You Will Ru(e) the Day: Developing Area-Selective Processes to Enable Ru-Based Interconnect at the 2 nm Node and Beyond

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CNF REU Project and Primary Source(s) of Research Funding: 2022 Cornell NanoScale Science & Technology Facility Research Experiences for Undergraduates (CNF REU) Program via the National Science Foundation under Grant No. NNCI-2025233

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Primary CNF Tools Used: Veeco Savannah, Oxford ALD FlexAL, Oxidation Furnace, Heidelberg Mask Writer - DWL2000, SC4500 Evaporator

Abstract:

For many years, scientists have used photolithography to layer patterns onto wafers. However, the minimum size of the features on the patterns is limited by the wavelength of the light used. Now, as the electronics industry seeks to create single digit nanometer features, photolithography is reaching the limits of its capabilities; a new method for patterning substrates is needed. One such way is through selective deposition of materials in which deposition is determined by the surface chemistry. In atomic layer deposition (ALD), a film is typically grown using half reactions in an AB cycle. First, the precursor (A) binds the substrate. Then, the co-reactant (B) reacts on the surface with the precursor to grow the desired film. Each AB cycle results in a film growth thickness of approximately one angstrom [1]. Because the user controls the number of cycle repetitions, thickness can be tailored with high precision. For area-selective ALD, if a chemical (co-adsorbate) is introduced before and alongside the precursor, the co-adsorbate can attach to certain surfaces and block film growth in order to achieve selectivity [2]. Additionally, the typical material used for electrical interconnects is copper. However, for single digit nanometer features, ruthenium is a better conductor. Overall, the purpose of this project is to create different sized line-and-space patterns of alternating ruthenium and dielectrics (Al_2O_3 and SiO_2) using a lift-off process. These patterns can then be used to test which co-adsorbates provide the best selectivity given the metals and dielectrics used in the patterns.

Summary of Research:

Ten 100 mm silicon wafers were utilized to create the patterns. First, all wafers were cleaned using an RCA clean. A 200 nm film of SiO_2 was thermally grown on five of the wafers using an oxidation furnace. A 50 nm film of Al_2O_3 was deposited via ALD on the other wafers using the Veeco Savannah and the Oxford ALD FlexAL. The negative photoresist nLOF2020 was spun on each wafer at 3000 rpm for one minute, followed by a one-minute bake. A GDSII file containing line-and-space patterns of 100, 30, 10, 3, and 1 μm was created using the gdstk python library and then used along with the Heidelberg Mask Writer - DWL2000 to create the mask pattern.

Each wafer was then exposed using the ABM contact aligner, baked on a hotplate for one minute, and developed in the Hamatech wafer processor.

The SC4500 evaporator was used to deposit the metals. Five nm of titanium was first deposited to help the ruthenium stick to the wafer. Then, 20 nm of ruthenium was deposited. After stripping the photoresist, the pattern was then examined using atomic force microscopy (the AFM).

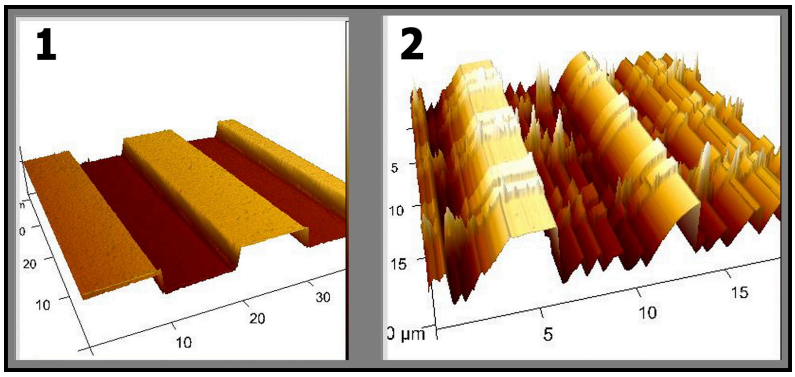

Figure 1, left: 10 µm line-and-space pattern. Figure 2, right: 3 µm line-and-space pattern.

Overall, the 100, 30, and 10 µm lines had good coverage and little surface roughness. However, there were holes and significantly more roughness in the 3 and 1 µm lines. This can be seen in the AFM images of the 10 µm and 3 µm lines as shown in Figures 1 and 2. This is likely due to the wafer not being clean enough before undergoing the photolithography process. Therefore, the 100, 30, and 10 µm lines can now be utilized for area-selective depositions.

References:

[1] S. M. George, "Atomic Layer Deposition: An Overview," ACS Publications, Nov. 2009. https://pubs.acs.org/doi/pdf/10.1021/cr900056b (accessed Aug. 13, 2022).

[2] T. Suh, et al., "Competitive Adsorption as a Route to Area-Selective Deposition," ACS Appl. Mater. Interfaces, vol. 12, no. 8, pp. 9989–9999, Feb. 2020, doi: 10.1021/acsami.9b22065.

Inkjet Printing of Epitaxially Connected Nanocrystal Superlattices

CNF Project Number: 1645-08

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User(s): Daniel M. Balazs, N. Deniz Erkan, Michelle Quien

Affiliation(s): School of Chemical and Biomolecular Engineering, Cornell University

Primary Source(s) of Research Funding: Department of Energy – Basic Energy Sciences (DE-SC0018026), National Science Foundation (DMR-1719875) for the use of Cornell Center for Materials Research tools

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Primary CNF Tools Used: Dimatix Printer

Abstract:

Access to a growing library of colloidal nanomaterials provides building blocks for complex assembled materials. The journey to bring these prospects to fruition stand to benefit from the application of advanced processing methods. Epitaxially connected nanocrystal (or quantum dot) superlattices present a captivating model system for mesocrystals with intriguing emergent properties. The conventional processing approach to create these materials involves assembling and attaching the constituent colloidal nanocrystals at the interface between two immiscible fluids. Processing small liquid volumes of the colloidal nanocrystal solution involves several complexities arising from the concurrent spreading, evaporation, assembly and attachment. The ability of inkjet printers to deliver small (typically picoliter) liquid volumes with precise positioning is attractive to advance fundamental insights into the processing science, and thereby potentially enable new routes to incorporate the epitaxially connected superlattices into technology platforms. This project identified the processing window of opportunity, including nanocrystal ink formulation and printing approach to enable delivery of colloidal nanocrystals from an inkjet nozzle onto the surface of a sessile droplet of the immiscible subphase. We demonstrate how inkjet printing can be scaled-down to enable the fabrication of epitaxially connected superlattices on patterned sub-millimeter droplets. We anticipate that insights from this work will spur on future advances to enable more mechanistic insights into the assembly processes and new avenues to create high-fidelity superlattices.

Summary of Research:

Bringing the heralded prospects of nanocrystal (NC) assemblies to fruition is contingent on better understanding of and control over the formation mechanism and the emerging structure-property relationships; both of these tasks rely critically on access to high-fidelity superlattices. Recent interfacial assembly and attachment studies point towards the need for more advanced processing methods to provide refined control over the delivery of the NC solution to the fluid interface. The volume of the deposited solution is a key consideration in the process of creating a liquid thin film from which NCs assemble on the surface of the sessile liquid subphase and attach to form epitaxially connected superlattices. Considering a typical NC colloidal concentration in the range of ~ 2-300 mg/ml, the formation of a monolayer NC film requires deposition of an ink film thickness of a least 100 nm. In the case of microliter droplets deposited from a conventional micro-pipettor, this film thickness requires spreading across an interface area of ~ 10^2 cm^2 [1]. Translating processing insights from earlier studies with cm2 scale surfaces to smaller interfaces in which dynamic processes can be better controlled therefore requires the ability to deposit smaller solution volumes. In this context, the ability of inkjet printers to deliver small (typically picoliter) liquid volumes with precise positioning is very attractive for both scientific and technological reasons. For example, Minemawari, et al. [2], successfully demonstrated inkjet printing of single crystals of organic semiconductors on the surface of micrometer-sized antisolvent droplet. Beyond providing an experimental testbed to refine our mechanistic understanding of the assembly and

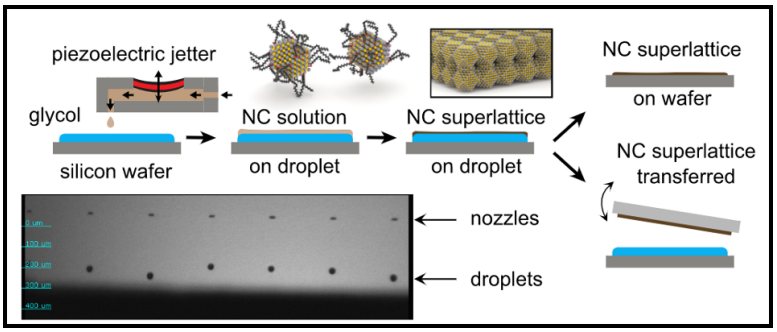

Figure 1: Sketch of the experimental setup. A colloidal NC ink is jetted on to of a sessile droplet of an immiscible subphase. NCs in the thin liquid film then assemble and attach to form an epitaxially connected superlattice (epi-SL) which can subsequently be transferred to a solid substrate.

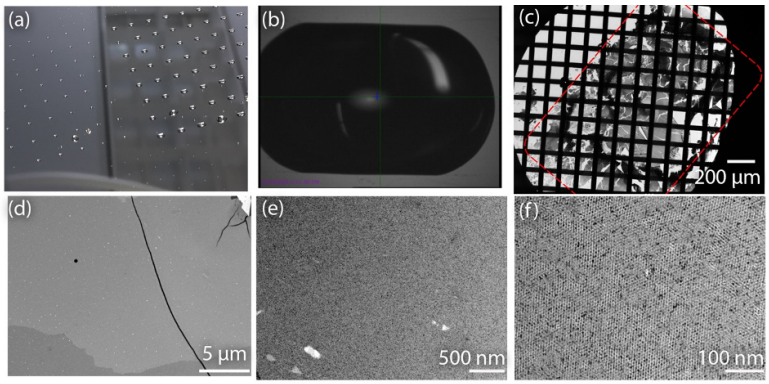

Figure 2: Multi-scale analysis of NC printed on patterned droplet. a) Optical image of droplets formed by spreading ethylene glycol on a patterned-fluorinated substrate; b) optical micrograph image of such a droplet; c) TEM image of a ~ 3 monolayer thick NC film prepared on a 1-by-1.5 mm droplet by inkjet printing; the shape of the droplet is marked showing complete spreading and coverage; d-f) the local homogeneity and superlattice structure are similar to those of samples prepared on larger scale.

attachment, inkjet printing of NC assemblies at fluid interfaces also has notable technological implications as this fabrication strategy could enable creation of epi-SLs in more complex geometries required for device integration. Inspired by these prospects, we set out to translate this approach to enable the delivery of colloidal NCs on top of an immiscible fluid interface.

In this project, we sought to build on these insights to identify a window of opportunities (including ink formulation and printing approach) to enable delivery of colloidal NCs onto the surface of a sessile droplet. Basic aspects of the processing workflow are summarized in Figure 1. We identified critical considerations for the NC ink formulation including NC solute concentration and NC surface ligand coverage, choice of solvent (with regards to NC solubility, vapor pressure and viscosity). The processing window of opportunity for stable inkjet printing is constrained by several factors. We examined inkjet printing of NC inks in the parameter space defined by the Reynold and Weber numbers. We established the basic relationship between fluid dynamic conditions during inkjet printing and the structural fidelity of the NC superlattice. We analyzed the structure of NC films formed on a geometrically contained droplet. The results of this project were recently published in Nano Research [3]. We anticipate that insights from this work will spur on future advances to enable more mechanistic insights into the assembly processes and new avenues to create high-fidelity superlattices.

References:

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Genetically Encoded Platform for Mucin-Induced Extracellular Vesicle Production

CNF Project Number: 2272-14

Principal Investigator(s): Dr. Matthew Paszek

User(s): Erik Chow

Affiliation(s): Department of Biomedical Engineering, Cornell University

Primary Source(s) of Research Funding: National Science Foundation Graduate Research Fellowship

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Primary CNF Tools Used: Malvern NS300 Nanosight

Abstract:

Extracellular vesicles (EVs) are critical in mediating intercellular communication. Because of the diverse nature of their cargoes — which include DNA, coding and noncoding RNA, and proteins — and their innate biocompatibility, EVs have quickly become a prominent focus in numerous biomedical engineering applications, including diagnostics, drug delivery, and targeted therapies. One largely unexplored area is the significance of the glycocalyx in EV biogenesis and function. Specifically, the capacity to rationally manipulate the glycocalyx to produce vesicular materials for biomedical applications remains poorly understood. We have previously demonstrated that overexpressing the mucin glycoprotein MUC1 in the glycocalyx leads to a dramatic increase in the production of EVs [1]. Here we summarize our recent efforts to develop and characterize a genetically encoded platform for the production of these so-called mucin-induced EVs (MUC-EVs).

Summary of Research:

Extracellular vesicles (EVs) have been shown to carry a wide range of cargoes, including DNA, coding and non-coding RNAs, and proteins. Because of the diverse nature of their cargoes, and their innate biocompatibility, EVs have quickly gained traction in numerous areas of biomedical engineering research, including disease pathogenesis, diagnostics, drug delivery, and targeted therapies. The glycocalyx is a polymer meshwork of proteins, nucleic acids, and glycans which dictates numerous intercellular interactions. However, the capacity for the production of rationally designed EVs through engineering of the glycocalyx remains poorly understood. It has been previously shown that engineering the glycocalyx via the overexpression of mucin can result in membrane morphologies which are favorable for the formation of EVs [1]. This report summarizes research from the last year characterizing a genetically encoded platform for increased generation of so-called "mucin-induced" EVs with tunable size characteristics and surface coatings.

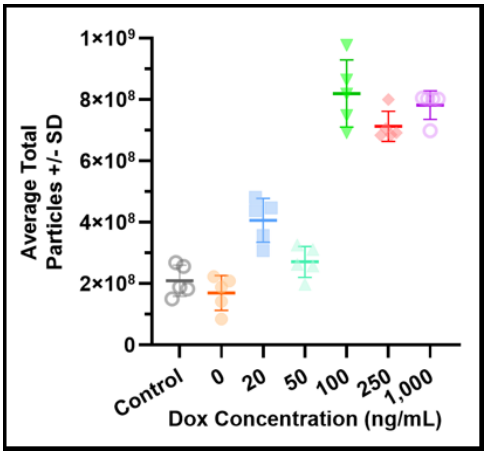

Figure 1: Tunable mucin-induced EV production. EV particle concentrations measured by NTA from MCF10A-rtTA cells (Control) and MCF10A-1E7 cells induced with a ranged of Dox concentrations. Plotted are the average reported total particle concentrations +/-SD from five video recordings.

To engineer the glycocalyx, MCF10A cells were genetically engineered to overexpress a MUC1-mOxGFP construct on the cell membrane. A single clone was expanded and used as a workhorse cell line for this

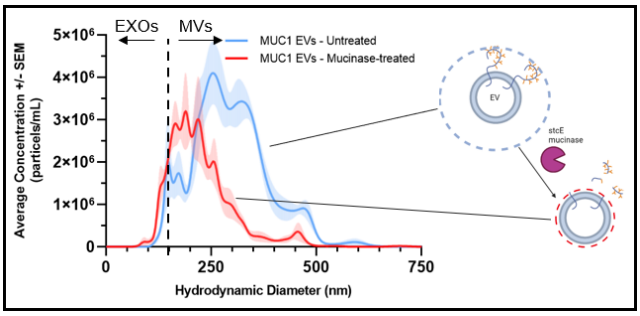

Figure 2: Mucin-induced EVs have removable mucin coatings. EV size distributions measured by NTA from MCF10A-1E7 derived EVs either untreated (Control) or treated with 100nM stcE mucinase. Histograms represent the average reported size from five video recordings.

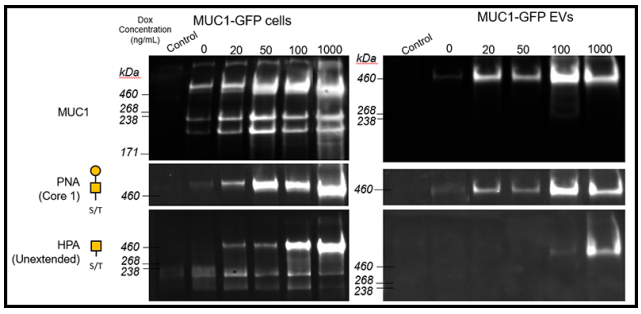

Figure 3: EVs from MCF10A-1E7 cells have similar mucin coating characteristics to their parent cells. Lectin blots comparing MUC1 glycosylation patterns in mucin-induced EVs and the cells from which they were derived.

research, hereafter referred to as MCF10A-1E7 cells. Expression of MUC1-mOxGFP in MCF10A-1E7s was tied to a tetracycline-inducible promoter, and cells were treated with doxycycline (Dox) for 24 h at a concentration of either 0.1 µg/mL or 1 µg/mL to induce MUC1-mOxGFP overexpression. MCF10A cells engineered with only the promoter but no MUC1-mOxGFP construct, hereafter referred to as MCF10A-rtTA cells, were used as a negative control. After Dox treatment, the cells were switched to serum-free media and cultured at 37°, 5% CO_2 for 15 h to 18 h. EV-containing media was harvested, and the EVs were isolated by PEG-enrichment [2]. EV mucin coatings were optionally removed by treatment with stcE mucinase [3], and EV sizes and concentrations were measured by nanoparticle tracking analysis (NTA) using the Malvern NS300 Nanosight.

Figure 1 illustrates the dose-dependent production of mucin-induced EVs based Dox titration. These data illustrate that tunable EV production in MCF10A-1E7 cells is achieved using our genetically encoded platform. Additionally, mucin-induced EVs were found to carry their own mucin coatings, as supported by Figure 2. Treatment of mucin-induced EVs with mucinase resulted in an overall decrease in EV size, consistent with the cleavage of MUC1 from the EV surface.

Figure 3 shows lectin staining of the mucins isolated from mucin-induced EVs. The EV-derived mucins show both similar expression and glycosylation patterns to cell-surface mucins from MCF10A-1E7 cells, suggesting that glycocalyx engineering at the cellular level can be used to tune mucin-induced EV coatings.

Conclusions and Future Steps:

Altogether, these data demonstrate that EV production and properties can be controlled by engineering the glycocalyx of cells. Further experiments are needed to explore the applications of engineered EV mucin coatings. Additionally, future experiments will strive to reliably segregate exosomes and microvesicles in order to more precisely study the exosome and microvesicle characteristics.

References:

[1] Shurer, C. R., Kuo, J. C.-H., Roberts, L. D. M., Gandhi, J. G., Colville, M. J., Enoki, T. A., Pan, H., Su, J., Noble, J. M., Hollander, M. J., O'Donnell, J. P., Yin, R., Pedram, K., Möckl, L., Kourkoutis, L. F., Moerner, W. E., Bertozzi, C. R., Feigenson, G. W., Reesink,

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Fabrication and Characterization Support for CCMR

CNF Project Number: 2974-21
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User(s): Philip Carubia

Affiliation(s): Cornell Center for Materials Research (CCMR), Cornell University

Primary Source(s) of Research Funding: National Science Foundation

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Primary CNF Tools Used: Universal Laser Systems VersaLaser VLS3.50

Abstract:

Over the last year, the Cornell NanoScale Facility (CNF) has been accessed three times on project number 2974-21. Once for training on the Universal Laser Systems VersaLaser VLS3.50, and twice for laser cutting 20 mm, 25 mm, and 40 mm discs from PSA backed grinding papers to be used with the DHR3 shear rheometer located in the Cornell Center for Materials Research (CCMR).

Summary of Research:

CNF Project 2974-21 was established for facilities staff from the Cornell Center for Materials Research (CCMR) to access basic instrumentation within the Cornell NanoScale Facility (CNF) for purposes of sample preparation and fabrication of accessories for CCMR instrumentation. The initial project proposal was started to gain access to the Universal Laser Systems VersaLaser VLS3.50 by the bard materials facility for cutting 20 mm, 25 mm, and 40 mm discs from PSA backed grinding papers to be used with our DHR3 shear Rheometer. These discs are used to increase the friction between stiffer samples and the instrument to reduce artifacts related to sample slippage.

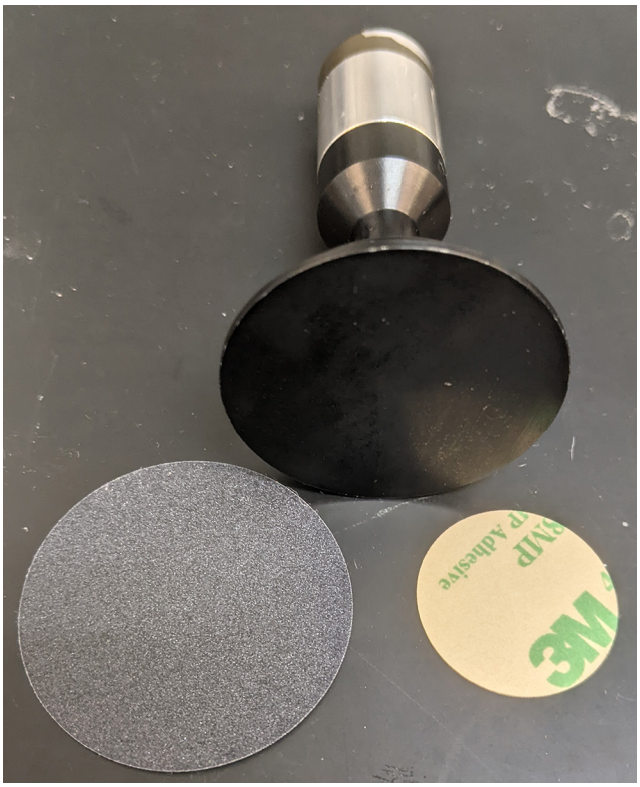

Figure 1: 40 mm upper parallel plate geometry with 40 mm disc front and 25 mm disc back.

Conclusions and Future Steps:

Access to this laser cutter has allowed us to test tougher hydrogels and viscoelastic materials at higher strains than previously available. It is likely that we will be using the Universal Laser Systems VersaLaser VLS3.50 in the future as we use up our existing stock.

Current Progress in Superconducting Device Fabrication

CNF Project Number: 2998-22
Principal Investigator(s): Valla Fatemi
User(s): Luojia Zhang, Haoran Lu

Affiliation(s): School of Applied and Engineering Physics, Cornell University

Primary Source(s) of Research Funding: Lab start-up account

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Primary CNF Tools Used: Heidelberg Mask Writer - DWL2000, ABM Contact Aligner, AJA Sputterer, AJA Ion Mill, Glen 1000

Abstract:

The Fatemi Lab is mainly interested in the intersection of low dimensional materials and quantum circuits. The current ongoing project is transport and microwave spectroscopy on graphene Josephson junction, and the main cleanroom activities are fabrication and packaging of those superconducting Josephson devices. So far, our efforts have been towards the deposition and measurement of base-layer superconducting niobium films.

Summary of Research:

The users from our lab have completed the cleanroom orientation and obtained the access in March this year. Later, Luojia got trained and started using the AFM to measure the thickness of boron nitride for our 2D materials stack. The majority of the fab work started in this summer. Haoran was trained on the wire bonder and used it to package preliminary resonator devices.Luojia started making devices with sputter deposition, photolithography, and RIE etching. The first contact mask was made using the Heidelberg DWL2000 mask writer. Later, the AJA sputterer was used to deposit a layer of niobium on top of a silicon wafer. The sputtered wafer was then patterned using photolithography. For that, we used the ABM contact aligner with AZ nLoF photoresist. After determining the optimal spin coating recipe and dose, we used the AJA ion mill to etch away the metal, and Glen 1000 to descum the wafer.

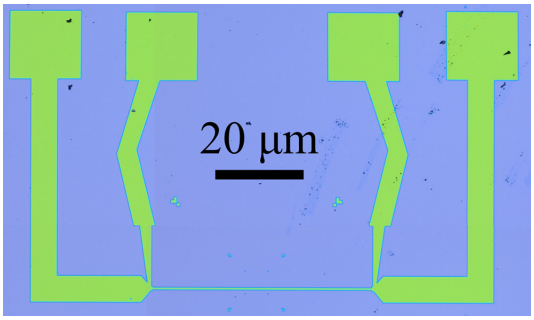

Figure 1: Image of etched niobium film patterned into a four-probe device structure for testing residual resistance ratio and the superconducting critical temperature.

Conclusions and Future Steps:

So far, we have made good first steps towards super-conducting niobium layers for use in Josephson and other superconducting devices. Next steps include:

(1) Determining the sputtering recipe to produce good quality nNB film with critical temperature larger than 9K.

(2) Print and use a stepper reticle for microwave resonators.

(3) Use E-beam lithography to make superconducting contacts with hBN-graphene-hBN stacks.

(4) Perform RIE side contacts on the 2D materials van der Waal stack, test the quality of the superconducting contacts.