 73, 109, 111, 112} Recently, Sodhi and co-workers achieved further insight by performing Parallel Angle Resolved X-ray Photoelectron Spectroscopy (PARXPS), and claimed that its surface consists of Ga$_2$O$_3$ native layer followed by a sub-oxide gradient Ga$_{2-x}$In$_x$O$_3$ and finally segregated In monolayer.\cite{113} The thickness of the heterogeneous oxide layer with the In monolayer was calculated to be 0.6 nm. This calculation is supported by the resistivity of the layer being more than five orders of magnitude lesser than Ga$_2$O$_3$ grown by other methods.\cite{73, 101} In addition, from Ga-O bond distances, we approximate that the layer consists of no more than three monolayers of the oxide, sub-oxide, and segregated In together.\cite{148} Thus, we deduce such a thin layer to be highly elastic as well as easy to engineer in contrast to conventional oxide films. Based on these results, we speculate that temperature driven oxidation of EGaIn coupled with interfacial
metastability in the form of an ultra-thin passivating oxide layer can lead to tunable surface texture and morphology.

Along these lines, we hypothesized two possible routes of oxidation via thermal treatment (Figure 1c). These routes depend on the competition between diffusion of oxygen, kinetics of oxidation, and thermal stress. The core shell particle consisting of EGaIn core and Ga$_2$O$_3$-ligand shell are illustrated by grey and faded green respectively whereas segregated In is represented by blue. The route on the left of Figure 1c illustrates Expansion induced Diffusion limited Oxidation (EDO). Since the oxide is extremely thin and elastic, heating causes it to expand and increase permeability to oxygen. Sub-oxides being naturally deprived of oxygen act as an oxygen sponge to absorb it and form stable oxides. Based on reduction potentials and heats of formation$^{149,150}$, we expect Ga to oxidize faster than In leading to the formation of a new Ga$_2$O$_3$ layer with the In$_2$O$_3$ beneath it. Later, oxygen diffuses through this layer, attacks the metal, and continues to form the oxides in a similar manner thus, yielding a stacked interface with alternating Ga$_2$O$_3$ and In$_2$O$_3$. Although our hypothesis implies that oxygen should oxidize all the liquid via anionic diffusion, growth of the oxide renders the material rigid and brittle like a conventional ceramic. In addition, increasing thermal expansion mismatch between the liquid and the growing oxide leads to massive thermal stress at the interface.$^{151,152}$ As a result, we expect the oxide shell to fracture at a critical point causing the liquid to flow out (analogous to a volcano), phase segregate under shear, and oxidize into Ga$_2$O$_3$ and In$_2$O$_3$ as depicted by the route on the right-hand side of Figure 1c (Thermo-mechanical Fracture induced surface Oxidation; TFO). Since, all parameters depend on temperature, regulating it can provide us particles with tunable surface texture and morphology.
Figure 1. Importance of surface texture and morphology. a) Superhydrophobicity and self-cleaning ability on textured surfaces, b) Application of textured particles in catalysis and drug delivery, c) Scheme outlining the possible pathways of oxide formation by thermal treatment. Heating the particle leads to thermal desorption of the ligand. In this process, growth occurs via two competing routes viz. Expansion induced Diffusive Oxidation (EDO) and Thermo-Mechanical Fracture induced surface Oxidation (TFO).
2.2 Experimental Section

2.2.1 Materials. Eutectic gallium-indium (Ga: In 75.5/24.5 wt %, Aldrich, ≥ 99.99% trace metal basis), glacial acetic acid (Fisher Scientific, Biotech, sequencing grade), and ethanol (Decon labs, 200 proof) were used as received in particle preparation and storage. Thermo Scientific Smart2Pure 6 UV water purifier system was used to obtain deionized water.

2.2.2 Particle preparation. We used a previously reported procedure of our group to synthesize core shell EGaIn@Ga$_2$O$_3$ particles.\textsuperscript{81} A 5 vol% solution of glacial acetic acid in deionized water (total: 100 ml) was prepared in a beaker, and then transferred to a Waring\textsuperscript{®} Laboratory Blender. Approximately 4g of EGaIn was weighed and added to the solution. The solution was sheared at 20,000 rpm for 10 minutes. Whatman 5 filter paper (1 µm particle retention) was used to separate the particles from the slurry. Residual slurry on the filter paper was washed out with ethanol. Particles were stored in ethanol.

2.2.3 Thermal treatment. Thermal treatment was carried out either in a TGA (Q50 TA Instruments) or a tube furnace (Thermolyne 79300). Silicon wafer chips were washed with acetone and dried with ultrapure nitrogen gas. The particles were drop casted onto the wafer with the solvent being allowed to dry in the oven at 60°C. Ambient air was used as the environment to facilitate oxidation. TGA was run by placing the silicon wafer containing particles on a platinum pan. Gas flow and ramp rate were set at 50 ml/min and 10°C/min respectively. For the tube furnace, the sample was placed on a ceramic crucible, and pushed carefully to the center of the tube to reach desired temperature. Following heat treatment, samples were stored in plastic boxes for imaging and analysis. A control experiment without heat treatment was performed for comparison.

2.2.4 Characterization. All samples were imaged by scanning electron microscopy (FEI Quanta 250 FE-SEM). False coloring was achieved by using Adobe Photoshop™. To observe internal
microstructure, we utilized the focused ion beam (FEI Helios Nanolab DualBeam). Elemental characterization was performed using energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy (Kratos Amicus 3400). In order to obtain elemental spectra for different morphological regions on the particle, scanning Auger microscopy (JEOL JAMP-7830F) was used. In addition, crystal structure was obtained using X-ray diffraction (Rigaku Smartlab Diffractometer).

2.3 Results and Discussion

The average particle size of control particles was between 1-5 micrometers. To confirm that our particles had a liquid core, we utilized the Energy Selective Backscattered detector while imaging, and observed no signs of phase segregation in the particles. In addition, broken particles depicted flow of the liquid metal thus confirming the liquid nature of the core.

2.3.1 Effect of temperature on surface texture and morphology

To investigate the effect of temperature on growth-induced surface morphology, we performed heat treatment from 300°C to 1000°C with increments of 100°C, and isothermal time scale of 45 minutes for each temperature. Figure 2 outlines the change in surface texture and morphology of EGaIn particles with temperature. The magnification is set to increase horizontally from left to right to show a cluster of particles followed by a single particle, and a magnified image of the same particle. Control EGaIn particles (Figure 2a-c) depict smooth texture on the surface with traces of adventitious contaminants. Particles heat-treated at 300°C (Figure 2d-f) do not show any changes in surface texture. Undulations observed on some particles depict that they cooled anisotropically, whereby the weakest region collapsed readily upon volume change. These features suggest that despite EDO the oxide was still thin enough to be elastic and withstand rapid changes in volume. Noticeable changes in texture begin to appear at 400°C (Figure 2g-i) with the
observation of patches with spots on it. We speculate this patchy growth to mediate from either mechanical fracture of the collapsed regions (TFO), or buckling of the loose outer layers due to thermal stress. Particles treated at 500°C (Figure 2j-l) show considerable roughness without any undulations. We noticed the healing of cracks that propagated from nucleation at the interface, and nonuniform growth of the surface. An additional uncontrolled experiment at 500°C was conducted to closely examine the emergence of surface roughness. We observed the presence of liquid emerging from the core thus confirming TFO. High magnification depicts the morphology to appear like nano ridges with size lower than 50 nanometers. We can therefore infer that surface roughening 1) occurs via TFO, 2) is comparable to a volcanic growth, and 3) is a continuous process such that the oxide layer undergoes repeated fracturing in a similar manner allowing fresh liquid to oxidize and form new outer layers. In addition, we discover the presence of a different phase material with higher contrast, giving rise to a second-tier of morphology. At 600°C (Figure 2m-o), the second-tier material appears to grow extensively, and cover the surface most likely due to sintering leading to a well-defined surface with two tiers of morphology. Particles at 700°C (Figure 2p-r) and 800°C depict accelerated growth of the second-tier material, which ultimately lead to them falling off under gravity. We also noticed the growth of tiny whiskers, a phenomenon close to crystallization. We observed another change in texture at higher temperatures, whereby the particles portrayed a high degree of coarsening, and concomitantly higher surface roughness as compared to lower temperatures. Backscattered images of particles treated at 600°C illustrated contrast differences between the two tiers of morphology suggesting composition differences between the two. From atomic mass differences, we speculate that the second-tier material must have higher concentration of In in it.
Figure 2. SEM images of EGaIn particles heat-treated at different temperatures under air atmosphere for 45 minutes. a-c) Control EGaIn. d-f) 300°C. g-i) 400°C. j-l) 500°C. m-o) 600°C. p-r) 700°C.

2.3.2 Effect of time on surface texture and morphology

To examine the effect of time on surface morphology, we treated particles from 15 minutes to 60 minutes at a constant temperature of 600°C. We chose 600°C as the temperature to conduct
time studies due to the clear presence of both tiers of morphology. We probed the growth of the second-tier material, as it was difficult to model the growth of the first-tier surface due to limitations in characterizations. An appreciable number of second-tier material were observed at 15 minutes giving rise to a sparse surface coverage (Figure 3a-c). More material appeared to grow at 30 minutes leading to an increase in coverage (Figure 3d-f). At 45 minutes, coverage increased considerably with the material forming a network most likely due to sintering. (Figure 3g-i). Coverage reached a plateau at 60 minutes with the formation of a dense chain-like network (Figure 3j-l).

**Figure 3.** SEM images of heat-treated EGaIn particles under isothermal conditions (600°C) for different time scales. a-c) 15 minutes. d-f) 30 minutes. g-i) 45 minutes. j-l) 60 minutes.
2.3.4 Effect of time and temperature on oxidation of the liquid

Since, oxidation of the liquid core led to surface growth and concomitant texture, we predicted our particles to have either a liquid core or a hollow core, and a shell with high thickness depending predominantly on the temperature and time of treatment. To observe this, we performed a series of heat treatment experiments ranging from 500°C to 1000°C and up to 360 minutes. To keep sample size constant, we drop casted a single drop of a very dilute suspension of EGaIn particles for each experiment. Finally, we scratched the wafer with the help of a thin disposable needle following heat treatment. Figure 4a-b depicts particles treated at 600°C and 60 minutes. We observed the flow of the liquid core as well as a broken shell with much higher thickness as compared to the control particle (0.6 nm). An EDS map of the cross-section of broken particles represented thick oxygen covered regions, which confirmed that the shell had grown considerably thicker due to oxidation. Further, ion milling of a particle treated at 1000°C and 120 minutes depicted a hollow cavity of uneven geometry (Figure 4c). Crystals (Figure 4d) are witnessed just underneath the oxide shell. We deduced that oxidation coupled with crystallization is primarily responsible for the liquid-less core. The phase diagram (Figure 4e) maps the transition from liquid core to hollow core with processing temperature and time. Clearly, we observed temperature dominated transitions in 700°C-800°C and 800°C-900°C regime, which can be attributed to rate of oxidation as well as crystallization, both being temperature dependent phenomenon. Time appeared to play an important role at higher temperatures, whereby most of the transitions occurred within 120 minutes.
**Figure 4.** Assessment of the core of the particle. a) A group of particles heat treated at 600°C for 60 minutes, and scratched by a needle shows that the core remains liquid after heat treatment. b) A magnification of the previous image outlining the broken fragments and thick oxide shell. c) SEM micrograph after ion milling of a particle heat-treated at 1000°C for 120 minutes depicting a hollow cavity of uneven geometry. d) High magnification image of the same particle revealing the growth of crystals beneath the shell. e) Temperature-Time phase diagram showing the transition from liquid core to hollow core.
2.3.5 Characterization and compositional analysis of the surface

To characterize the newly grown surface, we performed Scanning Auger Electron Spectroscopy (AES) on control and heat-treated particles. Figure 5 outlines Auger spectra from point analysis performed on a control particle as well as the two-tiered morphological regions on a particle heat-treated at 600°C. The assessment our peaks are consistent with literature.\textsuperscript{153-156} Comparison between control and treated particles show the emergence of an In M\textsubscript{4,5}N\textsubscript{4,5} peak at 398 eV, and a substantial decrease in the intensity of the C KVV peak at 262 eV in addition to the already present Ga L\textsubscript{3}M\textsubscript{4,5}M\textsubscript{4,5} at 1063 eV. We associated the shrinkage of the carbon peak to thermal desorption of the ligand at high temperature. The peak positions of Ga and In were approximately 5 eV lower than the metallic counterparts indicating the formation of Ga\textsubscript{2}O\textsubscript{3} and In\textsubscript{2}O\textsubscript{3} respectively. These shifts are due to reduced electron density owing to electron transfer during reaction, which in turn increases the binding energy of the remaining core electrons, and concomitantly reduces kinetic energy.\textsuperscript{157-159} To investigate whether the grown species were crystalline, we performed X-ray Diffraction (XRD) on particles treated at 600°C and 900°C respectively. We noticed the presence of two dominant peaks along with few tiny broad peaks in the 600°C particle, all of which can be attributed predominantly to Ga\textsubscript{2}O\textsubscript{3} respectively. At 900°C, we observed that the broad peaks at lower Bragg angle increased in intensity and sharpness along with the emergence of new peaks. We associated this to complete crystallization of the surface to yield mixed oxides of β-Ga\textsubscript{2}O\textsubscript{3} and cubic In\textsubscript{2}O\textsubscript{3} respectively, which translates well with the morphological changes observed in our SEM images. This result is in good agreement with previous work where the authors observed crystalline peaks of both species in such mixed oxides systems depending on solubility.\textsuperscript{160}
Figure 5. Composition of the surface of the particle. Vertical panels depict the spectra of the elements present whereas horizontal panels depict the region of spectral collection. a) Microscope image of a control particle with point analysis on the surface. b) Microscope image of a particle treated at 600°C with point analysis on the first-tier morphology. c) Microscope image of the same particle with point analysis on the second-tier morphology. d-f) Auger Spectroscopy of the Ga
LMM region. g-i) Auger Spectroscopy of the C KVV region. j-l) Auger Spectroscopy of the In MNN region.

Further, XPS was performed on particles after heat treatments ranging from room temperature to 600°C. We observed the presence of Ga$^{+3}$ on all our samples (Figure 6a) whereas In$^{+3}$ was not detectable from background until 400°C (Figure 6c), which, correlates well with our SEM observations. To model the growth of Ga$_2$O$_3$ and In$_2$O$_3$ at different temperatures, we calculated peak areas from the spectra and plotted them against temperature (Figure 6b and 6d). We witness that Ga$_2$O$_3$ and In$_2$O$_3$ begun to grow after 300°C. Thus, changes in surface texture observed at 400°C (Figure 2i) must be due to the growth of both oxides on the surface. In addition, we note that the data points corresponding to Ga are well spaced and fit a linear equation (R-Square value of 98.3%). However, data points corresponding to In have almost same ordinate values at 400°C and 500°C with the point at 600°C being well spaced from them. This suggested rapid growth of In$_2$O$_3$ that, correlates with the growth of the second-tier material after 500°C. EDS maps collected from these particles (600°C) support this observation. To obtain distinct spectra for both morphologies, we performed AES on both regions by utilizing its ability to scan and resolve smaller features. Figure 6e-f outline Auger spectra collected from the two tiers of morphology respectively (shown by the inset in both figures). We observed a greater peak height for In from the second-tier spectra whereas Ga showed the opposite trend. We calculated a rough quantitative estimate of relative composition between the two tiers based on peak-to-peak intensity from differential spectra. From calculations, we infer that the second-tier material was richer in In as compared to the first one.
Figure 6. Growth and composition of the surface depicted by XPS and Auger Spectroscopy. a) XPS of the Ga 2p$_{3/2}$ region at different temperatures. b) XPS of the In 3d$_{5/2}$ region at different temperatures. c-d) Auger spectra survey collected from the two tiers of morphology on a particle treated at 600°C. e) Growth of In$^{+3}$ with temperature. f) Plot depicting the composition inversion of the components with temperature.
2.3.6 Effect of thermal treatment on the native oxide layer leading to tunable surface texture

We visualized that the process of thermal oxidation leading to the change in surface texture depends on the diffusion of oxygen, kinetics of oxidation, thermal expansion mismatch between the metal and existing oxide, and mechanical properties of the growing oxide. At high temperature, expansion of the elastic native oxide leads to increase in oxygen permeability, and diffusion as per Arrhenius equation. Although there was no growth at 300°C, the crumples in particles communicate that the oxide expanded on heating, and shrunk anisotropically due to rapid volume change upon cooling. For the oxidation of a curved oxide metal interface at high temperature as in our case, the stress at the interface (σᵢ), depends on the difference in thermal expansivities of oxide and metal (Δα), modulus of the oxide (E_oxide), temperature difference (ΔT), particle radius (r), oxide thickness (ε), and Poisson’s ratio for the oxide (ν_oxide) as depicted in Equation 2.1. This stress at the interface is compressive in nature during heating as opposed to the stress in the oxide (σ_θ) that is tensile (Equation 2.2).\textsuperscript{161} Thus, based on this model, if the stress in the oxide is lower than its failure stress, we envisage the oxide to continue to grow thicker via EDO. However, since conventional ceramics are brittle, after a certain failure point, we expect the oxide to fracture and grow via TFO. In our case, as Ga has a lower reduction potential and heat of formation,\textsuperscript{151, 152} it oxidized faster than In to seal the cracks and restructure to form a Ga-rich surface. The emergence of surface texture is attributed to buckling of the loose outer layers in conjunction with thermal fracture oxidation (TFO). Analogous studies were conducted on Al nanoparticles where the authors observed significant restructuring after liquid Al leaked through cracks in the Al₂O₃ shell, albeit at a temperature beyond the melting point of Al.\textsuperscript{162} The presence of heterogeneous or stepped roughness can be associated to nonuniform growth of the fresh oxide layer over the previous layer. Previous studies conducted on titania rods have shown that the freshly grown oxide
is more fragile than the previous layer, which facilitates faster mechanical fracture and growth. Hence, we can assume that in our case, the subsequent layers grew rapidly after the first layer was formed. From Figure 6d, we observe the presence of In-richer second tier material only after the initial surface restructuring. Auger sputtering studies conducted by Chiechi and co-workers concluded that the segregated layer of In is permeable to oxygen and when fresh Ga$_2$O$_3$ is formed, it displaces In to the bottom.70, 71 Thus, repeated surface restructuring due to rapid oxidation of Ga leads to a buildup of In at the core. Later, this In-rich core oxidizes to form the second-tier material, which then sinter at higher temperatures. This process can best be visualized as a volcanic explosion. Further increases in temperature will only lead to the buildup of this material so that they fall off and spread around the particle. Considering the formation of an In-rich core, we shift to the hypereutectic point, which on cooling gives rise to eutectic and In-rich phases in the core.114 The detection of the In-rich phase and the relative composition of these two phases is beyond the scope of this study. Extensive surface coarsening is an indication of complete crystallization of Ga$_2$O$_3$ and In$_2$O$_3$ at high temperatures. The transitions from liquid to liquid-less core is associated to either complete oxidation of the core or crystallization, as higher temperatures can expedite these processes leading to a hollow core.

\[
\sigma_i = -\frac{\Delta \alpha \Delta T E_{ox} \epsilon}{(1 - \nu_{ox})} \tag{2.1}
\]

\[
\sigma_\theta = \frac{\Delta \alpha \Delta T E_{ox}}{(1 - \nu_{ox})} \tag{2.2}
\]

2.4 Conclusion

From this work, we demonstrate a simple, low-cost approach to engineer surface texture and morphology of liquid metal particles via surface oxidation. By considering the structure and
thermal-triggered evolution of the ultra-thin, yet complex, native passivating oxide on EGaIn, we infer that: 1) Thermal trigger oxidation induces surface roughness in a time-temperature dependent manner, 2) the liquid nature of the core, can be maintained by tuning the processing temperature and processing time, 3) thickness of the oxide shell, as expected, increases with processing time at a given temperature. The passivating nature of this oxide is, however, expected to limit growth at lower temperature in part due to diffusion limited permeation of the oxidant in accordance with Fick’s law, 4) the interfacial segregation of the low $E^\circ$ component (In) occurs with increased permeability, however fracture of the thickened oxide leads to release of an In-rich alloy. This spontaneously oxidizes leading to inversion of the composition of the most accessible surface components from the native Ga-rich to new In-rich, albeit limited to the loci where the fracture occurs.
CHAPTER 3.

BULK METASTABILITY AS A ROUTE TO ENGINEER HIGH ENERGY INTERFACES

3.1 Introduction

The role of material metastability is of paramount importance in material systems due to an alteration of the systems free energy and thus an alteration of its properties. Metastable systems can exist either in nature or can be generated via an array of different routes, one such example being undercooling. An example of a graded natural metastable layer is the ultra-thin passivating oxide layer on eutectic gallium indium (EGaIn, Ga:In 75.5:24.5 wt%, 15.5°C). This system can be closely associated to metastability due to its sub-nanometer thickness (0.6 nm), a hybrid chemical composition and a concomitant segregated pure metal underlayer. We utilized a modified emulsion technique (shear) to encapsulate EGaIn particles (6 nm-10 μm) in a smooth layer of the passivating oxide to form liquid-metal@oxide@organic core shell structure. Undercooled Field’s metal (In:Bi:Sn 51:32.5:16.5 wt%, 62°C) particles were similarly synthesized with the oxide@organic shell frustrating solidification of the metal melt.

The transition from liquid to solid phase, solidification, is an activated process, and for a system at equilibrium, the energy required to overcome this activation barrier at, ΔG_{LS}, at constant pressure can be expressed as following:

\[ \Delta G_{LS} = \Delta H_{LS} - T \cdot \Delta S_{LS} \]  

(3.1)

where ΔG_{LS}, ΔH_{LS}, and ΔS_{LS} are the free energy, enthalpy, and entropy differences between solid and liquid states, respectively. As the equilibrium transition requires equal free energies of the liquid and solid states, then
\[ \Delta H_f = T_m \cdot \Delta S_f \]  

Where \( \Delta H_f \) and \( \Delta S_f \) are the heat of fusion and the entropy of fusion, respectively, whereas \( T_m \) is the melting point of the transition. However, in non-equilibrium conditions, the thermal barrier is required for transition to occur, in other words, the solidification happens at temperatures below melting point. In that case,

\[
\Delta G_{LS} = \frac{\Delta H_f \cdot \Delta T}{T_m} - \int_T^{T_m} \Delta C_p \, dT - \int_T^{T_m} \frac{\Delta C_p}{T} \, dT 
\]

where \( \Delta C_p \) is the difference in the specific heat of liquid and solid states and \( \Delta T \) is the level of undercooling. Therefore, undercooling, \( \Delta T \), is required for solidification to happen and its level depends on the nucleation conditions of the solid crystals.

Generally, phase transformation from bulk liquid to solid phase occurs via the growth of crystal nuclei in the liquid.\textsuperscript{164} The formation of nuclei leads to a barrier in the form of free energy difference between the crystal and fluid, which is depicted by

\[
\Delta G = G_{crystal} - G_{fluid} = A \gamma - V \eta_s \Delta \mu
\]

Where \( V \) is the volume of the crystal nucleus, \( \eta_s \) is the number density of the particles in the crystal, and \( \Delta \mu \) (\( \mu_{\text{fluid}} - \mu_{\text{crystal}} \)) is the difference in chemical potential between the fluid and crystal. The term \( A \gamma \) refers to the interfacial energy (proportional to area \( A \)) due to the energetically unfavorable interface generated between the crystal and fluid.

As shown in chapter 2, the surface morphology of these particles was then tunably engineered to give different textures under different processing temperatures and processing times. This study relied on a metastable and dynamic interface whose stability could be perturbed, albeit with a support stable core. A more challenging case would entail perturbing the structure of the
passivating oxide in presence of a metastable core with the expectation that either the core metastability is sustained. Where core relaxation is feasible, couple morphological changes would occur either with evolution in the morphology of the oxide or with a similar time-temperature dependence as observed with EGaIn. With core relaxation, spinodal decomposition, difference in thermal expansivity, and/or crystallinity of the components of the alloy can lead to dendrite growth or increased internal stress leading to changes in the structure of the particle.

In this report, we demonstrate the effect of thermal energy on the metastable core in addition to the metastable oxide shell. We envision the role of relative thermal expansivity to be critical especially because Bi expands on cooling (negative coefficient of thermal expansion) as opposed to In and Sn. Thus, we envisage counter expansion of the elements, oxygen affinity of the same, and thermal expansivity mismatch between the shell and the core to control surface growth and composition.
Figure 1: Comparison of surface growth in metastable interface@stable core and metastable interface@metastable core. In the latter case, the surface could grow either via thermal fracture induced oxidation (similar to EGaIn particles) or via core relaxation leading to spinodal decomposition and dendritic growth.

3.2 Experimental Section

3.2.1 Materials. Field’s metal (In: Bi: Sn 51:32.5:16.5 wt %, Alfa Aesar), glacial acetic acid (Fisher Scientific, Biotech, sequencing grade), diethylene glycol (BioUltra), and ethanol (Decon labs, 200 proof) were used in particle preparation and storage.

3.2.2 Particle preparation. We used a previously reported procedure of our group to synthesize undercooled Field’s metal particles. A 5 vol% solution of glacial acetic acid in diethylene glycol (total: 5 ml) was prepared in a beaker, and then transferred to a scintillation vial (20 ml). Approximately 2g of Field’s metal was added to the solution. The vial was immersed half way through in an oil bath at 150°C to facilitate melting of the metal. Shearing was carried out via a dremel 3000 variable speed rotary tool at the rate of 20000 rpm with cross-shaped poly(tetrafluoroethylene) (PTFE) shearing implement. Heat was withdrawn after 10 minutes with the suspension being allowed to cool under shear for another minute. Whatman 5 filter paper (1 μm particle retention) was used to filter out the particles. Excess slurry was washed out with ethanol. Particles were stored in ethanol.

3.2.3 Thermal treatment. Thermal treatment was achieved by either utilizing a TGA (Q50 TA Instruments) or a tube furnace (Thermolyne 79300). Silicon wafer chips were washed and dried with ultrapure nitrogen gas. The particles were drop casted onto the wafer with excess solvent being allowed to dry in the oven at 60°C. We chose ambient air as the gas environment to facilitate
oxidation. TGA was run by placing the silicon wafer containing the particles on a platinum pan. Gas flow and ramp rate were set at 50 ml/min and 10°C/min respectively. For the tube furnace, a ceramic crucible containing the wafer with the particles was carefully pushed to the center of the tube to reach the desired temperature. Following heat treatment, samples were stored in plastic boxes for imaging and analysis. For comparison, we performed a controlled experiment without heat treatment.

3.2.4 Characterization. Imaging and elemental analysis was carried out by using the scanning electron microscopy (FEI Quanta 250 FE-SEM) with built in energy dispersive x-ray detector. Focused ion beam (FEI Helios Nanolab DualBeam) was used to mill the surface and observe internal microstructure. Crystal structure was obtained by x-ray diffraction (Rigaku Smartlab Diffractometer).

3.3 Results and Discussion

We utilize the previously reported SLICE procedure to synthesize undercooled Field’s metal particles, and investigate the effect of temperature on the same. Figure 2 outlines the changes occurring on the surface of Field’s metal particles with temperature. The magnification is set to increase horizontally from left to right to show a cluster of particles followed by a single particle and a magnification of the same particle. From Figure 2a-c, we observed that untreated particles were homogeneous, and had a smooth texture on the surface. Previous studies by Tevis and co-workers communicated that phase segregation would be observed if the core was in solidus phase or in other words thermodynamically stable. Based on these observations, we can conclude that our particles were characterized by a liquid core and thus were metastable. Particles treated at 200°C (Figure 2d-f) depicted crumples on the surface, albeit without any noticeable change in texture. We associated this to sudden volume change in the core during cooling with the weakest
region collapsing anisotropically. The effects of thermal stress became apparent at 300°C with the presence of cracks and deflation on few particles (Figure 2g-h). In addition, we observed minute changes in texture with the emergence of tiny particulates on the surface. Particles treated at 400°C (Figure 2j) do not show considerable difference in surface texture compared to those treated at 300°C. However, we did observe a direct consequence of thermal stress in the form of mechanical fracture of the shell on one particle (Figure 2k-l). The results at 300°C and 400°C are interlinked as an increase in temperature escalates expansion, which concomitantly increases thermal stress in the oxide leading to fracture. Thus, crumples, cracks, and deflation observed at lower temperatures translates well to fracture at higher temperature. Considerable changes in morphology were detected in particles treated at 500°C (Figure 2m-o) without mechanical deterioration, and the emergence of particles on the surface. Particles treated at 600°C (Figure 2p-r) depicted similar morphology to the ones at 500°C, albeit with marginally greater surface roughness. We noticed dendritic growth emerging from the particles on the surface (Figure 2q) that at higher magnification indicated to originate from the core (Figure 2r). By collecting micrographs using the energy selective backscattered detector, contrast differences were observed on the surface indicating phase segregation. Further, to investigate the elemental distribution of these phases, we collected energy dispersive X-ray spectroscopy maps (Figure 3). We observed segregation of Bi rich phase from the In and Sn phases with the presence of oxygen throughout the surface. In addition, the dendrites surrounding the particles appeared to be enriched in Bi and oxygen, thus indicating the presence of Bi$_2$O$_3$. Accordingly, we can infer that 1) surface growth occurs due to oxidation to form the oxides of the respective constituent elements, 2) phase segregation occurs to separate the Bi-rich phase from the other constituent phases, 3) The dendrites are rich in Bi$_2$O$_3$, which disintegrated and collapsed possibly due to counter expansion of Bi on cooling.
Figure 2. SEM images of Field’s metal undercooled particles heat-treated at different temperatures under air atmosphere for 30 minutes. a-c) Untreated particles, d-f) 200°C, g-i) 300°C, j-l) 400°C, m-o) 500°C, p-r) 600°C.
Figure 3: EDS map of undercooled Field's metal particles heat-treated at 600°C.

To examine the changes occurring in the core due to thermal treatment, we performed ion milling on particles treated at 400°C and 600°C (Figure 4a-d and Figure 4e-h respectively). For 400°C, we chose the particle with a mechanically fractured shell to ascertain the uniformity of the void. We discovered that the void disappears after approximately half the particle is milled away. Thus, particles with the mechanically fractured shell can best be visualized as a cup. In addition, we noticed that the core was in the solidus phase as opposed to undercooled control particles. For particles treated at 600°C, we rather observed two distinct phases in the core based on contrast differences. Interestingly, it appeared that the phase with higher atomic composition (brighter region) grew on the surface to form the particles or dendrites (Figure 4g). Based on EDS results, we can infer that the core underwent relaxation from an unstable equilibrium to segregate the Bi-rich phase from the In-rich and Sn-rich phases.
Figure 4. Ion milling of Field’s metal particles heat-treated at a-d) 400°C e-h) 600°C. The arrow denotes the progress of the experiment.
3.4 Conclusion

In this report, we have evaluated the influence of bulk metastability on surface growth dynamics. By considering the presence of a metastable core in addition to a metastable interface, we have inferred the following: 1) The effects of counter expansion induced thermal stress led to crumples, cracks, and fracture of particles at low treatment temperatures. 2) Higher temperatures caused the growth of dendrites on the surface of the particle, which from EDS was confirmed to be rich in Bi. 3) Ion milling depicted core relaxation and concomitant phase segregation that led to the growth of Bi-rich dendrites due to counter expansion.
CHAPTER 4.

CONCLUSIONS

In this work, we have successfully demonstrated the importance and applicability of liquid metal particles to tune surface texture for desirable applications. This was possible by envisaging a feasible approach to engineer the passivating native oxide layer existing on the surface of these liquid metals. By considering the metastable ultra-thin oxide shell in conjunction with a stable liquid (EGaIn), or metastable liquid (undercooled Field’s metal) core, we have inferred the following:

1) Surface texture tunability in EGaIn particles predominantly depends on processing temperature, primarily because of temperature dependent parameters governing the process of surface reorganization. Accordingly, we obtained particles characterized by crumples, patchy growth, and either multi-tiered morphology depending on temperature. In addition, as oxidation of the liquid core led to surface growth and reorganization, our heat-treated particles were characterized by shells with significantly higher thickness (compared to control particles), and either liquid or hollow cores.

2) We observed that the major element of the alloy (Ga) followed linear growth, whereas the minor element (In) observed step growth with temperature. Such dissimilar growth kinetics generated particles with two tiers of morphology, albeit after a minimum threshold temperature with the second-tier being richer in In as compared to first-tier.

3) In the case of undercooled Field’s metal particles, we observed greater effect of thermal stress compared to EGaIn particles with the presence of crumples, cracks, broken shells, and material loss except for the window between 500°C and 600°C. Interestingly, we observed core relaxation and subsequent phase segregation after 500°C. The Bi-rich phase
underwent dendritic growth, which then migrated to the surface due to its counter expansion.
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