Fabricating Van der Waals Heterostructures with Air Sensitive Materials: A Study of Flake Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$

By Liam Augustus Cohen

Submitted to the Department of Physics in partial fulfillment of the Requirements for the Degree of BACHELOR OF SCIENCE at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May, 2017 [June 2018]

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Signature redacted

__________________________________________
Department of Physics
(5/15/2017)

Signature redacted

Certified by

Signature redacted

Professor Raymond Ashoori
Thesis Supervisor, Department of Physics

Signature redacted

Certified by

Professor Nergis Mavalvala
Physics Associate Head, Department of Physics
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Thank you.

The images contained in this document are of the best quality available.
This work is dedicated to my Mother and Father, Anastasia Traina and Scott Cohen, who have sacrificed so much to give me the privilege to pursue my dreams.
I would like to thank Professor Raymond Ashoori who gave me the opportunity to work in his lab, and to continue my education in physics.

I would also like to thank Dr. Neal Staley for being my mentor the past two years and giving me this project. Our constant discussions, intellectual and non-intellectual have helped me grow not just as a scientist but as person as well: something I will be forever grateful for.

I want to thank everyone else in the Ashoori Group: Ahmet Demir, Heun Mo Yoo, Dr. Joonho Jang, Dr. Kuei-Lin Chu, and Spencer Tomarken. You all have made my two years with the group my best at MIT.

I would like to thank my many mentors over the years who have encouraged me to pursue my love of science, physics, and academia: Chris Udell, Daniel Newsome, Jennifer Udell, Peter Bonfanti, Preethi Thomas, Sarvjit Moonga, Sherezada Acosta.

Since I have the room, I would like to thank my dearest friend in the world, Charles Simpson-Brown. Our adventures together in New York City I think have left an indelible mark, and have shown through in my research in the form of ideas just crazy enough to work.
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Chapter 1:
Van der Waals Heterostructures: Preliminary

Ever since Novosolev et. Al [39] in 2004 were the first to isolate a monoatomic sheet of carbon - graphene - a wealth of research has been done on the various 2-D materials that can be isolated like graphene, via the mechanical exfoliation technique. In particular, as described by Geim and Grigorieva [40], 2-D materials like graphene, h-BN, WSe2, etc., can be stacked on top of each other like legos, creating a library of possible devices. As long as the material can be “picked-up” by other 2-d materials, in theory a stack of any set of 2-D materials can be made and its properties observed.

Nano-devices made in this manner present a unique opportunity to explore a plethora of new and interesting physics and electrical engineering applications. On the electrical engineering side, Van der Waals heterostructures (VDWHs) have been used to fabricate new electronic devices. For example, Roy T. et al [41], used a gated single-layer MoS2-WSe2 junction to create a gate-controlled semi-conductor device. This device was able to switch between being a forward rectifying diode, a backward diode, or an Esaki diode. From a more physics oriented perspective, VDWHs have been used by Cao, Fatemi, Jarillo-Herrero, Luo et. Al [42], to explore the effects of a Moiré lattice potential in twisted bilayer graphene. By taking two layers of graphene and transferring them on top of each other at an angle, a potential with periodicity much larger than the atomic spacing of the carbon-atoms forms. The Moiré pattern induces insulating states in graphene, which otherwise is a high-mobility conductor. These states were first able to be observed in VDWHs.
In theory, one could create a “dreamscape” of device structures as Geim et al., [40] puts it, however, in practice this is limited because the device quality drops every time a new piece of 2-D material is picked up and transferred. From a realistic standpoint, device architectures are limited to about 3-4 layers of material, after which creating larger stacks becomes increasingly more difficult. Ultimately, VDWHs is a technique that is barely a decade old, and will improve greatly over time. Already, multiple new techniques have arisen just within the last few years to improve upon some of the short-comings associated with the traditional set of techniques. One of these new techniques, viscoelastic based dry transfers, is the allowed us to make a major breakthrough in making low-resistance contact to a 2-D high-$T_c$ superconductor, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (BiSCCO).
Chapter 2:
Capacitance Spectroscopy: Preliminary

One of the most interesting pieces of information one could have about a physical system is its density of states (DOS). The electronic DOS, especially near the Fermi level, can give the electronic contribution to the specific heat, it can give a system’s magnetization, carriers available for conduction, etc. Characterizing the density of states for a given system, for the most part, classifies the system in its entirety. Capacitance spectroscopy is a technique, detailed by professor Ashoori in his graduate thesis [43], to measure the DOS of a material at the Fermi level. Originally, professor Ashoori developed the capacitance technique for a 2-D free electron gas (2DEG) in a GaAs/AlGaAs heterostructure. For this thesis we are interested in how the capacitance technique applies to VDWHs. The core concept is the same, but the practical technique is a little different. In this section I will only explain the idea behind capacitance spectroscopy in VDWHs, as it is most relevant to the work in this thesis.

To get the general feel for how measuring capacitance is related to the DOS of a material, lets consider a simple capacitance device of some 2D material of interest placed between two dielectrics.

![Figure-1: Flake Capacitance Device Model Used To Measure DOS of the Material of Interest](image)
From a classical E/M perspective, if we place a potential across the conducting plates, then an electric field will develop across the sample. To a zeroth order approximation, we can consider this setup as two capacitors in series, one going from the top gate to the material of interest, and another going from the material of interest to the bottom gate attached to ground. Typically, for VDWHs, $D$ is much much greater than $L$, and the capacitance going from the material of interest to the bottom gate is purely derived from classical Electromagnetism.

$$C_g = \frac{A \epsilon}{d}$$

We call this capacitance the geometric capacitance, since it encapsulates the capacitance of the device derived from its geometry, as opposed to its quantum nature.

For the other capacitance - from the top gate to the material of interest - we need to look at the density of states of the material. Since the dielectric near the top-gate is extremely thin, charge can tunnel into the material of interest proportional to the available density of states. This means that we can write down the DOS related capacitance as:

$$C_q = eA \frac{\partial n}{\partial \mu}$$

and the total capacitance as:

$$\frac{1}{C_T} = \frac{1}{C_g} + \frac{1}{C_q}$$

Since $C_g$ is constant, taking a measurement of the total capacitance allows one to extract out the DOS for a material of interest. It’s important to note here that the DOS is at a fixed energy, and
that the capacitance measurement reveals the DOS, in particular, at the Fermi energy of the material of interest.

In terms of taking an actual measurement, the model behind measuring capacitance is fairly simple.

The general idea is to apply a fixed $V_{\text{measure}}$ A.C. signal to the sample, and then apply a variable amplitude signal at the same frequency as $V_{\text{measure}}$, $V_{\text{std}}$, to a reference capacitor that is 180 degrees out of phase with $V_{\text{measure}}$. If the voltage at the node between the two capacitors is zeroed then a simple proportionality relation $V_{\text{std}} C_{\text{std}} = V_{\text{measured}} C_{\text{measured}}$ is achieved. Knowing
\( C_{\text{std}}, V_{\text{std}}, \) and \( V_{\text{measured}} \) one can extract out the value of \( C_{\text{measured}} \). The HEMT is in the circuit for both amplification purposes, and the gate-source capacitance of the HEMT forms a capacitive multiplier with the capacitance of the BNC cables connecting the sample to the measurement equipment, which increases the signal-to-noise ratio by a factor of \( C_{\text{cable}}/C_{\text{gs}} \).

As an additional note, the material of interest even in the simplest model will have some resistive component associated with it. If this is the case, and the resistive component becomes large, and if \( 1/RC - R \) here is the tunneling resistance - becomes smaller than the excitation frequency, then a drop in capacitance does not necessitate a gap in the DOS. It can be an indication of the device’s inability to fully charge in the time scale set by the excitation frequency. For this reason, any resistive component in the sample will introduce a phase shift at the balance point. Measuring this phase shift gives us a sense of the value of the resistive component in the device, and having both the capacitance information and the resistance information allows for a complete picture of a sample’s DOS.
Chapter 3:
Introduction to Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ and Previous Work

For this thesis, we were interested in studying the high-$T_c$ superconductor BiSCCO in the 2-D limit. In particular, we wanted to use capacitance spectroscopy to get a comprehensive look at the density of states of extremely thin BiSCCO in its pseudo-gap and Anti-Ferromagnetic insulator phases. This chapter will serve as a brief introduction to this material, what properties it has that make it an interesting material to study, and a review of the previous work that has been done on BiSCCO as a material in VDWHs.

The first thing to note about BiSCCO that makes it relevant for this thesis is that the material can be exfoliated. A single unit-cell of BiSCCO 2212 can be seen in figure-1. BiSCCO can be mechanically exfoliated with exactly the same method as graphene. In fact, the cleave

![Figure-1: BiSCCO 2212 Unit Cell](Image Credit [2])
planes are the CuO2 planes, and BiSCCO itself can be mechanically cleaved all the way down to a half-unit cell [1]. An interesting question in and of itself is at what flake thickness does superconductivity persist? It is not known whether or not superconductivity exists in the ultra-thin limit. Simply being able to take transport measurements on thin BiSCCO placed into a VDWH would be an interesting report.

BiSCCO is a d-wave symmetry spin-density-wave high temperature superconductor. The material is oxygen doped [4]: its charge carrier density can be tuned by the amount of interstitial oxygen. This means that BiSCCO is air sensitive and its doping level can change depending on how long its allowed to exchange oxygen with the ambient atmosphere [5]. As can be seen from

![Figure-2: Typical Phase Diagram of Multiple High Tc Superconductors as a Function of Doping](imagecredit)
figure-2, if BiSCCO is optimally doped, as in, it sits at the doping corresponding to the top of the superconducting dome, then the $T_c$ is roughly 95K. There are two interesting states in the phase diagram other than the superconducting state, and these are the anti-ferromagnetic insulator regime, and the pseudo gap regime.

The anti-ferromagnetic regime is interesting for a number of reasons. The first is that its an insulating regime, and the fact that an insulating regime and a superconducting regime can exist in the same material, and be related by a quantum phase transition no less, is very odd. Many other High $T_c$ superconductors exhibit this behavior, but BiSCCO is the only one that can be studied in the ultra-thin regime since its exfoliable. The pseudo gap phase is also interesting.
because it exhibits a density of states similar to that of a superconducting state, but instead of a complete gap where there is a range of energy with no available states, there is a range of energy with a very small number of states. Furthermore, at extremely low temperatures, it may be possible, in under-doped BiSCCO to transition between the AFM state, the pseudo-gap state, and the superconducting state by small charge carrier concentration changes induced by the electric-field effect. Observing this transition with a high resolution spectroscopic technique like capacitance may shed light on the fundamental mechanism behind superconductivity in BiSCCO and other high-\(T_c\) superconductors.

The pairing mechanism in BiSCCO and other high-\(T_c\) cuprate based superconductors is still widely debated. Literature [46] suggests superconductivity is related to a spin-density wave order parameter, and is related to the AFM insulating state. However, no model exists that cohesively explains the AFM insulator state, the pseudo-gap phase, superconductivity, and matches with experiments, there is still much to be understood. This project was originally intended with the goal of imaging with high resolution the the DOS of BiSCCO in the pseudo-gapped phase and the AFM phase in the ultra-thin limit. The project intended to start with optimal doping to gauge the gapped states in the superconducting regime. However, the ultimate goal was to work with under-doped BiSCCO and use high resolution spectroscopy to image the density of states between all three regimes in a single sample. By doing this work in the ultra-thin limit, we believed new details in the DOS might have shed some light on what the fundamental mechanism behind superconductivity is in this material. However, before fabricating a capacitance device, as a preliminary to this project, we first wanted to determine whether or not superconductivity could be observed in flake BiSCCO. As mentioned before this
was interesting in and of itself. However, this ended up being far more of a challenge than we expected.

Ever since 2004 when Novoselov and Geim [8] exfoliated graphene for the first time, it has been suggested that flake BiSCCO should be exfoliated in the same manner. However, only one group since 2004 has reported any transport measurements of flake BiSCCO [35]. Furthermore, this group has not published any follow-up reports since their initial paper in 2014, and no other group has been able to reproduce their results. Many of the the high-Tc cuprate based superconductors are sensitive to environmental parameters [37], thus requiring fabrication to be done in a carefully controlled environment. In particular, BiSCCO itself is known to form a highly resistive surface layer when exposed to water [14,17,23, 32]. This resistive layer can form as deep as several 10s of nanometers [14], which on a bulk scale is irrelevant, but encompasses the thickness of the entire flake on the scale of VDWHs. This environmental instability makes fabricating flake BiSCCO using traditional VDWH techniques incredibly difficult.

Most VDWH techniques involve using solvents of some type either as a cleaning step or part of the process of physically transferring a stack onto a final substrate. However, as is mentioned in [37] polar solvents in addition to water can also cause BiSCCO to form a resistive surface layer. Both acetone and IPA are polar (common solvents used in VDWH processes) and therefore can assist in degrading flake BiSCCO. In this thesis, we develop a means of fabricating VDWHs with BiSCCO using zero solvent steps. This allowed us to fabricate devices minimally affected by a resistive outer layer, achieving consistent low-resistance contacts on multiple devices. These devices are all supplemented with four-terminal transport data.
Throughout taking transport measurements we learned that there are other problems associated with working with flake BiSCCO in addition to just making low-resistance contacts. For one, as described in [5], BiSCCO thin-films change their phase based on the amount of dopants provided by interstitial oxygen. The oxygen content can easily be manipulated by an anneal in either air or Ar. For flakes, the rate at which oxygen is exchanged between the BiSCCO flake and the environment can only be assumed to be greater than in thin-films. Having no control over the oxygen content in our devices, it was difficult to achieve consistent transport data. Furthermore, the BiSCCO flakes, compared to graphene or h-BN, are fragile. We noticed via AFM imagery, that micro-cracks were appearing in the flakes after transfer, and we believe that thermally cycling the flakes caused these cracks to propagate and cause inconsistencies in our transport measurements.

However, although there is still work to be done, we in this thesis present a major leap forward in being able to make repeatable low-resistance contacts to flake BiSCCO. Despite the problems presented after making low-resistance contacts, we firmly believe that these problems are solvable with technology currently available. The following chapters of this thesis will detail all of the steps that we took in order to determine what is the correct process for making low-resistance contacts to flake BiSCCO. Many fabrication techniques that were attempted but ultimately failed are also presented along with the successful techniques and their corresponding devices. We hope that future work will be able to build off of the information presented in this thesis to be able to fully fabricate VDWHs with thin BiSCCO.
Section 2:
Fabrication Techniques
Chapter 1:

Application of Standard Van der Waals Heterostructure Techniques to Flake BiSCCO

As discussed in the previous chapter, the original goal of this thesis was to utilize the techniques developed to create VDWHs to analyze the DOS of thin BiSCCO in the AFM regime and the pseudo-gapped state. In the first chapter of this section we will review in detail the techniques used to create traditional VDWHs in the context of working with flake BiSCCO. The very first device that we attempted used entirely traditional VDWH techniques. We made a lot of progress with traditional VDWH techniques, and we were able to work around BiSCCO’s peculiarities to fabricate a device. It was by first attempting to use traditional transfer techniques to fabricate a transport device that we learned that it was difficult to make low-resistance contact to BiSCCO.

There are three important questions to ask of any VDWH material before attempting to fabricate a device. The first question: is it possible to mechanically exfoliate the material, and if so how does one go about doing it? The second question: is it possible to pick up the material with a PC transfer slide? And the third question: is it possible to pick up the material with other VDWH materials, like graphite or h-BN. These were the very first experiments that we performed when we started working with BiSCCO. We were successful at picking up BiSCCO by itself with a PC transfer slide, but we found that it was impossible to pick up BiSCCO with either h-BN or graphite. Although it may be possible to pick up BiSCCO with other VDWH materials, h-BN and graphite were the only relevant materials for our desired device structure.
The conclusion of this chapter is that although it is certainly possible to physically construct VDWH with BiSCCO using traditional techniques, a device architecture limitation exists which may affect the number of needed fabrication steps. Furthermore, the device built with these techniques did not conduct at room temperature, indicating that some step in the fabrication process was preventing the BiSCCO flake from making a low resistance contact to the Au leads.
Subsection 1:
Mechanical Exfoliation of BiSCCO

The first step in working with VDWH materials is to mechanically exfoliate the material of interest. For a detailed review of mechanical exfoliation see [7, 8]. Mechanical exfoliation involves taking the macroscopic crystal of a VDWH material and spreading it across a piece of scotch tape, and another piece of scotch tape is placed on top of the piece with crystals on it. The tape is then peeled apart and two new tapes are made, leaving crystals on both tapes. This

Figure-1: Graphical Description of Mechanical Exfoliation of Graphene - Crystals of graphite are placed onto a piece of tape as can be seen in frame-1. The graphite is then cleaved by pulling the two pieces of tape apart. This process is repeated several times before the tape is deposited onto a substrate where the crystal is cleaved once more leaving a piece of graphene or thin graphite on the substrate, as can be seen in frames 2-4.
process is repeated several times and the tape is then ultimately deposited onto a substrate. A graphical description of this process can be seen in figure-1. In addition we have provided two examples (graphite and h-BN on Si/SiO₂) isolated by mechanical exfoliation in figure-1: frames 5 and 6.

Typical substrates are Si with an oxide layer that is 285nm. The reason for the oxide layer is twofold. SiO₂ provides a strong Van der Waals interaction allowing for flakes to strongly adhere to the SiO₂, allowing thin layers to be cleaved off the crystals on the tape. The second reason for having an oxide layer is that the optical path now includes the SiO₂ in addition to the flake, which allows for even monolayers of VDWH materials to be seen optically [9].

Mechanically exfoliating BiSCCO requires minimal adjustment from the standard technique. However, as was discussed in section 1, BiSCCO is an oxygen doped material [11], its superconductive properties depend on the charge-carrier density provided by hole dopants introduced by interstitial oxygen. As such, some techniques used to increase yield for exfoliation [10] like heating the substrate before peeling off the deposition tape, or heat cleaning the substrate to remove glue, can amount to an anneal in atmosphere or forming gas. This can easily deplete BiSCCO of its oxygen content, and decrease the critical temperature or remove superconductivity completely. As such, even when working in an inert atmosphere, these techniques should be avoided. When exfoliating VDWH materials a common technique is to press down on the tape deposited onto the Si/SiO₂ substrate with a pair of carbon tipped tweezers. BiSCCO is a ceramic material and its flakes are structurally weaker than graphite or h-BN, as such one should avoid touching the substrate with hard objects, even carbon tipped tweezers.
An important step in preparing a Si/SiO₂ substrate is the solvent cleaning. Having a clean substrate is imperative in producing repeatable processes. In addition, different cleaning processes can have an effect on both how difficult it is to pick up the exfoliated material and also how large the yield is. An early test that we performed was experimenting with different substrate cleaning processes and optically determining which had larger yields for BiSCCO. We also tested to see how each cleaning process affected BiSCCO’s ability to be transferred, both via a PC transfer slide and via another VDWH material.

Three different processes to clean the SiO₂ substrates were used:

1. **Hydrofluoric Acid + Piranha (Nano-Strip™)**
   1.1. Sonicate wafer in Acetone for 5 min at highest power setting, then blow-dry
   1.2. Sonicate wafer in IPA for 5 min at highest power setting, then blow-dry
   1.3. Place wafer in 50mL of Nano-Strip™ for 15 min
   1.4. Place wafer in 10mL of Hydrofluoric acid mixed with 100mL of water for 15 seconds
   1.5. Rinse in DI water for 3 min

2. **Piranha (Nano-Strip™)**
   2.1. Repeat steps 1.1 - 1.3
   2.2. Repeat step 1.5

3. **O₂ plasma**
   3.1. Repeat steps 1.1 - 1.2
   3.2. Place wafer in an Asher (Oxygen plasma tool) with an RF set point of 150W for 1 min

The substrates in figures 2-4 were drawn from a 4th generation BiSCCO tape, each of which with approximately the same density of crystals per unit area. This made it appropriate to compare the yield across variously prepared substrates. This comparison process was repeated
three times, each with the same result. Wafers prepped with O$_2$ plasma had a much larger yield of thinner flakes per square centimeter. A disadvantage of using O$_2$ plasma as a cleaning step is that even without using a hot plate to increase flake yield a large amount of glue left over from the tape is deposited onto the substrate. However, this is an issue of minimal importance because flakes still tended to have large clean and usable areas. The conclusion is that preparing a substrate cleaned with O$_2$ plasma is ideal for finding large area thin BiSCCO flakes.
Subsection 2:
Transferring Flake BiSCCO

Figure 6: Graphical Description of Transferring a Flake with a PC Slide - The Van der Waals attraction between the flake and the heated PC is greater than that between the flake and the substrate allowing the PC slide to pick up the flake, as can be seen in frames G-L - Image Credit [12]

Besides preparing flakes with mechanical exfoliation, the other key technique in creating VDWHs is the use of a PC slide to transfer flakes to and from substrates. Fabricating VDWHs, as previously discussed, involves stacking layers of 2-D materials much like a child stacks legos (see figure 1 on p. 3). However, in order to actually stack these atomically thin layers on top of each other, the wet pick-up technique was developed.
The wet pick-up technique relies on the fact that flakes tend to stick more strongly to heated PC than to an Si/SiO₂ substrate. Van der Waals forces between different VDWH materials are also incredibly strong and can sometimes overcome the Van der Waals force between a flake and its substrate. This way, as in figure-6 frames J-L, an already picked up flake can be used to pick up an additional flake, thus creating a stack. This process can be repeated, creating stacks of arbitrary height. Ultimately the PC, with the VDWH stack is deposited onto a substrate (also Si/SiO₂). Chloroform is then used to dissolve the PC, leaving the VDWH stack clean and unaffected.

Figure-7: Graphical Description of PC slide fabrication - A thin layer of PC draped over a piece of PDMS, secured down with a piece of tape, forms the basis of a traditional transfer slide used to pick up VDWH materials
There are a wide variety of variations on the wet-transfer technique that are used to pick up VDWH materials. We will only describe the one that we found works for picking up flake BiSCCO. For picking up flake BiSCCO the correct type of PC to use is PPC dissolved in 6% chloroform. This type of PC evaporates very quickly, consequently one cannot create the thin layer of PC used to put on top of the polydimethylsiloxane (PDMS) with a resist spinner. Instead, one has to place a droplet of the PC dissolved in 6% chloroform onto a glass slide. After using a small amount of force to depress the liquid between two glass slides one must rapidly pull the glass slides apart to create the thin layer of PC (these steps can be seen in figure-7 frames 1-2). Afterwards, it is necessary to wait 10 minutes, allowing the chloroform to evaporate, before using the PC.

The next step in the process is to cut off a small chunk (~ 4 x 4 x 1 mm) of PDMS to place onto the glass slide. Making high quality transfer slides is dependent on having a clean PDMS surface. Having particulates lying on the surface causes bubbles once the PC has been transferred onto the PDMS. These bubbles are often the cause of de-lamination of the PC from the PDMS during the flake transfer process. Furthermore, it is difficult to use transfer slides that have bubbles in them in an inert atmosphere glove box. Transfer slides with bubbles do not survive the process of pumping down to vacuum before being introduced into the inert atmosphere. The damage this process does can be mitigated by poking a small hole in the side of the PC, but this is unfavorable.

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1 If you are working in a dry atmosphere it’s helpful to place the PC covered glass slides in a humid environment to facilitate ease of removal from the glass slides.
Getting a clean PDMS surface is a function of trial and error, but there are a couple of techniques that are useful in increasing the yield of small pieces of clean PDMS\(^2\). Typically, PDMS is synthesized by the reaction of the two compounds n-dimethyldichlorosilane and water; this reaction in the correct proportions is typically done in a petri-dish, and used to grow a uniform layer about 1mm thick. Instead of attempting to cut out pieces of PDMS directly from the petri-dish, cutting out larger pieces (~ 3 cm x 3 cm x 1mm) and cutting the smaller pieces from them allows for cleaner bits of PDMS. The surface of the larger bits of PDMS can be cleaned with isopropyl alcohol (IPA) and blow dried clean. Additionally, using a new razor blade pre-cleaned by sonicating in IPA for 5 minutes can help achieve cleaner PDMS surfaces. The most important tip for achieving clean PDMS surfaces is to always use the side of the razor blade to

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\(^2\) It’s good to clean the glass slide with IPA as well, but it’s not imperative since it will not affect PC de-lamination.
transport the PDMS from one place to another, do not use tweezers (unless transporting the 3cm x 3cm x 1mm chunk from the petri-dish to the glass slide). Any place that tweezers touch on the PDMS is unusable.

Moving forward, once the PDMS has been deposited onto the target glass slide it is necessary to transfer the PC onto the PDMS. This is done by taking a piece of tape, and punching a hole through it and placing it on top of a clean piece of PC (as can be seen in figure-7 frame 4). Using a razor blade one must cut the PC on the sides of the deposited tape, then using a pair of tweezers the piece of tape can be removed and the PC comes with it. On the glass slide side, a piece of double sided tape with a hole punched through it is placed down on the glass slide, with the PDMS poking through the hole. The tape with the PC on it is then deposited onto the glass slide such that the exposed PC (the PC not touching the tape) is draped over the PDMS. The double sided tape holds down the PC, and this completes the transfer slide fabrication process.

The actual process of transferring a flake is rather simple. The PC transfer slide is placed on a micro-manipulator with three axis control (as seen in figure-8). A microscope is focused on the transfer slide and the substrate with the flake to be picked up. Since both the PDMS and the PC are transparent, the target flake can be seen throughout the transfer process.

The transfer recipe for picking up flake BiSCCO is as follows: engage the PC close to the flake to be transferred. Keep the PC static while simultaneously raising the temperature of the substrate in increments of 5°C all the way up to 100°C. Wait at 100°C for 10 minutes, then

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3 Additional fabrication steps of using UV-Ozone or O2 plasma to clean the glass slide or the PDMS can increase how well the PDMS sticks to the glass slide, and how well the PC sticks to the glass slide.
Figure-9: 5x Image of BiSCCO flake deposited onto Ag contacts. As is mentioned previously, since the BiSCCO transfer process only has one step, when deposited onto the substrate after being picked up, the PC is heated to 180°C and then mechanically detached from the transfer slide.

Figure-10: 100x Image of Transferred BiSCCO Flake

Figure-11: Nearly Engaged BiSCCO Flake

Figure-12: Fully Engaged BiSCCO Flake

cool down in increments of 5°C until the substrate is at 40°C. At this point the flake should have been picked up and the PC fully disengaged, and it is safe to remove the transfer slide.
mechanically. With this technique we were able to pick up a thin piece of BiSCCO (~5nm) and place it onto a pair of Ag contacts (see figure-10).

Following up on transferring flake BiSCCO, we attempted to determine whether or not it could be picked up by another VDWH material. Specifically graphite or h-BN. We learned that neither h-BN nor graphite were able to pick up flake BiSCCO. Multiple attempts were made at modifying the transfer process described above. Transfers with both h-BN and graphite were attempted at temperatures up to 140°C in increments of 10°C. For each of these temperature levels, a wait time of up to 30 minutes was tested in increments of 5 minutes, starting at 10 minutes. Naturally, multiple types of flakes were also used. Unfortunately, no transfer recipe was able to successfully pick up BiSCCO using graphite or h-BN.

![Image of BiSCCO on GaAs](image.png)

Figure-13: 100x Image of BiSCCO on GaAs - Flake contrast is reduced on GaAs making it difficult to optically identify thin flakes.

The hypothesis generated was that the Van der Waals interaction between the BiSCCO and the oxide substrate was too strong for the VDWH materials to overcome. So we thought that perhaps using GaAS with no oxide layer would have a weaker Van der Waals attraction than an
oxide layer. The same tests were attempted on a GaAs substrate, but this was also a failure. BiSCCO could not be picked up even on GaAs with h-BN or graphite. This was probably for the best, since even if we could pick up BiSCCO with h-BN or graphite when BiSCCO was deposited on to GaAs, the contrast was reduced and it was difficult to optically determine flake thickness.

Figure-14: On the right this is a 100x image of a thin h-BN flake that was used to try and pick up the BiSCCO flake on the right. Multiple final temperatures and wait times, going up to 140°C for 30min, were used to try and pick up the flake BiSCCO, but none were successful.

Figure-15: On the right this is a 100x image of a thin graphite flake that was used to try and pick up the BiSCCO flake on the right. Multiple final temperatures and wait times, going up to 140°C for 30min, were used to try and pick up the flake BiSCCO, but none were successful.
Not being able to pickup BiSCCO with other VDWH materials extended the device fabrication process for flake BiSCCO based VDWHs. For example, if we wanted to use h-BN as a dielectric in a capacitance device, it would require two dissolution steps in chloroform. This was not ideal because the addition of more solvent steps degrades the quality of a device.

In conclusion for this section, it was shown that using the traditional PC transfer slides, BiSCCO can be picked up and transferred much like any other VDWH material. However, unlike other VDWH materials, the standard tool-box is not full. BiSCCO cannot be picked up with other VDWH materials like graphite or h-BN. This limits device topology and increases fabrication steps. However, this is okay because as we will learn in the following sections, the best fabrication technique to use for BiSCCO, which avoids solvents, removes this device topology limitation.

After learning what types of transfers were and weren’t allowed when working with flake BiSCCO under the umbrella of traditional VDWH techniques we attempted to fabricate a simple four terminal transport device using these techniques. We knew from previous literature reviews that BiSCCO was air sensitive, but we underestimated the time scale at which the flake degradation took place. We thought that by putting a protective graphite layer on top of the device, we might be able to protect the device from slow environmental damage. However, after testing the device, and not seeing superconductivity or any interesting signature other than the canonical resistance vs. temperature curve of flake graphite, we knew that some element of our fabrication process was ruining the integrity of the BiSCCO flake. So we had to go back to the drawing board and utilize non-traditional VDWH techniques in order to improve the fabrication process and make a successful device.
Figure-16: BiSCCO Transport Device - This device was fabricated using the traditional set of VDWH techniques. We were aware that BiSCCO was air sensitive, so we attempted to protect it from environmental degradation by placing a thin-graphite cover on top. To zeroth order the BiSCCO and the graphite act as if they are resistors in parallel, and we still expect to see a superconducting dip. However, no features were seen and contact between the lead connecting the pure BiSCCO and any of the leads touching the graphite flake exhibited MOhm two points resistance. This indicated an error in our fabrication process that needed to be corrected in order to make a measurable device.
Chapter 2:
Testing BiSCCO for Bulk Superconductivity

This chapter will be briefly dedicated to describing how to determine if BiSCCO is superconducting in bulk. Knowing that superconductivity could not be seen in devices made by traditional VDWH techniques, we figured before attempting to achieve superconductivity in flake BiSCCO we sought to confirm whether or not it still existed in the bulk crystals grown for us, and that the $T_c$ was consistent with the doping level listed by the crystal grower. As mentioned previously, the crystals that we worked with were grown by Dr. Genda Gu and her group at the Brookhaven National Laboratory as optimally doped BiSCCO 2212. Professor Raymond Ashoori's group had these crystals for over a year before we started our project, so it was possible that the doping may have changed over time. For an optimally doped sample, an expected $T_c$ would be 95K, however in bulk we observed a $T_c$ of 90K, a slight depression from the expected value. However, this is to be expected because over time oxygen from the sample is depleted effectively reducing $T_c$.

To fabricate the bulk conductivity test device, a macroscopic BiSCCO 2212 was cleaved and placed onto GaAs substrate with Au contacts patterned with photolithography and deposited via electron-beam deposition. The BiSCCO crystal was adhered manually to the Au contacts via silver epoxy, then wire bonded to a DIP socket. It is well known that BiSCCO forms a thin resistive layer [14] when exposed to water or atmospheric moisture. However, it is thought that the epoxy etches past the resistive layer, and makes direct contact to the CuO$_2$ planes [15], thus
making a good low resistance contact to the superconductor. The temperature measurement was taken in a liquid He⁴ cryostat. As shown in figure-18, this gave a sharp transition at a $T_c$ of roughly 90K.

Figure-18: Bulk BiSCCO Resistance Vs. Temperature Plot - The transition temperature happens at 90K, a slight depression from optimal doping. This was good to confirm since we at least know that any affects that were obscuring superconductivity were not originating in the bulk but were coming from some element of our fabrication process.
Chapter 3:
In Situ Ar-Ion Mill With E-Beam Deposition

To attempt and make low-resistance contact to flake BiSCCO we first started by adopting sputtering techniques developed for thin-film temperature superconductors (HTS). As discussed in [16, 17] a common technique to make contact to thin-film HTS is to etch down into the surface such that any metal contact forms a clean bond to the bulk of the superconductor. In this chapter we will discuss our attempts at trying to make contact to thick flake BiSCCO (greater than 50nm) by adopting this technique and using an Ar-ion Mill in situ with an electron beam deposition chamber. Ultimately this was the first test performed deviating from the standard VDWH fabrication techniques. We learned that using the Ar-ion mill to sputter the flake surface was not the new methodology needed to make good contact, the contacts were all highly resistive. However, this was surprising, but thinking carefully about why this was true, in fact lead to the key realization that allowed us to make low-resistance contact to flake BiSCCO.

Before trying to fabricate a full capacitance device it was important to establish whether or not it was possible to make a pure transport device, which would allow us to determine whether or not it was possible to see superconductivity in thin BiSCCO. This lent itself to a simple four-probe device structure as can be seen in figures-19 and 20. A four terminal measurement, using the outer two leads as a current source and the inner two leads as a voltage probe allows for measurement of the flake’s resistance without also measuring the contact resistance. This type of measurement setup is critical because in-plane resistance [18] of
BiSCCO thin-films is incredibly low: it can be several orders of magnitude lower than the contact resistance, even for low resistance contacts.

The first step in making an Ar-ion mill contact device was to make a pattern. Contacts were designed by first using an electron-beam lithograph to draw alignment markers near the flake. The sample with the alignment markers is then developed. Once the alignment makers are made, using microscope pictures and computer aided drawing software like KLayout a pattern can be precisely aligned to a flake. Going back to the lithograph, an aligned write is performed and the contacts are written. The sample with the contact pattern is then developed. After this is done, the sample is brought to an electron-beam deposition chamber with an in situ Ar-ion mill. The sample is then etched with a recipe calibrated to etch 10nm into the flake, using the PMMA as a mask. This process leaves the areas exposed via the electron beam lithograph etched through and the other areas untouched. Then while the sample is still under vacuum, such that no chemical reaction can occur to degrade the surface of the BiSCCO, 15 nm of Au is
deposited on top of 10nm of Ag as a capping layer. We chose Ag as the contact metal because Ag was the canonical metal used to make contact to BiSCCO tapes [19].

An important note to make before describing the details of the fabrication parameters is the use of Ag. The very first device we attempted to use the Ar-ion mill technique on we solely deposited 25nm of Ag. However, it was discovered that thin Ag contacts oxidize incredibly quickly (full oxidization occurs within a day) and become fully resistive, see figure-21. The solution to this problem was to deposit 10nm of Ag and then a 15nm capping layer of Au, which does not oxidize. This was successful, at least, in preventing the Ag from oxidizing, while still allowing for a Ag contact to the BiSCCO. An example of such a device can be seen in figures 19 and 20.

Each device was patterned using electron beam lithographic techniques. To do this a stack of negative PMMA resist (dissolved in anisole) is first spun onto the substrate. For the Ar-
ion mill devices the recipe that we used was a three layer stack: 2 layers of A11 PMMA and 1 layer of A4 PMMA (ordered from first spun on to last spun on). Each layer is spun at 4000 rpm for 45 seconds, resulting in a resist thickness of 750nm for A11 and 180nm for A4. A baking step is performed after each spin on a hot plate at 180°C for 2 minutes. The reason for the multiple resist stack is to aid in lift-off after depositing metal contacts. Stacking the PMMA in this manner results in a slight over-hang after development for 90 seconds in 1:3 MIBK:IPA (as seen in figure-22)

Figure-22: PMMA Stack - Stacking layers of PMMA of varying densities creates over hang upon development. This aids in liftoff by preventing the deposited metal from crawling up the sides

Differences in density between A11 and A4 PMMA cause more or less electron scattering in the material. A11 being the denser of the two ends up with more exposed area than the A11 due to increased amount of electron scattering. Having the overhang prevents deposited metal from creeping up the the sides of the PMMA, and eases lift-off. Liftoff is the process of removing the resist after the metal is deposited, leaving only metal in the exposed areas.
The electron beam lithograph itself that is used for the Ar-ion mill is the Raith 150.
Writes are performed with a dose of 400\textmu C/cm$^2$, with a beam current of 1nA. The column is set to a 30KeV acceleration potential, the aperture is set to 60um, and the step size is set to 20nm. Writes with contact pads that are 150um x 150um usually take about an hour. A faster tool like the Elionix may be able to complete the write in a much faster time.

When depositing metal contacts onto the flake the device was brought into an electron beam deposition chamber. The chamber was pumped down to less than 1E-6 Torr. The in-situ Ar-ion mill was run at a 200V accelerating voltage and 46mA of beam current. For the machine that we used in MIT’s Experimental Materials Laboratory, the calculated beam current density is 0.75mA/cm$^2$. The etch time that seemed to work the best was 10 seconds. This was determined optically (see figure-23). The etch parameters were varied continuously until a satisfactory etch
was achieved\textsuperscript{4}. From figure-22 it is optically clear that the parts that were protected by PMMA are thicker than those that were exposed, but not so much so that the flake was etched entirely through.

After milling to strip away the resistive outer layer, 10nm of Ag was deposited below 15nm of Au. Each material was deposited at a rate of 1Å/s to ensure smooth thin layers of each material. Again, the electron beam deposition was performed in situ with the Ar-ion mill such that no chemistry could occur to re-insulate the flake surface. Three devices in total were fabricated with this technique (as shown below in figures 24-26)\textsuperscript{5}. For each device the two terminal resistance was measured between each lead, and for each device fabricated with the ion mill, the 2-point resistance (which was dominated by contact resistance) was on the order of MOhm. This was rather puzzling, knowing that the flake was being etched and that the contacts were being deposited in-situ: this in theory should have worked. After doing some literature review in [16], we hypothesized that perhaps the Ag ions were not migrating into the CuO\textsubscript{2} planes.

As reference [16] suggests, we saw that for thin film HTS, annealing the sample in oxygen can cause the Ag to migrate deeper into the sample and make stronger contact to the CuO\textsubscript{2} planes. We attempted to take the previous three samples and anneal them in a tube furnace. The anneal was performed at 400°C for 15 minutes. The temperature ramp was done in N\textsubscript{2} at 8.5 SPCM, then at 400°C, O\textsubscript{2} was turned on at 2 SPCM and the N\textsubscript{2} flow rate was reduced to 0

\textsuperscript{4} One will notice that there is a spotted pattern on many of the Ar-ion mill devices. We hypothesized some Ar-ions had a large amount of kinetic energy due to the etch being performed at a finite temperature. These ions moved through the PMMA entirely and etched slightly into the flake.

\textsuperscript{5} After deposition, the PMMA is removed in a lift-off process via dissolution for 10 min in acetone
Figure-24: Devices 1-3 (upper left, upper right, bottom respectively) fabricated using the Ar-ion mill sputter technique. Small amounts of degradation can be seen by excessively energetic ions penetrating through the PMMA mask, but for the most part the flakes are clean and in theory should have produced conducting devices.

SPCM. This resulted in degraded flakes and contacts and no decrease in contact resistivity, as can be seen in figure-26.

One hypothesis was that since the contacts were a layered stack of Ag and Au, that the difference in the diffusion rate of each metal into the BiSCCO was causing the granularity in the contacts. Consequently we repeated the Ar-ion mill process but with purely Au contacts. This was successful in getting rid of the granular contacts, but the 2-point contact resistances were still on the order of MOhms (see figure-27).
Figure-25: Contact Resistivity of thin-film YBCO as a Function of Oxygen Annealing; this data was used to help us determine the initial anneal recipe for BiSCCO flakes- Image Credit [16]

An important note to make at this point is if we look at [21] we can see that for the size of our flake even in BiSCCO’s insulating phase (under-doped regime), the resistance of the flake should be nowhere near 1MOhm. At room temperature the resistivity for under-doped BiSCCO

Figure-26: Mixed Ag/Au Contact Ar-ion Mill Devices after Oxygen Annealing.- Metals diffused into the BiSCCO at different rates resulting in poor contact quality.
is 200μΩ-cm. Given a gratuitous order of magnitude estimate, assuming the flake width and length are on the order of 10μm, and the flake thickness is on the order of 10nm the total flake resistance is calculated to be on the order of 20kΩms. This is two orders of magnitude less than a 1MΩhm. Consequently, there were two conclusions we could draw: one the BiSCCO itself has been chemically modified beyond oxygen doping and has become strongly insulating, and two the surface chemistry has been affected and it is purely the interfacial contact between the Au

Figure-27: Various Ar-Ion Mill Devices Prepared With Purely Au Contacts and Oxygen Annealed - The contact quality problem was solved but no improvement in room temperature conductivity was found.
and the flake that is the cause of the large resistance we see. This sanity check allowed us to rule out the option that we were in fact making good contact, but we were measuring BiSCCO in an insulating regime, allowing us to focus our efforts on revising our fabrication process.

In conclusion for this section, although ion-milling seemed like a promising technique, ported over from thin-film HTS, to achieve low resistance contacts, it did not produce any improvement over traditional VDWH techniques. We were puzzled, by sputtering the flake in a vacuum before depositing metal, no chemistry should have been allowed to occur. However, after some careful thought, we realized that there may be some source of water somewhere causing the flake to degrade as we performed our process. The most likely candidate for where this water may have come from was water trapped on the surface of the Si/SiO₂ substrate. We also realized that it was possible the solvent steps in our process were aiding in the flake degradation. The next chapter details the experiments we performed and the literature we reviewed to narrow down the cause of the flake BiSCCO’s degradation.
Chapter 4:
Mechanism for High Resistance Contacts in Flake BiSCCO

After ion-milling proved to be an ineffective means of making low-resistance contact to BiSCCO we moved our efforts elsewhere. After some thought, it occurred to us that earlier solvent processes may destroy BiSCCO’s ability to make contact to any metal. We thought that this may be the case because, as you can see in figure-30, certain flakes after processing seemed to have degradation on the edges\(^6\). After sequential exposure to multiple solvents and other compounds used in our fabrication processes the BiSCCO flakes did not show any optical signs of degradation (see appendix at the end of this chapter). Not having any further indication as to what the key mechanism behind the loss in surface conductivity was, we delved into old literature on BiSCCO.

\[\text{Figure-28: BiSCCO flake pre-processing(left) and post-processing (right) - we thought that the slight degradation seen optically on the edges of the flake may be caused by solvents as opposed to ion milling, however this turned out not to be the case.}\]

\(^6\) It is true that the flake listed in figure-28 is an Ar-ion mill device but the degradation on the edges of the flake seemed inconsistent with the ion-mill degradation patterns seen more towards the center of affected flakes. This lead us to test multiple solvents to see if this degradation pattern could be repeated.
Looking at [23], even in 1988 it was known that water can degrade superconductivity in thin-film BiSCCO. This was one of the first experiments performed on BiSCCO when the material was first discovered because other CuO2 based HTS like YBCO were known to be extremely water sensitive. Moreover, other organic solvents, depending on their polarity can degrade BiSCCO as well [27]. [23] reported a large degradation in superconductivity in exposure to water for time scales as small as an hour. Considering flakes are much thinner than the thin films worked with in [23], we assumed that the loss in conductivity could have a more rapid onset in our samples.

Since we learned that water was the most damaging solvent to BiSCCO due to its highly polar nature, we hypothesized that moisture trapped on the SiO2 substrate was interacting with the BiSCCO flake and modifying the flake’s chemistry during the fabrication processes, changing the material into a full insulator. In addition, the numerous solvent steps in our processes were also contributing to the degradation of our samples. Looking at [26], we see that a study of water vapor effects on the surface layer of BiSCCO show that the insulating layer can penetrate up to 10s of nanometers. On non-flake scales this is hardly consequential, but since our flakes, even the thick ones are on the order of 10s of nm it is to be expected that exposure to water can degrade the entire flake, which explains why Ar-ion milling did not provide conductive samples.

This lends itself to a fundamental problem: even if one could work with BiSCCO in a completely inert atmosphere, free from exposure to water (in the atmosphere and on the substrate), the application of all standard VDWH techniques utilize solvents in their fabrication
processes. In order to solve this problem an entirely new technique needed to be developed in order to work with VDWH materials without any solvent steps. The following chapters will introduce the various techniques we employed to solve this problem, and ultimately make a true low-resistance contact to BiSCCO.

**Flake Degradation Test Results:**

In the following experiment, we took three different BiSCCO flakes and exposed them to a series of different solvents, attempting to see if extended exposure optically degraded the flake. The list of solvents that were used, from first to last (also in order of solvent strength), were: IPA, Acetone, TCE, MIBK, Water, and then after the solvents the PMMA11 was spun onto the flake and then dissolved in acetone.

**Flakes Pre-Solvents:**
Flakes Post-IPA:

Flakes Post-Acetone:
Flakes Post-TCE:

Flakes Post-MIBK:
Flakes Post-Water:

Flakes Post-PMMA A11:
Chapter 5: 
Solvent-Free Transfer Techniques

As we discussed in the previous chapter polar solvents degrade BiSCCO flakes and convert the BiSCCO into a strong insulator. Attempting to fabricate BiSCCO based VDHW with traditional techniques would be impossible. To solve this problem based on the work in [28], we developed a “dry” transfer technique for flake BiSCCO that involves no solvents and no wet chemistry. This technique involves using the viscoelastic material, GelPak®, on top of a block of PDMS, to create a new type of transfer slide. In this technique, the VDWH material is exfoliated directly to the GelPak®, then the material is deposited directly onto a desired substrate. By changing the engage or disengage speed of the transfer slide, the consistency of the viscoelastic material changes and allows for easy transfer of flakes. The rest of this chapter will be dedicated to describing the various fabrication techniques associated with GelPak® based transfers.

The first step in fabricating a GelPak® transfer slide is to exfoliate the material onto the GelPak®. For our devices we use GelPak® PF-Film. Using a pair of IPA cleaned scissors we cut a substrate sized (3cm x 3cm) piece of film. The PF-Film comes in three layers as can be seen in figure-29. The material that receives the exfoliated material is the Gel material. The other

![Figure-29: GelPak® PF-Film Layer Chart - Image Credit [29]](image-url)
two sheets are protective layers that cover the Gel material. The clear polyester substrate is an inflexible plastic sheet and the polyethylene coversheet is a thin flexible plastic layer that protects the top of the Gel material. To exfoliate the VDWH material onto the GelPak®, the Gel Material is removed from the clear polyester substrate and placed onto the end of a clean glass slide. Afterwards the polyethylene cover sheet is then removed so that a tape of VDWH material prepared by mechanical exfoliation can be deposited onto the Gel material (see figure-30). Once removed, the Gel material then has VDWH material on it and flakes can be found optically through a microscope (see figure-31).

![Figure-30: Graphical Representation of Exfoliation on GelPak®](image)

![Figure-31: BiSCCO Flake on GelPak® Film Under Microscope (right), and the same flake transferred onto Au Contact on an Si/SiO2 substrate (left)](image)
The next step, once the VDWH material has been exfoliated onto the GelPak© is to cut
the GelPak© into several small (3mm x 3mm) pieces using a pre-cleaned (sonicated for 5 min in
IPA) razor blade. Once the GelPak© has been cut one can use a microscope to optically search
for the flakes to be transferred. After the flakes have been found the 3mm x 3mm piece of Gel
material is transferred using a pair of fine metal tweezers onto a piece of PDMS (approximately
the same size as the Gel material) adhered to a glass slide. This completes the fabrication of a
GelPak© based transfer slide (see figure-34). An interesting note to make here is that it is
possible to use GelPaks© themselves as exfoliation tape. In this vein, two GelPaks© with crystals
on them can be pulled apart to create two new GelPaks© with VDWH material on them, exactly

![Figure-32: Graphical Description of Preparing a GelPak© Based Transfer Slide](image)

Figure-32: Graphical Description of Preparing a GelPak© Based Transfer Slide

mirroring the scotch tape method. Pulling the GelPaks© apart should be done rapidly to keep the
Gel film rigid, encouraging flakes to cleave in the c-axis. If this technique is used, then the step
where the exfoliation tape is pressed onto the GelPak© can be skipped.

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7 In discussing transfer techniques earlier in chapter 1 of section 2 an optional step was to clean the glass slide of
UV-Ozone or oxygen plasma. For the GelPak© transfer slides this step is recommended because there is no tape to
keep the PDMS attached to the glass slide, so cleaning the glass slide in UV-Ozone for 60 seconds can greatly
increase how well the PDMS adheres to the glass.
Before discussing how to physically perform a transfer with a GelPak® transfer slide, it is important to note a key advantage of the dry transfer technique beyond the fact that the transfers are solvent free. Exfoliating the material and making the transfer slide become one step in this process. The implication of this is that if the requirements of the transferred flake for the desired device are not stringent, the time between first exposure to air and transfer of a flake to a substrate is minimized. The average transfer time that we would spend making devices with BiSCCO, if not performed in inert atmosphere, would be 30 minutes. This time includes exfoliation, flake finding, and transfer onto a substrate. The technique is incredibly fast. This was extremely helpful for working with BiSCCO and even allowed us to make low-resistance contacts to the material while working in air, as opposed to an inert atmosphere like Argon. Naturally this process can be slowed down and the requirements for flake quality can be increased. However, if this is the case, one should perform the fabrication steps in an inert atmosphere, like Argon.

Figure-33: GelPak® Based Transfer of BiSCCO Flake — Movie of Transfer at: https://youtu.be/ZiTDfdBdiM
Performing a transfer with a GelPak© transfer slide is easy and requires very little change from the standard VDWH transfer techniques. Aligning the flake to be transferred to a substrate or to a pre-existing stack follows in the same manner. An important difference is that GelPak© transfer slides cannot pick up VDWH materials, but since there is no PC involved, any stack topology can be achieved with minimal fabrication effort. By simply exfoliating each layer onto a different sheet of Gel film any stack can be created by simply preforming GelPak© transfers in the stack order from bottom to top.

The key point in a GelPak© transfer is that since the stamp is viscoelastic, the material becomes softer when its shear velocity is low, and rigid when its shear velocity is high. So both engaging and disengaging the flake should be done slowly; this combined with doing the entire transfer at high temperatures (greater than 100°C) makes the Gel material liquid like and creates very flat transfers with minimal bubbles. If the GelPak© were to remain rigid, the transfer at worst would damage the flake, and at best the flake would fail to adhere since all of its area would not be in contact with the substrate. Since the GelPak© is made completely dry with no wet chemistry transfer temperatures can easily and safely exceed 180°C if needed. Furthermore, the transfer can start at any temperature without degradation of the Gel material. This proved to be a huge advantage in making low-resistance contact to the BiSCCO as will be discussed in the next chapter. Transfer speeds should be on the order of 5μm/min, as is seen in the video posted above in figure-33.

This concludes the chapter on how to make GelPak© transfer slides, and how to do physical transfers with them. We learned that the GelPak© transfer slides have many advantages over the traditional PC based transfer slides. These include the ability to do transfers with no
solvents, to do transfers at extremely high temperatures, to start a transfer at any temperature, the
ability to make very flat interfaces, and the ability to make a full scale BiSCCO transport device
in under 30 minutes, excluding preparation time (from exfoliation to transfer). These advantages
are great and are what allowed us to make low-resistance contacts to BiSCCO. However, there
is one major draw back to the GelPak based transfers that should be mentioned before moving
on.

Substrates are studied in great detail [30] to determine whether or not their optical
properties allow one to see thin flakes. Gel film is not very reflective and does not have the same
property as Si with a 285nm or 90nm oxide layer, thus it is much harder to see thin flakes.
Finding thin graphite or h-BN on a GelPak is very difficult. The contrast can be improved
slightly by depositing 10nm of aluminum onto a glass slide before searching for flakes on the
GelPak. A contrast of thin graphite transferred onto a piece of BiSCCO as compared to the

![Figure-34: Thin Graphite on GelPak (left), and the Same Graphite Transferred onto a Piece of BiSCCO on an Si/SiO2 (285nm) Substrate: As can be seen the contrast of a piece of graphite on a GelPak almost looks like how graphene would look on an Si/SiO2 substrate, this makes finding thinner flakes difficult.](image-url)
same flake on a GelPak®, can be seen in figure-34. However, although this may be a disadvantage of the GelPak® transfers, since even unit cell thick BiSCCO is relatively thick compared to graphene or h-BN, the reduced contrast was not an issue for our device fabrication.
Chapter 6: Making Low Resistance Contact to Flake BiSCCO

After figuring out how to perform completely solvent free transfers with GelPak® based transfer slides, we were able to fabricate low-resistance contacts to flake BiSCCO. This chapter is dedicated to elaborating on the additional steps needed to fully fabricate these devices. These devices were made by transferring BiSCCO flakes, using GelPak® transfer slides, onto pre-deposited Au transport pads defined via photolithography. The transport pads are baked at 180°C on a hot plate for 45 minutes in air before moving them to a VDWH transfer setup also sitting at 180°C. While the transport pads are left on the transfer setup, BiSCCO flakes are exfoliated onto a GelPak® transfer slide. The transport pads are then cooled down to 110°C, and the transfer is performed between 110°C and 160°C. This way during the entire transfer process the transport pads are kept at a temperature higher than the boiling point of water [32, 32]. Reducing the amount of moisture on the SiO₂ surface prevents the BiSCCO flake from degrading upon contact with the transport pads. Furthermore, since the device is completely ready to measure after the transfer, the flake itself is never exposed to any solvents before being placed in He⁴ for measurement.

The Au transport pads were made with a photolithographic image reversal process. We used a highly resistive (not-doped) Si substrate with a 285nm oxide with a layer of AZ5214 photo resist spun on at 4000 rpm for 45 seconds. The resist is pre-baked at 95°C for two minutes. This bake is to clean off any excess solvents present on the photoresist. A chromium mask is used to define the transport pads. The photoresist is exposed for 3 seconds under the
chromium mask. A reversal bake is then performed at $95^\circ C$ for two minutes. After the reversal bake the sample is then flood exposed (no mask) under UV for 43 seconds. This process defines all of the unexposed areas protected by the mask as the areas to be dissolved out by the developer. The develop is performed with AZ 422 for 3.5 minutes. The result can then be directly placed in the electron beam deposition chamber to deposit 5nm of Ti and 80nm of Au. The resulting pattern that we used can be seen in figure-36. A nice feature of the photolithographic pads over those defined by electron beam lithography is that many pads can be created in one exposure. Thus, many devices could be fabricated and tested rapidly.

Figure-35: Metalized Photolithographic Pattern for Transport Pads - The mask was repurposed from an old project so the leads had to be scratched to disconnect them.

In addition to heating the transport pads prior to transferring the BiSCCO flake onto them to get rid of residual water on their surface, the whole transfer can be performed above the

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This process was performed in a lab with 70% humidity. The reversal bake temperatures for labs with humidities kept at 10% is $115^\circ C$. 

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boiling point of water. Again, utilizing the GelPak\textsuperscript{®} transfer technique, being able to start the transfer at any temperature without cooling down below 100°C allows for extremely clean and water free transfers. Most transfers done on the photolithographic transport pads were done in air, the exfoliation and transfer were just done rapidly, in less than 30 minutes on average.

A natural question that we asked was once we were able to establish a low resistance contact was: is there a time limit on how long the contact remains conductive? So with the device in figure-36 after we made contact we were able to measure the room temperature resistance as a function of time in air. Two terminal resistance was measured between every pair of leads on this device, and the average resistance across all the leads was 34.33kΩ. This average resistance remained constant for up to an hour, after which we stopped measuring.

Figure-36: Flake BiSCCO Transferred onto Transport Pads - Maintaining low contact resistance over several days further indicated to us that the mechanism causing the high resistance contacts had to do with excess water on the substrate.
device in figure-36 was placed into He\textsuperscript{4} after an hour to take transport data. Other devices that were fabricated were found to maintain their contact resistance over several days exposed to air.

Two point resistances between contact pads were as low as a 1kΩ for some devices, like the one in figure-37\textsuperscript{9}. The samples in figures 36 and 37 are very thick flakes. Ignoring the possibility that the flakes were oxygen depleted, as mentioned in chapter 1, it is not known whether or not superconductivity persists in extremely thin BiSCCO samples. We wanted to be sure that if the flake was not in the under doped phase, that the flake would be thick enough to be considered “bulk.”

Finally, having the ability to make low resistance contact to flake BiSCCO was extremely exciting for us. It meant that we were finally able to take real transport measurements and see if

\textsuperscript{9} Two point resistances were calculated on a Keithly 2400 source meter at room temperature by sourcing voltage and measuring the resulting current, and taking the ratio. We found that these contacts were incredibly voltage sensitive, running voltages higher than 10mV ended up in destroying the leads on some devices.
we could see superconductivity. However, this measurement proved to be more difficult than we initially expected. The following chapters will discuss the problems that presented themselves in our measurements and how we attempted to go about fixing them.
Chapter 7:
Micro-cracks in Flake BiSCCO and Graphite Finger Devices

Having made low-resistance contact to flake BiSCCO we went about attempting to perform transport measurements to see if we saw superconductivity. However, we noticed that many of the measurements that we took had strong features in cool down, but lost those features upon warming the sample back up (as seen in figure-38). Looking at AFM images of the measured flakes we noticed that the BiSCCO flake had micro cracks running throughout it (see figure-39). These micro-cracks are particularly large near the transport pad edges. Our thought was that the inconsistencies seen between cool down and warm up could be explained by the micro-cracks expanding and propagating during a thermal cycle, changing the fundamental current path. Oftentimes we would need to switch device leads because upon thermal cycle the

\[\text{Overall resistance changes because device leads needed to be swapped upon thermal cycle. However, the qualitative behavior is fundamentally different.}\]
Figure 39: AFM Image of BiSCCO Flake Displaying Micro-cracks Pre-Measurement -

In the image above one can see wrinkles appearing between the Au contact leads. We believe these to be micro-cracks that propagate during a thermal cycle destroying features. A device would cease to be conducting, as in one or more of the transport contacts became completely unusable.

We believed that these micro cracks were formed when the BiSCCO was transferred onto the 5nm/80nm tall stack of Ti/Au. Since the BiSCCO is draped across several microns between Au leads, which is approximately an order of magnitude greater than the thickness of the flake, the force on the flake can easily cause these types of cracks. The simple solution would be to reduce the height of the contacts. However, Au contacts need to be at least 30nm in height: any less than 30nm, and the Au tends to ball up into grains and the contact no longer conducts. Our attempt to solve this problem was to remake the transport pads using graphite fingers. This
way, the height of the contact pads would be on the order of a nm, and the force on the flake upon transfer would be reduced.

Figure-40: BiSCCO Devices with BiSCCO Fingers - These devices were designed to alleviate the micro-cracks issue, but two-terminal resistance between all device leads were on the order of MOhms. Furthermore, these devices were fabricated in an inert atmosphere so the flakes should have never been exposed to water. This indicated that graphite was acting as a semi-conductor and was forming a Schottky barrier, preventing current from flowing into the BiSCCO flake.

Figure-41: Graphite Fingers Pre Etch

The graphite finger devices were fabricated first by using an e-beam lithograph to pattern the graphite flakes (using the same recipe defined on p.35-26), see figure-43. Once the pattern is made, using the PMMA as a mask, we used an O₂ plasma etch [33] to cut through the graphite
where the PMMA was developed. We ran the O\textsubscript{2} plasma etch at 120W for 1 min, and we found that this was satisfactory to completely etch through the graphite, see figure-44. We originally attempted to make 4 or 5 terminal devices, however sometimes after dissolving the PMMA mask in acetone, leads would be completely lost. After etching through the graphite the flakes were

![Figure-42: Graphite Fingers Post E-Beam (step one) Pre Etch - Large areas were developed in addition to the thinly spaced leads to help determine if the graphite was etched since the spacing was designed to be sub optical wavelength.](image)

![Figure-43: Graphite Fingers Post Etch - One of the reasons the leads were designed to be so closely spaced was to minimize the amount the BiSCCO flake sags between the leads. This was mean to reduce stress and reduce the number of micro-cracks formed.](image)
heat cleaned for 4 hours in forming gas (H₂ at 30 scpm, and Ar at 60 scpm) at 350°C to remove excess PMMA residue. After completing the clean step another e-beam write is performed to pattern the Au contacts that attach to the graphite fingers. The Au fingers are made with a 5nm layer of Ti, and 80nm of Au. Once the Au contacts are made, the last step was to use the dry-transfer method to place a piece of BiSCCO onto the graphite fingers (see chapter 5).

Once the graphite fingers were fully fabricated, including the Au contacts, they were transferred into an Ar atmosphere glove-box. The contacts were then placed on a hot plate at 180°C for an hour, while the BiSCCO flakes were exfoliated onto a GelPak® inside of the glove-box. Not only is the GelPak® transfer performed in the glovebox, but the BiSCCO mother tape itself is made inside the glove-box. This was done so that the BiSCCO flake placed onto the graphite leads was never exposed to air. After an hour, the transport pads were moved from the hot-plate onto the transfer setup, which has been preheated to 180°C. The BiSCCO is then transferred onto the graphite fingers, and much like the previous photolithography based devices, the entire transfer is performed above the boiling point of water to make extremely clean interfaces.

Two of the final devices made in this fashion can be seen in figure-40. We found that these devices did not conduct at room temperature. Measuring two-point resistances across all leads, all devices displayed over 1MΩ of resistance. As discussed previously, since 1MΩ is much greater than the expected resistance for an insulating state of BiSCCO, ultimately we believed it was the graphite making a high resistance contact to the BiSCCO flake, via a Schottky barrier mechanism. According to [34], they were successful in making a graphite-BiSCCO tunnel junction, however this was performed in bulk. The detailed mechanism causing
the potential barrier preventing contact to the BiSCCO is difficult to discern, and not much
theory work has been done on contacting thin graphite and thin-BiSCCO.

In conclusion, we attempted to make contact to BiSCCO with graphite leads using the
same technique we developed that allowed us to make contact to Au contact pads. We did this
with the intention of using thin graphite as a means of alleviating stresses induced in the
BiSCCO when transferred onto Au contacts. In theory, since graphite acts mostly like a metal,
we figured making contact to graphite should be similar to making contact to Au. However, we
learned that this was not true and thin graphite was not able to make contact to BiSCCO,
possibly due to some type of Schottky barrier mechanism.
Chapter 8:
Graphite Cover Devices

The next and last device structure we attempted was a thin-graphite cover device, based on the devices in [35], much like the device we made in chapter 1, but with the new techniques developed in chapter 5. Inside of an Ar glove-box, we would directly deposit a piece of thin-graphite on top of a piece of BiSCCO on a Si/SiO₂ substrate. Both the BiSCCO and the graphite were transferred using the GelPak® technique detailed in chapter 5 of this section. Afterwards, the device is removed from the glove-box and four Au leads are patterned onto the device via e-beam lithography, and 5nm of Ti and 80nm of Au are deposited onto the device. This process is done with the same steps listed on p.35-36. In the same manner as the Au photolithography based devices, the substrate is heated at 180°C on a hot-plate for 1 hour, and is kept above 100°C during all transfer steps. The graphite was designed to chemically protect the BiSCCO from atmosphere when we take the sample out of the glove-box and perform the various e-beam and

Figure-44: Graphite Cover BiSCCO Transport Device Device Electrical Model
deposition steps. Furthermore, since the BiSCCO was deposited directly onto the SiO2 substrate we were able to eliminate depositing the BiSCCO flake onto Au transport pads, potentially minimizing the micro-cracks during a thermal cycle.

One obvious problem with this is that thin-graphite tends to be extremely conductive, and to a zeroth-order approximation, the graphite cover device can be considered as two resistors in parallel, see figure-44. If the graphite resistance is low compared to the resistance of the BiSCCO flake, then the percentage change in the total resistance due to percentage change in the BiSCCO are small. Percent changes in the total resistance are given by the following:

\[ \Delta R_T \sim 1 + \left( \frac{R_G}{R_B} \right) \cdot \Delta R_B \]

However, in this approximation if the BiSCCO were to go superconducting we should still see the resistance of the sample drop to zero. On the other hand, if the BiSCCO is under-doped and in the pseudo-gap phase or in the AFM insulating state, then small changes in the resistance of the BiSCCO will be hard to see in the total resistance of the structure.

![Figure-45: Graphite Cover Transport Devices - Pre E-Beam](image)
To remedy this, attempts were made to apply O_2 plasma to the graphite layer to covert it into an insulator, however this proved difficult. It was hard to find an etch recipe that we could be sure only etched enough to fully convert the graphite layer to an insulator, but not expose the BiSCCO and keep it chemically protected. The other option was to use graphene as a cover for the BiSCCO. Graphene can be easily converted into an insulator by exposure to 30 seconds in
UV-Ozone\textsuperscript{11}. However, as is seen from figure-46, thin graphite is extremely difficult to see on a GelPak\textsuperscript{©}. Consequently, we found it impossible to find monolayer graphene on the GelPak\textsuperscript{©}, the contrast was not high enough.

These devices made contact, and we were able to take transport measurements. However, we never saw superconductivity, but the resistance vs. temperature curves and I-V curves were different than expected from just a pure piece of graphite. This will be discussed further in the data section.

\textsuperscript{11} UV-Ozone is much weaker than O\textsubscript{2} plasma, and doesn't etch very rapidly. Thus the conversion of graphene into an insulator is caused by a chemical reaction between the free ozone and the graphene to make graphene oxide.
Section 3:
Measurement Setup and Device Data
Chapter 1:
Transport Measurement Setup

As mentioned previously, we wanted to first verify if superconductivity could be seen in our flake devices before moving on to building a capacitance device. Superconductivity can be verified via two types of measurements: resistance vs. temperature curves and I-V curves. For resistance vs. temperature curves we expect to see metallic behavior with a sharp transition to zero resistance at the critical temperature. For I-V curves, we expect the curves to be flat at zero bias for a range of current, and linear outside of the absolute value of the critical current. Seeing both of these signatures would be enough to verify the flake was super conducting.

Before describing the details of the measurement setup we used to take these two types of curves, it will be good to review the basics of four terminal resistance probe measurements. Ultimately, four terminal probe measurements are designed to take resistance measurements of a sample without including the contact resistances.

![Figure-1: Graphite Cover BiSCCO Transport Device Device Model](image)
The essence of a four-probe resistance measurement involves sourcing current from the two outer probes and measuring voltage across the two inner probes. Voltmeters do not draw any current, hence the current across the three sections of the sample is the same as the current coming from the source-meter. Simple application of ohms law implies that the voltage measured across the voltmeter is:

\[ V_M = R_S \cdot I \implies R_S = \frac{V_M}{I} \]

The contact resistance does not come into play at all, and it is extremely easy to extract out the resistance of the sample. With this technique we can either fix the current bias and measure the change in the measured voltage as a function of temperature, thus giving a resistance vs. temperature measurement. Or at a fixed temperature, one can a source varying amount of current and measure the resulting voltage, thus giving an I-V curve. The detailed schematic of our measurement scheme is can be seen in figure-2.

Figure-2: Simplified Transport Measurement Block Diagram
In order to perform four-probe resistance measurements at various temperatures we would use a dip probe in order to place the sample inside of a He$^4$ dewar. The He$^4$ dewar has some amount of liquid He$^4$ at the bottom, and the He$^4$ that cannot be kept at 4K evaporates, and the gas forms a temperature gradient. This way, the top of the dewar is close to 300K (room temperature) and the bottom of dewar (in liquid) is at 4K. Taking a stick with a sample attached at the end, and slowly plunging the combination into the dewar allows for temperature selection over short time-scales. Naturally, even though the dewar is well insulated, it will inevitably exchange energy with the environment and the minimum temperature achievable will increase. However, as long as there is liquid He$^4$ in the dewar, a full temperature range resistance vs. temperature sweep can be achieved. In order to attach a sample to dip probe, a sample is mounted onto a blank D.I.P (Dual-Inline Package) with vacuum grease. Sample leads are then ultrasonically soldered (wire-bonded) to various pins on the D.I.P socket (see figure-3). The D.I.P socket is mounted onto the dip probe, which goes into the He$^4$ dewar, and the sample leads are attached to wires which are carried up through the probe, and into a Fischer 24-pin cable.
This cable and then be directly attached to a break-out box, which allows us to attach the various pins on a sample to measurement equipment.

To take four-terminal resistance measurements, we used a Keithly 2400 SourceMeter to source varying amount of D.C. current to the outer leads on our sample. The Keithly 2400 was typically set to a compliance of 2.1V to prevent excess voltage on device leads. To measure the voltage developed across the sample in response to an applied current, we used an Agilent 34401A digital multimeter (DMM), set to high-Z, 6-1/2 digits, and to average over 10 power line cycles. In addition, to measure the temperature inside of the dewar, inside of the dip probe two of the leads going to the breakout box were attached to a LakeShore Si diode sitting as close to the sample as possible. We would source a constant amount of current across the diode, using a battery powered current source also from LakeShore, and measure the corresponding voltage developed across it. The voltage across the diode, at a constant current, varies with temperature in a predictable manner. LakeShore, provides a lookup table that converts the voltage across the diode into a temperature. By reading out the voltage on the diode on another Agilent 34401A DMM, we were able to accurately measure the temperature of the sample.

The setup described above is enough for both types of measurements we wanted to take. For resistance vs. temperature curves, a constant amount of current would be sourced from the Keithly 2400, and the voltage across the sample would be measured by the Agilent 34401A. This would be repeated as we slowly lowered or lifted the dip probe in or out of the He\textsuperscript{4} dewar varying the temperature of the sample. This way a resistance vs. temperature plot could be made. For an I-V curve, leaving the dip-probe in place and keeping the sample at a constant temperature, the Keithly 2400 would sweep a range of current, and at each current point the
voltage across the sample would be measured. This would allow us to plot I-V curves at various temperatures.
Chapter 2:
Au Contact Pad Device Data

When measuring the various devices that we fabricated, although the original goal was to fabricate devices for capacitance measurements, we settled on trying to find evidence of superconductivity in thick flakes first. Since it’s not known whether or not superconductivity persists in thin flakes, like half-unit cell or single-unit cell, we attempted to find superconductivity in flakes that we knew we could consider “bulk.” However, even in these flakes no evidence of superconductivity was consistently found. However, across many different devices we did notice discernible features happening around an expected $T_c$ between 90K and 100K. Our assumption was that the BiSCCO flakes, especially being so thin, can easily change their doping level by exchanging oxygen with the atmosphere [37]. As can be

![Phase Diagram for BiSCCO 2212 - Image Credit [36]](image)

Figure-4: Phase Diagram for BiSCCO 2212 - Image Credit [36]
seen in figure-4, most likely the flakes, which should theoretically start at optimal doping (at the top of the superconducting dome), became de-doped, with no way to discern what the doping level was pre-measurement. Thus each transport measurement, in addition to being exposed to noise introduced by micro-cracks propagating upon thermal cycle, may be measuring BiSCCO in a different phase. This may explain the inconsistencies seen across various datasets. However, this chapter does not seek out to make any strong measurement.

Figure-5: Measured Au Contact Pad Device 1 ~ 30nm (15 layers)

Figure-6: Resistance Vs. Temperature Cool Down Measurement for Au Contact Pad Device 1
claims. However, presented in this chapter are the various devices that produced data with interesting features that could be observed due to the fact we achieved low resistance contacts and a high signal-to-noise ratio.

As can be seen from the plot in figure-6, although this device does not fit the typical superconducting resistance vs. temperature profile, there is clearly some large reduction in

![Image of a scatter plot showing resistance vs. temperature for Au contact pad device 1.](image)

Figure-7: Resistance Vs. Temperature Warm Up Measurement for Au Contact Pad Device 1

![Image of I-V curves at 4K for Device-1, showing short and long current sweeps.](image)

Figure-8: I-V Curve at 4K for Device-1: Short Current Sweep (left), Long Current Sweep (right)
resistance starting at 100K and ending around 90K. However, the rapid drop in resistance from 300K to 250K is very confusing since it drops almost as rapidly as the dip at 100K, and it lasts for much longer.

As was often the case with these devices, after measurement either leads would blow, or the flake itself would become unmeasurable. The resistance vs. temperature plot in

Figure-9: Differential Conductance Curves at 4K for Device-1: Short Current Sweep (left), Long Current Sweep (right)

Figure-10: Measured Au Contact Pad Device 2  50nm (30 layers)
Figure-11: Resistance Vs. Temperature Plots For Device 2

Figure-12: I-V Curves for Device-2 at 4K and 280K

figure-55 was taken at a lower current than the previous cool down because we found that
some of the leads used for the first cool down were not able to source current, and upon the next measurement we wanted to protect the currently used leads. However, the device did not show a repeatable measurement upon warm up, meaning thermally cycling the device had fundamentally changed either the flake itself, via the micro-crack mechanism, or the contacts had been degraded.

The I-V curves for device-1 device were interesting. Looking at the numerical differential conductance, we can see that at near zero current, there is a conductance peak\(^\text{12}\). However, outside of the conductance peak, the normalized dI/dV curves are quadratic. However, as we see in device-3, features of this kind seem to persist at room temperature, leading us to believe they are not related to superconductivity. We could not make any definitive claims as to what this signal was since we had no sense of a control, wherein we knew what signal we should see for a superconducting flake. However, the consistency of this data does indicate that what we saw is indeed a feature, and is of some physical interest.

\(^{12}\) It's important to point out that the voltage scaling is different for the two current sweeps, this is because between measurements device leads had to be changed due to accidental damage, giving over all different current and voltage ranges, but showing the same features.
One possible theory for why the differential conductance shows a peak at zero bias is that the BiSCCO flake forms domains of superconducting and non-superconducting material. This would explain the fact that we see features in the resistance vs. temperature curves reminiscent of a superconducting transition, yet the resistance remains finite. If the BiSCCO flake itself has lost superconductivity in some domains, then it is possible that the flake itself acts like a
superconductor in series with another normal metal with some finite resistance. If this were the case, then we could see that in regions near the Au device leads, if the BiSCCO is acting like a normal metal, then there is no energy cost associated with injecting a quasi-particle into the system. However, if the total current is low enough (below the critical current of the superconducting segment), then a portion of the flake may pass super-current, and the resistance should go down. This posits a possibility for an observed conductance peak. An additional possibility, is that the conductance peak is actually the two peaks seen in a classic superconducting gap [1], but our current resolution is not high enough to see the gap itself. To
determine this, one would have to work with a current source that can reliably source sub 10nA of current (the resolution on the Keithly 2400).

Device-2 had the most superconducting-like signature of every device that we measured. Furthermore, this device was interesting because the transition temperature seemed to happen at 120K, which is much higher than the expected 90K. Warming up the device at a lower current after taking I-V curves, attempting to obtain a resistance vs. temperature plot with the device living in the conductance peak, we found that the device had completely different behavior. It almost behaved as if the device was attempting to tunnel quasi-particles into a superconductor. That once the device was cooler than T_c, the energy cost to inject a quasi-particle increases, as reflected by the increase in resistance. This behavior can be seen in other devices as well.

For device-2, we see features distinctly opposite of that in device-1 for I-V sweeps at 4K. At low current, now we actually see a conductance trough, and at high current we see a conductance spike. This made analysis very difficult because even for devices that gave low-noise measurements, it was still difficult to get consistency across multiple devices. However, besides the conductance spike, the outer ranges of the differential conductance curve at high currents look flat, which is distinctly different than the parabolic shape we see in device-1.

Additionally, I-V curves at room temperature suggest that these features disappear, indicating that this device might display more similarities to a superconducting state than either device-1 or device-3.

For device-3, we saw similar results to device-1. And like device-1 the results did not disappear at room temperature. This lead us to believe that the features were not related to superconductivity, and were most likely a feature of either the device architecture, or the effect of
tunneling into the "strange-metal" phase of BiSCCO. However, we did see resistance vs. temperature signatures that were similar to device-2. This was what was so puzzling about working with flake BiSCCO, we got some sense of consistency on different measurement aspect across various devices, but no set of devices share every feature in common. This fundamentally made it impossible to make any definitive conclusions about our measurements.
Chapter 3:
Graphite Cover Device Data

The resistance vs. temperature curves for the graphene cover devices do not show any indication of superconductivity, nor do they show any discerning features near 100K. The resistance vs. temperature shapes were fundamentally odd. The curves show an insulating type behavior, which although may be expected from BiSCCO, should not be seen in graphite (which should be the dominating feature). Not to mention, the curves themselves are non-linear. This non-linear behavior could not be understood under any simple model of a graphite based resistor in parallel with a superconductor with varying thermal coefficients.

The I-V curves and the differential conductance curves could not tell us anything about the device. In particular the curves did not change qualitatively above and below the bulk critical temperature of BiSCCO. This lent us to believe that whatever features we were seeing were not in fact related to superconductivity, but perhaps some other BiSCCO phase. Ultimately,
for this device as well it was hard to draw any definitive conclusions, since the telltale sign of superconductivity could not be seen. This left us clueless as to what state the BiSCCO was in, making it impossible to interpret the data in any meaningful way.

Figure-18: Resistance Vs. Temperature Curves for Graphene Cover Devices

Figure-19: Differential Conductance Curves of Graphite Cover Device.
Section 4:
Conclusion
Chapter 1:
Project Conclusion and Suggestions for Further Work

To briefly conclude this thesis, we wanted to recap everything that was discussed and suggest possibilities for future work. The main takeaway from this thesis is that we constructed a means of making low resistance contacts to air sensitive VDWH materials, specifically BiSCCO. This project started out as an attempt to make a capacitance device and probe the density of states in BiSCCO’s AFM insulating phase. However, as a preliminary, we first set out to make contact and take basic transport measurements to guarantee that we could even see superconductivity in flakes before trying to observe more exotic physics.

Making a low-resistance contact to a BiSCCO flake proved much harder than originally thought. Fundamentally, this is what we believe is the reason for only one group [35] reporting transport measurements with no follow up publications since 2004. Working with this material is difficult. The bulk of our work became developing techniques to make contact and be able to take any kind of measurement. We first attempted to sputter the flake surface before depositing metal, however this proved ineffective in creating low resistance contacts. Eventually, we figured out that interfacial water left on any surface in contact with the BiSCCO completely degrades the ability to make contact. Furthermore, it was not only water, but any solvent step in the process could completely degrade the flake and render it impossible to make contact. To remedy this problem we developed a means of performing VDWH transfer techniques in an all-dry method that did not involve any solvent steps. This along with being able utilize the new
transfer process to perform the transfer entirely above 100°C minimized interfacial water in contact with the BiSCCO flake surface.

Once low-resistance contact was made, a host of other problems arose preventing us from seeing a repeatable superconducting signature or getting repeatable data that made sense. We discovered that micro-cracks in the BiSCCO propagate during a thermal cycle, and often prevented measurements from generating reproducible data. Furthermore, we knew that the doping in the BiSCCO flakes could change rapidly, and it seemed from our measurements like different devices had various domains mixing different phases, leading to uninterpretable data. Never being able to get a sensible transport measurement, we were not able to move on and take capacitance measurements.

BiSCCO itself is incredibly difficult to utilize as a VDWH material, however we believe its not impossible. We have already made a huge step forward in documenting a definitive process by which one can make consistent low-resistance contacts to flake BiSCCO. With this step forward, there are number of different suggestions that we would give for others attempting to work with this material in the future. One, pre-deposited Au contact pads are the best way to make contact, and we would suggest using photoresist, since devices leads patterned with photoresist had a higher yield for creating devices with low-contact resistance as compared to device leads patterned with PMMA. To get the advantages of the graphite finger device, but without the Schottky barrier, one can create a photoresist mask on an SiO₂ substrate, etch 30nm into the substrate with CF₄, and deposit 30nm of Au. This would create Au contacts that are flush with the substrate. This should reduce the creation of micro cracks in the BiSCCO flake when transferring it onto the “flush” transport pads. Additionally, having multiple sets of four
terminal transport pads extremely closely spaced together will minimize the possibility of a micro crack propagating through all four-terminal devices.

Something else that one could try is to have an oxygen tube furnace on-site, close to a measurement apparatus. If one could perform an oxygen anneal on a flake for an hour, and quickly exchange it into a Helium atmosphere, then it may be possible to re-dope a flake that has lost superconductivity. Also, using Raman spectroscopy as a means of measuring the optical conductivity of BiSCCO would give additional information as to whether or not the flake is insulating. This information would be extremely helpful in interpreting transport measurements, and would aid in understanding capacitance signals.

These ideas are just a few of the ones that could be used to make flake BiSCCO work. We’ve already taken steps to achieve low contact resistance, the next step in the process is to be able to control flake doping, or at least be aware of it before taking any kind of measurement without corrupting the flake itself. We will continue to work on this project in the future, and we hope that this thesis has given others useful information for continuing with this work.


[40] Novoselov, K. S., Mishchenko, A., Carvalho, A. & Castro Neto, A. H. 2D materials and van der Waals heterostructures.


[44] 221A Lecture Notes: Landau Levels. 221A Lecture Notes: Landau Levels
