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# Shear Alignment of Diblock Copolymers for Patterning Nanowire Meshes

K. T. Gustafson

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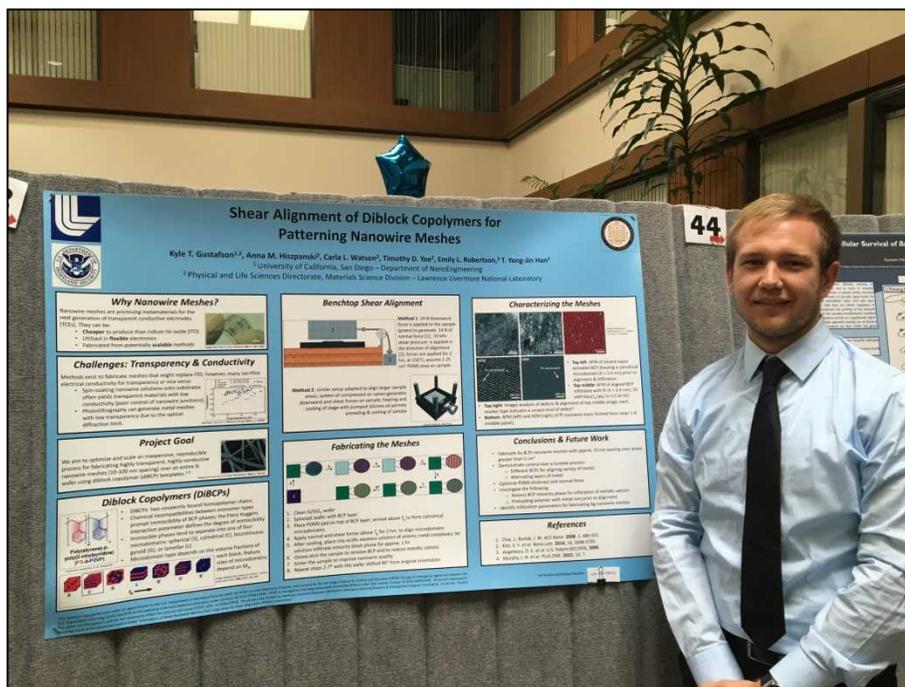
# Shear Alignment of Diblock Copolymers for Patterning Nanowire Meshes

**Kyle T. Gustafson**

**Hosting Site:** Lawrence Livermore National Laboratory

**Mentors:** Yong-Jin Han & Anna Hiszpanski

**Abstract:** Metallic nanowire meshes are useful as cheap, flexible alternatives to indium tin oxide – an expensive, brittle material used in transparent conductive electrodes. We have fabricated nanowire meshes over areas up to 2.5 cm<sup>2</sup> by: 1) mechanically aligning parallel rows of diblock copolymer (diBCP) microdomains; 2) selectively infiltrating those domains with metallic ions; 3) etching away the diBCP template; 4) sintering to reduce ions to metal nanowires; and, 5) repeating steps 1 – 4 on the same sample at a 90° offset. We aligned parallel rows of polystyrene-*b*-poly(2-vinylpyridine) [PS(48.5 kDa)-*b*-P2VP(14.5 kDa)] microdomains by heating above its glass transition temperature ( $T_g \approx 100^\circ\text{C}$ ), applying mechanical shear pressure (33 kPa) and normal force (13.7 N), and cooling below  $T_g$ . DiBCP samples were submerged in aqueous solutions of metallic ions (15 – 40 mM ions; 0.1 – 0.5 M HCl) for 30 – 90 minutes, which coordinate to nitrogen in P2VP. Subsequent ozone-etching and sintering steps yielded parallel nanowires. We aimed to optimize alignment parameters (e.g. shear and normal pressures, alignment duration, and PDMS thickness) to improve the quality, reproducibility, and scalability of meshes. We also investigated metals other than Pt and Au that may be patterned using this technique (Cu, Ag).



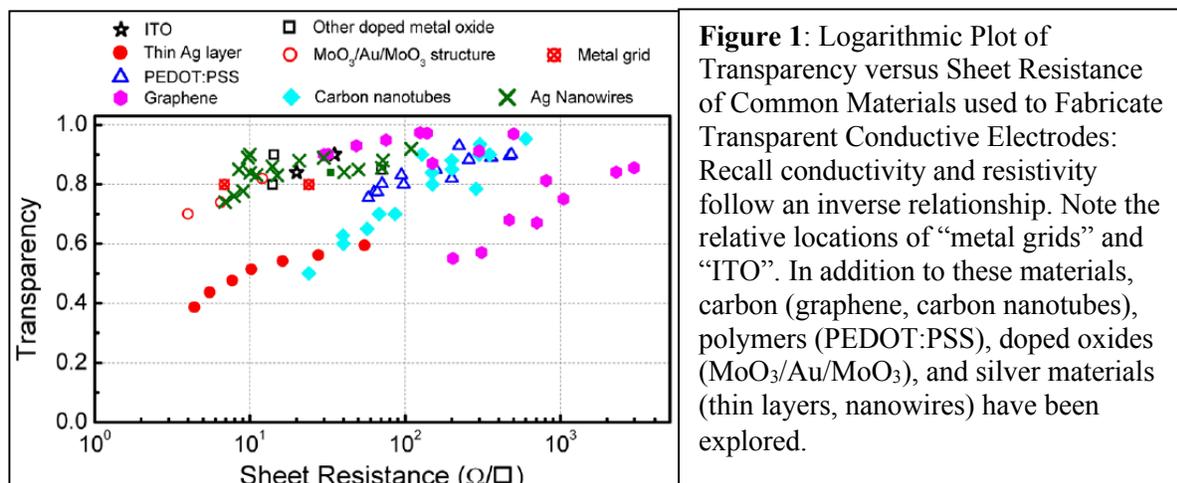
## I. Internship Project

This project demonstrates an inexpensive, reproducible, and scalable method for fabricating metallic nanowire meshes.<sup>1-3</sup> Nanowire meshes are potentially useful in applications that require unique optical and/or electrical properties. In particular, two-dimensional nanowire meshes are anticipated to be cheap, flexible alternatives for indium tin oxide (ITO) – an expensive and brittle transparent conductive electrode (TCE) used in electronic devices and solar cells. My portion of this project fixated solely on fabricating 2D nanowire meshes with high optical transparency and electrical conductivity; however, the ultimate goal of the project at large is to produce 3D nanowire meshes (i.e. layers of perpendicularly oriented nanowire arrays stacked upon one another) with optical and plasmonic properties characteristic of negative refractive index metamaterials (NIMMs). In particular, my primary role was to explore the chemical mechanism for metal ion infiltration of diblock copolymer (diBCP) microdomains and identify metals (other than Pt and Au) that can be patterned via mechanical alignment of PS-*b*-P2VP.

Common methods to fabricate two-dimensional metallic nanowire arrays as TCEs tend to sacrifice transparency for conductivity or vice versa. Photolithographic (PL) patterning of meshes is constrained by the optical diffraction limit of light. The wavelength of light used in PL typically cannot be set below 193 nm, the half-pitch or feature size of the resultant wires is limited to just below one-half said wavelength (approx. 50 – 97 nm). While techniques exist to circumvent the optical diffraction limit and lower the half-pitch further, the patterned nanowires remain too large for significant transparency. At the same time, meshes produced from PL techniques often contain few or no defects and discontinuities, and the regularity of these meshes yields high electrical conductivity. Therefore, PL is capable of producing highly conductive nanowire meshes with low optical transparency.

Another common method to generate meshes involves repeatedly spin-coating dispersions of nanowires onto a substrate. The benefit of this technique is that the aspect ratio of nanowires can be readily tuned by altering synthesis conditions – a field of research unto itself. The downside of this method is that, unlike PL, there is minimal control over creating junctions between nanowires. Researchers can tailor nanowire size sufficiently low for optical transparency; however, their inability to optimize the number of nanowire junctions often yields a mesh with low electrical conductivity. In order to increase the number of junctions formed across nanowires, researchers spin-coat additional layers. Doing so adds extra mass with which light interacts, reducing the optical transparency of the mesh.

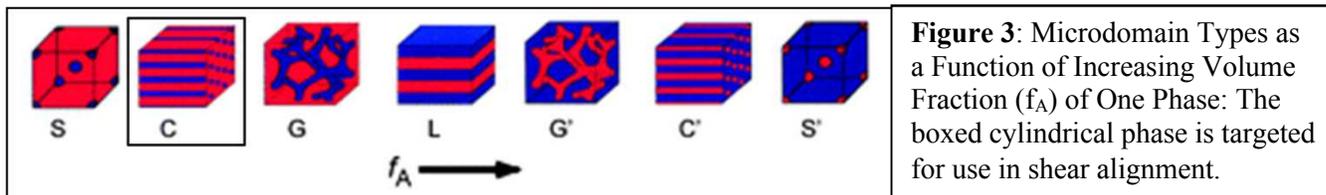
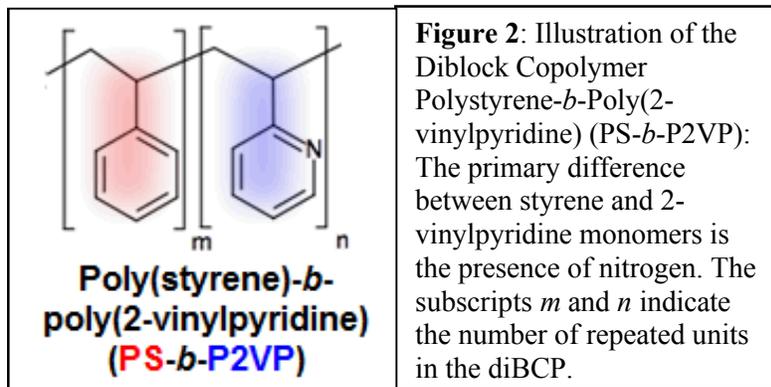
Therefore, a tradeoff between optical transparency and electrical conductivity occurs when spin-coating nanowire meshes. A plot of transparency versus sheet resistance for materials used in TCEs demonstrates this tradeoff, which is not specific to spin-coating techniques (**Figure 1**).<sup>4</sup>



The shear alignment of diBCPs as a template for patterning nanowire meshes offers a technique that is cheaper than producing ITO or meshes from PL; this method also lacks the inherent tradeoff between conductivity and transparency that is inherent to spin-coating layers of nanowire dispersions. The added benefit of being able to transfer shear-aligned nanowires to a variety of substrates means that these meshes could be used in flexible electronics – an area in which ITO, due to its brittleness, is typically not well-suited.

Central to this project is an understanding of diblock copolymers. DiBCPs can be considered two homopolymer chains covalently bound at a junction that fuses their two carbon backbones together, as shown in **Figure 2**.<sup>5</sup> These polymers will undergo microphase separation if chemical incompatibilities between monomer types are substantial. Microphase separation is the segregation of immiscible chemical species. The Flory-Huggins interaction parameter ( $\chi$ ) quantifies the degree of immiscibility between monomer types; high interaction parameters indicate substantial microphase separation. DiBCPs with high interaction parameters typically exhibit one of four morphologies, or microdomains, as shown in **Figure 3**: spherical (S), cylindrical (C), bicontinuous gyroid (G), or lamellar (L). Microdomain type is a function of volume fraction ( $f_A$ ) – the percentage of space occupied by a polymer chain that can be attributed to one monomer type.<sup>6</sup> Therefore, microdomain type is effectively set by the ratio of monomer types (i.e.  $m$  to  $n$  or  $n$  to  $m$ ; **Fig. 2**). Note that the phases invert as the volume fraction

of the minority phase (blue; from left to right) increases beyond roughly one-half. Maintaining that ratio while increasing or decreasing both  $m$  and  $n$  will either increase or decrease, respectively, the feature sizes of the microdomain.



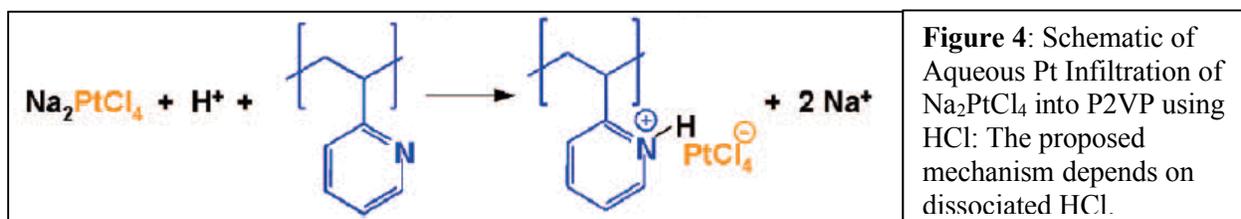
Chemical incompatibilities between diBCP monomer types, or phases, can also be exploited to form micelles in solution. If monomer type A is soluble in a given solvent while monomer type B is not, B will rearrange to minimize its contact with the solvent; consequentially, this rearrangement maximizes the contact between phase A and that solvent. For instance, the polymer in **Figure 2** (PS-*b*-P2VP) forms micelles in toluene because polystyrene is soluble and poly(2-vinylpyridine) is not. The slight chemical difference between styrene and 2-vinylpyridine (a single nitrogen atom in-place of carbon) ultimately accounts for this solubility difference. The diBCP solution can be spin-coated as a monolayer of nanoscale micelles on top of a substrate.

DiBCPs can be utilized as templates for patterning parallel rows of nanowires over macroscale areas. A few microliters of 1wt% solution of PS-*b*-P2VP (48.5-14.5 kDa) in toluene are spin-coated at 2000 rpm for 1 minute onto a SiO<sub>2</sub> substrate rinsed with isopropanol. The surface of the substrate is now a monolayer of PS-*b*-P2VP micelles. Annealing the substrate at 150°C for approximately 15 minutes will vaporize the toluene and prompt viscous flow of PS-*b*-P2VP ( $T_g \approx 100^\circ\text{C}$ ). As indicated by the rectangular box in Figure 2, we targeted a microdomain of P2VP cylinders (minority phase; blue)

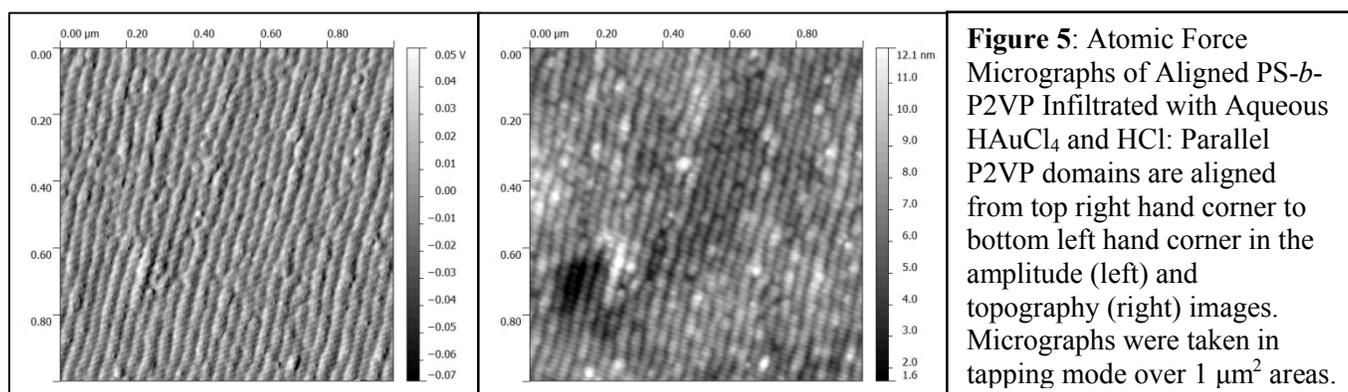
embedded within a PS matrix (majority phase; red) in a hexagonally close-packed (HCP) manner; the chosen molecular weights of the monomer types prompt microphase separation into this microdomain type. After annealing, we obtained a monolayer of HCP cylinders (P2VP) oriented perpendicularly to the substrate surface within a PS matrix. Application of shear force at temperatures above  $T_g$  for multiple hours rearranges the vertical HCP cylinders into parallel domains along the direction of shear. These parallel domains are several micrometers in length and approximately 5 – 10 nm wide.

To align these parallel P2VP domains, a PDMS pad (0.6 – 1.7 mm thick) is applied on top of the diBCP monolayer of micelles prior to annealing. The PDMS pad is pre-stamped on clean Si wafers to remove dust, oligomers, and other contaminants that might ultimately cause defects in the aligned domains. After annealing, shear pressure (33 kPa) and normal force (13.7 N) are applied to the sample at the elevated temperature (150°C) for multiple hours (1 – 3 hrs). The sample is allowed to cool well below  $T_g$  (to ~ 45°C) before the shear pressure and normal force are removed to ensure that viscous flow does not occur in the absence of shear.

At this point, the sample is purely polymeric; to pattern metal nanowires, the aligned domains must be infiltrated with metallic ions. The sample is placed polymer-side down atop the surface of an aqueous solution (15 – 40 mM) of platinates or aurates (anionic complexes containing oxidized metal) with added hydrochloric acid (0.1 – 0.5 M) for 30 – 90 minutes. Metal salt solutions were created from chloroauric acid (HAuCl<sub>4</sub>) and sodium tetrachloroplatinate (Na<sub>2</sub>PtCl<sub>4</sub>). Dr. Jillian Buriak's research group suggests a strong acid is necessary in order for: 1) the dissociated hydronium to coordinate to electron-rich nitrogen atoms in P2VP; and, 2) the anionic complexes to coordinate to the hydronium within the P2VP domains. **Figure 4** demonstrates the proposed mechanism.<sup>1</sup> The P2VP domains swell in the presence of aqueous solution, causing the PS corona surrounding said domains to burst. This permits further infiltration of ions.



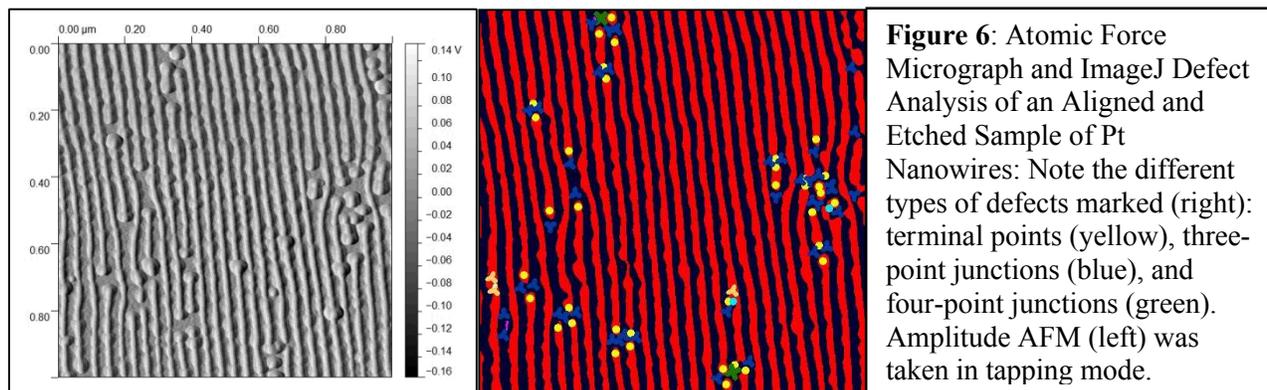
Infiltration alters the material properties of the P2VP domains, creating contrast differences with the PS matrix using atomic force microscopy (AFM). We utilize AFM to identify which samples are aligned well enough to be etched and sintered. AFM is a technique that utilizes changes in the resonant oscillation and deflection of a nanoscale cantilever as it scans across a sample with variations in material properties (e.g. elastic modulus) and topography (height). A laser is focused onto the back of the cantilever during a scan; a detector collects the reflected light, and differences between the incoming and outgoing laser light are outputted as contrast. To minimize damage to the sample from the AFM, tapping mode is chosen over contact mode. In tapping mode, the cantilever tip is prompted to oscillate such that it is not continuously touching the surface of the sample – that is, the tip “taps” the surface periodically to sample information as the cantilever is scanned. A typical micrograph of a pre-etched sample is shown in **Figure 5**.



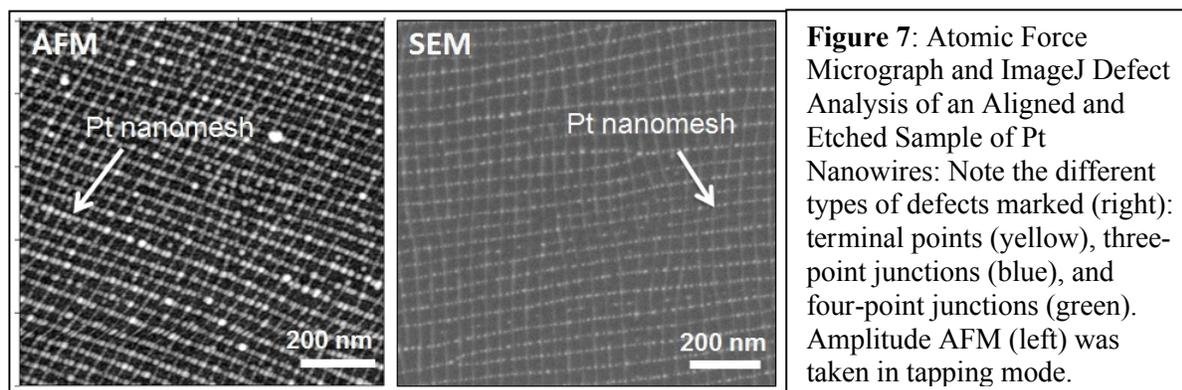
Ozone etching removes polymer from the substrate surface. While ozone is a strong oxidant, the two metals we are mostly interested in (Pt and Au) do not oxidize during ozone etching. A subsequent sintering step reduces Au<sup>3+</sup> and Pt<sup>2+</sup> to Au and Pt, respectively, and densifies the porous nanowires. Samples are typically sintered under shielding gas (4% H<sub>2</sub> in Ar) from room temperature to 800°C at a rate of 9.75°C per minute. The sample is held at 800°C for 5 minutes before it is cooled below 100°C and removed from the tube furnace for analysis.

Atomic force micrographs of samples are analyzed for orientation and defects using ImageJ macros and plugins modified from Dr. Jeffrey Murphy’s group.<sup>7</sup> Outputs of a modified Herman’s Orientation Parameter (values from 0 to 1) and planar defect density indicate the quality of alignment. Different types of defects are also tagged with respective markers, indicating junction and terminal points as well as their anticipated, weighted impact on conductivity. **Figure 6** shows a micrograph of an etched Pt

sample aligned over  $5.7 \text{ cm}^2$  that was processed by this software. The planar defect density was 48.9 defect-pairs per square micrometer; the modified Herman's Orientation Parameter proved to be 0.9831, indicating a well-aligned sample. Orientation and defect analysis is central to optimizing alignment parameters because it reveals experimental conditions that yield the best samples.



Well-aligned, sintered samples with minimal defects are identified using the ImageJ software and prepared for the next fabrication step: aligning a second layer of metal nanowires to form a mesh. The process outlined previously is repeated on a sample oriented such that the direction of shear during the first alignment step is perpendicular to the direction of shear in the upcoming alignment. A second layer of metal nanowires is patterned parallel to one another and perpendicular to the first layer of nanowires, yielding a nanowire mesh. **Figure 7** demonstrates a scanning electron micrograph and an atomic force micrograph of a Pt nanowire mesh. It has been demonstrated that nanowire meshes fabricated on  $\text{SiO}_2$  can be transferred to other substrates by embedding the meshes in a thin PDMS matrix.

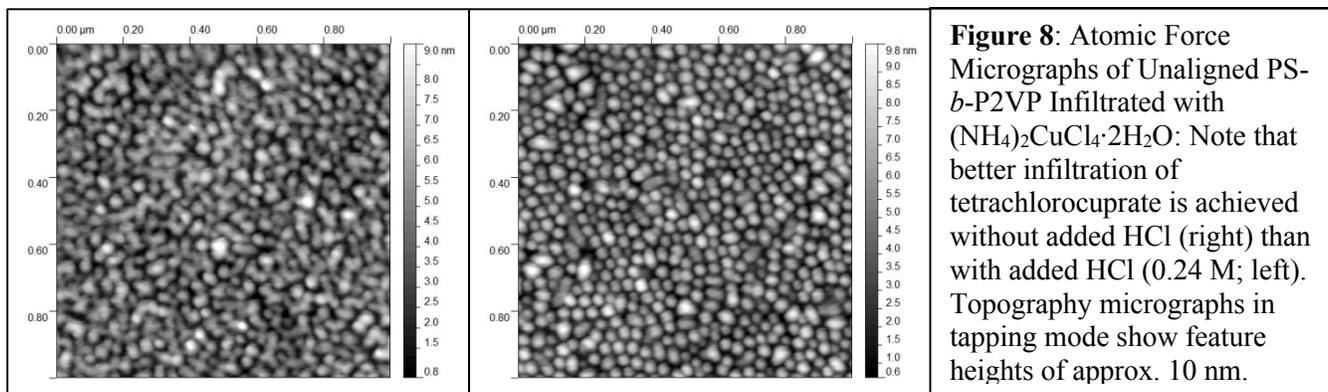


My contributions and observations to this project primarily involve the infiltration of metal ions in an effort to increase the number of metals available for patterning via shear alignment. My roles included fabricating samples of parallel diBCP domains, infiltrating those domains with aqueous metal

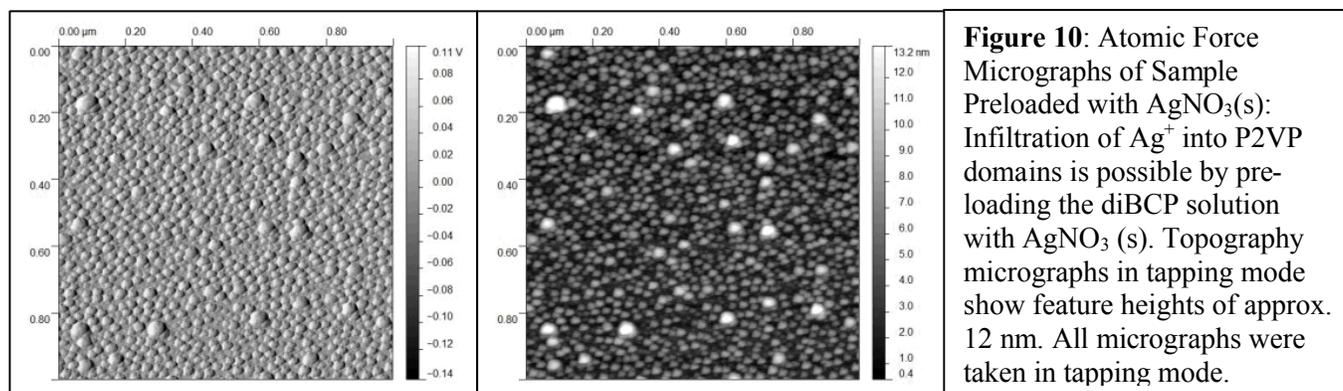
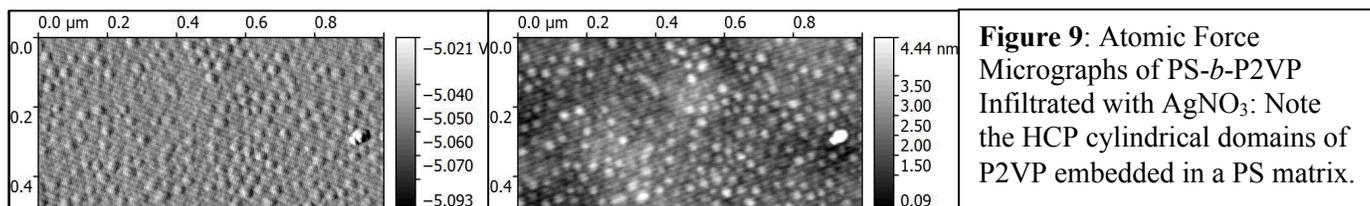
salt solutions, imaging parallel nanowires using AFM, analyzing the orientation and defect density of etched and sintered samples, optimizing relevant alignment parameters in order to improve the reproducibility and scalability of the process, and identifying salts other than  $\text{HAuCl}_4$  and  $\text{Na}_2\text{PtCl}_4$  that might infiltrate P2VP domains. I was not involved in the ozone etching and sintering processes, nor did I make PDMS stamps for use in alignment.

In an effort to identify other compatible metal salts for infiltration, I first explored Cu analogues of  $\text{Na}_2\text{PtCl}_4$ . Copper is commonly used in electronics because it is relatively inexpensive and electrically conductive. Synthesizing Cu nanowires, however, has proved to be quite challenging as copper is readily oxidized to one of several oxides. Ammonia tetrachlorocuprate dihydrate  $[(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}]$  was the closest analogue to the Pt salt that my mentors had been using. Based on the chemical mechanism for infiltration provided by Buriak's group and failed attempts to infiltrate P2VP with  $\text{CuCl}_2$  (aq), I felt confident a cuprate (like a platinate or aurate) was necessary; metal cations were not anticipated to infiltrate, while anionic complexes containing metal cations had been shown to infiltrate.

AFMs of annealed and unaligned PS-*b*-P2VP introduced to 20 mM  $(\text{NH}_4)_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$  (aq) with 0.24 M HCl demonstrated infiltration of cuprate anions ( $[\text{CuCl}_4]^{2-}$ ), as evidenced by HCP P2VP domains (**Figure 8**). Interestingly, however, a control showed that clearer infiltration was also achievable without HCl. This suggested to me the chemical mechanism proposed by Buriak's group might be incorrect – that hydronium is not necessary for the infiltration of metal ions. Buriak's previous publication does not highlight the use of HCl for infiltration of PS-*b*-P2VP, which opposes the proposed infiltration mechanism.<sup>8,9</sup> This investigation was important for several reasons: 1) it would be beneficial to remove HCl from the fabrication process if possible; 2) it suggested that  $\text{Ag}^+$  might infiltrate P2VP domains, potentially allowing us to pattern highly conductive Ag nanowire meshes; and, 3) PS-*b*-P2VP might be loaded prior to spin-coating, saving one hour per aligned layer.

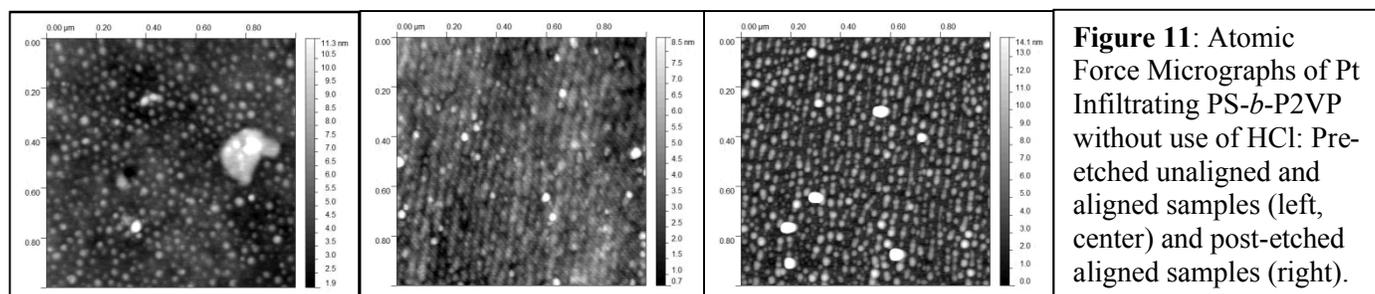


Buriak's group demonstrated that PS-*b*-P2VP micelles can be loaded internally with Ag<sup>+</sup> before spin-coating them onto a substrate, etching away the BCP, and reducing the ions to pure metal. While my previous attempts to load metal cations (Cu<sup>2+</sup>) directly into P2VP were largely unsuccessful, I investigated Buriak's about Ag<sup>+</sup> infiltration. AFMs of pre-etched, unaligned diBCP samples that were infiltrated with 20 mM AgNO<sub>3</sub> (aq) for 30 minutes after annealing show HCP of P2VP domains, indicating Ag<sup>+</sup> infiltration (**Figure 9**). Interestingly, solutions of PS-*b*-P2VP in toluene (1wt%; 48.5-14.5 kDa) with added AgNO<sub>3</sub> (s) demonstrated successful preloading of Ag<sup>+</sup> in unaligned, etched P2VP domains, as Buriak's group reported (**Figure 10**). Therefore, we believe that preloading diBCP micelles in-solution with metal ions or metal ion complexes is possible and might reduce the overall time required for nanowire mesh fabrication; furthermore, aligning Ag nanowires is likely possible, and the infiltration of metal ions is not necessarily restricted to anionic complexes as previously thought.



Other pertinent contributions include an investigation into the role of HCl during the infiltration step. Samples introduced to 20 mM (NH<sub>4</sub>)<sub>2</sub>CuCl<sub>4</sub>·2H<sub>2</sub>O (aq) showed infiltration of what we believe to be tetrachlorocuprate. Comparable infiltration with and without HCl suggests that HCl might not be necessary. I attempted to infiltrate P2VP domains with 20 mM Na<sub>2</sub>PtCl<sub>4</sub> (aq) to test our assumption that HCl was necessary for infiltration. AFMs of aligned and unaligned samples show that infiltration of tetrachloroplatinate is possible without HCl (**Figure 11**). While infiltration of tetrachloroaurate has not

yet been tested, we anticipate that HCl is also unnecessary in this case. This presumption is borne from the similarities between tetrachlorocuprate, tetrachloroplatinate, and tetrachloroaurate anions.



Not all conclusions reached over the course of this project have been positive. Attempts to preload a diBCP containing a polyanionic block (polystyrene-*b*-poly(acrylic acid), or PS-*b*-PAA) with Ag<sup>+</sup> were apparently unsuccessful. I thought Ag<sup>+</sup> might coordinate to the anionic monomer units in the PAA block once they deprotonated in water of neutral pH; however, little information was available regarding the microphase separation and microdomains of PS-*b*-PAA, which made it difficult to select appropriate molecular weights for each block; I was unable to spin-coat a monolayer of PS-*b*-PAA micelles that annealed into a cylindrical HCP microdomain. Consequently, AFM data did not confirm infiltration of Ag<sup>+</sup> into PAA domains for both preloaded samples and samples infiltrated by exposure to AgNO<sub>3</sub> (aq).

I encountered another setback when trying to pattern Cu nanowires. As previously mentioned, ozone etching typically oxidizes any metal present except for Pt and Au, which are mostly inert. Given that unintentional oxidation of Cu nanoparticles is a common occurrence, it is no surprise that Cu samples post-etching show minimal alignment or AFM contrast. While etched Cu samples have not been analyzed for composition using energy dispersive x-ray spectroscopy (EDX) or other compositional characterization methods, I anticipate that copper oxides are present instead of pure copper.

Other accomplishments this summer included biweekly presentations of data and conclusions to my mentors, coworkers, and fellow interns. I also created and presented a scientific poster at the LLNL Summer Scholars Poster Symposium. Perhaps one of the most important accomplishments over the course of this project was learning to use the AFM, which is something I had wanted to do since learning about it as an undergraduate student.

If I were to continue this project beyond my internship, I would investigate the infiltration of other metal salts analogous to those currently used for infiltration:  $\text{NaAlCl}_4$ ,  $\text{NaPdCl}_4$ ,  $\text{NaCoCl}_4$ ,  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{ZnCl}_4$ ,  $\text{NH}_4\text{AuCl}_4$ , and  $(\text{NH}_4)_2\text{SnCl}_6$ . As discussed with my mentors, it would also be interesting to investigate PS-*b*-P2VP with molecular weights other than 48.5-14.5 kDa to see how much control we can exhibit over the spacing and size of nanowires in the mesh. Further tunability of mesh dimensions might be achievable by adding homopolymer (PS or P2VP) to PS-*b*-P2VP. I would also like to continue to investigate preloading PS-*b*-P2VP with metal ions; while it is possible to preload with  $\text{Ag}^+$ , I have yet to see whether or not we see similar results with platinates, aurates, and cuprates. I anticipate relevant preloading parameters include the duration and vigor of mixing (e.g. sonication, vortex mixing, stirring), temperature, and whether or not the initial solvent needs to be vaporized and micelles re-suspended in different solvent prior to spin-coating. Identifying etching and sintering steps that would enable patterning pure Cu nanowire meshes would also be an interesting task. Finally, producing high quality nanowire meshes and continuing to optimize alignment parameters is an imperative step for this project.

The benefits I received from working on this project are substantial. I believe my input was sought and valued by mentors and peers, which had not been the case in previous academic research experiences. From the very beginning of this internship, I felt like an actual member of the group whose ideas were encouraged and whose conclusions were respected. Perhaps the most beneficial outcome that this internship had on me was to be confident in my own work. Noticing that people more experienced and knowledgeable than me depended on me to communicate scientific results showed me that I am capable of executing my responsibilities and that I was not chosen for this internship by virtue of good luck. I look forward to learning more from this internship as I move on in my career and reflect back on my experience this past summer.

## **II. Impact of Internship on My Career**

This project ties into my undergraduate and Masters curriculum as a student in the Department of NanoEngineering at UC San Diego studying materials science at the nanoscale. I believe that the overall internship experience will impact my career planning more than the specifics of the project will impact my academic planning because I plan to shift my academic focus toward developing nanoscale components for ultrasensitive disease sensors. Prior to the internship, I wanted to become a project

scientist at a national research laboratory after a decade or so in industry. Now I am certain this career path is what I will pursue. Much of the value of this experience comes from the privilege of working onsite; it is difficult to understand the dynamic of a national laboratory without experiencing it firsthand.

Perhaps the most valuable technical skill I gained over the course of this project is operating an atomic force microscope. AFM is essential to almost all researchers of nanomaterials or nanoscale devices because it provides information about topography and material properties at dimensions that cannot be probed with optical microscopy. This means that we cannot take photographs and optical micrographs, which depict macroscale and microscale objects as they appear to us (albeit often magnified), of nanoscale objects. In the absence of photos, we must piece together the geometry, morphology, composition, and material properties of nanoscale objects using a variety of characterization instruments and techniques including the AFM. I anticipate that I will operate AFMs often throughout my career as an engineer of nanoscale devices. Other knowledge I gained throughout this project includes all information stated in Section I except for the background regarding diBCPs, which I learned during two separate polymer engineering classes at UC San Diego.

Because my internship began a few weeks into the DHS Lecture Series for summer interns at LLNL, I was unable to attend the first few lectures – DHS Overview, DHS Nuclear Detection Portfolio, and Energy, Exergy, the Carbon Cycle, and Nuclear Security Research. The next lecture in the series, Heart Model, was one of the best research talks I have ever attended, largely because the speaker (Fred Streitz) was so engaging and enthusiastic about his job, fellow team members, and the context of his work. I left invigorated about the project I had just begun, even though it was entirely unrelated to the work presented in the talk. Fred Streitz encompassed a bit of what I had hoped to become, and his passion for collaborative science and learning was inspiring.

Other lectures in the series were interesting predominantly for their content. The Hypothetical Biological Attack Scenario by Holly Franz taught me a lot about anthrax, in particular, and the modes by which biological agents can be disseminated across human communities. Another favorite lecture was Homemade Explosives by Sabrina DePiero, in which I learned about the components of explosive devices (oxidizers and fuels), the differences in detonation between high power and low power reactions (explosives and enhanced blasts; propellants, thermites, and pyrotechnics, respectively), and the shock-

driven nature of detonation. One of the most interesting pieces of information about that lecture was that homemade explosives often include common kitchen items like sugar.

I also had the opportunity to tour the National Ignition Facility while at Lawrence Livermore National Laboratory. This tour was inspiring to me in a way similar to Fred Streitz's passion for scientific collaboration. The sheer amount of collaboration that went into designing the billion-dollar facility and that goes into operating the lasers demonstrates the scope of the scientific community's capability. While most of these lectures and tours were not of substantial benefit to my professional development, I felt they were inspirational and educational on a personal level.

I believe DHS should continue research in cybersecurity and the protection of digital records at national laboratories, given the amount of classified or sensitive information stored electronically at these locations. I also think that continued research of ultrasensitive sensors for biological and chemical warfare agents, negative refractive index metamaterials for invisibility cloaking, and nanoporous carbon for strong, lightweight materials are essential upcoming technologies relevant to the DHS Mission Statement. Another important technology is quantum dot-based inks, which might be printed onto materials (e.g. currency, passports, important documentation, trade goods) to identify counterfeiting.

### **III. Acknowledgements**

I would like to thank Dr. Yong-Jin Han, Dr. Anna Hiszpanski, Tim Yee, and Carla Watson at Lawrence Livermore National Laboratory for their mentorship and guidance throughout my portion of this project. I would also like to thank Dr. Sadik Esener and Dr. Milan Makale for recommending me to the DHS HS-STEM internship through ORISE and the U.S. Department of Homeland Security. Finally, I would like to thank Lisa Palmer and Barry Goldman at for their help managing the logistical end of my stay at Lawrence Livermore National Laboratory.

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