

Transfer of 2D Materials in an Inert Atmosphere

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I. Introduction & Motivation

The field of two dimensional materials (2DMs) is currently an expanding area of research, with potential applications in electronics, catalysis, biomedical devices, optoelectronics, and more. 2DMs are a class of materials whose crystal structures are naturally layered, where intralayer atoms are held together by strong covalent bonds, but layers are only held together by weaker van der Waals bonds. This results in individual layers with pristine interfaces free of dangling bonds, allowing us to reach the limits of scaling while maintaining certain properties, such as carrier mobility, that would degrade in typical, 3D (bulk) materials at the sub-nm thickness scale [1].

2DMs cover a diverse range of mechanical, optical, thermal, and electrical properties. For example, the bandgaps of 2DMs can range from metallic and semimetallic (e.g., graphene), to semiconducting (such as the transition metal dichalcogenides (TMDs), e.g. MoS₂), to insulating (hexagonal boron nitride, hBN). This makes 2DMs attractive for a wide range of applications and possible structures, for example the concept of van der Waals (vdW) heterostructures, where different 2DMs can be stacked in any desired order without having to worry about lattice mismatching, allowing great control over band alignments.

Because of their increasing role in nanoscale electronics research, it is crucial that SNF and SNSF develop greater capabilities to fabricate, process, and characterize 2DMs. The most critical step in 2DM processing is the transfer of material to arbitrary substrates. Currently, there are two main methods of obtaining thin 2DMs, down to monolayers: mechanical exfoliation and growth. Mechanical exfoliation, also known as the “Scotch-tape” method, involves cleaving thin layers of material from a bulk crystal, typically using tape or some other sticky polymer. This process can be repeated to yield thinner and thinner samples, until the limit of a single layer can be reached. These flakes can then be transferred to a substrate of choice. The other method used to obtain 2DMs is by directly growing them, most commonly using chemical vapor deposition (CVD). This bottom-up approach, as opposed to the top-down approach of exfoliation, allows for much greater control of the number of layers. For example, here at Stanford we have the capability to grow several TMDs directly as monolayers. One issue with CVD growth of TMDs (and other 2DMs) is that it can require high temperatures (up to 900°C), and thus is only compatible with substrates such as Si, SiO₂, quartz, or sapphire. If we want to transfer 2DMs onto arbitrary substrates, such as polymers for thin, flexible circuits, we need a transfer technique.

It is well known that many 2DMs, for example MoTe₂, HfSe₂, or black phosphorus (BP) are highly unstable in air when exfoliated and can quickly degrade. These materials have highly

attractive properties, such as phase-change behaviors or very high mobility values. It is therefore necessary to be able to transfer and encapsulate them in an inert atmosphere. The glovebox in the ExFab provides an inert environment to store, transfer, encapsulate, and work with unstable materials, 2D or otherwise. The transfer station on the right side of the glovebox is designed for aligned placement of 2DM flakes, enabling 2D transfer, but the process has yet to be fully optimized. The goal of this project was to improve the transfer process in the glovebox, as well as to create a user guide for the transfer station.

II. Transfer Process

Transfers of 2DMs fall into two basic categories- those involving water or some kind of aqueous solution (“wet” transfers) and those that do not (“dry” transfers). Because of the low humidity, controlled conditions in the glovebox, only dry transfers are allowed. Most dry transfers follow the same basic principle – use a rigid material (typically a polymer or stack of polymers) to pick up the 2D material from its original substrate, and then “stamp” it onto the target substrate. Once in contact, the polymer stamp is then removed, leaving behind the 2DM on the new substrate [2]. This removal must be done carefully to ensure the 2DM adheres to the new substrate and doesn’t come off with the stamp; typically this is achieved by removing the stamp very slowly while introducing some heating step. Heating helps to release the stamp from the target substrate. This process is illustrated in Fig. 1.

There is a careful balancing act when developing the transfer process. You want a stamp that is sticky enough to pick up or exfoliate your material, but can release it onto a new substrate that holds onto it stronger (with vdW bonds). The optimization of this stamp process was the focus of our project.

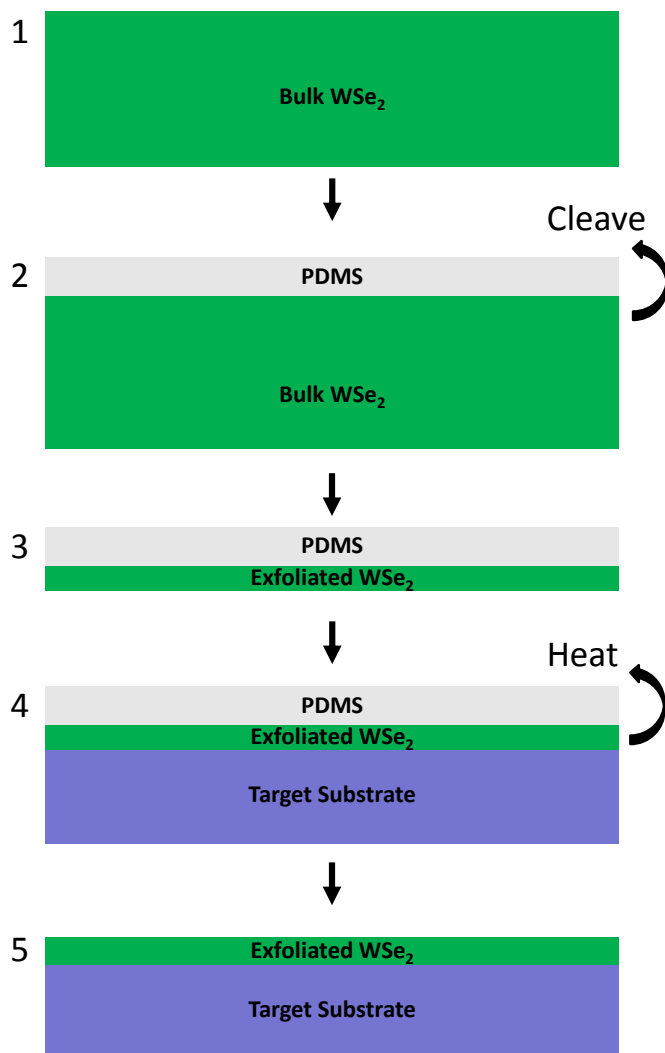


Figure 1: The transfer process used and optimized in the glovebox. Step 1 – Begin with a bulk crystal to exfoliate. 2 – Apply PDMS and remove slowly to exfoliate thin flakes. 3- The PDMS now acts as a semi-rigid stamp holding exfoliated flakes. 4-Align and place the stamp onto the target substrate. Heat the stack to aid in release, then slowly remove the PDMS. 5 – What is left are exfoliated flakes on the new target substrate. Rinse with solvents to remove bulk residue.

III. Choice of Materials

With so many different 2DMs available, in an ideal world we could test every single one and develop an optimized process for each material. However, given the time scale of this project (one quarter), we determined it best to focus on the transfer process, namely the polymer layer and temperature conditions, by keeping the 2DM fixed. Controlling this material, while not exploring the full gamut of possible 2DMs, does allow us to eliminate one source of variation, while still providing useful trends and results regarding the transfer process. Our choice of 2DM acts as a case study, which can then be applied and tweaked for other materials.

Our choice of material was WSe₂. There were three main reasons for this: first, WSe₂ is a relatively popular 2DM for research. It is a semiconducting TMD and is the most promising candidate for p-type conduction in the common TMDs. Second, it is relatively air stable, lasting for a time scale of weeks to months after exfoliation. This is important because our characterization techniques require the transferred material to be exposed to air. While other materials, such as MoTe₂, are less stable and perhaps better candidates for transfer in the glovebox, they would require encapsulation before characterization of the transfer. This could introduce additional variables that would have to be controlled and would be less indicative of the transfer quality. The third reason behind the choice of WSe₂ is our ability to grow it via CVD at Stanford in the Pop group. Specifically, one group member (Connor) focuses on the growth of WSe₂ for his research. That's why we chose WSe₂, rather than other 2DMs that we can grow at Stanford like

graphene or MoS₂. Ultimately this reason became irrelevant because we later decided to only focus on exfoliated material in our transfer process due to time constraints. Figure 2 shows exfoliated and CVD grown WSe₂.

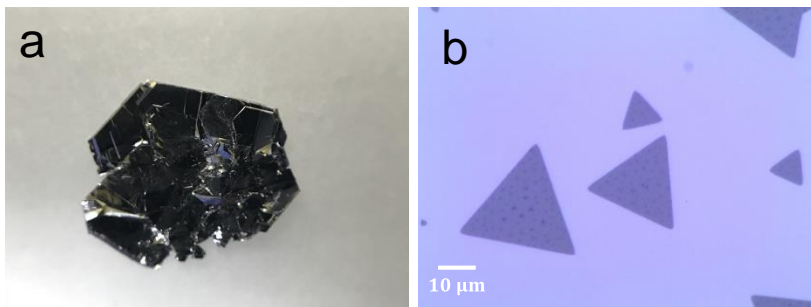


Figure 2: (a) A bulk crystal of WSe₂, which can be exfoliated to yield thin samples. (b) Optical Micrograph of single grains of WSe₂ grown by CVD at Stanford.

Several polymers have been used in the literature to form the “stamps” for the dry transfer process, including polypropylene carbonate (PPC) and poly(methyl methacrylate) (PMMA). However, for our project we decided to focus on polydimethylsiloxane (PDMS), as it is the most common choice. Additionally, it is easy to obtain in a thicker, rigid layer than something like PMMA (which comes in a solvent that must be evaporated or spin-coated). The composition/consistency of PDMS can be easily varied as well, because it is prepared by combining a base and curing agent to yield a solid polymer. We suspected that the consistency, rigidity, and “stickiness” of the PDMS could affect transfer quality – ranging from how much material could be picked up, how easily it could be released, and how much residue would be left on the target substrate. The use of PDMS, therefore, is a process that could be optimized, and it became the main focus on our project.

Finally, the effects of different substrates were taken into account. We chose two target substrates to act as case studies: SiO₂ (on Si) and polyethylene naphthalate (PEN). SiO₂/Si is the quintessential substrate in SNF and is by far the most common substrate currently used when working with 2DMs. It is rigid, has low surface roughness, and is incredibly well studied and understood. PEN is a polymer substrate that is optically transparent, mechanically flexible, and chemically resistant, allowing for lithography and processing in SNF. It is one of the most commonly used substrates for flexible applications. The reason to use PEN was to both demonstrate the transfer of 2DMs onto flexible substrates as well as to elucidate any possible differences between the transfer process onto a rigid substrate (SiO₂) versus a flexible one.

IV. Design of Experiment (DOE)

As discussed in the previous sections, we decided that our project should focus on the PDMS layer of the transfer process, rather than on the 2DM being transferred. The source material was exfoliated WSe₂ from a bulk crystal purchased from 2D Semiconductors Inc (<http://www.2dsemiconductors.com/>). Two target substrates were used, SiO₂/Si and PEN. PDMS consistency was varied by changing the relative ratio of the base to the curing agent. Three base:curing agent ratios were used: 5:1, 7.5:1, and 9:1. With more base, the PDMS is less cured and more sticky. It is important to note that the recommended ratio from the PDMS vendor is 10:1, but we found that at this ratio the PDMS would barely cure using the recommended curing conditions. It was recommended to us by SNF staff that we use Sylgard 182 PDMS, as it has a longer shelf life once cured. We found that the trade-off with this is that it takes a long time to cure, which may lead to issues with getting a fully cured stamp. In general, any PDMS can be used, but it should be cured and yet sticky enough to pick up material. Fig. 3 shows an example of PDMS that has not fully cured. Release temperature was also varied. 140°C is a typical choice, so we used 130°C and 150°C to look at trends with temperature. Release bakes were performed for 20 minutes once the set temperature was reached.

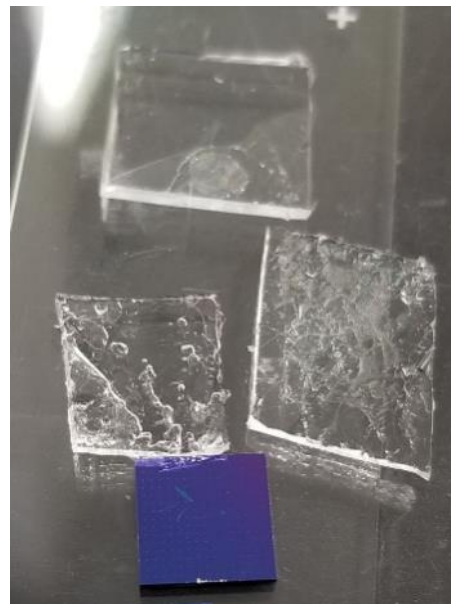


Figure 3: Example of PDMS that has not fully cured. Notice the bubbles and other defects that appear due to part of the PDMS being solid while part is still uncured.

Because there were only three main variables that we were changing, we performed transfers for all combinations of conditions (as opposed to a fractional factorial approach when dealing with more variables). This led to 12 total transfers, each of which were then characterized to determine the quality of transfer. The DOE is summarized in the table below.

PDMS Base:Curing Agent	Release Temperature (°C)	Target Substrate
5:1	130	300 nm SiO ₂ /Si
7.5:1	150	PEN
9:1		

V. Characterization of Transfers

In order to determine the success of our transfers, it is necessary to decide on metrics which quantify “success”. Qualitatively, we can use optical microscopy to identify flakes and see bulk residue. However, more advanced techniques are necessary for quantification of residue and material quality. Below we discuss the four main techniques used for our project’s characterization: Optical Microscopy, Raman Spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM).

Optical Microscopy

Optical microscopy served as the preliminary technique in order to identify a successful transfer. It allows for a quick way to locate and map transferred flakes prior to later in-depth characterization. Figure 4 shows typical images of transferred WSe₂ flakes.

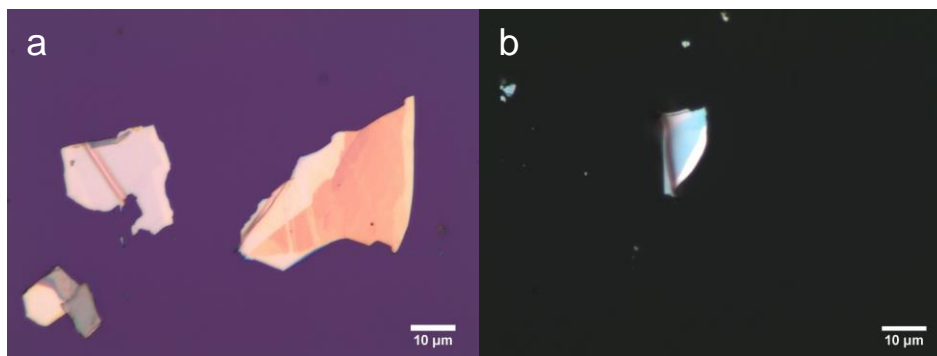


Figure 4: Optical images of typical WSe₂ flakes. (a) Flakes transferred to PEN. (b) Flake on the PDMS stamp, before being transferred to a new substrate. For both, lateral dimensions tend to be in the 10s of microns, and thicknesses are on the order of 10s-100s of nanometers.

Raman Spectroscopy

Raman spectroscopy uses the scattering of light to measure the vibrational modes of a crystalline solid. These vibrational modes occur at frequencies/energies that are very specific to a given material – acting as a “fingerprint” unique to a given material; this is the case with 2DMs as well. In Raman, monochromatic, coherent laser light is shined onto a sample. Most light is simply backscattered/reflected with no change in energy (“Rayleigh” scattering). However, a very small proportion of light interacts with the material’s vibrations/phonons, which can result in the scattered light losing a small amount of energy (Stokes) or gaining a small amount of energy (anti-Stokes). These shifts are normally reported as a change in wavenumber (cm⁻¹); the number of photons with this energy shift is the signal received in a Raman spectrometer (counts/intensity).

The size and shape of these Raman peaks are related to material conditions and quality. For example, in WSe₂ there are two main peaks: the E_{2g} peak, associated with in-plane vibrational modes, and the A_{1g} peak, associated with out-of-plane modes (See Fig. 5). The E_{2g} peak position can be correlated to in-plane strain; the A_{1g} peak can be shifted with doping. For both of these peaks, height and width (typically reported as the full width at half maximum, FWHM) are related to the material quality. The sharper these peaks, the more pristine the material is, as fewer defects, adsorbed material, etc. allows for shifted energies.

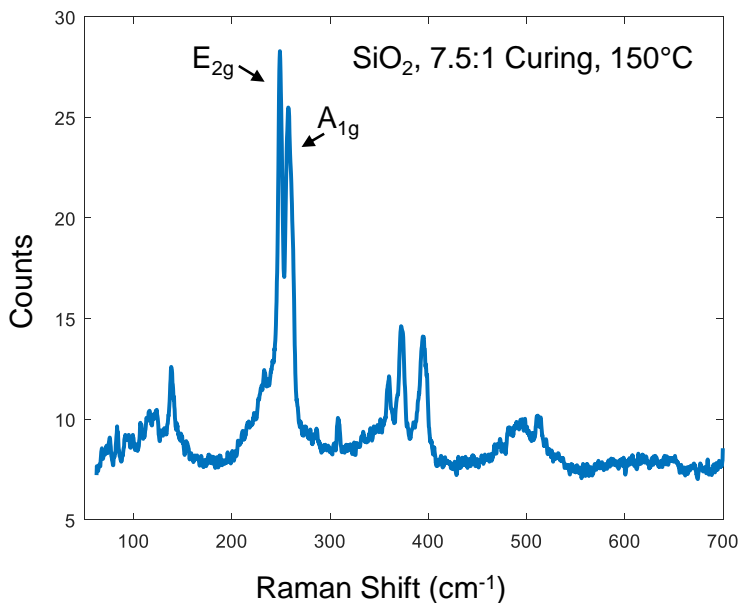


Figure 5: A typical Raman spectrum of WSe₂ on SiO₂. The E_{2g} and A_{1g} are the most intense peaks, which were used to quantify transferred material quality.

For the purposes of our project, we used the FWHM of the E_{2g} peak (the strongest peak) as a quantitative measure of material quality after transfer. In all experiments, we used a 532 nm laser at 10% power in the Horiba Labram Raman system, located in SNSF (Spilker 007). A 20 second acquisition time and 10 accumulations were used to boost signal and get clearly defined peaks; these conditions were constant across all samples and baseline measurements for an accurate comparison. Plots of the FWHM versus curing ratio, for both release temperatures and both substrates, are shown in Fig. 6.

We observe that for SiO₂ substrates, using less curing agent (hence, a less cured or “stickier” PDMS) yields a sharper E_{2g} peak (smaller FWHM), which means a better transfer. This at first seems counterintuitive, because a stickier polymer should leave more residue. The physical explanation for this is currently unclear; more data is needed to get a more accurate trend. Higher temperature bakes lead to worse transfers on SiO₂, which may be due to baking on more polymer residue.

For PEN substrates, we see the same trend with curing agent ratio, but the opposite for bake temperature: 150°C bakes appear to lead to better transfers on PEN. This may be due to the fact that 150°C begins to approach a temperature where the PEN begins to soften, but not quite melt [3]. This may lead to better sticking and wetting to the WSe₂, and hence fewer defects in the material and a sharper Raman peak.

For SiO₂, there is a noticeable increase in FWHM in transferred samples when compared to a control sample of WSe₂ exfoliated directly onto SiO₂ (no PDMS – the blue exfoliation tape is stuck directly onto the SiO₂ substrate), which has a FWHM of ~5 cm⁻¹. This indicates that the

transfer process onto SiO₂ induces some damage in the WSe₂ which is unavoidable. However, on the PEN substrates, a baseline of ~5.5 indicates that there is very little difference between exfoliated directly onto PEN vs. using PDMS, which would allow for an aligned transfer.

X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique for measuring elemental composition by irradiating a sample with x-rays and measuring the energy and number of photoelectrons that are emitted. The incoming x-ray photons cause electrons to be ejected from the sample material; the binding energy can then be calculated by taking the difference between the measured photoelectron kinetic energy and incoming photon energy. These binding energy values allow for composition identification, with the counts providing an estimate for the relative amounts of each element present.

While this technique cannot be used to quantify precise amounts of species on the surface of samples, we use it to obtain a qualitative idea of the relative residue levels that are left by each transfer procedure. It is first important to note that we deliberately avoided doing XPS measurements on the transferred WSe₂ flakes themselves, instead opting to measure points around the flakes on the same substrate, which would have undergone the same transfer conditions. This is because there is a Se Auger peak that overlaps with the C peak, and this would convolute the analysis as we are using the C peak for part of the residue analysis. In addition, the x-ray spot size was chosen to be 200 μm (for better signal), and this is an order of magnitude greater than the average exfoliated flake size that we obtain.

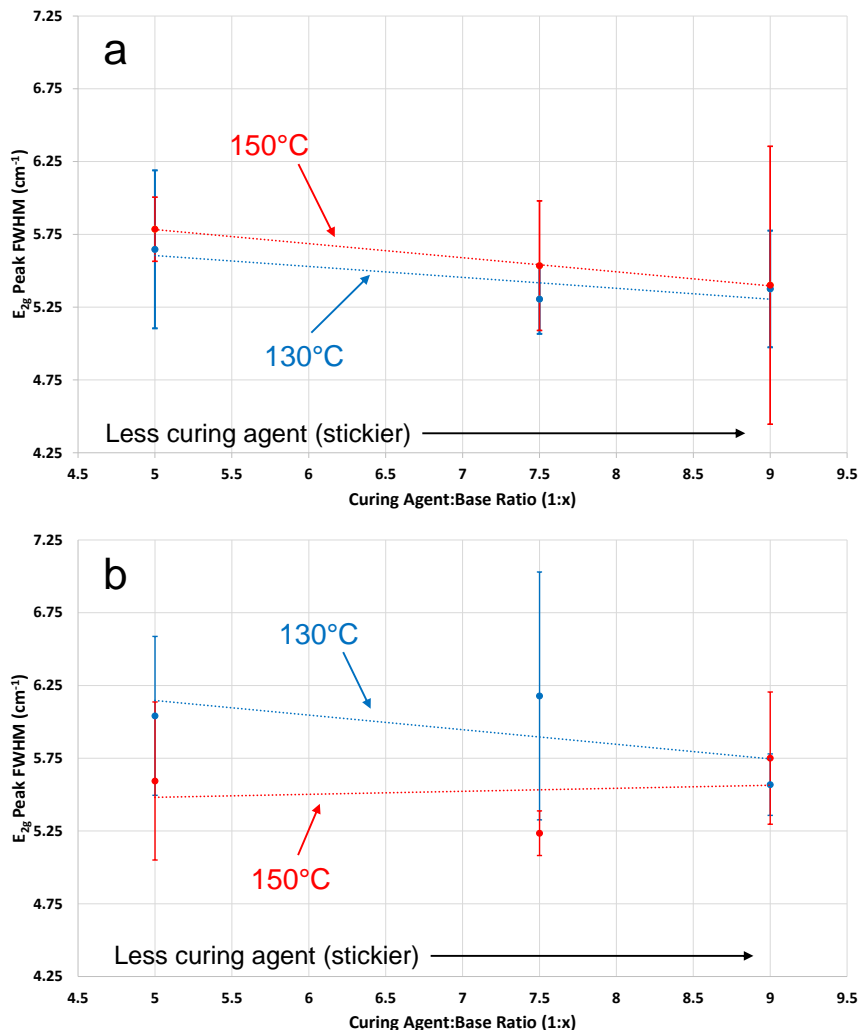


Figure 6: FWHM of the E_{2g} peak in WSe₂ as a function of PDMS level of curing for both 130°C bake (blue) and 150°C (red) on (a) SiO₂ substrate (b) PEN substrate.

For the SiO₂/Si substrate, we assume that there should not be any C inherent to the material. Therefore, any C that we measure through XPS is likely from contamination, although it could be from hydrocarbons in the air. In order to get an estimate of what conditions lead to the cleanest transfer, we take the ratio of the C to Si peaks, where a higher value for this ratio would indicate more contamination. This is plotted in figure 7a.

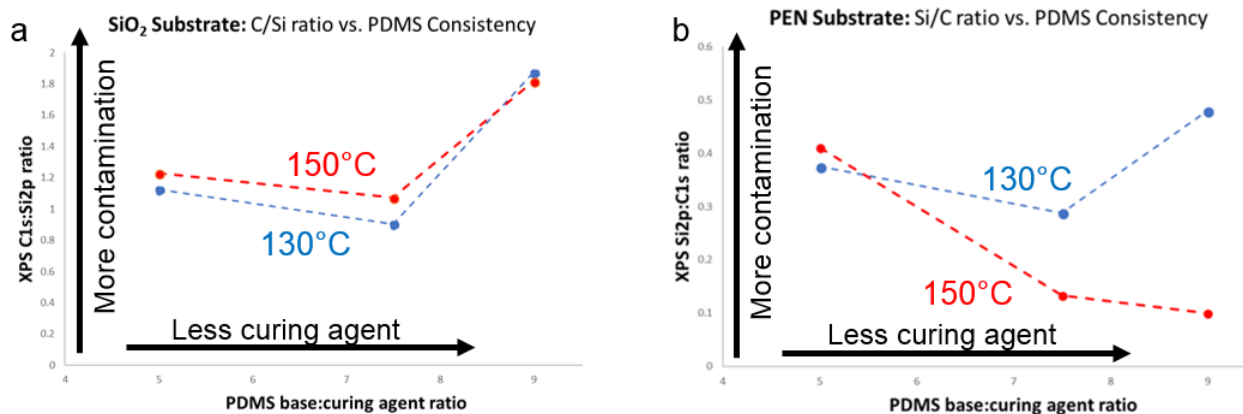


Figure 7: Ratio of contaminant species to native substrate species in order to compare residue levels for (a) SiO₂ and (b) PEN

For the PEN substrate, we assume that there should not be any Si inherent to the material. Therefore, any Si measured through XPS must be contamination, and we assume that this contamination is primarily from the PDMS, although it is possible that there is additional Si contamination from processing. So, to estimate relative levels of residue, we take the Si to C peak ratio where a higher ratio implies more contamination. While there may be additional C from residue as well, we assume that the C in PEN will dominate this peak. These data are plotted in figure 7b.

Atomic Force Microscopy (AFM)

Atomic Force Microscopy (AFM) is a type of scanning probe microscopy (SPM) that is capable of obtaining nanometer resolution surface topographical micrographs. In this technique, a sharp tip is attached to a cantilever and raster scanned over the sample. For this work, we used intermittent (tapping) mode, which preserves AFM tip lifetime and minimizes potential damage to the sample as compared to contact mode. In intermittent mode, as the topography of the sample changes, forces (Van der Waals or electrostatic) will change the amplitude of oscillation of the cantilever. A laser reflects off the back of the cantilever and hits a photo-sensitive detector, which is used to measure deflection of the cantilever and therefore, changes in topography.

After completing the transfer procedure with each set of parameters as defined in our DOE, we did an AFM scan of a flake on each sample. Our assumption is that increased levels of root mean square (rms) surface roughness are due to added polymer residue that would have been induced during the transfer process. This technique would therefore allow us to quantify levels of residue that were too small to see optically. In addition, we scanned an area of bare substrate in order to ensure that the surface roughness of thin flakes would not be solely due to the substrate roughness.

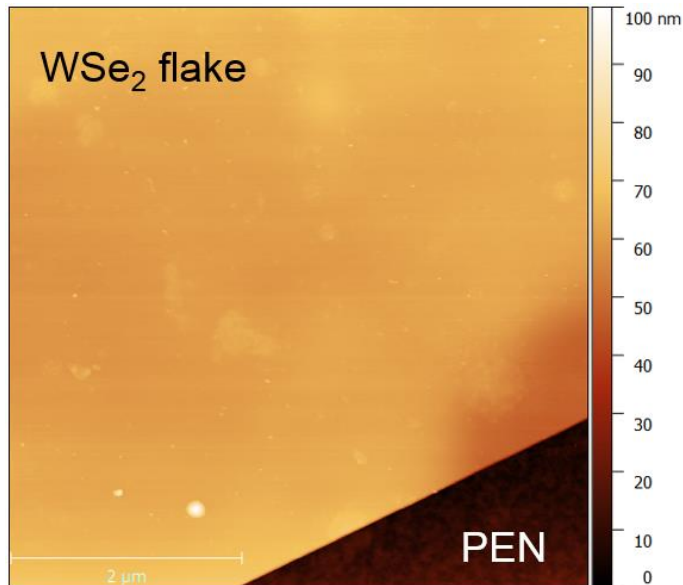


Figure 9: A representative AFM micrograph of a WSe₂ flake transferred to a PEN substrate

A representative AFM micrograph is shown in figure 9. The surface roughness data is compiled in figure 10. The rms surface roughness of each flake is relatively close to the values for the substrates and these values indicate that there was not a significant amount of contaminant particulates left from the transfer process. There does not seem to be a very clear trend between the PDMS base to curing agent ratio, but we may tentatively conclude that the 7.5 to 1 ratio yields the cleanest transfer. In addition, it appears as though a higher release temperature is cleaner for the PEN target substrate, while lower is better for SiO₂. This data is presented in figure 10.

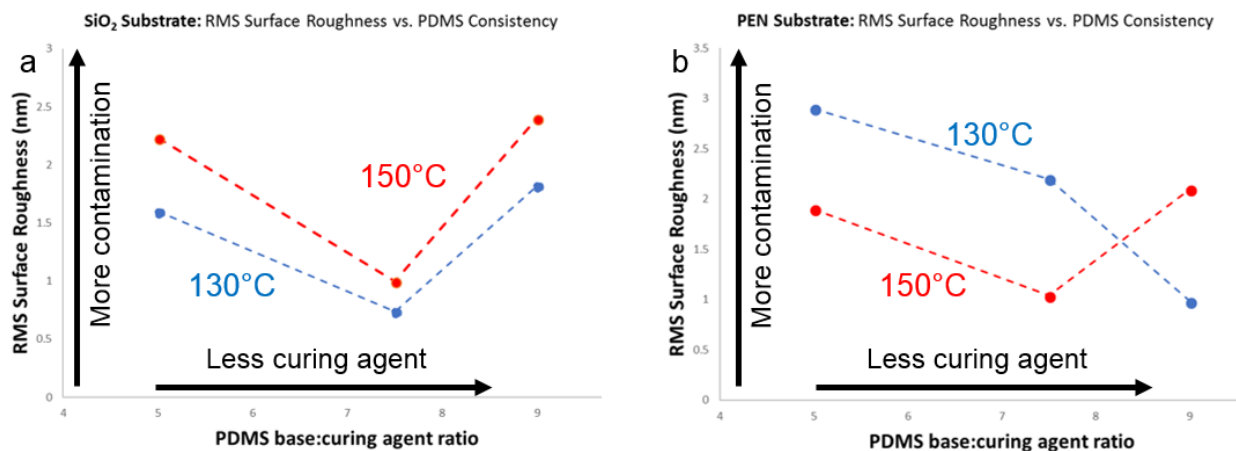


Figure 10: Compiled surface roughness data for the substrates (a) SiO₂ and (b) PEN

VI. Conclusion

Although we had a limited number of data points, we tentatively conclude that the 7.5 (base) to 1 (curing agent) ratio leaves the minimum amount of residue. We further conclude that the higher PMDS release temperature is more optimal for the PEN target substrate while the

lower temperature is better for the SiO₂ substrate. This may be due to the higher temperature getting closer to the melting point of the PEN substrate (approximately 260°C), which could potentially “wet” the surface of the PEN and allow the transfer of WSe₂ to adhere more strongly. On the other hand, the release temperatures are well below the melting point of SiO₂, and so this phenomenon would not affect the SiO₂ data. While not definitively conclusive, this work still provides a starting point for successful 2D material transfers in an inert atmosphere. Our survey paper has the specific transfer process in the ExFab glovebox documented with more in-depth details.

VII. Future Work

With more time, this experiment would benefit from a greater number of data points – both in number of transfers and in characterization. In addition, while many of the transfers in the glovebox are done with exfoliated materials, there is a significant amount of uncontrollable variation that occurs with exfoliated flakes. They range in size, shape, and thickness, with many flakes having “step” like structures where they are made up of different numbers of layers. With this in mind, a DOE using chemical vapor deposition (CVD) grown monolayer material would also be useful, as the transferred material could be standardized to remove one source of variation.

VIII. Acknowledgments

We would like to acknowledge Prof. Howe and Mary Tang for organizing and leading this course. Additionally, we’d like to thank our mentors Michelle and Hye Ryoung for their advice and guidance, as well as members of the Pop group (specifically Connor M. and Isha D.) for helpful discussions.

IX. References

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