### SURFACE ENGINEERING AT THE NANO- AND MACRO-SCALE

By

Tyler Nathaniel Johnson

### A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Materials Science and Engineering - Doctor of Philosophy

2023

#### ABSTRACT

Surface engineering plays a pivotal role in enhancing material performance and functionality at both the macro and nano scales. At the macro scale, surface engineering is crucial for improving the mechanical, chemical, and thermal properties of materials, thereby extending their lifespan, and enabling them to withstand harsh environmental conditions. This is especially relevant in industries such as aerospace, automotive, and construction where materials are exposed to extreme temperatures, corrosive substances, and mechanical stress. Surface patterning is a technique that involves creating specific patterns or structures on the surface of materials. This approach can significantly impact the thermal properties of materials, leading to improved heat transfer, thermal conductivity, and overall thermal performance.

Surface engineering at the nano scale becomes increasingly important due to the unique properties and behaviors exhibited by materials at this level. Nanostructured surfaces offer enhanced strength, durability, and responsiveness to external stimuli. Tailoring the surface properties at the nanoscale allows for precise control over factors like adhesion, friction, and wettability, leading to improvements in areas such as lubrication, wear resistance, and composite manufacturing. These advancements are critical in the development of cutting-edge technologies, such as nanoelectronics, biomaterials, and sensors. In the realm of energy conversion and storage, surface modifications at the nano scale can significantly enhance catalytic activity, promoting more efficient fuel cells and batteries.

Plasma processing offers a promising approach to modify the basal plane of graphene, bridging the gap between chemical and physical methods. This document investigates the effects of  $C_4F_8$  and  $O_2$  plasma source gases on graphene nanoplatelets. Precise control allows lowtemperature plasma treatment to modify the graphene nanoplatelet surface without altering its intrinsic structure. This provides new opportunities for surface engineering in advanced composites. Plasma treatments enable tailored immersion characteristics and the introduction of functional groups, creating desired bonding environments.

Currently, battery thermal management systems in pouch cell systems rely on the use of cold plates. The design of these cold plates creates limitations, such as increased weight and reduced energy density. To overcome these challenges, the integration of cold plate designs into existing pouch cell materials is investigated, and a novel manufacturing method is developed.

The novel manufacturing process is based on roll-molding, which allows for easy adoption at the manufacturing level by leveraging existing roll-to-roll lamination processes. Proof-ofconcept experiments conducted using laboratory-scale equipment demonstrate the feasibility of the approach. Furthermore, the document presents insights into scaling up the manufacturing process and identifies semi-optimized rolling conditions to produce state-of-the-art cold plate designs.

Additionally, advanced materials were developed as superior alternatives to current 3-layer laminates, offering enhanced properties and manufacturability. These materials have the potential to enhance battery pack performance and functionality beyond existing limitations. The findings presented in this document provide valuable insights for advancing battery packing technologies, paving the way for more efficient, reliable, and high-performance battery systems in various applications.

Copyright by TYLER NATHANIEL JOHNSON 2023

#### ACKNOWLEDGEMENTS

I am sincerely grateful to my advisor, Dr. Andre Lee, for his unwavering guidance and encouragement throughout my academic journey. I would like to express my deep appreciation to Dr. Carl Boehlert, Dr. Martin Crimp, Dr. Qi Hua Fan, and Dr. Hui Chia Yu, my committee members, for their valuable time and contributions. My heartfelt thanks go to my family and friends for their constant support. I also want to acknowledge the contributions of Dr. Per Askeland and Dr. Ed Drown, whose expertise greatly enriched my technical knowledge. Special thanks to Brian Robert and Ford Motor Company for their years of technical assistance and support. Lastly, I am grateful to the dedicated departmental support staff for their invaluable assistance over the years.

CHAPTER 1: THE CRUCIAL ROLE OF SURFACE ENGINEERING IN MATERIALS SCIENCE
CHAPTER 2: PLASMA FUNCTIONALIZATION OF GRAPHENE NANOPLATELET SURFACES
CHAPTER 3: NOVEL PRODUCTION PROCESS FOR ELECTRIC VEHICLE BATTERY THERMAL MANAGEMENT SYSTEMS
CHAPTER 4: ALTERNATE MATERIALS SELECTION FOR BATTERY THERMAL MANAGEMENT SYSTEMS160
CHAPTER 5: SUMMARY AND OUTLOOK182
BIBLIOGRAPHY189

# CHAPTER 1: THE CRUCIAL ROLE OF SURFACE ENGINEERING IN MATERIALS SCIENCE

### **1.1 Introduction to Surface Engineering**

Materials science is a multidisciplinary field that explores the properties, structure, and performance of materials. Within this realm, surface engineering emerges as a pivotal aspect, wielding transformative influence on the functionalities and applications of diverse materials. This chapter delves into the profound importance of surface engineering in materials science, elucidating its role in tailoring material surfaces to meet specific requirements across various industries.

At its core, surface engineering is the strategic modification of a material's surface to enhance its properties and performance. This branch of materials science acknowledges that the surface characteristics of a material often dictate its interaction with the environment and its suitability for a particular application. By employing a myriad of techniques, from coatings and treatments to surface patterning and modification, scientists and engineers can fine-tune material surfaces with precision.

The ability to functionalize material surfaces is a hallmark of surface engineering. By selectively altering surface properties, such as hardness, wear resistance, and corrosion resistance, materials can be tailored to excel in specific applications. For example, in industries where components are subjected to abrasive wear, surface engineering techniques can be employed to fortify materials against degradation, thereby extending their lifespan and reducing maintenance costs.

One of the most pressing challenges in materials science is the degradation of materials due to corrosion and wear [1] [2] [3] [4]. Surface engineering serves as a formidable ally in addressing

this challenge. Through the application of coatings and treatments, materials can be shielded from corrosive environments and abrasive forces [5] [4]. This not only ensures the longevity of materials but is also pivotal in applications ranging from aerospace components to everyday household items. The evolution of intermetallic compounds and their interface with the matrix is a dynamic and critical aspect of understanding the behavior and properties of metallic alloys and solders [6] [7] [8]. Surface engineering is a powerful tool to control and tailor the formation and evolution of intermetallic compounds. Understanding the evolution of intermetallic compounds and their interface with the matrix is essential for optimizing material properties in various industries, including aerospace, automotive, and electronics. Ongoing research continues to deepen our understanding of these complex interactions, paving the way for the development of advanced materials with enhanced performance and durability.

In the realm of medical applications, where materials often interact with biological systems, surface engineering is paramount [9] [10] [11] [12] [13]. The biocompatibility of materials, a measure of their ability to coexist with living tissues, is linked to surface properties. Surface engineering allows for the creation of medical implants and devices with surfaces optimized for compatibility, reducing the risk of adverse reactions, and improving patient outcomes [9] [10] [11] [12] [13] [14]. Surface engineering allows for improved imaging conditions using various nanoparticles, modifying their interactions with cells and in vivo processes [15].

Friction and wear are challenges in mechanical systems [1] [4] [2] [3]. Surface engineering techniques play a pivotal role in mitigating these challenges. Through the manipulation of surface textures [16], introduction of lubricating coatings [3], and optimization of material properties, engineers can enhance the efficiency and durability of components. This has far-reaching

implications, from improving the reliability of machinery to reducing energy consumption in various industrial processes.

In the fast-evolving fields of electronics [17] and photonics [18], where nanoscale precision is needed, surface engineering takes center stage. The properties of materials at the surface significantly influence device performance. Surface engineering allows for the precise tuning of conductivity [19], adhesion [20], and other critical characteristics, enabling the development of advanced electronic components, sensors, and photonics devices.

### **1.2 Surface Engineering for Surface Functionalization**

In the dynamic field of materials science, the ability to tailor material surfaces to achieve specific functionalities is a cornerstone of innovation. Surface engineering serves as a powerful tool for functionalizing material surfaces, providing avenues for enhancing performance, enabling new applications, and addressing diverse industrial challenges.

Functionalization refers to the deliberate modification of material surfaces to introduce specific properties or functionalities. This can include alterations in chemical composition, surface energy, topography, or the introduction of functional groups. The goal is to enhance or introduce characteristics that are tailored to meet the demands of diverse applications.

Surface engineering is instrumental in tailoring the electrical and electronic properties of materials. For instance, the introduction of conductive coatings or the manipulation of surface states in semiconductors can enhance electrical conductivity [19], opening possibilities for applications in electronics, sensors, and energy devices.

Controlling wettability is a fascinating aspect of surface functionalization. Creating superhydrophobic or superhydrophilic surfaces through plasma treatments, engineered coatings, or nanostructuring allows for control over water repellency or attraction [16]. This has implications in fields such as self-cleaning surfaces, anti-fogging materials, and microfluidic devices [4].

Surface chemistry modification is a versatile strategy for functionalization. By introducing specific functional groups or altering the chemical composition, surface properties such as hydrophobicity [16], adhesion [20] [21], and reactivity [22] [14] can be finely tuned. This approach is crucial in applications ranging from catalysis to sensors and responsive materials.

Surface coatings represent a fundamental approach to functionalizing material surfaces [22]. Whether through thin films, polymers, or nanostructured coatings, surface engineering allows

4

for the deposition of materials with specific properties. Coatings can provide functionalities such as corrosion resistance [3], biocompatibility [9], or enhanced electrical conductivity [19], expanding the utility of the underlying material.

Coating does present some disadvantages though, when compared to other surface functionalization methods, such as plasma treatment. The thickness of coatings can sometimes be challenging to control precisely, leading to variability in the functionalized layer [23] [24]. Achieving uniformity across large surfaces can be especially difficult. Plasma treatment, when well-controlled, can provide a more consistent modification depth. The treatment penetrates the material surface, and the depth of modification can be adjusted with careful control of plasma parameters. Ensuring strong adhesion between the substrate material and the coating may be challenging [20], especially if the substrate surface is not properly prepared. Poor adhesion can result in coating delamination over time. Plasma treatment often enhances adhesion by modifying the surface chemistry of the material, leading to better compatibility with subsequently applied materials. Plasma treatment is generally more versatile in terms of material compatibility. It can be applied to a wide range of materials, including polymers, metals, and ceramics. Some coating processes involve the use of solvents and chemicals that may have environmental implications. Additionally, the disposal of excess coating material can be a concern. Plasma treatment is typically a cleaner process, as it often involves gases and does not generate significant chemical waste. However, the environmental impact depends on the specific gases used in the treatment. The range of functionalities that can be introduced through coating may be limited by the types of materials available for coating. Achieving multifunctionality may require the application of multiple coatings. Plasma treatment offers a broader range of functionalization possibilities, as it can modify surface chemistry and structure, enabling diverse functionalities in a single treatment [25] [26].

While surface engineering has made significant strides in functionalizing material surfaces, challenges persist. Issues such as long-term stability, scalability, and the environmental impact of certain surface treatments require continued attention. Functionalizing material surfaces through surface engineering is a dynamic and continually evolving field with broad-reaching implications. By tailoring surfaces to exhibit specific functionalities, researchers and engineers unlock a spectrum of possibilities across industries. As technology advances, the synergy between surface engineering and materials science promises innovations that will shape the next generation of materials and their applications.

### **1.3 Surface Engineering for Battery Thermal Management Systems**

The quest for efficient heat management spans numerous industries, from electronics and energy systems to aerospace and beyond. Surface engineering emerges as a pivotal domain in the pursuit of optimizing thermal properties. Diverse strategies and techniques are employed in surface engineering to enhance the thermal conductivity and overall thermal performance of materials.

Surface coatings serve as a cornerstone in surface engineering for thermal enhancement. Applying coatings with high thermal conductivity materials, such as metals or ceramics, provides an additional avenue for efficient heat transfer [27] [28]. These coatings act as conduits, facilitating the rapid movement of thermal energy across the surface.

Incorporating thermally conductive fillers into material matrices is a classic technique in surface engineering [29] [30] [31] [32]. Metals, ceramics, and carbon-based materials serve as effective fillers, creating pathways for efficient heat transfer. The strategic use of fillers allows engineers to tailor thermal properties to meet the demands of specific applications. The integration of nanomaterials into surfaces is an effective approach to thermal enhancement. Nanostructured surfaces, such as those incorporating graphene or carbon nanotubes, offer increased surface area and provide pathways for efficient heat conduction [33]. The nanoscale architecture promotes superior thermal properties, making these surfaces promising for applications demanding exceptional thermal conductivity.

Control over surface roughness emerges as a nuanced strategy in surface engineering for thermal optimization. By tailoring micro and nano-level roughness, the contact area between materials can be influenced, allowing for improved thermal contact and enhanced heat transfer efficiency [34] [35]. The relationship between surface topography and thermal properties opens avenues for fine-tuning materials for specific thermal needs. Controlling wettability is also possible by simply controlling the surface roughness of material. Creating superhydrophobic or superhydrophilic surfaces through surface roughness allows for control over water repellency or attraction [16]. This has implications in fields such as passive corrosion resistance of metallic alloys [16].

Controlling surface topology has emerged as a transformative strategy in the pursuit of optimizing thermal conductivity. As the demand for efficient heat management continues to rise across various industries, understanding how surface features influence thermal properties becomes essential. Surface topology refers to the geometric characteristics of a surface, encompassing features such as roughness, texture, and pattern. Understanding the interplay between these surface attributes and thermal conductivity is foundational to the development of advanced thermal materials.

The electronics industry stands to benefit significantly from advances in controlling surface topology for enhanced thermal conductivity. Efficient heat dissipation is critical in microelectronics, and tailored surface features can mitigate heat buildup, improving device performance and reliability [36] [37] [38] [39] [40]. Despite notable strides, challenges persist in fully harnessing the potential of surface topology engineering for thermal conductivity. Issues such as scalability, manufacturing precision, and durability warrant further exploration.

Controlling surface topology represents a frontier in the pursuit of enhanced thermal conductivity. By manipulating surface features at macro, micro, and nanoscales, researchers and engineers unlock unprecedented opportunities to tailor thermal properties according to the demands of diverse applications. As industries continue to push the boundaries of heat management, the synergy between surface topology and thermal conductivity promises a future where materials are finely tuned to conduct heat with unparalleled efficiency.

## CHAPTER 2: PLASMA FUNCTIONALIZATION OF GRAPHENE NANOPLATELET SURFACES

### 2.1 Graphene Structure and Properties

Graphene has remained an attractive material, due to its intrinsic properties [41] [42] [43]. Graphene has a considerable Young's modulus, on the order of 1 TPa [44], and an excellent thermal conductivity of 4800-5300 W/mK [45]. Graphene also exhibits very interesting electrical properties, with reported carrier mobilities over 200,000 cm<sup>2</sup>V<sup>-1</sup>S<sup>-1</sup> and various quantum effects, such as the Quantum Hall Effect and Klein Tunneling [46]. These properties make graphene desirable as both a filler material in various composites and as a standalone material for electronics applications. Many of graphene's properties are a result of its atomic structure. Graphene is composed of a single layer of carbon atoms arranged in a hexagonal configuration with sp<sup>2</sup> bonding, assuming it exists in its perfect state without defects. In real graphitic materials, including mass-produced graphene-like products, vacancies, substitutional impurities, grain boundaries, and other structural modifications and variants are possible. Molecular dynamic simulations on vacancies in graphene have shown a linearly decreasing Young's modulus as vacancy concentration increases [47]. The spacing of defects can also play a significant role in the degradation of mechanical properties. For defect spacings greater than 4.686 nm, there is little difference between single- or double-atomic vacancies in terms of the reduction in the critical strain to failure [47]. If defects are spaced far enough apart, more attachment points can be created without degrading properties. This implies that modification to graphene's structure must be minimized during surface functionalization to maintain desirable properties.

A single carbon atom in graphene is connected to its three nearest neighbors by covalent ( $\sigma$ ) bonds. These are formed from electrons in the 2s, 2p<sub>x</sub>, and 2p<sub>y</sub> valence orbitals, while the remaining fourth valence electron occupies the  $2p_z$  orbital oriented perpendicular to the plane of the graphene sheet. These  $2p_z$  orbitals overlap and form delocalized valence and conduction bands throughout the graphene sheet. Each carbon atom contributes one electron, completely filling the valence band and resulting in a Fermi energy at the energy where the valence and conduction bands meet [48]. These points are known as Dirac points, and the dispersion relation around them is shown to be linear between energy and momentum [49]. These conditions give rise to many unique electrical phenomena. However, disruption of the basal plane bonding will result in degradation of these properties.

Due to the sp<sup>2</sup> bonding in graphene, covalent chemical functionalization of the sheet face requires the breaking of these bonds. To create graphene composites more effectively, attachment points need to be added to allow dispersion in solvents and facilitate good interfacial bonding [50]. There are various methods to incorporate these attachment points, including chemical treatments and physical processes. Chemical treatments, such as the Hummers' method for creating graphene oxide [51], are batch processes. They require harsh chemicals for intercalation and oxidation, which can be time-consuming and result in the degradation of many properties that make graphene desirable in the first place. Moreover, the chemicals and reactions involved create exothermic conditions that are not conducive to large-scale manufacturing. Other chemical processes, such as Diels-Alder chemistry, may use less hazardous chemicals but remain unattractive due to the length of the reaction and batch process restrictions [46]. On the other hand, physical processes, such as sonication in solvents [52] and mechanical grinding procedures [53], are simple and more environmentally friendly but less effective in creating strong interfacial bonding. These physical processes can also require large amounts of energy to physically break the bonds within the graphene and ensure an environment where those broken bonds will reform according to the desired bonding schemes [53].

Bottom-up processes such as chemical vapor deposition (CVD) growth of graphene are highly technical and difficult to perform at large scales [54]. This limitation restricts the availability of large sheets of chemically pure single-layer graphene. On the other hand, top-down processes involving graphite as a starting material are much more common. Large batches of graphite can be processed, either chemically or physically, to break them down into as few layers as possible. However, this process can cause significant damage to the basal layer structure and is ineffective in producing monolayer graphene [55].

Chemical intercalation to promote exfoliation leaves residual acid content [56]. Moreover, it incompletely intercalates and results in partial exfoliation, making precise control of the layer count impossible. Subsequently, the exfoliated product undergoes ball milling for a set duration to produce a range of flake sizes. Due to the ball milling process mechanically fracturing partially exfoliated flake agglomerates randomly, the resulting flake size range tends to be large [55]. With process control, a range of layer counts and flake diameters can be determined. This process produces what is known as graphene nanoplatelets (GnP) or graphene nanosheets (GnS). While this material can be produced at large scales, it suffers from poor homogeneity in surface chemistry and basal structure [56]. To effectively utilize this available graphene alternative, the surface must be efficiently modified and controlled through simple, high-throughput methods. Although thermal treatments can be effective in healing the basal plane, they do not offer straightforward routes for surface modification.

### 2.2 Introduction to Plasma Surface Functionalization of Graphene

Graphene, since its first documentation in 2004 by researchers Novoselov and Geim [57], has garnered extraordinary interest and become a material of significant research. Substantial advancements in graphene research have yielded exciting results in the electronics and composites industries. However, to fully harness the potential of graphene and its properties, current strategies for surface modification must be optimized, and new strategies need to be developed.

To enhance the production of composites with graphene-like materials as fillers, the surface of graphene-like materials must undergo functionalization [58]. Numerous strategies exist for surface functionalization of graphene, which can be broadly categorized as primary functionalization and secondary functionalization. Primary functionalization involves breaking bonds and converting sp<sup>2</sup> to sp<sup>3</sup> bonds on the surface of graphene [58]. On the other hand, secondary functionalization capitalizes on the significant Van der Waals interactions present at the surface of graphene due to sp<sup>2</sup> hybridization and  $\pi$ - $\pi$  stacking present [58].

Among the various strategies, plasma modification stands out as particularly attractive due to its flexible processing and absence of harsh chemicals. By utilizing different source gases, a wide range of radicals can be generated, enabling tailored functionalization of graphene for specific applications. Plasma can be generated under various environmental conditions, allowing for scalable processes and continuous treatment of materials. This document explores plasma treatment of graphene as a surface functionalization strategy.

Plasma is a collection of free charged particles moving in random directions, which, on average, maintains electrical neutrality [59]. Plasma processing is crucial as this collection of charged particles enables the creation of surface structures that are not achievable through any other commercial method. Different types of plasmas can be generated depending on the types and energy levels of ions and electrons. Plasma is formed in low-pressure gases through a discharge process, where a voltage source drives current between parallel plate electrodes. Under the influence of the electric field, electrons and ions are accelerated, but due to the low mass of electrons, they can respond much faster to electric fields. Electrons collide with ions and neutral molecules, leading to ionization and deionization. Ions, too, are accelerated by the electric fields and collide with the electrodes, resulting in secondary electron emission.

In this research, electron acceleration in radio frequency (RF) alternating current discharge is utilized. In alternating currents, electrons oscillate back and forth between the electrodes, while heavier ions are unable to respond within the timeframe of the alternating discharge. This electron acceleration leads to increased ionizing collisions with neutral molecules in the gas. Consequently, RF discharges operate at lower voltages, as they rely less on secondary electron emission from ion impacts at the electrodes. It is worth noting that most plasmas used for materials processing are not in thermal equilibrium, meaning that the electron temperature within the plasma is significantly higher than the ion temperature [59].

Many plasmas are utilized in etching processes due to their high energy and reactivity, which enables efficient material removal. Ions are generated through electron collisions, and these ions exhibit reactivity with the substrate. They are accelerated towards the substrate, and upon collision with the substrate surface, they react to form volatile gaseous by-products, which are subsequently carried away. With careful control and optimization, plasma can also be employed for film deposition using similar mechanisms. Reactive ions are created, which exhibit reactivity with the substrate, and they are accelerated towards the substrate. However, the accelerating potential is reduced, and instead of forming gaseous by-products, the reactive ions form physical or chemical bonds with the substrate surface, facilitating surface functionalization and film growth. The vast range of possibilities in terms of source gases, accelerating fields, and environmental conditions allows for the attainment of various plasma conditions suitable for diverse material processing applications. This flexibility has led to significant interest in plasma as a field of study for materials processing, particularly for surface treatment and functionalization.

Plasma treatment of graphene surfaces has been shown to successfully modify the basal plane of graphene without the creation of harsh by-products [60] [61] [62] [63]. Plasma modification of graphene utilizes energetic and/or reactive radicals in the plasma to interact with the surface and can have several effects, such as breaking the C-C bonds, removing surface atoms, "cleaning" the surface, and modifying the surface chemistry [64]. The surface reactions are determined by the types of plasma species and energy, which depend on the plasma system, source gas and pressure, and excitation power. Oxygen plasmas have been used to increase bonding between graphene and various matrix materials. Oxygen plasma functionalized graphene has been shown to increase adhesion and stress transfer in metal composites [65]. Oxygen plasmas have also been shown to increase the functionalizability of graphene materials in general, creating more active reaction sites for further functionalization [66]. Oxygen plasma functionalization on nitrogen-doped graphene has been shown to increase supercapacitor performance by inducing pseudo-capacitance incorporating nitrogen and oxygen functional groups [67]. Other carbon-based materials, such as carbon black, have been treated with oxygen plasma; aiming to improve its dispersibility without changing intrinsic structure. Using oxygen plasma functionalization, carbon black was transformed from easily agglomerating nanoparticles to a network with high surface area and hydrophilicity, increasing its usability as a desalination agent [68]. Carbon nanotubes have been modified with plasma for various applications. Treatment with mixtures of oxygen and argon gasses have been shown to increase oxygen content and improve electrochemical sensing

performance [69]. Plasma produced using mixtures of carbon dioxide and nitrogen have been shown to alter the nanotubes surface, by producing isocyanate functionalities, and increase the wear resistance of polyurethane-nanotube composites [70]. Amine functionalization using nitrogen plasma has been performed on reduced graphene oxide, with amine functionals providing enhanced interfacial bonding [71]. Nitrogen plasma has been used to produce successful biosensors using graphene as a base material [72]. Mixtures of argon and nitrogen gasses have been used to produce a plasma that can reduce and functionalize graphene oxide simultaneously [73]. Previous reports show that octafluorocyclobutane plasma can functionalize graphite, while oxygen plasma can etch single layer chemical vapor deposited graphene in a few seconds [74] [75]. In this work, radio frequency (RF) power is used to excite gases in a lab-scale plasma reactor, enabling the radicals to interact with graphene nanoplatelets (GnP). The interactions of the plasma species with the GnP create surface disorder, making it possible to introduce covalently bonded functional groups to the graphene surface.

In conventional plasma treatment systems, the sample remains static within the reaction chamber and electrodes are positioned such that the plasma plume interacts with the sample surface. This setup geometry limits the plasma interaction with the sample materials, especially powder samples, to the exposed surfaces. Depending on the energy of the radicals in the plasma, treatment of the bulk material, or at any depth below a few layers of surface atoms, becomes improbable. As radical energy increases, interactions deeper into the surface of the material become possible but implantation and ablation become issues, destroying bonds, and creating disorder within the material. In this work, we report using our patented rotary plasma reactor to overcome these limitations [76]. The rotary plasma reactor is particularly attractive for treating the surface of powders like GnP. The rotation of a tumbler will expose fresh GnP surfaces to the plasma for effective modifications. The goal of the plasma treatments is to modify the GnP surface to allow easy incorporation into solvents and composites, while not significantly changing the structure of the GnP and preserving the intrinsic properties. By utilizing the rotary reactor, lower energy plasma can be utilized to fully treat powder samples, especially large quantities of powders that are difficult to treat in conventional stationary sample set-ups. Using lower energy plasma limits the structural modifications of the GnP, preserving the intrinsic properties, and promoting chemical modification of the surface without implantation or ablation. This minimal change in the GnP structure would allow for more efficient reinforcement in composites.

### 2.3 Plasma Conditions

Plasma modification of graphene involves utilizing reactive radicals in the plasma to bombard the surface, and the effects on graphene depend on the energy of these radicals. At high energies, the radicals vigorously collide with the graphene surface, leading to broken bonds and etching, which removes layers and 'cleans' the surface [64]. For surface chemistry modification, low-energy plasma species are more effective. However, it's important to note that the terms 'high energy' and 'low energy' are subjective and vary depending on the type of plasma system, source gas, and excitation power.

Previous studies have demonstrated the functionalization of graphite using octafluorocyclobutane (C<sub>4</sub>F<sub>8</sub>) source gas with plasma powers of 100 Watts (W) for 10-20 minutes [74]. Conversely,  $C_4F_8$  plasma has been shown to etch silicon dioxide at 350 W for 1 minute [75]. Oxygen plasma (O<sub>2</sub>) has been observed to etch single-layer CVD-grown graphene at 50 W for 5 seconds [75]. In this work, 70 watts of RF power is used to excite oxygen and fluorine-containing gases in a lab-scale plasma reactor, enabling the radicals to interact with the surface of GnP. At this power level, radicals are transported to the surface of graphene, allowing them to interact with the graphene surface. However, it's important to acknowledge that some radicals may still cause surface ablation and introduce disorder. In this way, covalently bonded functional groups are introduced to the surface of graphene.

### **2.4 Initial Plasma Treatments**

Plasma treatment of graphene surfaces has proven to be a successful method for modifying the basal plane of graphene without generating harsh by-products [60] [61] [62] [63]. In the process of plasma modification, energetic and/or reactive radicals within the plasma interact with the graphene surface, leading to various effects, such as the breaking of C-C bonds, removal of surface atoms, surface 'cleaning', and surface chemistry modification [64]. The specific surface reactions depend on the plasma species and their energy levels, which are determined by factors such as the plasma system, source gas, pressure, and excitation power. Previous studies have demonstrated that C<sub>4</sub>F<sub>8</sub> plasma can functionalize graphite, while O<sub>2</sub> plasma can etch single-layer graphene grown by chemical vapor deposition within a matter of seconds [74] [75].

The objective of the plasma treatments is to modify the GnP surface, enabling easy incorporation into solvents and composites, while preserving the intrinsic structure and properties of GnP. To evaluate the effects of the plasma treatment, X-ray Photoelectron Spectroscopy (XPS) was used to assess surface functionalization, Raman Microscopy and X-ray Diffraction (XRD) to monitor structural changes in GnP and conducted rudimentary immersion experiments to qualitatively visualize the surface modifications.

### 2.4.1 Initial Plasma Treatment Materials and Methods

GnP of grade M25 was obtained from XG Sciences [56] and used without further modification. According to XG Sciences, this particular grade of GnP was produced through a mechanical milling process involving acid-assisted intercalated graphite powders. The M grade particles have thicknesses ranging from approximately 6 to 8 nanometers and a surface area of 120-150 m<sup>2</sup>/g. Specifically, the M25 grade has an average particle diameter of 25 microns [56].

The plasma system consisted of a rotary tumbler chamber measuring 63 mm in diameter and 200 mm in length, which served as the vacuum chamber. Additionally, the system included a mechanical vacuum pump, a 13.56 MHz RF power supply, a matching network, a vacuum gauge, and a gas flow controller. A matching network is used to manually tune the impedance of the RF power source to the characteristic impedance of the generated plasma, minimizing the power reflected from the plasma.

The experimental procedure involved loading 1g of M25 GnP into the rotary tumbler, followed by evacuating the chamber. Subsequently, the gas flow rate was adjusted to maintain a stable pressure range of 660-680 mTorr (87.9-90.7 Pa), achieved with a flow rate of 8 standard cubic centimeters per minute (sccm). For the plasma generation and treatment of the samples,  $C_4F_8$  and  $O_2$  gases were used, respectively.

Afterward, the RF power was activated, and the matching network was manually tuned to minimize reflected power. A constant RF power of 70 W was applied throughout all the treatments. The samples were treated for a duration of 10 minutes, with the rotation direction reversed every 30 seconds. This rotation scheme ensured that the GnP particles were moved back and forth from one end to the other, facilitating uniform treatment.

These plasma parameters were selected as starting points to evaluate ease of processing, with a relatively low power (<100 Watts) and poor vacuum (>>0.7 mTorr) selected. If these plasma parameters prove successful, then processing according to these parameters should be accomplished with relative ease and with lower cost equipment.

XPS analysis was performed using a Perkin Elmer Phi 5600 ESCA system equipped with a magnesium K $\alpha$  x-ray source. The measurements were conducted at a take-off angle of 45°. Survey scans were obtained with a step size of 1.6 eV and a pass energy of 187 eV, while detailed region scans were performed with a step size of 0.05 eV and a pass energy of 11.75 eV. The acquired spectral data were analyzed using CasaXPS software.

Raman spectroscopy measurements were carried out using a LabRAM ARAMIS instrument (HORIBA JOBIN YVON, Inc) equipped with a 50x objective lens. The Raman spectra were acquired in the range of 1200-3000 cm-1 with an excitation laser wavelength of 532 nm. Scans were performed using a 1800 gr/mm grating, with each spectrum being accumulated for 180 seconds.

XRD analysis was conducted using a Bruker D2 Phaser instrument (Bruker Corporation). Scans were performed at a voltage of 30 kV and a current of 10 mA, with a step size of 0.01° and a dwell time of 0.5 seconds.

For the immersion experiments, deionized water and isopropyl alcohol were utilized as the immersion liquids. Approximately 20 milligrams of sample materials were added to approximately 60 mL of the liquid. Samples were compared to assess the effects of surface treatment on behavior in water and alcohol. Prior to immersion, the samples were weighed, and then added to a beaker containing the liquid. Manual stirring was performed using a glass stir rod, and the experiments were recorded on video.

### 2.4.2 Initial Plasma Treatment XPS Results and Discussion

The XPS spectrum peak fitting was conducted using the CasaXPS software. Background subtraction was performed, and the spectra were charge-referenced to the 284.5 eV C=C peak. To analyze the C1s spectrum from Raw M25 (Figure 1), a modified version of the general fitting scheme suggested by Biesinger [77] for graphitic/graphene/carbon nanotube materials was utilized. Some adjustments were made to enhance the fit. Specifically, the full width at half maximum (FWHM) restrictions for the shake-up peak ( $\pi$ - $\pi$ \*) were relaxed to 3.47 eV, allowing for broadening of the peak to better match the experimental data. The origin of this  $\pi$ - $\pi$ \* peak is the extensive stacking interactions in graphene-like materials [78]. The peak assignments and constraints based on this modified fitting scheme are provided in Table 1.



Figure 1. XPS Spectrum of the C1s region of Raw M25 before plasma modification. Peaks were fit using CasaXPS software.

Species	Peak	Starting Position (eV)	Common Range (eV)	FWHM (eV)	Lineshape	Area Constraint
C=C	А	284.5		0.4 to 0.8	LA (1.2, 2.5, 5)	
С-С, С-Н	В	A+0.5	A+0.3 to A+0.5	0.9 to 1.5	GL (30)	
С-ОН, С- О-С	С	A+2.0	A+1.8 to A+2.2	B*1	GL (30)	
С=О	D	A+3.5	A+3.3 to A+3.5	B*1	GL (30)	
O-C=O	Е	A+4.5	A+4.3 to A+4.8	B*1	GL (30)	
π-π*	F	A+6.41		2.7	GL (30)	A*0.0696
CF <sub>2</sub>	G	A+6.7 [79]		B*1	GL (30)	
CF <sub>3</sub>	Н	A+8.6 [79]		B*1	GL (30)	

Table 1. Constraints used in CasaXPS software to fit XPS spectra.

This fitting scheme serves as an appropriate initial approach for most graphitic materials. The C=C peak, which is typically the most prominent peak, can be utilized for charge correction. Due to the use of graphene nanoplatelets, a significant contribution from the  $\pi$ - $\pi$ \* peak is anticipated [78]. XG Sciences' data suggests the presence of ethers, hydroxyl, and carboxyl groups resulting from residuals of the intercalation process [56]. Therefore, these groups must be considered when analyzing the starting material. Peak fitting in the 4-6 cm<sup>-1</sup> range, adjacent to the C=C peak, can be challenging due to potential overlap between oxygen and fluorine functional group peaks. Notably, the O-C=O and C-F peaks may be convoluted and appear in the same region; thus, these peak assignments should be considered tentative.

The same fitting scheme was subsequently applied to the spectrum obtained from the fluorine plasma-treated materials. Interestingly, two additional peaks became apparent upon applying the general fitting scheme (Figure 2).



Figure 2. XPS Spectrum of the C1s region of  $C_4F_8$  Plasma treated M25. Peaks were fit using CasaXPS software.

These peaks are attributed to the plasma treatment process and have been assigned accordingly. The assignment of the CF<sub>2</sub> and CF<sub>3</sub> peaks aligns well with literature values for energy shifting [79]. Based on the molecular structure of C<sub>4</sub>F<sub>8</sub>, it is not expected to observe a significant number of C-F functional groups. Instead, the ionization process of C<sub>4</sub>F<sub>8</sub> is likely to cause a breakdown, resulting in an abundance of CF<sub>2</sub> radicals [80]. However, the presence of C-F functional groups would overlap with the  $\pi$ - $\pi$ \* peak and the O-C=O peak. Therefore, the broadening and increased intensity in the 290-293 eV region could be attributed to fluorine functionalization.

Fitting of the oxygen plasma-treated samples did not reveal any additional peaks, but only showed increases in intensity for the oxygen functional peaks (Figure 3). On the other hand, fitting of the F1s peak for the fluorine plasma-treated samples required multiple component peaks, as depicted in Figure 4 for the  $C_4F_8$  plasma treated samples.



Figure 3. XPS Spectrum of the C1s region of O<sub>2</sub> Plasma treated M25. Peaks were fit using CasaXPS software.



Figure 4. XPS Spectrum of the F1s region of C<sub>4</sub>F<sub>8</sub> Plasma treated M25. Peaks were fit using CasaXPS software.

These results support the presence of multiple fluorine species at the surface of the GnP after plasma modification. At least two peaks are expected due to the two additional peaks observed in Figure 2. However, due to overlaps in the C1s spectrum between oxygen and fluorine bonded carbons, there may be additional peaks convoluting the F1s spectrum. The fluorine treatment resulted in a reduction of oxygen content from 3.31 at% in the as-received GnP to 2.0 at% after the 10-minute fluorine plasma treatment. Peaks at lower binding energies are indicative of ionically bonded fluorine (<688 eV), while higher binding energy peaks are more covalent in nature [74] [79]. The peak at 688 eV indicates primarily covalently bonded fluorine, but additional shoulders can be fitted to this peak to reduce the residual standard deviation of the fit. This suggests the presence of multiple bonding environments for fluorine, which is expected due to variations in the energy of the radicals interacting with the surface. Further treatments should be conducted to study the evolution of the F1s peak and gain a better understanding of the changing bonding environment. Importantly, fluorine peaks are not observed in the XPS spectra of the raw material or the oxygen plasma-treated material.

Peak fitting of the O1s peaks for oxygen plasma-treated samples reveals the presence of two distinct peaks (Figure 5).



Figure 5. XPS Spectrum of the O1s region of O<sub>2</sub> Plasma treated M25. Peaks were fit using CasaXPS software.
These peaks can be roughly associated with a double-bonded oxygen in a carbonyl-type carbon group and a single-bonded oxygen in a carboxylic-type carbon group [81]. The doublebonded carbonyl-type oxygen peaks are typically located at low eV values (530 eV - 533 eV), while the single-bonded carboxylic-type oxygen peaks are located at higher eV values (533 eV -537 eV) [81]. Further deconvolution of these peaks with additional assignments becomes challenging due to the noise-to-signal ratio. The XPS O1s spectrum for raw M25 (Figure 6) shows two peaks at 530.6 eV and 532.4 eV. Comparison of the spectra between raw M25 and oxygen plasma-treated M25 reveals an increase in the ratio of single-bonded oxygen species. This is consistent with the observation in Figure 3, which shows an increase in the C-H and C-OH peaks and a decrease in the C=O and O-C=O peaks compared to the raw spectrum in Figure 1. This change in ratio suggests an increase in preferential single-bonded oxygen groups over the more difficult-to-functionalize double-bonded oxygen groups. After a 10-minute C<sub>4</sub>F<sub>8</sub> plasma treatment (Figure 7), the two peaks have shifted to slightly higher binding energies, specifically at 531.1 eV and 532.9 eV, respectively. This suggests that the oxygen species present are becoming more carboxylic and single-bonded in nature. Overall, the oxygen content has increased in the oxygen plasma-treated samples compared to the raw M25. The oxygen density increased from 3.31 at% in the as-received GnP to 5.74 at% after a 10-minute oxygen plasma treatment. On the other hand, fluorine plasma treatments resulted in an oxygen content of 2.0 at% after 10 minutes. These results indicate that fluorine plasma treatments either remove oxygen species through sputtering or functionalize these oxygen attachment points.



Figure 6. XPS Spectrum of the O1s region of Raw M25 before plasma modification. Peaks were fit using CasaXPS software.



Figure 7. XPS Spectrum of the O1s region of  $C_4F_8$  Plasma treated M25. Peaks were fit using CasaXPS software.

Raman microscopy is a powerful tool for the structural characterization of carbon materials [82] [83] [84] [85]. Raman scatter can obtain information about the structure and properties of molecules using their vibrational transitions. Raman scattering is a two-photon event, measuring the change in the polarizability of the molecule with respect to its vibrational motion [86]. The Raman microscopy results reveal changes in the spectrum for different plasma treatments. Table 2 summarizes the approximate peak positions and peak intensities, which were used to determine the ratios between peak intensities. It is noting that the spectrum of the  $C_4F_8$  plasma-treated samples (Figure 8) is the only one that exhibits a D-peak.

Sample	D-Peak	G-Peak	D'-Peak	2D-Peak
M25 Raw	N/A	1568 cm <sup>-1</sup>	NI/A	2700 cm <sup>-1</sup>
		38773 cnts.	$\mathbf{N}/\mathbf{A}$	8417 cnts.
M25 O <sub>2</sub> 10 min	N/A	1571 cm <sup>-1</sup>	NI/A	2693 cm <sup>-1</sup>
		38243 cnts.	$\mathbf{N}/\mathbf{A}$	4426 cnts.
M25 C <sub>4</sub> F <sub>8</sub> 10	1342 cm <sup>-1</sup>	1568 cm <sup>-1</sup>	1605 cm <sup>-1</sup>	2680 cm <sup>-1</sup>
min	18996 cnts.	37162 cnts.	2870 cnts.	1633 cnts.

Table 2. Table summarizing Raman peak position and intensities used to calculate intensity ratios.



Figure 8. Raman spectrum for samples comparing Raw M25, 10 Minute  $O_2$  Plasma, and 10 Minute  $C_4F_8$  Plasma samples.

The D-Peak at around 1350 cm<sup>-1</sup> represents the breaking of symmetry in the carbon basal plane, resulting from the breaking of pi bonds in carbon atoms and allowing non-symmetrical stretching. A transverse zone boundary phonon interacts with defects to create this shift. The intensity of the D-Peak relative to the G-Peak can be used to measure the level of "disorder" in the basal plane [87]. The G-Peak at around 1580 cm<sup>-1</sup> corresponds to the symmetric "breathing" of the perfect carbon basal plane. Perfect graphene will exhibit only a G-Peak and a G'-Peak.

The C<sub>4</sub>F<sub>8</sub> plasma treatment resulted in an I<sub>D</sub>:I<sub>G</sub> ratio of 0.51, which is significantly higher than that of the Raw M25 and O<sub>2</sub>-treated M25 samples. Oxygen plasma treatments did not result in a significant D-Peak, indicating relatively little disorder in the basal plane. This suggests that functional groups were mainly added at the edges of the GnP sheets. These results indicate a preference for oxygen containing functional groups to attach at edges, where there is natural disorder, rather than create disorder on the basal plane. For some applications, basal plane disorder is not desired, and this type of treatment scheme would be preferred. If we were to increase RF power or increase treatment times, we could possibly increase the basal disorder generated and implant oxygen containing functionals within the basal plane. These results highlight the versatility and tunability of plasma treatments.

Additionally, the spectrum of the C<sub>4</sub>F<sub>8</sub>-treated samples (Figure 8) shows a shoulder at approximately 1605 cm<sup>-1</sup>, which corresponds to the D'-Peak. The D'-Peak arises from an intravalley double resonance process, where a longitudinal phonon interacts with a defect around an equivalent k point in the Brillouin zone. In contrast, the G'-Peak is an intervalley process involving nonequivalent k points and does not require defects to appear in perfect graphene spectra. The presence of the D'-Peak provides further evidence of defects generated during the C<sub>4</sub>F<sub>8</sub> plasma treatment.

The G'-Peak is sensitive to doping and strain in graphene, as well as the number of graphene layers with AB Bernal stacking [84]. Reducing the layer count or increasing strain will result in a redshift of the G'-Peak, while increased doping will dampen the peak intensity. Graphene produced through mechanical exfoliation typically exhibits predominantly AB stacking. However, the sample material used in this study underwent unknown chemical processes that may have altered the stacking order and produced randomly stacked graphene platelet agglomerates. In this case, the G'-Peak can provide information about the relaxation associated with double resonant selection rules and the random stacking [84]. Our observations show that plasma treatment leads to both a redshift and dampening of the G'-Peak (Figure 8), with  $C_4F_8$  plasma resulting in more pronounced shifting and dampening. This is consistent with the  $I_D:I_G$  ratio results, indicating a higher degree of disorder in the  $C_4F_8$ -treated samples. Furthermore, the peak shape changes from a Lorentzian type for the raw materials to a broader, more convoluted Lorentzian for the  $C_4F_8$ -treated samples.

X-ray diffraction can be used in conjunction with Raman spectroscopy to determine the crystallite size in the c-axis [84]. The diffraction scans are compared in Figure 9, where the Raw M25 samples exhibit a peak at 26.75°, and the diffraction angles decrease with the progression of the treatment. The peak positions, intensities, and FWHM values are reported in Table 3.



Figure 9. X-Ray Diffraction results for Raw M25, 10 Minute O<sub>2</sub> Plasma, and 10 Minute C<sub>4</sub>F<sub>8</sub> Plasma. Intensity has been normalized.

Table 3. Table summarizing the peak position, intensity, and full-width at half maximum of the X-Ray Diffraction results.

Sample	Diffraction Angle (°2 $\theta$ )	Intensity (counts)	FWHM (°2 $\theta$ )
M25 Raw	26.75	4355	0.55
M25 O <sub>2</sub> 10 min	26.74	4565	0.51
M25 C <sub>4</sub> F <sub>8</sub> 10 min	26.67	3831	0.61

From Figure 8, it is observed that the Raw M25 material has the most blue-shifted peak, and as it is treated with plasma, the peak redshifts and changes shape. This is supported by the diffraction results (Figure 9), where the shift towards lower 2 $\theta$  angles and the broadening of the peak FWHM indicate a smaller crystallite size according to the Scherrer equation. Plasma has been shown to exfoliate graphene under certain conditions [88]. The slight shifting, coupled with the increases in FWHM, could indicate a peeling of layers due to plasma interactions. The slight shifting could also indicate a larger inter-galley spacing for the GnP, but this effect is negligible as the d-spacing remains 0.33 nm.

Immersion experiments were conducted to observe how the plasma treatments changed the behavior in deionized (DI) water and isopropyl alcohol. Still images of the immersion experiments are displayed in Figure 10 and Figure 11 for qualitative inspection.



Figure 10. Still image of immersion experiments, 20 milligrams of GnP in 60 milliliters of DI Water. A is C<sub>4</sub>F<sub>8</sub> treated M25, B is O<sub>2</sub> treated M25, and C is Raw M25. Beakers are 100 mL Kimble beakers with a 50 mm outer diameter.



Figure 11. Still image of immersion experiments, 20 milligrams of GnP in 60 milliliters of Isopropyl Alcohol. A is C<sub>4</sub>F<sub>8</sub> treated M25, B is O<sub>2</sub> treated M25, and C is Raw M25. Beakers are 100 mL Kimble beakers with a 50 mm outer diameter.

The results of these experiments demonstrate that fluorine surface treatments significantly increase the hydrophobicity of the M25 GnP. Figure 10 shows that the C<sub>4</sub>F<sub>8</sub> 10 Minute Plasma sample does not disperse in DI water, indicating enhanced hydrophobic behavior. Increased hydrophobicity suggests the presence of C-F bonds on the surface of graphene [79] [89]. In terms of dispersibility in isopropyl alcohol, the fluorine-treated samples exhibit similar behavior to untreated GnP. Figure 11 shows little difference in the appearance of the solutions, although the oxygen plasma-treated sample appears slightly more dispersed upon visual inspection. The oxygen plasma-treated samples exhibit increased dispersibility in both water and isopropyl alcohol compared to the untreated samples. This enhanced dispersibility is attributed to the increased disorder on the basal plane of graphene and the presence of oxygen-containing functional groups.

In this series of experiments, commercially available graphene nanoplatelets (GnP) underwent low-temperature plasma processes for modification. The modifications were characterized using XPS, Raman microscopy, and XRD techniques. Immersion experiments were also conducted to observe the behavior of the modified GnP in solvents. The results indicate that  $C_{4}F_{8}$  plasma treatments successfully attached fluorine-containing functional groups to the surface of GnP. The addition of fluorine is evidenced by the presence of F1s peaks in the XPS scans, indicating modified immersion characteristics in water and alcohol. X-ray diffraction and Raman experiments showed no significant change in the structure of GnP, which is crucial for maintaining its desirable properties. However, there was some ambiguity in assigning peaks in the 290 cm<sup>-1</sup> region due to overlap between oxygen and fluorine-containing functionals. Multiple distinct peaks in the C1s spectrum and the need for two or more peaks in the F1s spectrum suggest the addition of more than one type of fluorine-containing functional to the GnP structure. The predominant addition of CF<sub>2</sub>-type fluorine functionals aligns with literature data on radical density in C<sub>4</sub>F<sub>8</sub>

plasma [77]. The fluorine atomic percentage increased from zero in the as-received GnP to 12.6 at% after a 10-minute  $C_4F_8$  plasma treatment. Oxygen plasma treatments were successful in adding oxygen-containing functionals to GnP without inducing basal plane disorder.

The density of oxygen increased from 3.31 at% in the as-received GnP to 5.74 at% after a 10-minute oxygen plasma treatment. These results suggest that most oxygen functionalization occurs at the edges of GnP, where natural disorder provides dangling bonds.  $C_4F_8$  plasma treatment led to decreased dispersibility in water but had no noticeable effect on dispersibility in alcohol. On the other hand, oxygen plasma treatments qualitatively increased dispersibility in both water and alcohol. These changes in the interaction of GnP with solvents provide further evidence of a functionalized surface. The results are promising for future functionalization of plasma-treated GnP, with the ability to control the types of functional groups present at the surface.

## **2.5 Solder Incorporation**

Initial goals of the project were to improve the thermomechanical fatigue properties of solders and tin alloys for microelectronic applications. Electrical devices, and the components and circuits that comprise them, are continually getting smaller. The need for smaller circuits with greater densities of interconnections will only increase. With this need for miniaturization, unfamiliar problems will emerge, and some existing problems will be amplified. Gradient-driven mechanisms such as diffusion will be exacerbated by the micro-scale of future solder bumps. Not only will miniaturization impact the performance requirements of interconnect materials, but the adoption of more electrical components in electrical vehicles will increase the performance and lifetime requirements to meet safety standards. Due to the toxicity of lead, consumer electronics have adopted lead-free solders. Currently, SAC305 is the standard solder material.

To minimize the material's compositional migration, research has been focused on the addition of inert particles as physical barriers. To hinder the diffusion of single atoms, the addition of point-like particles can only be so effective, as there is a probability that a diffusing atom will encounter a barrier particle. As the surface area of the particle is increased, the probability that a diffusing atom will encounter that particle increases. This can be maximized by introducing a particle with a 2-dimensional plate-like morphology and ensuring they are aligned correctly and dispersed well. This concept has been the basis of under bump metallization (UBM) [90]. The addition of a metallic layer on the substrate will minimize the diffusion of copper from the substrate into the solder. This UBM layer will only hinder diffusion of copper from the substrate into the solder; it does nothing to prevent the migration of atoms within the bulk of the solder or at the chip-solder interface. Through the addition of well-dispersed, plate-like particles, this UBM effect

may be applied to the bulk of the solder. Many particles are available in plate-like morphology, but other factors must be considered when selecting a particle.

With the popularization of electronic vehicles, more reliability is needed for solder materials if they are to be widely adopted by the automotive industry, as expected lifetimes for soldered connections are increased. For this reason, it is important to focus research efforts on the service reliability of the solder and mitigation of "aging effects" that impact the reliability of the solder.

The most critical properties for a solder are the melting temperature, range, and solidification kinetics. The melting temperature and range will determine the processing conditions and the minimum temperature that the electrical components must be able to endure. The melting temperature and range will also determine the maximum service temperature of that part. Solidification kinetics and the as-reflowed microstructure are crucial to the service lifetime of the solder. The creation of a finer microstructure with well-dispersed IMCs leads to enhanced mechanical properties compared to a coarser microstructure with agglomerated IMCs.

The coefficient of thermal expansion has become increasingly more important as electronics become smaller. As electronics and circuits become smaller, so do their interconnects. Coefficients of thermal expansion may be approaching length scales comparable to solder bump size, threatening thermally induced shorts. Coefficients of thermal expansion may play a role in whisker formation [91], as the imparted stress may be enough to produce plastic extrusion of Snrich phases through holes in the IMC layer at the interface of the solder.

Surface tension at the liquid-solder interface plays a key role in the application of the solder [92]. Surface tension will dictate wettability and aid in the self-alignment of parts and circuitry through capillary flow. Poor wettability will lead to a poor solder-substrate interface and, in turn, affect the mechanical and electrical performance of the interconnect.

Resistivity is important in electronic interconnects, as the flow of electrons is the goal of a circuit and should be optimized to extend the lifetime and improve the reliability of soldered joints. The flow of electrons through the solder material can have several effects on the microstructure and properties of the solder joints. Electromigration can become an issue when dealing with solder alloys comprised of two or more phases and can result in deleterious effects on the performance of the joint [39]. Electromigration can cause the growth of intermetallic compounds and have adverse effects on the mechanical properties of soldered joints. Materials with high electrical resistivities are also susceptible to Joule heating, which will further exacerbate any electromigration and thermal effects [93].

Once the soldered joint has been reflowed, the mechanical properties of the joint are crucial factors that affect the reliability and performance of the joint. The most important stress state that occurs in solder joints is creep [93]. Creep is any time-dependent, monotonic deformation that occurs through a variety of mechanisms. All creep processes are thermally activated, and due to the requirement of low melting temperatures, creep occurs at exceptionally low temperatures in solder. Cyclic deformation is another particularly important stress state and can be isothermal or thermal. Isothermal cyclic deformation can be any imposed cyclic displacement that occurs at a constant temperature. Thermal cyclic deformation can be caused by a difference in the coefficient of thermal expansion between two dissimilar materials. Unfortunately, fatigue in solder is complex because it will occur in parallel with creep. Resistance to these deformation modes is critical in extending the lifetime of soldered joints.

Other mechanical properties that are important to solder materials are monotonic properties, such as ultimate tensile strength, shear strength, and elongation. Ultimate tensile strength is the maximum engineering stress a material can withstand in tension without fracture. Ultimate tensile strengths can vary depending on the strain rate imposed. Shear strength is analogous to tensile strength; however, because the testing is conducted in shear, plastic instability (neck formation) does not play a role in the deformation. Elongation is important in the overall performance of the solder joint. Though most solder joints are not meant to be mechanically supportive of stress, they need to be able to withstand any accidental strains without failure, and ductility is important in this aspect.

Among the issues affecting reliability, thermomechanical fatigue, electromigration, and thermomigration are major contributors to damage in lead-free electronic solders [36] [94]. These contributors are not listed in order of importance, and there are significant mutual interactions among them, such that a solution to mitigate one issue may also prove beneficial for other issues. Thermomechanical fatigue, electromigration, and thermomigration are particularly significant in the context of electronics miniaturization.

Even small temperature differences can result in exceptionally large temperature gradients in miniaturized solder joints. A temperature gradient of ~1000 °C/cm can cause thermomigration in solders [39]. Micro-bumps, approximately 10  $\mu$ m in size, are used to achieve joint densities of 105 to 106 joints/cm<sup>2</sup> [93]. Following Moore's law, the density of 2-dimensional integrated circuits on Si chips will double every 18-24 months. Due to the geometry of new miniaturized circuits, large gradient forces are expected to pose reliability issues for electronic interconnects. Joule heating becomes a greater concern as the density continues to increase, and the excess heat needs to be conducted away. A temperature gradient is necessary to facilitate heat conduction. An effective solder material must have adequate thermal conductivity to remove the excess heat generated by Joule heating or the service environment. Thermal migration has been studied in PbSn solders, and it has been found that Pb diffuses from the hot end to the cold end of the solder bump, resulting in Sn redistributing from the cold end to the hot end of the solder bump [39] [95]. It is unclear whether the Sn diffusion is a result of the Pb atoms being the dominant diffusing species and forcing a reverse flux of Sn to maintain volume, or if the Sn possesses a negative transport heat.

To study the thermal migration of Sn in lead-free alloys, inert markers such as holes produced by a focused ion beam are needed. Using this method and under a thermal gradient of 2829 °C/cm, thermomigration was observed in  $SnAg_{3.5}$  solder joints [96]. Hillocks, small mounds at the interface comprised of Sn, are caused by the thermally induced mass transport of the Sn atoms. It was found that the net mass transport of Sn was from the cold end to the hot end of the solder joint.

The mechanism by which these atoms migrate is a simple diffusion mechanism of vacancy exchange. According to the requirements of thermodynamics of irreversible processes, any atomistic mechanism that underlies a finite-field effect must also underlie the zero-field effect [37]. This means that a mechanism that underlies thermomigration must not be dependent on a thermal gradient and must be present in isothermal conditions. For this reason, vacancy-driven diffusion is accepted as the primary mechanism at work in solid binary alloys [40].

Strategies to mitigate thermomigration are aimed at limiting the diffusion of atoms within the solder. The addition of inert particles, such as titanium carbide, has been shown to limit microstructural evolution in SAC305 solders during thermal stressing [97]. The results show that particles at the interface of solder-substrate will act as barriers to diffusion and limit the diffusivity of Cu into the solder under large temperature gradients.

Electromigration is the mass transport of atoms due to several driving forces, more complicated than just a concentration gradient of the diffusing species. The driving forces for electromigration include both the direct field force, as well as an electron wind force. The electron wind force is the transfer of momentum from moving electrons to an ion or atom due to the scattering of valence electrons [98] [39]. Electromigration, like thermomigration, is a diffusion-controlled phenomenon. The formation of hillocks and voids occurs during electromigration, just as with thermomigration. In electromigration, the hillocks will form at the interface of the solder and the anode while voids will form at the interface between the solder and cathode.

If the hot side of a solder joint corresponds to the cathode and the cold side corresponds to the anode, then thermomigration and electromigration will act in the same direction and compound. If the opposite is true, and the hot side corresponds to the anode and the cold side corresponds to the cathode, then thermomigration and electromigration will compete [98]. In the case of microelectronics, the smaller electronic interconnects become, thermomigration becomes dominant [98] [38].

Electromigration has several driving forces but acts through vacancy diffusion mechanisms. This is beneficial to engineering solutions for thermomigration and electromigration, as one only needs to control the diffusion of atoms to mitigate both issues. Where thermomigration and electromigration differ are the driving forces that influence each. The main job of the electronic interconnect is to transfer charge through a circuit, so the flow of electrons through the solder is unavoidable. Depending on the service conditions and resistance of materials involved, thermomigration may not be a critical issue. Often electromigration will result in modified microstructures and void formation, leading to current channels developing and narrowing, resulting in current crowding and Joule heating. Mitigating electromigration will therefore play a role in mitigating thermomigration by reducing current crowding and the production of waste heat. Strategies to mitigate electromigration are focused on limiting the diffusivity of atoms. The actual failure mechanism of electromigration is due to the coarsening of IMC layers at the interface reducing the electronic conduction across the interface and/or void formation at the IMC-solder interface resulting in loss of conduction. The average current density in flip-chip solder joints has reached as high as 104 A/cm<sup>2</sup> [99]. Under these types of current densities, the failure mode of SnAgCu flip-chip solder joints occurs by a pancake-type void formation and propagation at the interface between the solder and  $Cu_6Sn_5$  [99]. The electron wind effect and the direct field effect cannot be removed, so the strategy to mitigate the electromigration effects will change the way atoms respond to these driving forces. When adding a particle to mitigate electromigration, the thermal stability of the particle is not important, but the electronic properties of the particle are important as far as the addition of particles does not decrease the electronic conductivity of the solder.

Corrosion can be an issue whenever two dissimilar metals are electronically interconnected. This is certainly the case with solder, especially in elevated temperature and high humidity environments. As with other reliability issues, miniaturization only exaggerates the potential failure modes. Corrosion products nanograms or less can result in complete device failure due to the small scale of interconnects [100]. Corrosion in lead-free alloys is between the Sn-rich phase and the other phases present. In the case of Sn-Ag-Cu, the galvanic corrosion is due to the potential difference between the Sn-rich phase and the intermetallic compounds (IMCs). The intermetallic compounds within the bulk of the solder consist of Ag<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub> which are very chemically stable [101]. A layer of Cu<sub>3</sub>Sn will form at the interface of the solder and the copper substrate. The corrosion products consist of SnO, SnO<sub>2</sub>, Sn(OH)<sub>4</sub>, and Sn<sub>3</sub>O(OH)<sub>2</sub>Cl<sub>2</sub> [102].

The mechanism of corrosion begins with the dissolution of Sn at anodic sites within a galvanic couple of Sn-rich phases and IMCs within the solder and at the solder-substrate interface. Hydroxyls are produced at the cathode, and electrons are transferred through the material while ions are transported away from the reaction site and combine with hydroxyls and other ions. The corrosion products are then deposited, and in some cases, the cycle continues as a pit is initiated at the reaction site [103]. While in some other instances, the corrosion products will passivate the surface.

Strategies to mitigate galvanic corrosion are focused on manipulating the morphology of the solder microstructure through processing or alloy design. It has been demonstrated that changing the cooling rates of solder joints will influence the microstructures produced. A fine and homogeneously distributed Cu-Sn intermetallic is produced in an SnCu<sub>2.8</sub> alloy using a cooling rate of 15 °C/s, while a coarsened microstructure appeared with a cooling rate of 1.2 °C/s [104]. The microstructure with the coarser IMC morphology resulted in improved electrochemical resistance. This can be attributed to the interface of the Sn-rich phase and the IMC being much more susceptible to corrosion than the bulk IMC. This area is more susceptible to corrosion due to atomic level straining resulting from the lattice mismatch of the Sn-rich and IMC phases. A fine microstructure will also provide more accentuated pitting corrosion due to the higher number of galvanic couples formed. The same results are true for  $SnAg_{0.3}Zn_{0.9}$  solder alloys with different cooling rates. It was found that water-cooled samples were less corrosion resistant than furnacecooled and air-cooled samples [101]. This is not a correlation between cooling rate and corrosion resistance, but a correlation between microstructure and corrosion resistance. The corrosion resistance of SnAg<sub>2</sub> solder alloy increases with an increase in cooling rate [104]. In this case, the morphology of the IMCs changed from a fiber-like + plate-like Ag<sub>3</sub>Sn at slower cooling rates to a

mixture of spheroid-like + fiber-like Ag<sub>3</sub>Sn at higher cooling rates. In any case, decreasing the area of the anode-cathode galvanic couples will be beneficial to the corrosion resistance of Sn-based alloys.

Graphene is a 2D hexagonal array of carbon atoms with sp<sup>2</sup> bonding. Much of the interest in graphene was initially driven by its excellent electrical properties. A single carbon atom in graphene is connected to its three nearest neighbors by covalent (sigma) bonds. These bonds are formed from electrons in the 2s, 2px, and 2py valence orbitals, while the remaining fourth valence electron occupies the 2pz orbital oriented perpendicular to the plane of the graphene sheet [105]. These 2pz orbitals overlap and form delocalized valence and conduction bands throughout the graphene sheet. These delocalized bands meet at highly symmetric K and K' points. Each carbon atom contributes one electron, filling the valence band and giving rise to a Fermi energy at the energy where the valence and conduction bands meet. These points are known as Dirac points, and the dispersion relation around these Dirac points is shown to be linear between energy and momentum [105]. Due to the sp<sup>2</sup> bonding in graphene, covalent chemical functionalization of the sheet face requires breaking these bonds. Non-covalent functionalization can be achieved through van der Waals forces. Chemical bond strength plays a role in determining the mechanical properties of the material. The intrinsic strength of graphene is considered greater than that of any other material, due to its three-fold coordinated C-C bonding.

The isolation of single sheets of graphene from graphite in the early 2000s [106] [107] allowed for the characterization of graphene's experimental strength. Atomic Force Microscopybased techniques have been applied to determine the mechanical properties of single-layer graphene. By depositing single-layer graphene flakes onto an etched silicon substrate with circular wells of known diameter and depth, researchers were able to use AFM tips with known spring constants to deflect the graphene sheets and calculate mechanical properties. A fracture strain of 25% was achieved, and a Young's modulus of around 1 TPa and an intrinsic strength of 130 GPa were calculated [108] [109] [110].

The thermal properties of graphene are, like its other properties, impressive due to its unique 2D structure. The conductivity within a graphene sheet makes it an excellent heat spreader. Many carbon materials have excellent thermal conductivity, such as diamond, but a diamond will spread heat in all three dimensions throughout its lattice, while graphene is only two-dimensional. The strong covalent network that forms graphene provides an efficient means for heat transfer by lattice vibrations, or phonons. The determination of the thermal conductivity of graphene was first achieved through modified Raman spectroscopy experiments, in which the temperature dependence of certain Raman peaks was tracked. The frequency shift of the G-peak from ~1584 cm<sup>-1</sup> at -200°C to ~1578 cm<sup>-1</sup> at 100°C is linear and can be used to track the temperature of the sample with the Raman spectra. By using the Raman excitation laser power to heat the sample, the amount of heat dissipated can be tracked through the integrated Raman spectra [45] or by placing a detector underneath the graphene layer [111]. Using these methods, values for thermal conductivity of ~3000 W/mK [5] and ~2500 W/mK [58] were found. However, other studies using similar Raman setups found thermal conductivity values of ~600 W/mK [112] using different values for laser absorption. Had [112] used comparable numbers for laser power absorption, a value of ~3600 W/mK would have been extracted, highlighting the importance of an understanding of the laser light absorption characteristics. Even a thermal conductivity of 600 W/mK is exceptionally good, with bulk copper having a thermal conductivity of ~400 W/mK. Graphene is unique in that it has a negative thermal expansion coefficient at room temperature [113]. This is a consequence of its 2D structure and was predicted by Lifshitz in 1952 [114].

Unfortunately, defects will tend to degrade the mechanical properties of graphene, and pristine graphene itself is not extremely useful in composites. To incorporate graphene into other materials, there must be some attachment sites to interact with other materials. When the basal plane of graphene is disrupted, oxygen-containing functional groups can be attached. When this process takes place, the graphene is said to be oxidized and is more easily dispersed in composites. This can have detrimental effects, both on the electronic structure of the valence and conduction bands, but also on the mechanical properties of graphene as the out-of-plane, sp<sup>3</sup> structures are more easily bent and weaken the sheet. The degree of functionalization will determine the effect on the electrical, chemical, thermal, and mechanical properties. In most studies of graphene-like material incorporation, there exists a balance between the amount added and property improvements, with a point of diminishing returns and, in some cases, detrimental effects. This amount is a function of surface modifications, as nickel decoration of graphene can modify this threshold to allow greater incorporation of graphene.

The addition of carbon nanotubes (CNT) in Sn<sub>95.8</sub>Ag<sub>3.5</sub>Cu<sub>0.7</sub> using powder metallurgy techniques results in increases to 0.2% yield strength, ultimate tensile strength (UTS), and creep resistance, while decreasing the coefficient of thermal expansion (CTE) and ductility [115]. The decrease in ductility was partly attributed to the agglomeration of the CNTs and poor bonding to the solder matrix. This was partially alleviated by the decoration of the CNTs with nickel nanoparticles. Additions of nickel-coated CNTs to Sn<sub>95.8</sub>Ag<sub>3.5</sub>Cu<sub>0.7</sub> solder enhanced the corrosion resistance by forming a physical barrier that hindered the initiation and development of defect corrosion [116]. Mechanical studies were not performed on the Ni-coated CNTs. Graphene in the form of GNS resulted in enhanced corrosion resistance as well as improved mechanical properties. The addition of GNS to Sn<sub>96.5</sub>Ag<sub>3</sub>Cu<sub>0.5</sub> solders through powder metallurgy results in increases to

the UTS and wettability of the solder while decreasing the CTE and ductility [117]. This improvement in corrosion resistance is attributed to the formation of a compact corrosion layer of the GNSs, which will provide an inert physical barrier that prevents the initiation and development of corrosion [118] [119]. This same idea is what will be applied to mitigating the diffusion of copper in solder interconnects. Graphene plates should act as inert barriers to atom diffusion and stop atom migration. By modifying the basal plane with plasma, matrix interactions may be strengthened, and mechanical properties may be further improved.

The use of oxygen plasma to treat the surface of GnP will further help the bonding between the GnP and the solder matrix. Studies performed on thermally annealed graphene oxide show that the degree to which the surface has been modified plays a role in the performance improvement of composites [120]. Too many functional groups on the surface of the reduced graphene oxide resulted in poorer improvements to mechanical properties than a less modified surface. The same is true for too few functional groups as well, with samples being thermally treated at higher temperatures having less oxygen-containing functional groups and similarly less improved mechanical properties. Best mechanical performance of the alloy being obtained at an I<sub>D</sub>/I<sub>G</sub> ratio of 0.67, compared to 1.17 and 0.06 for too many and too few functional groups, respectively. A study of the amount of geometrically necessary dislocations contained in these aluminum alloys shows that the surface modification of graphene also plays a part in how dislocations are allowed to propagate through the material. The composite produced with the least surface-modified graphene had the largest density of geometrically necessary dislocations. Since dislocations move through a material through vacancy-driven diffusion mechanisms, a hindrance to dislocation motion is a hindrance to vacancy-driven diffusion. So, the tuning of graphene's surface is a vital step in alloy optimization. Modifying the graphene's surface with oxygen plasma will remove the

need for oxidation with harsh chemicals and subsequent thermal reduction of the graphene oxide. Plasma treatment is also a low-cost alternative for the large-scale functionalization of graphene, being already a proven technique for the modification of carbonous materials for sterilization and impurity absorption [121].

Atoms are diffused by driving forces, and as a result, microstructural modification takes place. This modification usually involves the coarsening of the interfacial IMC due to the diffusion of Cu from the substrate into the interfacial IMC layer. IMC coarsening also occurs in the bulk microstructure. This IMC coarsening is detrimental to the mechanical, electronic, and thermal properties of the joint. Attempts at mitigating this focus on introducing barriers to diffusion. With the increasing importance of thermomigration in miniaturization, these diffusion barriers must be thermally stable and possess good thermal conductivity. Ceramic particles have been used as they are thermally stable, but they lack adequate thermal conductivity to alleviate Joule heating. The addition of graphene-like materials can introduce a diffusion barrier and favorable properties such as electrical and thermal conductivity. Surface modification of graphene-like materials with oxygen plasma is a low-cost and simple method to improve adhesion between the particles and the matrix by introducing oxygen-containing functional groups.

## **2.5.1 Solder Incorporation Materials and Methods**

Pure tin paste was used as the basis of this study. The paste used was E-127 Pure Tin FLUX-'N-SOLDER, Lot: 17735, supplied by Johnson MFG. CO.

GnPs were used as the graphene-like material for this study. The GnPs were supplied by XG Sciences. The R10 GnP has a surface area of 30-60 m<sup>2</sup>/g, while the M25 GnP has a surface area of 120-150 m<sup>2</sup>/g [56]. The oxygen plasma treatments were performed at 70 W power for 10 minutes. The oxygen plasma treatments were conducted at room temperature and at 200°C. The plasma system included a rotary tumbler chamber with a diameter of 63 mm and a length of 200 mm, which served as the vacuum chamber, a mechanical vacuum pump, a 13.56 MHz RF power supply, a matching network, a vacuum gauge, and a gas flow controller. Firstly, 1g of M25 GnP was loaded into the rotary tumbler, and then the chamber was evacuated. Next, the gas flow rate was adjusted to achieve a stable pressure of 660-680 mTorr (87.9-90.7 Pa), which was achieved at a flow rate of 8 sccm. The unmodified GnP powders will be referred to as M25 GnP Plasma200. Similarly, for the R10 samples.

The plasma-treated GnP flakes were subsequently blended into the Sn pastes. The GnP flakes were characterized by Raman spectroscopy, XRD, and XPS before and after plasma treatment.

To simplify the incorporation process of GnP into Sn, GnP powders were directly incorporated into commercially available Sn paste. This was done using a Thinky Mixer (THINKY MIXER SR-500, Non-Vacuum Solder Paste Mixer). Samples weighing approximately 1.8 grams of paste and 0.018 grams of GnP powders were mixed at 2000 revolutions per minute for 5 minutes. The pastes were then reflowed on a hot plate under flowing argon. These bulk solder samples were cross-sectioned and metallographically prepared to study the bulk microstructure of

the solders. Sn samples, with and without graphene, were also reflowed on clean copper substrates, cross-sectioned, and metallographically prepared to characterize the interfacial intermetallic compounds.

## **2.5.2 Solder Incorporation Results**

Characterization of surface modified GnP became the focus of the study once preliminary incorporation experiments began. A complete understanding of the surface chemistry would allow more applications to be identified for the surface modified material. Focusing on solder incorporation limited the scope of the applicability of these materials. Incorporation experiments were paused, and further characterization studies of the modified materials were performed; and more careful plasma parameter controls were implemented and studied.

Now that the surface chemistries are more well understood, any performance enhancements can be described mechanistically. This enhances the ability to anticipate performance impacts from future incorporations; and allows better experimental design for future incorporation experiments. Preliminary experiments included the incorporation of GnP into pure tin pastes. For industry application to be more readily proven, a more common solder such as SAC 305 should be used. Incorporation and reflow experiments utilized a Thinky mixer and were reflowed in a nitrogen atmosphere. Reflow characteristics, such as wetting and time to melt were modified. Tin pastes containing no GnP had a higher wettability on clean copper substrates (Figure 12).



Figure 12. Still image of reflow experiments. Samples were reflowed under nitrogen atmosphere on clean copper substrate.

Tin pastes containing some GnP had higher weight loss during reflow and showed lower wettability and poor adhesion to clean copper substrates. This indicates that some GnP is segregating to the interface of the tin and flux during reflow and hindering copper diffusion into the molten tin. This hypothesis is supported by SEM imaging of the interface of tin and the copper substrate. Micrographs of the interface of pure tin without GnP incorporation show a continuous intermetallic compound (IMC) layer of both Cu<sub>3</sub>Sn and Cu<sub>6</sub>Sn<sub>5</sub>, with Cu<sub>3</sub>Sn layer thicknesses ranging from around 0.5 microns to 0.9 microns (Figure 13). This is a typical scalloped IMC layer morphology expected for tin alloys on copper substrates. When GnP is added, the Cu<sub>3</sub>Sn layer formation is retarded and the Cu<sub>3</sub>Sn layer becomes discontinuous along the interface (Figure 14).



Figure 13. SEM micrographs of the interface of pure tin and copper substrate. Arrow A indicates copper substrate, Arrow B indicates Cu<sub>3</sub>Sn layer, Arrow C indicates Cu<sub>6</sub>Sn<sub>5</sub> layer. Layer thicknesses for Cu<sub>3</sub>Sn layer are labeled at various places along interface.



Figure 14. SEM micrographs of the interface of M25 tin and copper substrate. Arrow A indicates copper substrate, Arrow B indicates Cu<sub>3</sub>Sn layer, Arrow C indicates Cu<sub>6</sub>Sn<sub>5</sub> layer. Layer thicknesses for Cu<sub>3</sub>Sn layer is labeled at interface. Circles indicate areas where the Cu<sub>3</sub>Sn layer formation is retarded.

This is evidence of GnP altering the IMC formation kinetics, the mechanism of this alteration is most likely tied to its segregation to the interface. This is further evidenced by imaging of GnP aggregations near the tin-copper interface (Figure 15). These large aggregations can be seen along the interface, specifically the IMC-tin interface.

Further studies should be conducted to observe how plasma treatment affects the agglomeration and IMC layer retardation effects of modified GnP materials. Incorporation and reflow processes have been standardized using repeatable mixing procedures and inert atmosphere reflowing. Initial results indicate agglomeration may be beneficial to alter reflow kinetics. Additionally, surface energy may play a large part as samples reflowed with GnP showed greater weight loss during reflow, indicating more solid material is being segregated and confined to the flux. This is observed qualitatively in Figure 12, the flux from "No GnP" sample is very low viscosity whereas the flux from GnP containing samples is solid and ash-like. Plasma treatments were able to alter the behavior of GnP in solvents, the fluxed tin paste in this case could be considered a solvent. Therefore, the oxygen- and fluorine-based plasma treatments should alter the behavior of the GnP in the fluxed paste; this alteration could impact the reflow behavior of the GnP-fluxed paste composite materials.


Figure 15. SEM micrographs of GnP aggregation near tin-copper interface.

The results of the XPS (Table 4) show that the increased temperature makes the plasma treatments less effective at implanting oxygen species on the GnP. Samples that received the plasma treatment at room temperature had oxygen levels of 5.74 at% and 4.08 at% for the M25 and R10, respectively, while at 200°C the M25 and R10 samples had 3.7 at% and 3.49 at%, respectively.

Sample	Carbon (at%)	Oxygen (at%)
Raw M25	96.69	3.31
M25 70W 10 minutes	94.26	5.74
R10 70W 10 minutes	95.92	4.08
M25 70W 10 minutes 200C	96.3	3.7
R10 70W 10 minutes 200C	96.51	3.49

Table 4. XPS results giving approximate carbon and oxygen atomic percentages of the plasma treated GnP powders, with raw M25 for comparison.

These results show the healing effect increased temperature has on the modification of the GnP. From these results, it was determined that elevated temperature treatments would not be pursued further. These results also lead to the down selection of M25 as the primary material of interest due to the increased modifiability. This is most likely tied to the wide, flat structure of the M25 platelets. The increased surface area of the M25 allows greater modification to the surface through plasma treatments.

### 2.6 Treatment Time Effects of C<sub>4</sub>F<sub>8</sub> Plasma Modification

Plasma treatment has been employed to surface treat various materials for different purposes. High-energy plasmas are commonly used for etching and surface cleaning due to the energetic radicals that ablate the surface. Advancements in plasma systems have enabled the creation of lower energy plasmas at relatively low vacuum pressures, reducing costs and simplifying the modification process. Thus, further research on the effects of plasma on graphene and graphene-like materials is warranted. This study aims to treat graphene nanoplatelets with  $C_4F_8$  plasma for varying durations and investigate changes in surface compositions and structures. To assess the effects of plasma treatment, XPS was utilized to evaluate surface functionalization, while Raman Microscopy and XRD were employed to monitor structural changes in the graphene nanoplatelets.

The obtained Raman microscopy results demonstrate changes in the spectrum corresponding to different plasma treatments. The D-Peak, observed at around 1350 cm<sup>-1</sup>, indicates the breaking of symmetry in the carbon basal plane due to the disruption of pi-bonded carbons, allowing for non-symmetrical stretching. The intensity of the D-Peak relative to the G-Peak can be used to assess the degree of "disorder" in the basal plane. [87]. The G-Peak, observed at approximately 1580 cm<sup>-1</sup>, represents the symmetric "breathing" mode of the pristine carbon basal plane. Additionally, the C4F8-treated samples exhibit a shoulder at around 1605 cm<sup>-1</sup>, which corresponds to the D'-Peak. The D'-Peak arises from an intravalley double resonance process, where a longitudinal phonon interacts with a defect in a circular path around an equivalent k-point in the Brillouin zone. On the other hand, the G'-Peak, which is intervalley in nature and arises from the interaction of two longitudinal phonons, does not require the presence of defects and is present in the spectra of perfect graphene.

The G'-Peak has been shown to be sensitive to doping, strain, and the number of graphene layers with AB Bernal stacking. [84]. Reducing the number of layers in few-layer graphene leads to a redshift in the G'-Peak, while increasing strain causes a similar redshift. Doping, on the other hand, results in a decrease in the intensity of the G'-Peak. It should be noted that the sample material used in this study underwent unknown chemical processes that may have altered the stacking order and resulted in rotationally random graphene platelet agglomerates. In this case, the G'-Peak can provide insights into the double resonant selection rule relaxation associated with the random stacking [84].



Figure 16. Comparison of Raman Spectra for all C<sub>4</sub>F<sub>8</sub> treated samples.

From Figure 16, the structure of the graphene nanoplatelets (GnP) undergoes changes as the plasma treatment time increases. Initially, from 0 to 3 minutes of treatment, there is minimal structural alteration observed in the Raman spectroscopy results. However, there is a slight dampening and broadening of the G'-Peak, as well as a slight increase in the intensity of the G-Peak.

Significant structural changes start to occur between 3 to 10 minutes of treatment, as indicated by the increasing intensity of the D-Peak. Additionally, at 10 minutes of treatment, a distinct D'-Peak becomes prominent, which suggests the generation of disorder on the basal plane. Notably, the G'-Peak experiences a significant dampening at the 10-minute treatment mark, which could be an indication of a heavily doped basal plane.

As the treatment time increases from 10 to 15 minutes, interesting trends begin to emerge. It would be expected that the disorder of the basal plane would continue to increase with longer treatment times, but the opposite is observed. At 15 minutes of treatment, the spectrum appears more similar to the raw material. Both the D-Peak and the D'-Peak have disappeared, indicating a reduction in basal plane disorder. The only noticeable modification is the dampened G'-Peak, which could suggest increased rotational randomness in the stacking of the graphene nanoplatelets (GnP). This could be an indication that the plasma treatment has etched the surface, removing the previously functionalized layer and exposing a fresher, more pristine basal layer.

However, as the treatment time is further increased, evidence of functionalization reemerges. At 30 minutes of treatment, the D-Peak reappears, albeit with reduced intensity, and the D'-Peak is also present, indicating the creation of basal plane disorder. This supports the notion that there is functionalization of the basal layer up to a certain point, followed by the removal of the fully functionalized layer, exposing a fresh basal layer. With decreased layer count, the intensity of the G'-Peak would be expected to increase, which is indeed observed at the 30-minute treatment mark, as the G'-Peak shows a significant increase in intensity.

X-ray diffraction can be combined with Raman spectroscopy to assist in determining the crystallite size along the c-axis of graphene [84]. By deconvoluting the G'-Peak and analyzing the results alongside XRD scans, empirical formulas have been established to estimate the c-axis crystallite size based on the intensity ratio of the deconvoluted G'-Peak. In essence, the relationship discovered suggests that as the G'-Peak becomes more shifted towards higher Raman shifts, the crystallite size should increase.



Figure 17. Comparison of X-Ray Diffraction spectra for all C<sub>4</sub>F<sub>8</sub> plasma treated samples.

The XRD results (Figure 17) support the hypothesis of a functionalization, peeling, refunctionalization process. An interesting observation is made at 3 minutes treatment time. At low treatment times, there is a shift in the XRD peak from around 26.75° to 26.24°. This represents the most significant shift among the treated samples, and the shift decreases from 3 to 10 minutes treatment time. This finding contrasts with the Raman results, which indicated minimal changes to the structure of the GnP. Raman spectroscopy provides information about the bonding of the basal plane by measuring the energy of emitted photons from vibrating bonds. On the other hand, XRD provides structural information about the platelets by diffracting X-rays off the crystal structure, without providing bonding information. Based on these results, it can be infered that at 3 minutes treatment time, the structure of the platelets is affected without modifying the bonding of the basal layer. This could be attributed to edge functionalization and slight exfoliation of the platelets.

Plasma has also been demonstrated to exfoliate graphite under specific conditions [88]. The samples treated for more than 3 minutes exhibit a consistent trend of shifting to slightly lower diffraction angles and narrowing of the FWHM. These results suggest a potential slight exfoliation of the samples.

# CHAPTER 3: NOVEL PRODUCTION PROCESS FOR ELECTRIC VEHICLE BATTERY THERMAL MANAGEMENT SYSTEMS

# **3.1 Motivation**

As the demand for electric vehicles increases, there is a growing need to extend the service life of these vehicles. The performance and lifespan of the batteries, which are crucial components of electric vehicles, are significantly influenced by temperature [122]. In situations where hundreds of cells are connected in series or parallel, inconsistencies among cells can lead to the formation of hot spots and variations in heating. This temperature gradient can further degrade the cells and create a potential cycle of runaway heating. To enhance battery life and maximize efficiency, precise temperature control is essential. Various thermal strategies have been developed to create battery thermal management systems (BTMS) that aim to maintain module temperature homogeneity by utilizing internal or external heating or cooling methods. The ideal temperature range for the battery module is typically between +15 to +30 degrees Celsius, and it should be uniformly maintained throughout the module. One crucial aspect considered in this study is the relationship between the cell's dimension and the temperature distribution. As the cell's dimension increases, the surface area-to-volume ratio decreases, resulting in more heat being retained within the battery [122]. Therefore, by increasing the cell's surface area while keeping the volume constant, the retained heat within the battery can be reduced. Many BTMSs rely on modifying the module configuration to enhance their performance. One approach is to arrange the cells in cooling channels, and these channel geometries can be modified, such as transitioning from a simple channel to a wedge channel. This wedge channel improves the BTMS efficiency without altering the cell morphology by increasing the air velocity around these cells (Figure 18).



Figure 18. Schematic of (A) simple channel and (B) wedged channel configurations.

However, there are drawbacks associated with the use of wedged channels, as it requires an increase in parasitic power to accelerate the coolant [122]. Another approach is to arrange the cells in arrays within cooling channels. These cells can be organized in aligned banks or in staggered banks, where every other row is offset by half a period, as shown in Figure 19. These banks can then be placed in either simple channels or wedge channels. The efficiency of the cooling system can also be enhanced by modifying the direction of coolant flow and the flow geometry. In simple channels, efficiency can be increased by implementing reciprocal coolant flow, as depicted in Figure 20. Additionally, coolant flow can be directed in U-parallel and Zparallel configurations, where the coolant flows past all cells simultaneously, reducing temperature differences between cells (refer to Figure 21).



Figure 19. Schematic of (A) aligned bank and (B) staggered bank.



Figure 20. Schematic of (A) simple channel and (B) simple channel with reciprocating cooling.



Figure 21. Schematic of (A) Z-parallel configuration and (B) U-parallel configuration.

These configurations are more appealing for their ability to homogenize cell temperatures within a module and create venting conditions for the removal of any gases. All of these approaches focus on modifying module and flow geometry while ignoring cell-level modifications.

Other strategies involve adding cooling components at the module level to control temperature homogeneity. The addition of cold plates between each cell of the module is currently employed in many pouch and prismatic cell modules for electric vehicles [122]. Experiments on cooling channel performance indicate that channel geometry plays a significant role in cold plate performance. Serpentine flow channels outperform straight channels in terms of cooling performance. While the addition of cold plates improves the system's performance, it comes at the cost of energy density. To enhance energy density, cold plates should be minimized or removed from modules. The integration of flow channels at the cell level will further increase battery module performance in electric vehicles.

The motivation for this project was to advance battery thermal management systems for electric vehicle applications. The battery setup of interest was a pouch cell-type battery system. This type of set-up allows for flexibility in the types of modules available. These types of set-ups allow the user to quickly reconfigure modules to address changing enclosure geometry in various vehicle body designs. In these setups, pouches are constructed of a 3-layer laminate. The innermost layer is polypropylene ( $80 \mu m$ ), followed by aluminum ( $50 \mu m$ ), and then nylon ( $16 \mu m$ ). An adhesive layer of 15  $\mu m$  exists between the aluminum and nylon. The polypropylene layer acts as an inert chemical barrier for the electrolyte, while the aluminum layer provides gas barrier properties, mechanical integrity, and thermal conductivity. The nylon layer offers scratch resistance.

Current thermal management systems for such battery systems involve using a cold plate between each pouch cell in the system. These cold plates are 3 mm thick aluminum blocks with channels that allow for the circulation of a cooling medium. However, these cold plates add considerable bulk to the system and do not contribute to the energy density. The subsequent sections will discuss the designs for these cooling channels.

To increase energy density and reduce weight, it is necessary to eliminate these cold plates. One approach is to pattern the side of each pouch cell. When the cells are placed into the enclosures and compressed together, the patterns imprinted into the side of the pouch cell will form cooling channels. The goal was to create features up to 3 mm in height to fully utilize the space where the cold plate was positioned, while still conforming to the current enclosure geometry.

For this application, it was crucial that only one side of the aluminum layer be patterned, while the other side remained flat. This requirement ruled out the use of deep-drawing techniques. As a result, a novel production strategy needed to be developed to create featured surfaces on one side of thin sheet aluminum.

This strategy, to incorporate cold plates into pouch cell batteries, utilizes the intrinsic ductility of aluminum to facilitate extrusion. By studying the currently used state-of-the-art materials this research is more amenable to quick industry adoption. However, other materials could be leveraged to increase the ability to create features. Non-monolithic materials, such as metallic foams, can be utilized to create these surface features without the need to plastically deform the material. Collapsing the voids within the foam material takes less pressure than plastically deforming the monolithic material. Metallic foams are available in various metals and in closed- and open-cell varieties. Additionally, it will be shown that most metallic foams will maintain adequate thermal conductivities to be used as a feature material.

In addition to metallic foams, other advanced materials were investigated as replacements to the aluminum layers. Aluminum has good thermal conductivity, as do most metals, but the thermal conductivity of this layer could be increased through careful materials selection. By modifying GnP with a surfactant, a suspension of GnP can be created which can then be filtrated and dried into a GnP paper. This GnP is flexible and has good thermal conductivity [123]. Studies were undertaken on this advanced GnP paper material into its patternability and lamination characteristics. Different patterns were replicated on the GnP paper through various pressing procedures. These papers were then tested in enclosed thermal cells, and their lamination characteristics were studied.

## **3.2 Proof-of-Concept Roller**

In the early experiments, patterns optimized for heat sink applications were investigated for their manufacturability. Pin/fin arrays, commonly used in heat sink applications, were of particular interest. Various forming strategies were explored to create these pin/fin arrays. Among them, a compressional roll molding technique showed the most promising results. While this technique had not been experimentally investigated at these length scales before, it had demonstrated potential at smaller scales and in simulations [124] [125]. One notable advantage of this method was its potential for continuous processing.

A small roller system was obtained, and a custom roller was machined. One roller had cavities to create the features, while the other roller remained flat. This enabled the production of features on one side of the aluminum while minimizing any impact on the other side.

### 3.2.1 Proof-of-Concept Roller Introduction

The creation of pin/fin arrays on surfaces is of interest for both thermal and fluid-flow management [126] [127] [128]. Typically, features on sheet metal are achieved through extrusion-forging or compression molding processes [129]. However, these processes have two significant disadvantages: they require high forming pressures and are batch processes [130] [131]. Sheet-bulk metal forming processes, as defined by Merklein et al., aim to apply bulk metal forming techniques to sheet metals in order to achieve three-dimensional material flow [132]. In addition, conventional press forging processes are sometimes employed with sheet processes to produce complex surface geometries [133].

Experimental results have indicated that creating pins using extrusion forming processes can necessitate pressures exceeding 500 MPa, thereby limiting the feasibility of creating large-area pin arrays [125].

Numerical simulations and experimental results have highlighted the benefits of rollextrusion processes for creating surface features [125] [124]. While roll-extrusion processes introduce more complex stress states compared to uniaxial extrusion, they offer the advantage of continuous production with similar properties [134]. In this study, a combined forging-rolling procedure, similar to roll-coining, was developed to produce surface features on aluminum sheets [135] [136]. Unlike roll-coining [137], the rollers used in this procedure were non-interlocking. One roller remained flat, while the other had patterned cavities to facilitate the extrusion process.

Previous studies on roll molding have primarily examined simple pin or straight fin designs [125] [124]. The motivation for this study is to explore the use of roll-extrusion for generating complex patterns on flexible metal substrates. Pin- and fin-arrays are particularly relevant for thermal and flow management in electronic heat sinking systems. In order to assess the

manufacturing feasibility, experimental prototypes of pin- and fin-arrays with various sizes and spacings were created.

# 3.2.2 Proof-of-Concept Roller Materials and Methods

For rolling experiments, a jewelry rolling mill was employed. A custom roll made of O1 tool steel was machined, incorporating several diagnostic patterns. Figure 22 provides comprehensive information on the design spacings and measurement locations.



Figure 22. Full Schematic annotated with measurement locations shown. All measurements are in inches.

Two aluminum alloys, namely 1100 and 3003, were obtained from McMaster Carr and used in their as-received condition. These materials are the current industry standard and were selected to increase the ease of industrial adoption to any new process. The samples used for rolling experiments had approximate dimensions of 38 mm width and 72 mm length. Initially, all samples had a thickness of 1 mm. The rolling process was conducted at room temperature using a hand crank. The thickness of the samples was measured using a point-to-point micrometer with an accuracy of +/- 0.001 mm. The roller gap was set to zero, and the actual reduction in thickness (draft) was determined by the deflection of the rollers.

### 3.2.3 Proof-of-Concept Roller Results and Discussion

Measurements were taken along the centerline of the roller within each designated section, as specified in Figure 22. To determine feature heights, the average of the troughs on both sides of a feature was calculated and subtracted from the measured height of the feature. Transverse spacing refers to the distance between two features measured across the width of the roller. On the other hand, longitudinal spacing is the distance between two features measured around the circumference of the roller.

The pin and fin section comprises the most closely spaced fins and a segment featuring pins. The design is particularly intriguing because of the improved thermal management offered by pin arrays [138]. Regarding the pin structure, Figure 23 illustrates both the in-line and staggered arrangements. Both arrangements can be defined by the transverse pitch ( $S_T$ ) and longitudinal pitch ( $S_L$ ).



Figure 23. (a) In-line pin fin arrangement; (b) staggered pin fin arrangement.

In addition to increasing the heat transfer surface area, pin fins also generate more air turbulence, resulting in enhanced heat transfer rates. The Nusselt number (Nu) values for an inline pin fin array with various ranges can be calculated using equations (1) and (2):

$$Nu = 0.9Re_D^{0.4} \cdot Pr^{0.36} \cdot \left(\frac{Pr}{Pr_s}\right)^{0.25} for \ 0 < Re_D < 100$$

$$Nu = 0.52Re_D^{0.5} \cdot Pr^{0.36} \cdot \left(\frac{Pr}{Pr_s}\right)^{0.25} for \ 100 < Re_D < 1000$$

Where,

$$Re_D = \frac{v_{max}D}{v}$$
 3

$$v_{max} = \frac{vS_T}{(S_T - D)} \tag{4}$$

where v represents the free-stream air velocity, D denotes the diameter of the pin, and Pr<sub>s</sub> represents the Prandtl number at the battery surface temperature. The Prandtl number is a dimensionless number and represents the ratio of the momentum diffusivity and the thermal diffusivity. It is worth noting that the Prandtl value (Pr) of air does not exhibit a significant dependence on temperature. Therefore, the value of Pr<sub>s</sub> is assumed to be the same as the value of Pr for the air temperature. The Nusselt number (Nu), is the ratio of convective heat transfer and the conductive heat transfer. The Nu values for a staggered pin fin array can be calculated using equation (5):

$$Nu = 1.04Re_D^{0.4} \cdot Pr^{0.36} \cdot \left(\frac{Pr}{Ps}\right)^{0.25} for \ 0 < Re_D < 500$$
 5

Once the Nu values are determined, the  $R_{conv}$  values as a function of air velocity are calculated and summarized in Table 5.

Air velocity (m/s)	Plain	Plate fin	Pin fin (in-line)	Pin fin (staggered)
0.1	0.02369	0.03104	0.03164	0.02710
0.2	0.02368	0.03099	0.02397	0.02054
0.3	0.02368	0.03092	0.02150	0.01746
0.4	0.02366	0.03084	0.01862	0.01556
0.6	0.02363	0.03064	0.01520	0.01323
0.8	0.02359	0.03039	0.01317	0.01179
1.0	0.02354	0.03011	0.01178	0.01079

Table 5.  $R_{conv}$  (m<sup>2</sup>\*K/W) values for plain, plate-finned, and pin-finned batteries.

As indicated in Table 5, the values of  $R_{conv}$  (convective resistance) for a plate-fin array are consistently higher than those of a plain surface for air velocity ranges between 0.1 m/s and 1 m/s. On the other hand, for a pin-fin array, the value of  $R_{conv}$  is initially higher than that of a plain surface at low air velocities. However, as the air velocity increases, the value of  $R_{conv}$  becomes lower than that of a plain surface. This decrease in  $R_{conv}$  for the pin-fin array is attributed to the enhanced air turbulence at higher velocities. This high sensitivity to air velocity is not observed in a plate-fin array. Consequently, the pin-fin array is expected to be more effective in enhancing the heat transfer rate compared to the plate-fin array.

It is important to note that the pins created using this process were sloped, with the front edge being the tallest and the trailing edge being the shortest, in relation to the rolling direction. Furthermore, the pins were taller in the center of the design space, closer to the roller center, and closer to the design center. Pin #4 was the tallest among the pins. The average feature height for pin #4 in the 1100 series was 0.9 mm. The average feature heights for all the pins were 0.54 mm for the 3003 series aluminum and 0.72 mm for the 1100 series aluminum.

Pins proved to be the most successful features created, with average feature heights exceeding 0.5 mm in both the 3003 and 1100 series aluminum. Pin sections were less prone to wrinkling compared to the fin sections of the design spaces. Wrinkling is mainly influenced by variations in draft along the contact length of the roller. Design spaces with long continuous features, particularly those oriented transverse to the rolling direction, tend to cause significant differences in the roller gap and result in substantial wrinkling. Discontinuous features, such as pins, along the contact length of the roller help mitigate these wrinkling issues.

In the transverse sections of the crosshatch design, cavity wall deformation was observed in 21 out of the 24 tested cavity walls. The increased feature density led to a decrease in feature height

for the crosshatch fins. Unfortunately, trough measurements could not be taken within the crosshatch section due to the diameter of the micrometer tip. Instead, trough measurements were taken before and after the design space and then averaged. The unsatisfactory results from this design section indicate the need to adjust the spacing between fins to allow for the proper extrusion and flow of material into the features.

Design section 2 focuses on evaluating the spacing limits of fins in both the transverse and longitudinal directions. During the rolling experiments, the first wall of the transverse section between features 1 and 2 experienced failure. The failure of the cavity wall at point B (Figure 22) can be attributed to lateral pressure exerted during the extrusion rolling process. The dividing wall rolled over into the feature 2 cavity, eliminating the trough between features 1 and 2. Consequently, only the height of feature 1 was measured and reported. The first trough, which was 0.22 mm wide, could not be measured directly with the micrometer due to the tip diameter. Instead, the measurement was taken just beside the features, as indicated in Figure 22.

In terms of feature height, the transverse section of features was consistently taller than the longitudinal section. This height difference is a result of material flow in the rolling direction. As a result, the longitudinal section of features exhibits a sloped profile from the front to the rear. The front tip of the longitudinal features, in relation to the rolling direction, is always taller than the rear tip. This sloping pattern of the longitudinal fins is similar to the results observed in design section 1 with the formed pins displaying a similar sloping pattern.

Transverse fins in the design also experienced issues related to the interaction between the roller cavity and the sample features. One such issue is referred to as "lipping," which involves the tearing of the front edge of a transverse-oriented fin. This tearing results in a small lip of material being left on top of the feature, leading to a sloped leading edge. One hypothesis for the formation

of these lips is that the front edge of the roller cavity peels away this material as the sample is removed from the roller. Figure 24 provides a schematic illustrating this process.

Another issue associated with the feature-cavity interaction is referred to as "hair-trimming." This issue is characterized by the presence of a thin strip of material at the top rear edge of transverse-oriented fins. This thin strip resembles a hair and remains connected at one end, sometimes being completely detached from the sample piece. Similar to lipping, this phenomenon arises from the interaction between the feature and the cavity, but it exclusively occurs at the back edge of rolled features. Figure 25 highlights a possible mechanism for the creation of these hairtrimming occurrences.



Figure 24. Schematic representation of "lipping" issue encountered when rolling. This schematic is further reinforced by a micrograph imagining the cross section of a rolled feature highlighting the issue.



Figure 25. Schematic representation of "hair-trimming" issue encountered when rolling. This schematic is further reinforced by optical imaging of a rolled feature highlighting the issue.

In this scenario, the back edge of the cavity wall scrapes the backside of the feature from bottom to top, resulting in a thin strip of material being left on the top, rear edge of the feature. These issues were observed exclusively in the transverse-oriented fins. However, the sloping of the longitudinal features is not affected by these problems.

Continuous features, such as fins, are susceptible to wrinkling issues. This wrinkling may be caused, in part, by geometric constraints during material extrusion. The roll gap must be perfectly parallel; otherwise, one edge of the sheet will experience a greater reduction in thickness than the other, leading to bowing and wrinkling of the sheet.

Design section 3 focused on studying the longitudinal feature spacing and feature transverse width. To observe the effect of feature transverse width on cavity wall integrity, a section of offset shortened transverse fins was included. Design set 3 was divided into three sections with different longitudinal feature spacings: the narrowest spacing was 0.44 mm, the second narrowest was 0.89 mm, and the third spacing was 1.70 mm.

The results indicated that the sidewall pressure on the roller cavity led to cavity wall failures. The shortened offset features remained undamaged at the narrowest spacings, while the cavities that extended across the width of the roller experienced failures. During the rolling process, the three sets of fins with 0.44 mm spacing all exhibited cavity wall failures. However, some samples that were rolled before the failure occurred were still measurable. Another observed failure in this section was the shearing of the sample at the beginning of the design space near the 0.44 mm spaced features.

When comparing analogous features, there was good uniformity between the sets of fins. Comparing the first fin of each set to the shortened transverse fins, it was found that the first continuous fin was taller than the shortened transverse fins. For example, in the 1100 series,
Feature #1, #7, and #13 measured 1.16 mm, 1.15 mm, and 1.13 mm, respectively. On the other hand, Feature #2, #3, #8, #9, #14, and #15, which were the shortened transverse fins in each set, measured 1.09 mm, 1.08 mm, 1.09 mm, 1.09 mm, 1.06 mm, and 1.08 mm, respectively.

Similar to design section 2, design section 3 also experienced many of the same rollcavity/feature interaction issues. Hair-trimming effects and lipping effects were observed in the long continuous lines of design section 3 but not in the discontinuous line sections of the design space.

This section involved a modification to the pin design, where the pins were elongated along the 45° diagonal in relation to the flow direction. These design modifications were based on flow channel studies conducted to gain a better understanding of the relationship between flow regimes and different designs. In these flow channel experiments, a smoke generation apparatus was used to produce smoke, which was then cooled and stored. Subsequently, air was forced through the storage chamber, pattern chamber, and smoke trails were recorded. Still images extracted from the recordings have been annotated to highlight areas of smoke pooling and flow channels, as shown in Figure 26, Figure 27, and Figure 28.



Figure 26. Still image from flow channel studies with arrows overlayed to highlight laminar flow through the design space and dashed circles to highlight areas of air pooling and stagnation.



Figure 27. Still image from flow channel studies with arrows overlayed to highlight laminar flow through the design space and dashed circles to highlight areas of air pooling and stagnation.



Figure 28. Still image from flow channel studies with arrows overlayed to highlight laminar flow through the design space and dashed circles to highlight areas of air pooling and stagnation.

The flow channel study revealed that elongated features with their major axis oriented at a 45° angle to the vertical allow for continuous airflow and reduce stagnation, while still maintaining the offset pin fin basis of feature spacing. Figure 26 and Figure 27 demonstrate that designs with elongated features oriented at 0° or 90° angles to the vertical result in air pooling and stagnation. However, when the features are rotated 45°, as shown in Figure 28, continuous flow is achieved. These results prompted modifications to the designs in order to channel airflow. To further reduce drag on airflow, vesica piscis shaped features were incorporated. Vesica piscis shaped features are created by intersecting circles of equal radius and also served to direct flow patterns and minimize drag caused by sharp corners.

Design space 4.1 consistently exhibited the tallest measured features in both series of aluminum. This design space had the largest longitudinal and transverse spacing between features among the four designs. Decreasing the transverse spacing from 4.49 mm to 2.54 mm resulted in an average decrease in feature height of 0.06 mm in the 1100 series and 0.02 mm in the 3003 series. Likewise, reducing the longitudinal spacing from 2.26 mm to 2.00 mm led to an average decrease in feature height of 0.11 mm in the 1100 series and 0.08 mm in the 3003 series. These findings suggest that the longitudinal spacing between features has a greater impact on the average feature height compared to the transverse spacing. Additionally, increasing the feature size did not lead to a decrease in feature height, as design space 4.3 and 4.4 exhibited equivalent feature heights.

This design section also benefits from the advantages of discontinuous roll gap differences, which mitigate wrinkling similar to pin arrays. Moreover, the diamond patterns employed in this design section help alleviate various roll-cavity/feature interaction issues. These issues, such as lipping and hair-trimming, can result in undesired topologies on the features. The cavities machined into the roller for these features had sloped walls, not 90° like other design sections, and chamfered edges. By sloping the front and back edges of the roller cavity many of these unwanted effects can be eliminated.

Features were successfully created using the roll-extrusion process. All samples had an initial thickness of 1 mm. Therefore, design sets that resulted in an absolute height greater than 1 mm can be considered to have undergone extrusion processes. A comprehensive summary of the rolling experiments' results, including the average height of all features, is presented in Figure 29.



Figure 29. Full Results of rolling experiments, with all features in a design space averaged.

In terms of materials, the 1100 series aluminum alloy exhibited greater compliance compared to the 3003 series. When rolled with the 1100 series, the same designs resulted in taller features. However, the overall trends in data were consistent across both alloys. Pins were the most successful in terms of extrusion, with average heights of up to 1.5 mm for pin #4 in the 1100 series samples. Other design sets did not achieve extrusion conditions, with design section 1, cross-hatched, transverse, and longitudinal averaging 0.87 mm and 0.83 mm, respectively. These results resembled a forging process where the entire workpiece underwent deformation. The pins did exhibit some topology issues, with sloped tops in relation to the rolling direction. This could be mitigated by creating shallower cavities on the roller surface.

From design section 2, it was observed that transverse fins were more successful than longitudinal fins in achieving workpiece extrusion. However, transverse fins also exhibited more roller cavity - feature interaction issues compared to longitudinal fins. These issues included lipping and hair-trimming effects, which were topological defects in the rolled features. These issues were somewhat alleviated by the sloping of the roller cavity wall in design section 4. Wrinkling issues were also present, resulting from differences in draft along the contact length of the roller. Addressing these issues was challenging, as the design required a change in draft along the roller's contact length. Design section 3 aimed to address wrinkling issues by incorporating both continuous and discontinuous features along the contact length of the roller.

In design section 3, cavity walls that were 38 mm wide and 0.22 mm thick experienced failures, while walls that were 38 mm wide and 0.44 mm thick did not. Similarly, cavity walls that were 76 mm wide and 0.44 mm thick failed, while those that were 2.25 mm wide and 0.44 mm thick did not experience failures. The spacing between longitudinal features did not reach a limit, with the shortest spacing attempted being 0.22 mm. The failure of the roll at tight transverse

spacings could be mitigated by either shortening the transverse length of the feature or by using a harder roll material. Shortening the transverse length of the feature also helped address wrinkling issues. Similar to design section 2, the same roller cavity - feature interaction issues were observed in the continuous features of design section 3, but not in the discontinuous features.

Design section 4 focused on the effects of cavity wall sloping on the topology of the rolled features. The ellipsoidal features in this section also benefited from the discontinuous effects, which reduced wrinkling. The machined ellipsoidal features had sloped cavity walls to address roller cavity - feature interactions. Lipping and hair-trimming issues were not observed in any features of design section 4. These ellipsoidal features were designed to channel the flow of a medium through the design. Larger spacings between features, both transverse and longitudinal, resulted in increased feature height. Decreasing the longitudinal spacing had a greater negative impact on feature height compared to the transverse spacing. Increasing the feature size did not significantly affect feature height.

This study explored a manufacturing technique for patterning substrates within a roll-toroll process. Initial designs were followed by diagnostic designs aimed at identifying issues with the extrusion rolling method. Rolling issues were identified, and some potential solutions were implemented and studied. This method offers a straightforward solution for large-scale heat sink manufacturing that can be implemented using existing rolling infrastructure.

## 3.3 Replication of State-of-the-Art Cold Plates

After successfully proving the concept on a small scale with several designs, the focus shifted towards creating a process that could be implemented on a larger scale. To demonstrate this, currently used cold plate designs were chosen, and a larger rolling system was acquired. A battery calendaring roller was modified, and a custom roller was manufactured with cavities replicating the current cold plate designs. The rollers had a diameter of 100 mm and a length of 300 mm, allowing for the creation of larger designs and complete prototypes. This rolling system was also equipped with a heating system, enabling preheating of the rollers and conducting elevated temperature rolling experiments.

At this stage of the project, the lamination process for the final prototypes became a focal point. The objective was to develop a lamination process that would ensure good conformation of the outer nylon layer to the featured aluminum layer. Initial experiments with heated conformal pressing using high durometer rubbers yielded inadequate pressure on the troughs of the designs. When softer rubbers were used, better results were obtained due to increased isotropic pressure applied at the base of the features. However, softer rubbers did not transfer enough pressure, leading to delamination at the feature peaks during bending. As a result, the investigation shifted towards vacuum systems in combination with high durometer rubber heated compression. The heat supplied by the platens in the hydraulic press was transferred through the vacuum plate beneath the prototype, enabling the sealing of the polypropylene layer. Meanwhile, the rubber on the top of the prototype reduced temperature embrittlement of the nylon. The vacuum pressure provided sufficient pressure to ensure good conformation at the troughs of the designs, while the high durometer rubbers facilitated the sealing of outer layers and adhesion at the peaks. Detailed results and issues regarding this development are discussed in subsequent sections.

## **3.3.1 Replication of State-of-the-Art Cold Plates Introduction**

Current pouch cell battery systems rely on the use of cold plates placed between cells for thermal management. However, the inclusion of cold plates adds weight to the system and reduces its energy density. To address these drawbacks, integrating cold plate designs directly into the pouch cells themselves would decrease the overall weight by eliminating the need for separate cooling plates.

The construction of current pouch cell batteries involves a 3-layer laminate structure. This laminate consists of an inner polypropylene barrier layer, an aluminum layer, and an outer nylon layer. The polypropylene layer functions to contain the electrolyte, the aluminum layer acts as an impermeable barrier against gas diffusion, and the nylon layer provides scratch and abrasion resistance. The production of these laminates is typically carried out using roll-to-roll manufacturing processes. Once the pouch cells are fabricated, they are filled with electrolyte, and multiple pouches are assembled into a cell with cold plates serving as separators. There is a gap between each pouch cell where the cold plate is positioned, and the cold plate features channels that enable the flow of a cooling medium, such as gas or liquid.

By introducing features onto the aluminum layer of each pouch cell, it becomes possible to eliminate the need for cold plates. The creation of these features on sheet metal is commonly facilitated through extrusion-forging or compression molding processes [129]. However, these processes have notable drawbacks, including the requirement for high forming pressures and their batch nature [130] [131].

To overcome these limitations, sheet-bulk metal forming processes have been developed. These processes combine conventional sheet processes with bulk processes to achieve the desired properties [132] [133]. Experimental findings have indicated that creating pins through extrusion forming processes can necessitate significant pressures, thereby restricting the production of large pin arrays [124] [125] [139].

Numerical simulations and experimental results have showcased the advantages of rollextrusion processes in generating surface features [125] [124]. Although roll molding processes introduce more complex stress states compared to uniaxial pressing processes, they enable continuous production while maintaining comparable properties [134]. In the context of this study, a procedure inspired by roll-coining, a forging-rolling procedure, was developed to create surface features on aluminum sheets [135] [136]. Unlike roll-coining, the rollers employed in this procedure are non-interlocking, with the bottom roller being flat and the top roller featuring patterned cavities to facilitate extrusion [124] [137]. Prior investigations into roll molding have primarily focused on simple pin or straight fin designs [125] [124] [140].

Commercial cold plate designs incorporate curved channels throughout the cold plate area to facilitate the flow of a medium and facilitate heat removal from the entire pouch area. The use of roll molding processes to generate intricate patterns on flexible metal substrates serves as the motivation behind the current study.

## 3.3.2 Replication of State-of-the-Art Cold Plates Materials and Methods

A battery calendaring roller, along with a custom roll, was acquired for the project. The provided rollers had dimensions of 100 mm in diameter and 300 mm in length. Schematics of the custom machined roller can be found in Figure 30.



Figure 30. Overview of design space, all measurements are in inches. Top left design is A1, bottom left design is A2, top middle design is B1, bottom middle design is B2, top right design is C1, bottom right design is C2. Colored designs indicate chamfering.

The roller was equipped with a motor that allowed for speed control and rotational direction control. The heating system of the roller consisted of four heating rods positioned near the front and back of both the top and bottom roller, which were enclosed behind thin steel sheeting. This heating system had the capability of maintaining a continuous temperature of 120°C. Pressure was applied using a screw-driven wedge system at each journal of the top roll, and the gap between the rollers could be adjusted from 0 to 2 mm, with measurements taken using a micrometer at each journal of the top roll. Detailed information about the design of the custom roller can be found in Figure 31 through Figure 36. The roller itself was 300 mm long and had a diameter of 100 mm. The designs of the roller were based on current state-of-the-art cold plate designs used in commercial vehicles. Design A1 was based on a same-side inlet/outlet serpentine pattern, oriented transverse to the rolling direction, while design A2 had the same pattern but was oriented longitudinal to the rolling direction. Design B1 was based on an opposite-side inlet/outlet arcshaped pattern, oriented longitudinal to the rolling direction, while design B2 had the same pattern but was oriented transverse to the rolling direction. Design C1 was based on an opposite-side inlet/outlet serpentine pattern, oriented transverse to the rolling direction, while design C2 had the same pattern but was oriented longitudinal to the rolling direction. To investigate the effect of cavity edge/feature interaction, the edges on design B2 and C2 were slightly chamfered.



Figure 31. Detailed schematic of Design Space A1, all measurements are in inches.



Figure 32. Detailed schematic of Design Space A2, all measurements are in inches.



Figure 33. Detailed schematic of Design Space B1, all measurements are in inches.



Figure 34. Detailed schematic of Design Space B2, all measurements are in inches.



Figure 35. Detailed schematic of Design Space C1, all measurements are in inches.



Figure 36. Detailed schematic of Design Space C2, all measurements are in inches.

Three different aluminum alloys, namely 1100 series aluminum, 1224 series aluminum, and 3003 series aluminum, were utilized in this study. The samples were prepared at various thicknesses and were subjected to annealing at a temperature of 500°C for a duration of 4 hours prior to rolling. The sample dimensions were 133 mm by 95 mm, which allowed for the entire design space to be rolled without interference from adjacent design spaces. For lamination purposes, samples varied in size, ranging from smaller 133 mm by 95 mm samples to larger 133 mm by 190 mm folded samples. Thin aluminum foils, obtained from McMaster Carr and used as received, were employed to create 3-layer laminates for mechanical and permeability testing. The size of the vacuum plate area limited the sample size for lamination.

The roller was modified to enable manual control of the rolling process. This modification involved drilling two holes in the drive gear of the upper roll to accommodate the mounting of a lever arm. The lever arm allowed for the application of additional torque to the rollers, providing manual control during the rolling process.

However, it should be noted that the heating system of the roller had limitations, and therefore, the samples were heated to elevated temperatures on an external hot plate. The temperature of the samples was verified using a thermocouple before being rolled through the rolling system, which itself was heated to 120°C by the roller's heating system. Once the samples reached the desired temperature, they were immediately rolled. To assist with the rolling process, a 500 mm long lever arm was utilized manually.

Sample measurements were conducted using a point-to-point micrometer with an accuracy of  $\pm 0.001$  mm to ensure precise and accurate measurements.

The lamination process involved the use of a laboratory vacuum pump and a heated 50-ton hydraulic press. For the lamination, commercially available nylon and polypropylene materials were purchased and used as received. Additionally, a thin pressure-sensitive adhesive tape from 3M was obtained and used in its original form.

To facilitate the lamination process, a piece of vacuum fabric was placed on the vacuum plate. This fabric helped create air channels and improve the vacuum pressure during the lamination process. A schematic illustrating the lamination process is provided in Figure 37.



Step 1. Bare Plate



Step 4. Second Non-stick



Step 7. Nylon vacuum sheet coated with nonstick



Step 2. Non-stick layer



Step 5. Vacuum fabric



Step 8. Plate placement and vacuum pump



Figure 37. Schematic of lamination process.

Step 3. Sample with Nylon



Step 6. Sealant tape



Step 9. Pressure removal and unloading



The next step in the lamination process is to outline the vacuum plate with gasket tape. The 3-layer laminate is composed of the following layers: a polypropylene inner layer, PSA (Pressure-Sensitive Adhesive) tape, an aluminum layer, another PSA tape, and a nylon outer layer.

The PSA tape is first applied to both sides of the aluminum layer, ensuring that the protective film is left intact. This creates a sandwich structure of tape-aluminum-tape. The tapealuminum-tape sandwich is then vacuum-pressed, while keeping the protective film on. This step allows for proper conformation of the adhesive layer.

Next, the protective film is removed, and the polypropylene inner layer is carefully applied to the flat side of the aluminum sample. The nylon outer layer is then gently placed over the patterned side of the aluminum.

The completed laminate sandwich is placed on the vacuum fabric, and a nylon vacuum sheet is placed over the entire vacuum plate, sealing it to the gasket tape.

The vacuum plate, with the laminate assembly, is then placed in the press. A 2 mm thick rubber pad is positioned directly over the sample, and a vacuum hose is attached to the plate and pump. Vacuum is pulled, and the setup is pressed at a force of 10 tons for a duration of 1 minute.

To verify the viability of the lamination process, the experimentally produced 3-layer laminates are cut into tensile samples. These samples are then tested for mechanical properties and analyzed for oxygen permeability.

Mechanical testing was conducted using an Instron model 4302 equipped with a 10 kN static load cell. The testing was performed at a strain rate of 200 mm/min. Dog bone-shaped samples were prepared according to ASTM D638 standards, with a gauge length of 50 mm, a gauge width of 13 mm, and an overall length of 165 mm.

Samples that broke near the grip region were excluded from the data set to ensure accurate measurements and reliable analysis. The purpose of this exclusion is to focus on the representative samples that provide meaningful information about the mechanical properties of the tested materials.

Permeability testing was carried out using a Mocon Ox-Tran 2/20 MH System. The tests were considered complete when the measurements obtained in three consecutive tests were within 5% of each other. The permeability testing was conducted with a continuous flow of 100% permeant gas, using medical grade oxygen as the permeant gas and a carrier gas mixture of 2% hydrogen and 98% nitrogen.

The testing duration for each sample was 30 minutes, and the permeation module was rezeroed every 30 minutes to ensure accurate measurements. The permeation samples had a testing area of 0.78 cm<sup>2</sup>, allowing for precise assessment of the permeability properties of the materials under investigation.

## 3.3.3 Replication of State-of-the-Art Cold Plates Results and Discussion

Measurements were conducted at different locations on the rolled samples, with only the maximum feature height and minimum trough depth being reported. The measurement locations for each design space are indicated in Figure 38.

To investigate the directional effects on the designs, some samples were rolled in both rolling directions. The complete results of the rolling experiments, including the measured feature heights and trough depths, are provided in Figure 39.

The results of the mechanical testing, including tensile strength and elongation at break, are summarized in Table 6. Additionally, Table 7, presents the results of the permeability testing, indicating the oxygen permeability values for the laminates. These tables provide a comprehensive overview of the mechanical and permeability properties obtained from the experimental testing conducted on the rolled samples.



Figure 38. Schematic of measurement locations for each design space. Red circles indicate areas where fin/feature measurements were taken, and blue circles indicate areas where trough measurements were taken. Magenta patterns (B2 and C2) had chamfered edges.



Figure 39. Overview of results for rolling experiments. Sample labels are "alloy: initial thickness: rolling gap: rolling temperature: direction (if applicable)".

Aluminum Thickness	Laminate Thickness (mm)	Tensile Strength (MPa)
(mm)		
0.012 (1100 series)	0.183	23.03
0.05 (Benchmark)	0.1	60.04
0.055 (1100 series)	0.231	33.82
0.076 (3003 series)	0.233	29.15
0.11 (1100 series)	0.279	34.83
0.25 (1100 series)	0.429	54.94

Table 6. Results for mechanical testing of flat laminates.

Tuote (, Rebuild for permeasing) testing of nut furthing testing		
Sample	Permeation (cc/m <sup>2</sup> per day)	
Benchmark 0.113 mm (0.1 mm Aluminum)	$33 \pm 0$	
0.175 mm Laminate (0.012 mm Aluminum)	$47.5 \pm 4.5$	
0.29 mm Laminate w/Copper (0.012 mm Aluminum)	51.5 ± 2.5	

Table 7. Results for permeability testing of flat laminates.

Designs A2 and C2 were found to be the most successful in terms of feature heights. These design spaces have specific areas where large troughs are followed by thin transverse-oriented fins. These fins exhibited significantly greater height (up to 0.99 mm) compared to the longitudinally oriented fins (up to 0.74 mm) and other areas of the design space. The extrusion of these features can be attributed to the substantial displaced volume preceding them [141].

Designs A1 and A2 are similar designs, but they are rotated by 90°, resulting in either longitudinal or transverse orientation relative to the outlet/inlet and rolling direction. Interestingly, it was observed that the analogous feature on design space A2 consistently exhibited greater height than the same feature on design space A1. This difference in feature height may be attributed to the orientation of the troughs relative to the rolling direction. In a rolling process, extrusion tends to occur more easily along the rolling direction compared to the transverse direction [124] [140] [141].

The parameters of the lamination process play a crucial role in achieving proper layer conformation in the laminate. If the nylon layer is wrinkled during the application process, it can result in ridges and delamination in the final laminate. The forming pressure applied during lamination is a critical factor that determines the degree of conformity in the laminate.

Increasing the pressure leads to improved conformity of both the adhesive layer and the plastic layer in the laminate. However, lamination can become more challenging when dealing with larger radius curves, as seen in designs B1 and B2 (Figure 30). The larger radius curves at the edges of these designs show less conformal lamination compared to those at the center of the design space. This indicates that achieving uniform conformity in the laminate becomes more difficult as the curves become larger in radius.

Wrinkling issues were present in rolled samples, particularly near the design corners. This wrinkling occurs in areas surrounding large, undeformed features such as in designs B1 and B2. Wrinkling issues were lessened at elevated rolling temperatures, where the sample material was more compliant. This wrinkling may be due, in part, to geometric constriction on material extrusion. If the roll gap is not parallel, one edge of the sheet will be decreased more in thickness than the other and result in bowing of the sheet. Designs A1, A2, B1, and B2 are offset on the roller with respect to the center, and as such will receive inconsistent roller deflection along the width of the design, with areas near the roll center deflecting more. This results in the areas of the design space nearest the edge of the roller being decreased more in thickness and causing wrinkling [141]. Wrinkling issues are highlighted in CAD schematics of Figure 40 through Figure 45 with circles and associated optical imaging of samples.



Figure 40. Image of (a) tin sample and (b) schematic highlighting areas of wrinkling for design space A1 and (c) rolled aluminum samples with rolling direction indicated by arrows.



Figure 41. Image of (a) tin sample and (b) schematic highlighting areas of wrinkling for design space A2 and (c) rolled aluminum samples with rolling direction indicated by arrows.



Figure 42. Image of (a) tin sample and (b) schematic highlighting areas of wrinkling for design space B1 and (c) rolled aluminum samples with rolling direction indicated by arrows.


Figure 43. Image of (a) tin sample and (b) schematic highlighting areas of wrinkling for design space B2 and (c) rolled aluminum samples with rolling direction indicated by arrows.



Figure 44. Image of (a) tin sample and (b) schematic highlighting areas of wrinkling for design space C1 and (c) rolled aluminum samples with rolling direction indicated by arrows.



Figure 45. Image of (a) tin sample and (b) schematic highlighting areas of wrinkling for design space C2 and (c) rolled aluminum samples with rolling direction indicated by arrows.

Tin samples showed evidence of wrinkling in all samples. Some samples, especially at room temperature, suffered from issues related to the feature-cavity interaction during the rolling process. One issue in this category is referred to as lipping. This issue was evidenced by a tearing of the front edge of a transverse-oriented fin such that a small lip of material is left on the top of the feature and the feature is left with a sloped leading edge. One hypothesis for the evolution of these lips is the front edge of the roller cavity peels away this material as the sample is removed from the roller, Figure 24 shows a schematic of this process.

Another issue related to the feature-cavity interaction is an issue referred to as hair-trimming. This issue was evidenced by a thin strip of material being present at the top rear edge of transverseoriented fins. This thin strip of material resembles a hair and is left connected at one end, sometimes being completely removed from the sample piece. Like lipping, this phenomenon results from the feature-cavity interaction, but different in that it appears only at the back edge of rolled features. A schematic showing hypothesized creation mechanism is highlighted in Figure 25.

In this scenario, the back edge of the cavity wall will scrape the backside of the feature from bottom to top, resulting in a thin strip of material left on the top, rear edge of the feature. This issue can be solved by a slight chamfering of the edge of the cavity wall, as evidenced by hair trimming being non-existent on designs B2 and C2. An issue was observed on longitudinally oriented troughs which manifested as arc-shaped surface texturing. This issue, referred to as "scalloping" due to the similarity to scalloped texturing, was observed in wide, longitudinally oriented troughs. An example of this scalloping can be seen in Figure 46, where consecutive arc shapes are formed on the surface of the troughs.



Figure 46. Scalloping issues on design space C2, a 2mm 3003 series aluminum sample rolled at 350°C is shown here. Inset highlights scalloping issues.

As the workpiece passes through the rolls all elements across the width experience some tendency to expand laterally. The tendency for lateral spread is opposed by the transverse friction forces. Because of the friction hill, these are higher toward the center of the sheet so that the elements in the central region spread much less than the outer elements near the edge [141] [142]. This tendency for the sample to spread near the edge of compression zones may result in these surface artifacts. The scalloping is oriented such that the "U" is pointed towards the rolling direction. This could be due to the center of trough being more easily strained than areas near the edge which are under less transverse friction forces but confined geometrically by the wall of the feature on the roller. This effect is more severe when draft is increased.

From designs B1 and B2, curves with a smaller radius of curvature are more easily laminated. The outer curves on designs B1 and B2, which have larger radii of curvature, are less conformally laminated than inner curves with smaller radii of curvature. Outer curves on design space B2 show signs of delamination and poor conformity (Figure 47 and Figure 48).



Figure 47. Image highlighting conformity issues with lamination of curves. Black arrows indicate areas of good conformity and red arrows indicate areas of poor conformity.



Figure 48. Image highlighting the conformity issues with lamination of curves and conformity at smaller radius of curvature. Black arrows indicate areas of good conformity and red arrows indicate areas of poor conformity.

Insets on Figure 47 and Figure 48 highlight these conformity issues, red arrows indicate areas of poor conformity while black arrows indicate arrows of good conformity. Outermost fins show consistent lines of poor conformity running the entire radius. Inner fins show some areas of poor conformity but also areas where the nylon has conformed well. The top, transverse segment of first fin and rounded "nose" in center of design space B2 are well conformed (Figure 47, bottom inset and Figure 48, bottom inset). There may be several reasons for this lack of conformity on outer most curves. One reason could be the strain state achieved when pressing the nylon. The nylon may be strained more in the vicinity of smaller radius inner most curves than larger radius outer most curves. This extra strain in the small radius curves may be enough to plastically deform the nylon film, causing it to stay conformed to the curves once the force is removed. In the larger radius curve case, the nylon film may only be elastically deformed, resulting in relaxation and delamination once the force is removed. Alternatively, there may be issues with the lamination process itself, such as the stiffness of the rubber pad. If the rubber pad used to apply pressure is too stiff, then it will be less likely to conform at the base of fins. A lack of conformity of the rubber pad will result in a lack of conformity of the nylon film, this also may be the cause of further lamination issues discussed below.

Highlighted in Figure 49, concave curvature was more easily conformed to when laminating, compared to convex curvature.



Figure 49. Image highlighting conformity issues on convex and concave curvatures. Black arrows indicate areas of good conformity and red arrows indicate areas of poor conformity.

This effect was evidenced on the equivalent curves in design space B2 shown in Figure 49. Each of these curves has an equivalent radius unlike the curves shown in Figure 47 and Figure 48. When comparing the convex and concave side of each curve, there is evidence of good conformity on the concave side of each curve and poor conformity on the convex side of each curve. This may be due, in part, to the lipping effect and the sloped leading edge of the features. The convex side of these curves are the front edge with respect to the rolling direction, resulting in them becoming sloped during the rolling process. The concave side of these curves are the trailing edge with respect to the rolling direction and, in this case, remain relatively straight walled 90° features. The straight walled concave side of the features strains the nylon more and plastically deforms it, resulting in better conformity after the pressure is removed. The sloped leading edge does not impose enough strain to plastically deform the film and results in lower conformity once vacuum pressure is removed.

The stiffness of the rubber pad and curvature of padding may have contributed to this issue. A cartoon schematic of the process shown in Figure 50 illustrates the issue.



Figure 50. Cartoon schematic of possible cause of lamination issues. Here the rubber pad is "squished" out due to the curvature of the rubber padding, this squishing could result in one side of the base of a fin receiving little to no pressure from the pad.

A pad with curvature convex with respect to the sample was used to prevent air bubbles from becoming trapped at the center of the design space. In this way the center of the pad will contact the sample first and be "squished" towards the edges. Due to this effect, the base of one side of a fin may receive little to no pressure from the pad, highlighted by the blue circles in Figure 50. Similarly, the base of one side of a fin may receive more pressure, highlighted by red circles in Figure 50.

Fin tips that extended to the end of the design space were shown to have lamination issues when compared to similar fin tips that resided within the design space. This can be seen in Figure 51 and Figure 52, the former highlighting edge fin issues while the latter compares one of these edge fins to equivalently sized fins from the center of two different design spaces.



Figure 51. Image highlighting edge fin issues and length of straight fin dependance on conformity. Black arrows indicate areas of good conformity and red arrows indicate areas of poor conformity.



Figure 52. Image showing conformity issues with external fin tips and flattened fin tips. Black arrows indicate areas of good conformity and red arrows indicate areas of poor conformity.

The left most and center fin from Figure 52 are roughly equivalent in shape as well as size, with the main difference being the left most fin coming from the edge of B2 and the center fin coming from the center of A1. The A1 fin shows less area of non-conformity than the B2 fin. Again, this may be due to the "squishing" effect shown in Figure 50, with the center of the pad coming into contact first and receiving the most time under pressure.

The lamination conformity of the fins that extend to the edge of the design space on B2 seem to be influenced by the length of the straight section that precede it. Highlighted by the insets of Figure 51, fins at the bottom of the design space begin to achieve good conformity before fins at the top of the design section with shorter straight sections of fin. Accumulation of gas bubbles at the ends of these fins could cause this poor conformity. In addition, the fins themselves are taller at the ends, meaning the nylon at the ends of the fins needs to accommodate extra height change. The stiffness of the rubber pad could also contribute to these issues. The rubber pad must bend in one plane to accommodate the height change of the fin; in straight fin sections this is the only bending the pad must accommodate. When the fin is curved, the pad must now bend in two planes to accommodate the height change and curvature.

In addition, the A1 fin is slightly more rounded than the B2 fin, the right most fin in Figure 52, from the center of C2, is more rounded than the A1 fin and B2 fin. These results indicate fin tips with a continuous curve are more easily conformed to than flattened fin tips. The fin from C2 shows areas of good conformity near the tip of the fin.

In addition to the shape of the fin tip, the size of the fin will also affect conformity. A fin from the center of C2 and the fin from the center of B2 are compared in Figure 53, the fin from B2 is roughly twice the size of the fin from C2. The fin at the center of B2 has much better conformity than that of C2, with the top of the fin being almost completely conformed.



Figure 53. Image highlighting the effect of size on conformity of rounded fin tips. Black arrows indicate areas of good conformity and red arrows indicate areas of poor conformity.

Testing results indicated the laminating process is adequate to reproduce benchmark performance within orders of magnitude for both mechanical strength and oxygen permeability. Table 6 shows that for similar aluminum thicknesses, benchmark laminates are almost twice as strong. This can be attributed to optimized processes producing well adhered layers and the composition of benchmark aluminum. The benchmark sample utilizes an unknown 8000 series aluminum alloyed with iron. Summarized in Table 7, permeation data, permeation values for lab-made laminates are slightly higher than that of the benchmark material.

The most successful design elements were fins oriented transverse to the rolling direction. These features are especially effective when preceded by a large trough due to the displaced material from the trough being extruded into these thin transverse fins. Fins oriented longitudinal to the rolling direction were not as tall as those oriented transverse to the rolling direction. Designs A2 and C2 contained thin transversely oriented fins that were the tallest areas of the design space. These thin transversely oriented fins were the tallest features measured of all design spaces, especially A2. Design space A2 has long troughs which end in thin transverse fins, these fins are the tallest features measured with an absolute height of 2 mm and a feature height of 0.91 mm from a 1.81 mm thick tin sample.

Design spaces A2 and C2 can be compared to examine the effects of transverse-fin longitudinal thickness on feature height, as both designs include long longitudinal troughs. Comparing A2 and C2, as the thickness of the fins in the longitudinal direction increases, in most cases, feature height decreases.

Design spaces B1 and C2 were less consistent. Design space B1 was taller at the corners of the input channels preceding and following longitudinal troughs than the center of the design space, which contained only transverse troughs. These results support the conservation of material and indicate that to get better feature heights, it is beneficial to place longitudinal troughs preceding thin transverse fins. These results also indicate transverse troughs may induce more transverse extrusion of material, leading to the corners highlighted in Figure 38 (red circles) being taller than straight sections of the fin.

This approach of using thin, transverse oriented fins has its disadvantages related to the topography of the rolled features. Transverse fins suffered from a category of issues here called "Lipping Effects" which encompasses two issues, related to the roller cavity/feature interaction. Hair-trimming was mitigated by chamfering the cavity edges of Design B2 and C2. Lipping was still observed in design space C2, but only when feature height was 0.7 mm, which was the tallest feature achieved in aluminum.

The tallest features formed in tin were 0.91 mm and 0. 81 mm for design spaces A2 and B1, respectively. For aluminum, 0.7 mm was the tallest feature height achieved. This was for design space C2 in 2.03 mm thick 1100 aluminum through a 0.9 mm gap at 350 °C and 2.48 mm thick 1100 aluminum through a 1.3 mm gap at 350 °C. Here, tin is rolled at a higher homologous temperature than 1100 aluminum, meaning that tin should be more compliant and thus, more conducive to extrusion. Tin samples for design space B1 were tallest at the corners highlighted in Figure 38 (red circles); areas where transverse and longitudinal extrusion are being deposited. Design space B1 has the narrowest troughs in terms of transverse width. Design space B1 also had the thinnest troughs, this could be due to the increase in the rolling pressure on these troughs due to decreased length along the contact line over which the rolling force is applied. An increase in rolling pressure would increase the amount of extrusion possible which could explain why B1 was more effective for tin samples than aluminum.

For all aluminum samples except 2.03 mm 3003 aluminum rolled through a 0.9 mm gap at room temperature, design A2 or C2 had the thinnest troughs. The inlet and outlet of A2 and C2 were consistently thinner than the thinnest troughs of other design spaces. Especially the outlet of C2, these are areas where the length of the line of contact has been decreased, theoretically increasing the rolling pressure in these areas. At the inlet/outlet of A2 and the inlet of C2, there is

a considerable decrease in the length of the line of contact. This could account for the decreased thickness of these areas specifically and should also be considered for future design optimization.

There were design spaces with outliers, in terms of feature heights, caused by the wrinkling of large, undeformed areas. Design spaces A1, B1, and B2 suffered from wrinkling near the undeformed areas highlighted in Figure 40, Figure 42, and Figure 43, respectively. Design A2 did not suffer from as severe wrinkling as Design A1. This could be because more longitudinal features allow for continuous longitudinal extrusion of material, whereas Design A1 contains transverse troughs which force more transverse extrusion. This causes the undeformed areas of A1, B1, and B2 to bow and wrinkle, making these areas of the designs difficult to measure and inconsistent in thickness. Interestingly, design space C1 had fewer wrinkling issues despite being transverse troughs. Design space C2 had more wrinkling associated with the large, undeformed fins next to the inlet and outlet (Figure 45). This may suggest that undeformed area, or transverse width, is a more dominant factor in wrinkling than trough orientation.

Complex designs were produced on the surface of sheet aluminum. These aluminum samples were then able to be laminated to replicate current benchmark materials.

## CHAPTER 4: ALTERNATE MATERIALS SELECTION FOR BATTERY THERMAL MANAGEMENT SYSTEMS

## 4.1 Metallic Foams

During rolling experiments, alternative materials were trialed to examine their processability with compressional roll molding. Of the alternative materials, one standout was a metallic foam. Metallic foams can be strained up to 60-70% at almost constant stress, making them an ideal candidate for compressional roll molding [143]. Foams can be classified as either closed cell or open cell, with closed cell having faces separating the voids of each cell. Open cell foams have excellent heat dissipation because of high thermal conductivity and high internal surface area [143]. As foams are strained, they first undergo a linear elastic region when recoverable bending occurs. Once yielding occurs, the foams undergo a plateau region where plastic yielding is occurring, and voids are being closed. As most voids are closed, the stress beings to rise as densification occurs. This densification phenomena could be leveraged to optimize heat conductivity in selected areas, such as near the tabs in pouch cells, and reduce hot spots.

Previous calculations on staggered arrays assume that the fin has high thermal conductivity, such that the fin temperature is the same with the battery surface temperature. This assumption might not be satisfied if the fins are made from polymeric or non-monolithic material which have lower thermal conductivity than most monolithic metals. Fin arrays manufactured from polymeric materials are more appealing due to their low cost and light weight. However, polymeric materials generally have a low thermal conductivity, almost three orders of magnitude lower than metals. Metallic foams are also attractive due to their lighter weight but suffer from decreased thermal conductivity over the monolithic metals. If the heat conduction along the fin is not fast enough, the temperature along the fin drops. This results in a lower average temperature difference between

the fin surface and the cooling air. A lower temperature difference leads to a lower heat transfer rate based on the convective resistance derived from Newton's Law as given in (6).

$$Q_s = h(T_s - T_\infty) \tag{6}$$

Thus, the amount of heat that a fin array made from polymeric materials can remove is decreased. The following equations are based on equations for external forced convection from [138]. The effect of the thermal conductivity of the fin material on the overall heat transfer rate can be quantified using (7).

$$\frac{d^2\theta}{dx^2} - a^2\theta = 0 7$$

Where,

$$a^2 = \frac{hp}{kA_c}, \quad \theta = T - T_{\infty}, \qquad 8$$

and *h* is the convection heat transfer coefficient, *p* is the fin perimeter,  $A_c$  is the cross-section area of the fin, and *k* is the thermal conductivity of the fin. *T* is the temperature at any given point from the battery surface to the fin tip and  $T_{\infty}$  is the mean temperature of the cooling air. The fin connects two pouch battery surfaces. Thus, the boundary conditions for the fin equation can be given as (9) and (10), respectively.

$$\theta(0) = T_s - T_\infty \tag{9}$$

$$\theta(L) = T_s - T_{\infty} \tag{10}$$

where *L* is the length of a fin and  $T_s$  is the surface temperature of the battery. The heat transfer rate from a fin is obtained by solving the fin equation with the two boundary conditions and provided in the following, (11).

$$q_f = M \frac{(\cosh mL - \theta_L/\theta_S)}{\sinh mL}$$
11

Where,

$$M = \sqrt{hpkA_c\theta_S}.$$
12

To simplify the calculations, the following assumptions are made: the convective heat transfer coefficient, *h*, is 40 W/(m<sup>2</sup>·K); the mean air temperature is 22°C; the surface temperature is 45°C and remains constant. The fin length, *L*, is 3mm. The diameter of a pin fin is 3 mm, which gives a cross-section area of  $7 \times 10^{-6}$  m<sup>2</sup> and a perimeter of  $9.4 \times 10^{-3}$  m. With these given conditions, the heat transfer rate of a single pin fin is plotted as a function of the thermal conductivity in Figure 54.



Figure 54. Heat transfer rate of a single fin as a function of thermal conductivity of the fin material.

Overall, the heat transfer rate from a fin array does not exhibit strong dependence on the thermal conductivity of the fin material, although the heat transfer rate increases faster when the thermal conductivity increases from 0.3 to 3 W/m·K. Many simulations and experiments have been conducted on thermal conductivity of metal foams as a function of porosity. In many systems, metallic foams will maintain an effective thermal conductivity above 3 W/m·K up to very high porosities. Simulation and experimental data show that copper foams up to 97.9% porosity maintain effective thermal conductivity above 3 W/m·K [144]. Aluminum foams maintain an effective thermal conductivity of 4.65  $\pm$  0.41 W/m·K at 92.7% porosity [145]. Further, copper foams have been shown to be amenable to paraffin impregnation up to 95% on average with vacuum assistance [146]. For these reasons, and due to aluminum's oxide formation, both copper and aluminum foams were investigated.

The metallic foam used was an open cell copper foam with 93% porosity, purchased in 12" x 12" sheets of approximately 1.52 mm thickness. This foam was able to be easily rolled and patterned, as well as laminated. The aluminum foam used was a 91% porosity closed cell foam with initial thickness of approximately 5 mm.

Copper foams were used to recreate current manifold designs using the roller outline in previous sections. Another huge advantage to the metallic foam is the ability to stack layers and compress those layers into one homogenous structure. Copper foam was able to be rolled at 0 mm rolling gap very easily and was able to be reduced to a thickness of 0.38 mm for a stack of 4 copper foam sheets, while features of 1.7 mm in height were formed. In experiments, layers that were compressed together showed good adhesion while the uncompressed regions could be susceptible to delamination between the layers. Once compressed regions had edges trimmed, it was very difficult to differentiate or otherwise separate individual layers. Edges of compressed regions and

the edges and bases of features were somewhat susceptible to delamination (Figure 55). Lamination with the nylon and polypropylene prevents the delamination of the foam layers in use for the 3-layer laminate application. Another advantage of the metallic foams is the preservation of the pore structure in both the compressed and uncompressed regions. A single sheet, rolled and featured, was sectioned, and imaged with stereomicroscopy (Figure 56). This shows that even in areas of compression, there is still some pore structure remaining. This remaining pore structure could indicate that further strain is possible before densification begins.

Additional metal foams were experimented with, an aluminum closed cell foam was also rolled and featured. Due to the stability and ready formation of aluminum oxide, the aluminum foams were more brittle and would crumble during the rolling procedure. This meant that less draft was possible before fracture, but features were still able to be formed. Design space C2 in aluminum foam was cross sectioned and imaged (Figure 57).



Figure 55. 4 Layer stacked copper foam featured sample.



Figure 56. Cross section of rolled copper foam sample.



Figure 57. Cross section of aluminum foam sample. Inset shows full sample clamped for imaging.

This closed cell foam was able to be deformed but fractured at large drafts in the interface between compressed and uncompressed areas. Ductility of the base metal plays a large role in the processability of the metallic foam. Copper being much more ductile than alumina means the copper foam can be deformed more readily and to higher drafts.

Another advantage to the metallic foams was less variation in feature height throughout the design space. When measuring rolled samples, the measurement location is extremely important as highlighted in Figure 38. Certain areas of the design space are consistently taller than other areas, this is not the case with the foam materials. The foam materials remain at a consistent height in the non-compressed regions and give greater sample uniformity, this could also be beneficial to temperature homogenization throughout the pouch cell.

Lamination of the foam materials was accomplished with the same lamination procedures as monolithic materials. This is promising for the future incorporation of foam materials into current production processes. Lamination prevented the delamination of the foam layers post rolling procedure. This ease of lamination and structural stability are desirable for pouch laminate materials. Copper foams, once laminated, were very flexible and able to be folded into 2-sided pouch prototypes, ready for sealing (Figure 58). Aluminum foams remained rigid but were able to be laminated with preliminary lamination procedures (Figure 59).



Figure 58. Laminated copper foam sample, double sided and foldable.



Figure 59. Aluminum foam sample laminated using preliminary lamination procedures not reported here.

In this prototype, a textured vacuum bag was used to provide vacuum pressure and seal laminate. The lamination here was successful but future lamination experiments with combined vacuum pressure and heated platen pressure were not attempted. Also, both foam materials were able to be bonded to a thin aluminum foil layer; this is important to provide gas barrier properties. Copper foam was laminated with aluminum layers on both sides. Permeation testing from previous experiments (Table 7) show that this lamination process with one side aluminum foil covered copper foam is adequate to recreate the benchmark material performance within an order of magnitude. At the laboratory scale, this is a promising result as industry optimization would improve this figure significantly.

Another major advantage to open cell metallic foam materials is the ability to be back-filled with phase changing materials (PCMs). This would enable greater heat absorption and allow for more precise control of temperature within the range of the transformation temperature of the PCM. This process is currently used in many electric vehicle systems, specifically those utilizing prismatic cells. Producing the laminate material with a porous center layer would allow filling of PCM and give the best temperature uniformity throughout the cell.

## 4.2 Graphene Paper

As alternative materials were explored, a replacement material for the aluminum layer was considered. The goal of replacing the aluminum was to increase the ability to produce features and increase the thermal conductivity. For this application, a GnP composite paper was considered.

This GnP composite paper was produced using a suspension/filtration process of surfactant modified GnP [123]. As received M25 GnP was mixed in a 1:1 ratio with polyethyleneimine (PEI) to create a suspension in DI water. This suspension was then sonicated for 3 minutes at 120 Watts and then mechanically stirred for 12 hours. This suspension is then vacuum filtered through a support membrane and died in a vacuum at 75 °C for 24 hours.

Features were formed by pressing silicone masks onto filtrated GnP discs using a hydraulic press. Samples were pressed at 2000 lbs. pressure for 3 minutes. Trials were conducted featuring this material both before and after drying. Features formed before drying were successful, whereas attempting to feature dried discs result in fracture of the disc. Arrays of circular and square features were able to be formed.

These discs were tested in a modified flow chamber heating cell. A heating pad was connected to a variable ac power supply which supplied a constant 4.34 Watts heating power at 25 Volts. The heating pad was fixed to an aluminum plate at the bottom of a thermally isolated heating chamber, simulating a heating battery pack. Distance from heated plate to top of chamber was approximately 3 mm, simulating the space between battery packs. Air temperature was measured at the inlet and outlet of the system.

Featured graphene paper was subjected to lamination procedures reported in previous sections (Figure 37).

Featured samples used in samples are as follows: Flat, Least Dense Square, Most Dense Square, Least Dense Circular, Most Dense Circular, and a 3-D Printed sample. Samples are shown in Figure 60, the 3-D Printed sample is an aluminum sheet with 3-D printed graphene dots. Square features are approximately 5 mm by 5mm, circular features are approximately 4 mm in diatemer. The Flat sample contains no features and is 0.774 grams in weight. The Least Dense Square sample contains 10 features with x-spacing of 20 mm, y-spacing of 15 mm and weighs 1.422 grams. The Most Dense Square sample contains 24 features with x-spacing of 5 mm, y-spacing of 5 mm and weighs 0.749 grams. The Least Dense Circular sample contains 33 features with x-spacing of 7 mm, y-spacing of 7 mm and weighs 0.687 grams. The Most Dense Circular sample contains over 100 hundred features with x-spacing of 3 mm, y-spacing of 3 mm and weighs 0.706 grams. The 3-D Printed sample contains 36 features with x-spacing of 10 mm, y-spacing of 10 mm and weighs 4.063 grams.


Figure 60. Graphene paper samples used in heat chamber experiments. (A) Flat, (B) Least Dense Square, (C) Most Dense Square, (D) Least Dense Circular, (E) Most Dense Circular, and (F) 3-D Printed.



Figure 61. Cooling Curves from Heat Chamber Experiments. Temperatures have been selfnormalized.



Figure 62. Cooling Curves from Heat Chamber Experiments.

Cooling curves have been reported as outlet temperatures, both self-normalized (Figure 61) and raw data (Figure 62). From the raw data (Figure 62), the starting air temperature was lowest for the empty set-up with no heat conducting sample. At time = 0, no air is flowing in the heating chamber. This means that less heat is being conducted to the air when no sample is present in the chamber and no air is flowing. Least Dense Circular samples achieved highest outlet air temperatures at all points throughout the test. Because constant power is supplied to the heating pad, it can be assumed that the Most Dense Circular sample is the most efficient at transferring heat from the thermal plate to the air. After time = 0, air flow is initiated in the chamber and cooling begins. Normalizing data to itself allows visualization of percentage of heat removed and cooling rates for different sample materials. Most Dense Square and Flat samples were able to produce highest initial cooling rates, while Least Dense Square and Flat samples were most efficient in removing heat from the chamber. It should also be noted that the Least Dense Square sample was twice as heavy as other graphene paper samples, with the Flat sample being the second heaviest graphene paper sample. The 3-D Printed sample is the heaviest sample but is also mainly aluminum. The difference in heat conduction between aluminum and GnP paper is likely the main factor in this reduced efficiency. The Most Dense Circular and 3-D Printed samples were least efficient in heat removal. The Most Dense Circular sample is very heavily featured, forming very narrow flow channels and creating large pressure drops through the featured area. This effect can cause stagnation of air at the surface of the sample [138]. This will reduce the efficiency in removal of heat from the surface.

The Most Dense Square sample was selected to attempt lamination on. This sample was selected as it was produced using twice as much treated GnP and was therefore more mechanically robust. Preliminary lamination experiments involved attempting to laminate and feature GnP paper

discs in one step. This resulted in fracture of the GnP paper disc, however features were successfully formed on one side of the disc (Figure 63). As lamination procedures developed, GnP paper was able to be laminated without fracture. This was accomplished through a 2-step, featuring then lamination procedure. Flat, wet GnP disc were pressed at 2000 lbs. pressure for 3 minutes with a silicone mask. Holes or depressions were cut into the silicone pad to allow material extrusion through the holes or into the cavities. In this way, features were formed on the surface of the GnP discs. These featured samples were then subjected to lamination procedures reported in previous sections. This produced interesting results, in that the features are visible on the back side of the GnP discs.



Figure 63. GnP paper sample that was featured and laminated in one step using heated, masked platen pressing.



Figure 64. GnP paper laminated using procedures reported in previous sections.

#### **CHAPTER 5: SUMMARY AND OUTLOOK**

## 5.1 Summary

Surface engineering will become more important as more complex composites are needed. Understanding the complex interactions that occur at all surfaces and length scales are key to creating better composites. Being able to selectively modify surfaces allows greater control of bonding at interfaces, which in turn will dictate composite properties. Methods to modify surfaces will become more advanced as the need to modify new surfaces arise.

In this work a rotary chamber was utilized to maximize surface treatment homogeneity in plasma processes. Oxygen and fluorine functional groups were able to be successfully attached to the GnP surfaces.

In this work, a novel rolling procedure was developed to satisfy industry requirements while allowing complex patterns to be formed on the surface of the cells. This concept was proven on various length scales and geometries, with results promising for scale up and implementation in a continuous process. With the novel rolling procedure came a need to develop a lamination procedure that would allow conformity of outer polymer layers. A novel, combined vacuum/compliant pad lamination procedure was developed and compared to benchmark processes. Experimental laminates were shown to be within an order of magnitude of commercial, benchmark laminates for both mechanical strength and oxygen barrier properties.

Along with an advanced process for manufacturing of featured 3-layer laminates, advanced materials concepts were also proven. Non-monolithic materials were tested, and metallic foams were found to be ideal materials for this new rolling procedure. These materials are easier to compress and form complex shapes without the wrinkling issues present in monolithic materials. These materials also present opportunities for post-processing and backfill with PCMs. The

structure allows the foams to be compressed into densified regions, with stacking of layers presenting unique design strategies for hotspot mitigation.

In this work, material development of the pouch cell outer layer led to production of graphene paper which could increase the overall heat transfer of the laminate. This material was able to be patterned and laminated. Lamination post-featuring led to interesting results where features were transferred through the midplane of the sheet.

#### 5.2 Research Outlook of Plasma Processing

Many of the unique results from the fluorine plasma seem to be time dependent, according to preliminary results from extended treatment time studies. It would be a worthwhile effort to better understand the surface evolution with oxygen plasma treatments as well. Extended treatment time experiments were conducted. Full characterization of modified materials should be concluded to monitor surface evolution. The current hypothesis is that as the GnP materials are being treated, their surfaces become saturated with functional groups and as treatment continues the saturated layer is somehow removed and treatment recommences on the freshly exposed layer. The mechanism through which the saturated layer is removed could be better understood through more careful treatment parameter controls and thorough characterization.

The application of plasma treatment in surface engineering for functionalization stands as a powerful and versatile strategy in materials science. Plasma treatment offers unparalleled versatility in functionalizing material surfaces. Through careful control of plasma parameters, including gas composition, pressure, and power, researchers can tailor surface chemistry, structure, and properties with precision. This versatility extends across a broad spectrum of materials, from polymers and metals to ceramics. One of the key advantages of plasma treatment is its ability to enhance adhesion between surfaces and coatings. This has profound implications for diverse applications, particularly in the biomedical field where improved adhesion and biocompatibility are crucial. By modifying surface chemistry, plasma treatment creates a conducive environment for subsequent functional coatings, promoting better integration with biological systems.

Plasma treatment exhibits exceptional uniformity in modifying material surfaces, especially when utilizing a rotary sample chamber. The treatment can penetrate complex geometries and porous structures, ensuring that even intricate surfaces are effectively functionalized. This capability makes plasma treatment particularly advantageous in applications where consistent modification across diverse surface morphologies is essential. The rotary tumbler system allows large batches of powder to be treated continuously and uniformly.

The environmentally friendly nature of plasma treatment sets it apart from certain chemical processes. It often involves gases and does not generate significant chemical waste, aligning with sustainability goals. This aspect makes plasma treatment an attractive option for functionalization, especially when considering the environmental impact of material processing. From enhancing the wettability of surfaces for improved printing and coating processes to modifying the surface energy of polymers for better adhesion in packaging, the impact spans industries such as electronics, healthcare, and manufacturing.

While plasma treatment offers numerous advantages, challenges persist, including scalability, the need for specialized equipment, and the potential for unintended side effects. Ongoing research endeavors focus on addressing these challenges and further refining plasma treatment techniques. Advances in plasma diagnostics, modeling, and novel gas compositions are driving the field towards new frontiers. The future of plasma treatment in surface engineering holds promising prospects. Continued advancements in understanding plasma-material interactions, along with innovations in plasma sources and techniques, will likely expand the scope of applications and enable even finer control over surface functionalities. The integration of plasma treatment with other surface engineering approaches and emerging technologies is poised to unlock new possibilities in materials design and functionality.

In summary, plasma treatment offers a dynamic and powerful tool for functionalizing material surfaces. The continued synergy between research, technological innovation, and

185

industrial applications will undoubtedly shape the landscape of materials science and engineering, with plasma treatment playing a central role.

# **5.3 Research Outlook of Rolling Experiments**

From these two preliminary experiments, some design and process guidelines can be determined. This rolling method is conducive to continuous manufacturing, something current heat sink production methods lack. This method also produces monolithic heat sinks, improving the thermal conductivity from plate to pin in comparison to top-down methods of attaching pins through additive manufacturing. Optimization for pin arrays would allow for continuous production of large arrays which could then be sectioned to appropriate size.

Surface engineering for patterning surfaces to enhance thermal conductivity represents a transformative avenue in materials science and engineering. Through meticulous control of surface topography at macro and nanoscales, researchers and engineers have unlocked unprecedented possibilities to tailor materials for optimized heat transfer. Surface engineering allows for precision engineering of surface topography, influencing thermal conductivity at the fundamental level. Techniques such as surface texturing and advanced manufacturing methods enable the creation of intricately patterned surfaces designed to enhance heat transfer. The versatility of surface engineering in patterning surfaces for increased thermal conductivity extends across various industries. From microelectronics and energy storage to aerospace and beyond, tailored surface patterns address specific thermal challenges, providing solutions for enhanced performance and efficiency.

While significant strides have been made in surface engineering for thermal optimization, challenges persist. Scalability and the integration of sustainable approaches are areas that warrant continued research. Ongoing efforts in these domains aim to further refine surface patterning techniques and broaden their applicability. As the field evolves, future directions in surface engineering for thermal conductivity include the integration of bio-inspired designs, advanced

computational modeling for predictive engineering, and the exploration of novel materials with inherent thermal functionalities. These directions hold promise for pushing the boundaries of what is achievable in tailoring surfaces for optimized heat transfer.

Surface engineering's role in patterning surfaces for increased thermal conductivity is emblematic of the precision and innovation at the heart of materials engineering. The ability to fine-tune thermal properties through surface patterning not only addresses current challenges but also paves the way for the development of next-generation materials with unprecedented thermal capabilities. As the field continues to advance, the synergy between surface engineering and thermal conductivity promises to shape the future of materials design and innovation.

### BIBLIOGRAPHY

- [1] J. R. Davis, Surface Engineering for Corrosion and Wear Resistance, Materials Park, OH: ASM International, 2001.
- [2] A. Matthews, A. Leyland, B. Dorn, P. R. Stevenson, M. Bin-Sudin, C. Rebholz, A. Voevodin and J. Schneider, "Plasma-based surface engineering processes for wear and corrosion protection," *J. Vac. Sci. Technol. A*, vol. 13, pp. 1202-1207, 1995.
- [3] C. B. Breslin, A. M. Fenelon and K. G. Conroy, "Surface engineering: corrosion protection using conducting polymers," *Materials & Design*, vol. 26, no. 3, pp. 233-237, 2005.
- [4] N. Dalili, A. Edrisy and R. Carriveau, "A review of surface engineering issues critical to wind turbine performance," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 2, pp. 428-438, 2009.
- [5] A. L. Yerokhin, X. Nie, A. Leyland, A. Matthews and S. J. Dowey, "Plasma electrolysis for surface engineering," *Surface and Coatings Technology*, vol. 122, no. 2-3, pp. 73-93, 1999.
- [6] P. Xue, B. L. Xiao and Z. Y. Ma, "Effect of Interfacial Microstructure Evolution on Mechanical Properties and Fracture Behavior of Friction Stir-Welded Al-Cu Joints," *Metallurgical and Materials Transactions A*, vol. 46, pp. 3091-3103, 2015.
- [7] L. Sun, M. Chen and L. Zhang, "Microstructure evolution and grain orientation of IMC in Cu-Sn TLP bonding solder joints," *Journal of Alloys and Compounds*, vol. 786, pp. 677-687, 2019.
- [8] M. Berthou, P. Retailleau, H. Fremont, A. Guedon-Gracia and C. Jephos-Davennel, "Microstructure evolution observation for SAC solder joint: Comparison between thermal cycling and thermal storage," *Microelectronics Reliability*, vol. 49, no. 9-11, pp. 1267-1272, 2009.
- [9] A. Kurella and N. B. Dahotre, "Review Paper: Surface Modification for Bioimplants: The Role of Laser Surface Engineering," *Journal of Biomaterials Applications*, vol. 20, pp. 5-50, 2005.
- [10] F. Poncin-Epaillard and G. Legeay, "Surface engineering of biomaterials with plasma techniques," *Journal of Biomaterials Science, Polymer Edition*, vol. 14, no. 10, pp. 1005-1028, 2003.
- [11] R. Vasita, K. Shanmugam and D. S. Katti, "Improved Biomaterials for Tissue Engineering Applications: Surface Modification of Polymers," *Current Topics in Medicinal Chemistry*, vol. 8, pp. 341-353, 2008.

- [12] G. Wu, P. Li, H. Feng, X. Zhang and P. K. Chu, "Engineering and functionalization of biomaterials via surface modification," *Journal of Materials Chemistry B*, vol. 3, no. 10, pp. 2024-2042, 2015.
- [13] Y. P. Jiao and F. Z. Cui, "Surface modification of polyester biomaterials for tissue engineering," *Biomedical materials,* vol. 2, no. 4, p. R24, 2007.
- [14] R. Morent, N. De Guyter, T. Desmet, P. Dubruel and C. Leys, "Plasma surface modification of biodegradeable polymers: a review," *Plasma processes and polymers*, vol. 8, no. 3, pp. 171-190, 2011.
- [15] J. Nam, N. Won, J. Bang, H. Jin, J. Park, S. Jung, S. Jung, Y. Park and S. Kim, "Surface engineering of inorganic nanoparticles for imaging and therapy," *Advanced Drug Delivery Reviews*, vol. 65, no. 5, pp. 622-648, 2013.
- [16] X. Xiao, W. Xie and Z. Ye, "Preparation of corrosion-resisting superhydrophobic surface on aluminium substrate," *Surface Engineering*, vol. 35, no. 5, pp. 411-417, 2019.
- [17] L. Miozzo, A. Yassar and G. Horowitz, "Surface engineering for high performance organic electronic devices: the chemical approach," J. Mater. Chem., vol. 20, pp. 2513-2538, 2010.
- [18] M. Batzill, "Fundamental aspects of surface engineering of transition metal oxide photocatalysts," *Energy Environ. Sci.*, vol. 4, pp. 3275-3286, 2011.
- [19] C. Yang, C. P. Wong and M. M. Yuen, "Printed electrically conductive composites: conductive filler designs and surface engineering," *Journal of Materials Chemistry C*, vol. 1, no. 26, pp. 4052-4069, 2013.
- [20] J. Robertus, W. R. Browne and B. L. Feringa, "Dynamic control over cell adhesive properties using molecular-based surface engineering strategies," *Chem. Soc. Rev.*, vol. 39, pp. 354-378, 2010.
- [21] E. M. Liston, L. Martinu and M. R. Wertheimer, "Plasma surface modification of polymers for improved adhesion: a critical review," *Journal of adhesion science and technology*, vol. 7, no. 10, pp. 1091-1127, 1993.
- [22] J. Lahann, M. Balcells, H. Lu, T. Rodon, K. F. Jensen and R. Langer, "Reactive Polymer Coatings: A First Step toward Surface Engineering of Microfluidic Devices," *Analytical Chemistry*, vol. 75, no. 9, pp. 2117-2122, 2003.
- [23] T. Lin, L. Wang, X. Wang and A. Kaynak, "Polymerising pyrrole on polyester textiles and controlling the conductivity through coating thickness," *Thin solid films*, Vols. 1-2, pp. 77-82, 2005.

- [24] L. Cisneros-Zevallos and J. M. Krochta, "Dependance of coating thickness on viscosity of coating solution applied to fruits and vegetables by dipping method," *Journal of Food Science*, vol. 68, no. 2, pp. 503-510, 2003.
- [25] H. Yasuda, "Plasma for modification of polymers," *Journal of Macromolecular Science*, vol. 10, no. 3, pp. 383-420, 1976.
- [26] F. Zhu, "Plasma modification of starch," Food Chemistry, vol. 232, pp. 476-486, 2017.
- [27] H. Hatta and M. Taya, "Thermal conductivity of coated filler composites," *Journal of applied physics*, vol. 59, no. 6, pp. 1851-1860, 1986.
- [28] W. Chi, S. Sampath and H. Wang, "Ambient and high-temperature thermal conductivity of thermal sprayed coatings," *Journal of Thermal Spray Technology*, vol. 15, pp. 773-778, 2006.
- [29] I. L. Ngo, S. Jeon and C. Byon, "Thermal conductivity of transparent and flexible polymers containing fillers: A literature review," *International Journal of Heat and Mass Transfer*, vol. 98, pp. 219-226, 2016.
- [30] G. W. Lee, M. Park, J. Kim, J. I. Lee and H. G. Yoon, "Enhanced thermal conductivity of polymer composites filled with hybrid filler," *Composites part A: Applied science and manufacturing*, vol. 37, no. 5, pp. 727-734, 2006.
- [31] Y. X. Fu, Z. X. He, D. C. Mo and S. S. Lu, "Thermal conductivity enhancement with different fillers for epoxy resin adhesives," *Applied Thermal Engineering*, vol. 66, no. 1-2, pp. 493-498, 2014.
- [32] W. S. Lee and J. Yu, "Comparative study of thermally conductive fillers in underfill for the electronic components," *Diamond and related Materials*, vol. 14, no. 10, pp. 1647-1653, 2005.
- [33] Z. Han and A. Fina, "Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review," *Progress in polymer science*, vol. 36, no. 7, pp. 914-944, 2011.
- [34] P. Martin, Z. Aksamija, E. Pop and U. Ravaioli, "Impact of phonon-surface roughness scattering on thermal conductivity on thin Si nanowires," *Physical review letters*, vol. 102, no. 12, p. 125503, 2009.
- [35] M. Kazan, G. Guisbiers, S. Pereira, M. R. Correia, P. Masri, A. Bruyant, S. Volz and P. Royer, "Thermal conductivity of silicon bulk and nanowires: Effects of isotopic composition, phonon confinement, and surface roughness," *Journal of Applied Physics*, vol. 107, no. 8, 2010.

- [36] K. S. Subramanian, Lead-free Solders: Materials Reliability for Electronics, New Jersey: Wiley, 2012.
- [37] R. A. Oriani, "Thermomigration in solid metals," *Journal of Physics and Chemistry of Solids*, vol. 30, no. 2, pp. 339-351, 1969.
- [38] Y. Hua, B. Cemal and H. Douglas, "Thermomigration in Pb-Sn solder joints under joule heating during electric current stressing," *Applied Physics Letters*, vol. 82, no. 7, pp. 1045-1047, 2003.
- [39] C. Chen, H. M. Tong and K. N. Tu, "Electromigration and Thermomigration in Pb-Free Flip-Chip Solder Joints," *Annual Review of Materials Research*, vol. 40, pp. 531-555, 2010.
- [40] I. V. Belova, Z.-K. Liu and G. E. Murch, "Exact phenomenological theory for thermotransport in a solid binary alloy," *Philosophical Magazine Letters*, vol. 101, no. 3, pp. 123-131, 2021.
- [41] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics*, vol. 81, pp. 109-162, 2009.
- [42] Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, "Graphene and Graphene Oxide: Synthesis, Properties, and Applications," *Advanced Materials*, vol. 22, pp. 3906-3924, 2010.
- [43] K. Cao, S. Feng, Y. Han, L. Gao, T. Hue Ly, Z. Xu and Y. Lu, "Elastic straining of freestanding monolayer graphene," *Nature Communications*, vol. 11, 2020.
- [44] C. Lee, X. Wei, J. W. Kysar and J. Hone, "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene," *Science*, vol. 321, pp. 385-388, 2008.
- [45] A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C. N. Lau, "Superior Thermal Conductivity of Single-Layer Graphene," *Nano Letters*, vol. 8, no. 3, pp. 902-907, 2008.
- [46] C. S. Allen and J. H. Warner, "Properties of Graphene," in *Graphene*, Oxford, Elsevier, 2013, pp. 74-80.
- [47] M. H. Rummeli, "The Mechanical Properties of Graphene," in *Graphene*, Oxford, Elsevier, 2013, pp. 99-113.
- [48] C. S. Allen and J. H. Warner, "Properties of Graphene," in *Graphene*, Oxford, Elsevier, 2013, pp. 61-64.

- [49] A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov and A. K. Geim, "The electronic properties of graphene," *Reviews of Modern Physics*, vol. 81, pp. 109-162, 2009.
- [50] D. G. Papgeorgiou, I. A. Kinloch and R. J. Young, "Mechanical properties of graphene and graphene-based nanocomposites," *Progress in Materials Science*, vol. 90, pp. 75-127, 2017.
- [51] W. S. Hummers Jr. and R. E. Offeman, "Preparation of Graphitic Oxide," *Journal of the American Chemical Society*, vol. 80, no. 6, p. 1339, 1958.
- [52] P. May, U. Khan, A. O'Neill and J. N. Coleman, "Approaching the theoretical limit for reinforcing polymers with graphene," *Journal of Materials Chemistry*, vol. 22, pp. 1278-1282, 2012.
- [53] M. Bastwros, G.-Y. Kim, C. Zhu, K. Zhang, S. Wang, X. Tang and X. Wang, "Effect of ball milling on graphene reinforced Al6061 composite fabricated by semi-solid sintering," *Composites Part B: Engineering*, vol. 60, pp. 111-118, 2014.
- [54] X. Chen, L. Zhang and S. Chen, "Large area CVD growth of graphene," *Synthetic Metals*, vol. 210, no. A, pp. 95-108, 2015.
- [55] W. Zhao, M. Fang, F. Wu, H. Wu, L. Wang and G. Chen, "Preparation of graphene by exfoliation of graphite using wet ball milling," *J. Mater. Chem*, vol. 20, pp. 5817-5819, 2010.
- [56] X. Sciences, "Grade M Technical Data Sheet," [Online]. Available: https://xgsciences.us/docs/Grade%20M%20Data%20Sheet.pdf. [Accessed June 2023].
- [57] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, "Electric Field Effect in Atomically Thin Carbon Films," *Science*, vol. 306, pp. 666-669, 2004.
- [58] T. Kuila, S. Bose, A. Mishra, P. Khanra, N. Kim and J. Lee, "Chemical functionalization of graphene and its applications," *Progress in Materials Science*, vol. 57, no. 7, pp. 1061-1105, 2012.
- [59] M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, Hoboken, New Jersey: John Wiley & Sons, 2005.
- [60] X. Wang, Q. Fan, Z. Chen, Q. Wang, J. Li, A. Hobiny, A. Alsaedi and X. Wang, "Surface Modification of Graphene Oxides by Plasma Techniques and Their Application for Environmental Pollution Cleanup," *The Chemical Record*, vol. 16, pp. 295-318, 2015.

- [61] A. Dey, A. Chroneos, N. Braithwaite, R. Gandhiraman and S. Krishnamurthy, "Plasma engineering of graphene," *Applied Physics Reviews*, vol. 3, no. 2, pp. 1-19, 2016.
- [62] I. Bertoti, M. Mohai and K. Laszlo, "Surface modification of graphene and graphite by nitrogen plasma: Determination of chemical state alterations and assignments by quantitative X-ray photoelectron spectroscopy," *Carbon*, vol. 84, pp. 185-196, 2015.
- [63] Q. Wang, X. Wang, Z. Chai and W. Hu, "Low-temperature plasma synthesis of carbon nanotubes and graphene based materials and their fuel cell applications," *Royal Society of Chemistry*, vol. 42, pp. 8821-8834, 2013.
- [64] C. Jin, T. Huang, Y. Yang, M. Wu, Y. Xu, Z. Wu, L. Zhuge, X. Wu and C. Ye, "Synthesis of Few-layer Graphene-on-Insulator Films by Controllable C4F8 Plasma Etching SiC," *Plasma Processes and Polymers*, vol. 12, pp. 1061-1068, 2015.
- [65] Z. Dong, S. Zhao, Y. Zhang, J. Yang and D.-B. Xiong, "Evaluating and manipulating bonding strength at multilayer graphene-copper interface via plasma functionalization," *Materials Science and Engineering: A*, vol. 848, no. 143391, 2022.
- [66] A. Jafari, H. Mortaheb and F. Gallucci, "Plasma treatment for enhanced functionalization of graphene nanosheets by octadecylamine," *Chemical Engineering Research and Design*, vol. 187, pp. 251-260, 2022.
- [67] K. Joseph and V. Shanov, "Symmetric Supercapacitor Based on Nitrogen-Doped and Plasma-Functionalized 3D Graphene," *Batteries*, vol. 8, no. 12, p. 258, 2022.
- [68] R. Cao, J. Zhou, D. Wang, J. Zhang, Y. Zhang, H. Zhou and J. Li, "Improving capacitive deionization performance by using O2 plasma modified carbon black," *Chemical Engineering Journal*, vol. 451, no. 1, p. 138530, 2023.
- [69] F. Bohlooli, A. Anagri and S. Mori, "Development of carbon-based metal free electrochemical sensor for hydrogen peroxide by surface modification of carbon nanowalls," *Carbon*, vol. 196, pp. 327-336, 2022.
- [70] D. Ogawa, S. Morimune-Moriya and K. Nakamura, "Effective polymerization technique for plasma-treated multiwalled carbon nanotubes to maximize wear resistance of composite polyurethane," *Journal of Vacuum Science and Technology B*, vol. 40, no. 2, p. 022803, 2022.
- [71] A. Ackermann, M. Fischer, A. Wick, S. Carosella, B. Fox and P. Middendorf, "Mechanical, Thermal and Electrical Properties of Epoxy Nanocomposites with Amine-Functionalized Reduced Graphene Oxide via Plasma Treatment," *Journal of Composites Science*, vol. 6, no. 6, p. 153, 2022.

- [72] Y. Wang, Y. Shao, D. W. Matson, J. Li and Y. Lin, "Nitrogen-Doped Graphene and Its Applications in Electrochemical Biosensing," ACS Nano, vol. 4, no. 4, pp. 1790-1798, 2010.
- [73] K. Akada, S. Obata and K. Saiki, "Radio-frequency plasma assisted reduction and nitrogen doping of graphene oxide," *Carbon*, vol. 189, pp. 571-578, 2022.
- [74] C. Lee, Y.-J. Han, Y. D. Seo, K. Nakabayashi, J. Miyawaki, R. Santamaria, R. Menendez, S.-H. Yoon and J. Jang, "C4F8 plasma treatment as an effective route for improving rate performance of natural/synthetic graphite anodes in lithium ion batteries," *Carbon*, vol. 103, pp. 28-35, 2016.
- [75] Y. Liu, J. Chang, H. Yang, S. Lin, S. Akhbari, Q. Zhou, K. Heo and L. Lin, "Self-aligned, direct-write graphene channel FETs," in 2013 Transducers & Eurosensors XXVII: The 17th International Conference on Solid-State Sensors, Actuators and Microsystems (TRANSDUCERS & EUROSENSORS XXVII), Barcelona, Spain, 2013.
- [76] Q. H. Fan and M. Toomajian, "Rotary Plasma Reactors". United States of America Patent 11,545,343, 3 January 2023.
- [77] M. C. Biesinger, "Accessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review," *Applied Surface Science*, vol. 597, p. 153681, 2022.
- [78] J. Liu, J. Tang and J. Gooding, "Strategies for chemical modification of graphene and applications of chemically modified graphene," *J. Mater. Chem*, vol. 22, pp. 12435-12452, 2012.
- [79] L. Cheng, S. Jandhyala, G. Mordi, A. Lucero, J. Huang, A. Azcatl, R. Addou, R. Wallace, L. Colombo and J. Kim, "Partially Fluorinated Graphene: Structural and Electrical Characterization," ACS Applied Materials & Interfaces, vol. 8, no. 7, pp. 5002-5008, 2016.
- [80] K. Miyata, M. Hori and T. Goto, "Infrared diode laser absorption spectroscopy measurements of CFx (X=1-3) radical densities in electron cyclotron resonance plasmas employing C4F8, C2F6, CF4, and CHF3 gases," *Journal of Vacuum Science & Technology A*, vol. 14, pp. 2343-2350, 1996.
- [81] J.-H. Zhou, Z.-J. Sui, J. Zhu, P. Li, D. Chen, Y.-C. Dai and W.-K. Yuan, "Characterization of surface oxygen complexes on carbon nanofibers by TPD, XPS and FT-IR," *Carbon*, vol. 45, no. 4, pp. 785-796, 2007.
- [82] A. C. Ferrari, "Determination of bonding in diamond-like carbon by Raman spectroscopy," *Diamond and Related Materials*, vol. 11, pp. 1053-1061, 2002.

- [83] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim, "Raman Spectrum of Graphene and Graphene Layers," *Physical Review Letters*, vol. 97, pp. 1-4, 2006.
- [84] L. M. Malard, M. A. Pimenta, G. Dresselhaus and M. S. Dresselhaus, "Raman spectroscopy in graphene," *Physics Reports*, vol. 473, no. 5-6, pp. 51-87, 2009.
- [85] A. C. Ferrari and D. M. Basko, "Raman spectroscopy as a versatile tool for studying the properties of graphene," *Nature Nanotechnology*, vol. 8, pp. 235-246, 2013.
- [86] L. A. Nafie, "Theory of Raman Scattering," in *Handbook of Raman Spectroscopy*, New York, Marcel Dekker, 2001.
- [87] M. M. Lucchese, F. Stavale, E. H. Martins Ferreira, C. Vilani, M. V. O. Moutinho, R. B. Capaz, C. A. Achete and A. Jorio, "Quantifying ion-induced defects and Raman relaxation length in graphene," *Carbon*, vol. 48, pp. 1592-1597, 2010.
- [88] K. Wang, M. Xu, Y. Gu, Z. Gu, J. Liu and Q. H. Fan, "Low-temperature plasma exfoliated n-doped graphene for symmetrical electrode supercapacitors," *Nano Energy*, vol. 31, pp. 486-494, 2017.
- [89] W. Feng, P. Long, Y. Feng and Y. Li, "Two-Dimensional Fluorinated Graphene: Synthesis, Structures, Properties and Applications," *Advanced Science*, vol. 3, pp. 1-22, 2016.
- [90] J. Lin, A. De Silva, D. Frear, Y. Guo, S. Hayes, J. Jang, L. Li, D. Mitchell, B. Yeung and C. Zhang, "Characterization of Lead-Free Solders and Under Bump Metallurgies for Flip-Chip Package," *IEEE Transaction on Electronics Packaging Manufacturing*, vol. 25, no. 3, pp. 300-307, 2002.
- [91] C. Xu, Y. Zhang, C. Fan and J. Abys, "Driving Force for the Formation of Sn Whiskers: Compressive Stress - Pathways for Its Generation and Remedies for Its Elimination and Minimization," *IEEE Transactions on Electronics Packaging Manufacturing*, vol. 28, no. 1, pp. 31-35, 2005.
- [92] Z. Moser, W. Gasior and J. Pstrus, "Surface Tension Measurements of the Bi-Sn and Sn-Bi-Ag Liquid Alloys," *Journal of Electronic Materials*, vol. 30, no. 9, pp. 1104-1111, 2001.
- [93] K. N. Tu, "Reliability challenges in 3D IC packaging technology," *Microelectronics Reliability*, vol. 51, pp. 517-523, 2011.
- [94] K. N. Subramanian, Lead-free Electronic Solders, New York: Springer, 2007.

- [95] A. T. Huang, A. M. Gusak, K. N. Tu and Y.-S. Lai, "Thermomigration in SnPb composite flip chip solder joints," *Applied Physics Letters*, vol. 88, no. 141911, pp. 1-2, 2006.
- [96] H.-Y. Hsiao and C. Chen, "Thermomigration in Pb-free SnAg solder joint under alternating current stressing," *Applied Physics Letters*, vol. 94, no. 9, pp. 1-3, 2009.
- [97] C. Guang, C. Xinzhan, W. Yaofeng and W. Fengshun, "Microstructural, compositional and hardness evolutions of 96.5Sn-3Ag-0.5Cu/TiC composite solder under thermomigration stressing," *Journal of Materials Science: Materials in Electronics*, vol. 31, no. 12, pp. 9492-9503, 2020.
- [98] M. F. Abdulhamid, C. Basaran and Y.-S. Lai, "Thermomigration versus electromigration in microelectronics solder joints," *IEEE Trans. Adv. Packag.*, vol. 32, pp. 627-635, 2009.
- [99] L. Zhang, S. Ou, J. Huang, K. N. Tu, S. Gee and L. Nguyen, "Effect of current crowding on void propogation at the interface between intermetallic compound and solder flip chip solder joints," *Applied Physics Letters*, vol. 88, no. 012106, pp. 1-3, 2006.
- [100] R. B. Comizzoli, R. P. Frankenthal, P. C. Milner and J. D. Sinclair, "Corrosion of Electronic Materials and Devices," *Science AAAS*, vol. 234, no. 4774, pp. 340-345, 1986.
- [101] M. Wang, J. Wang, H. Feng and W. Ke, "Effect of AG3Sn intermetallic compounds on corrosion of Sn-3.0Ag-0.5Cu solder under high-temperature and high-humidity condition," *Corrosion Science*, vol. 63, pp. 20-28, 2012.
- [102] S. Li, X. Wang, Z. Liu, Y. Jiu, S. Zhang, J. Geng, X. Chen, S. Wu, P. He and W. Long, "Corrosion behavior of Sn-based lead-free solder alloys: a review," *Journal of Materials Science: Materials in Electronics*, vol. 31, pp. 9076-9090, 2020.
- [103] B. Liao, H. Cen, Z. Chen and X. Guo, "Corrosion behavior of Sn-3.0Ag-0.5Cu alloy under chlorine-containing thin electrolyte layers," *Corrosion Science*, vol. 143, pp. 347-361, 2018.
- [104] W. R. Osorio, L. R. Garcia, L. C. Peixoto and A. Garcia, "Electrochemical behavior of a lead-free SnAg solder alloy affected by the microstructure array," *Materials & Design*, vol. 32, no. 10, pp. 4763-4772, 2011.
- [105] J. H. Warner, F. Schaffel, A. Bachmatiuk and M. H. Rummeli, "Chapter 3 Properties of Graphene," in *Graphene: Fundamentals and Emergent Applications*, Amsterdam, Elsevier Science, 2013, pp. 61-127.
- [106] C. Wei, K. Cho and D. Srivastava, "Tensile strength of carbon nanotubes under realistic temperature and strain rate," *Physical Review B*, vol. 67, no. 115407, pp. 1-6, 2003.

- [107] A. K. Geim and K. S. Novoselov, "The rise of graphene," *Nature Materials*, vol. 6, pp. 183-191, 2007.
- [108] R. Ansari, B. Motevalli, A. Montazeri and S. Ajori, "Fracture analysis of monolayer graphene sheets with double vacancy defects via MD simulation," *Solid State Communications*, vol. 151, no. 17, pp. 1141-1146, 2011.
- [109] F. Liu, P. Ming and J. Li, "Ab initio calculation of ideal strength and phonon instability of graphene under tension," *Physical Review B*, vol. 76, no. 064120, pp. 1-7, 2007.
- [110] S. Ogata and Y. Shibutani, "Ideal tensile strength and band gap of single-walled carbon nanotubes," *Physical Review B*, vol. 68, no. 165409, pp. 1-4, 2003.
- [111] W. Cai, A. L. Moore, Y. Zhu, X. Li, S. Chen, L. Shi and R. S. Ruoff, "Thermal Transport in Suspended and Supported Monolayer Graphene Grown by Chemical Vapor Deposition," *Nano Letters*, vol. 10, no. 5, pp. 1645-1651, 2010.
- [112] C. Faugeras, B. Faugeras, M. Orlita, M. Potemski, R. R. Nair and A. K. Geim, "Thermal Conductivity of Graphene in Corbino Membrane Geometry," ACS Nano, vol. 4, no. 4, pp. 1889-1892, 2010.
- [113] C. N. Lau, W. Bao, F. Miao, Z. Chen, H. Zhang, W. Jang and C. Dames, "Controlled ripple texturing of suspended graphene and ultrathin graphite membranes," *Nature Nanotechnology*, vol. 4, no. 9, pp. 562-566, 2009.
- [114] I. M. Lifshitz, "Thermal properties of chain and layered structures at low temperatures," *Zh. Eksp. Teor. Fiz*, 1952.
- [115] J. Wei, S. M. L. Nai, X. F. Ang and K. P. Yung, "Advanced high density interconnect materials and techniques," in 2009 International Conference on Electronic Packaging Technology & High Density Packaging, Beijing, 2009.
- [116] Y. D. Han, L. Chen, H. Y. Jing, S. M. L. Nai, J. Wei and L. Xu, "Effect of Ni-Coated Carbon Nanotubes on the Corrosion Behavior of Sn-Ag-Cu Solder," *Journal of Electronic Materials*, vol. 42, pp. 3559-3566, 2013.
- [117] X. D. Liu, Y. D. Han, H. Y. Jing, J. Wei and L. Xu, "Effect of graphene nanosheets reinforcement on the performance of Sn Ag Cu lead-free solder," *Materials Science and Engineering: A*, vol. 562, pp. 25-32, 2013.
- [118] H. Ming, J. Wang, Z. Zhang, S. Wang, E.-H. Han and W. Ke, "Multilayer Graphene: A Potential Anti-oxidation Barrier in Simulated Primary Water," *Journals of Materials Science & Technology*, vol. 30, no. 11, pp. 1084-1087, 2014.

- [119] L. Xu, Z. K. Zhang, H. Y. Jing, J. Wei and Y. D. Han, "Effect of graphene nanosheets on the corrosion behavior of Sn-Ag-Cu solders," *Journal of Materials Science: Materials in Electronics*, no. 8, 2015.
- [120] L. Zhao, T. Lee, S. Ryu, Y. Oshima, Q. Guo and D. Zhang, "Mechanical Robustness of Metal Nanocomposites Rendered by Graphene Functionalization," *Nano Letters*, vol. 21, no. 13, pp. 5706-5713, 2021.
- [121] M. A. Mackinder, INTERACTIONS BETWEEN PLASMA AND MATERIAL SURFACES FOR STERILIZATION AND IMPURITY ASDORPTION, East Lansing: Michigan State University, 2022.
- [122] G. Xia, L. Cao and G. Bi, "A review on battery thermal management in electric vehicle application," *Journal of Power Sources*, vol. 367, pp. 90-105, 2017.
- [123] Z. Yu, *GRAPHENE NANOPLATELET BASED POLYMER COMPOSITES AND THEIR MULTIPLE APPLICATIONS*, East Lansing: Zeyang Yu, 2019.
- [124] P. A. Primeax, B. Zhang, X. Zhang, J. Miller, W. J. Meng, K. C. P and A. L. Moore, "Aluminum-based one- and two-dimensional micro fin array structures: high-throughput fabrication and heat transfer testing," *J Micromech Microeng*, vol. 27, no. 2, pp. 1-9, 2017.
- [125] J. Wang and Z. Feng, "Manufacturing of surface features from extrusion forging and extrusion rolling of sheet metals," *Manuf Lett*, vol. 15 (Part A), pp. 42-5, 2018.
- [126] D. E. Metzger, W. B. Shepard and S. W. Haley, "Row resolved heat transfer variations in pin-fin arrays including effects of non-uniform arrays and flow convergence," in *Proceedings of the ASME 1986 International Gas Turbine Conference and Exhibit*, Dusseldorf, West Germany, 1986.
- [127] A. I. Zografos and J. E. Sunderland, "Natural convection from pin fin arrays," *Exp Therm Fluid Sci*, vol. 4, no. 3, pp. 440-9, 1990.
- [128] P. Yoav, A. Kosar, C. Mishra, C. J. Kuo and B. Schneider, "Forced convective heat transfer across a pin fin micro heat sink," *Int J Heat Mass Transf*, vol. 48, no. 17, pp. 3615-27, 2005.
- [129] M. S. Hashmi and F. B. Klemz, "Axisymmetric extrusion forging: effects of material property and product geometry," *Int J Mach Tools Manuf*, vol. 26, pp. 157-70, 1986.
- [130] L. Brayden and J. Monaghan, "An analysis of closed-die extrusion/forging," J Mater Process Technol, vol. 26, pp. 141-57, 1991.

- [131] J. Vickery and J. Monaghan, "An upper-bound analysis of a forging-extrusion process," J Mater Process Technol, vol. 55, pp. 103-10, 1995.
- [132] M. Merklein, J. M. Allwood, B. A. Behrens, A. Brosius, H. Hagenah and K. Kuzman, "Bulk forming of sheet metal," *CIRP Ann Manuf Technol*, vol. 61, pp. 725-45, 2012.
- [133] C. Sun, S. H. Zhang, W. D. Tang and Z. T. Wang, "Press forging of magnesium alloy notebook case with complex geometry," *Mater Manuf Process*, vol. 25, pp. 534-8, 2010.
- [134] P. Haldar, J. G. Hoehn Jr, J. A. Rice and L. R. Motowidlo, "Enhancement in critical current density of Bi-Pb-Sr-Ca-Cu-O tapes by thermomechanical processing: Cold rolling versus uniaxial pressing," *App Phy Lett*, vol. 60, no. 4, pp. 495-7, 1992.
- [135] H. Ike, "Properties of Metal Sheets with 3-D Designed Surface Microgeometry Prepared by Special Rolls," *J Ma Proc Techn*, vol. 60, pp. 363-8, 1996.
- [136] H. Ike, "Surface Deformation vs. Bulk Plastic Deformation A Key for Microscopic Control of Surfaces in Metal Forming," J Ma Proc Techn, vol. 138, pp. 250-5, 2003.
- [137] J. R. Davis, ASM Specialty Handbook Copper and Copper Alloys, Ohio: ASM International, 2001, p. 220.
- [138] Y. A. Cengel, Heat Transfer: A Practical Approach, 2 ed., New York: McGraw-Hill, 2002.
- [139] J. Jiang, W. J. Meng, G. B. Sinclair and E. Lara-Curzio, "Futher experiments and modeling for microscale compression molding of metals at elevated temperatures," *Journal of Materials Research*, vol. 22, no. 7, pp. 1839-1848, 2007.
- [140] B. Lu and W. J. Meng, "Roll Molding of Microchannel Arrays on Al and Cu Sheet Metals: A Method for High-Throughput Manufacturing," *Journal of Micro- and Nano-Manufacturing*, vol. 2, no. 1, pp. 1-9, 2014.
- [141] G. E. Dieter, Mechanical Metallurgy, New York: McGraw-Hill, 1961.
- [142] M. P. Groover, Fundamentals of Modern Manufacturing: Materials, Processing, and Systems, New York: John Wiley & Sons, 2002.
- [143] L. J. Gibson, "Mechanical Behavior of Metallic Foams," Annual review of materials science, vol. 30, pp. 191-227, 2000.
- [144] J. Skibinski, K. Cwieka, S. H. Ibrahim and T. Wejrzanowski, "Influence of Pore Size Variation on Thermal Conductivity of Open-Porous Foams," *Materials*, vol. 12, no. 12, p. 2017, 2019.

- [145] Y. Amani, A. Takahashi, P. Chantrenne, S. Maruyama, S. Dancette and E. Maire, "Thermal conductivity of highly porous metal foams: Experimental and image based finite element analysis," *Internation Journal of Heat and Mass Transfer*, vol. 122, pp. 1-10, 2018.
- [146] X. Xiao, P. Zhang and M. Li, "Effective thermal conductivity of open-cell metal foams impregnated with pure paraffin for latent heat storage," *International Journal of Thermal Sciences*, vol. 81, pp. 94-105, 2014.
- [147] J. Jiang, F. Mei and W. J. Meng, "Fabrication of metal-based high-aspect-ratio microscale structures by compression molding," *Journal of Vaccum Science and Technology*, vol. 26, pp. 745-751, 2008.