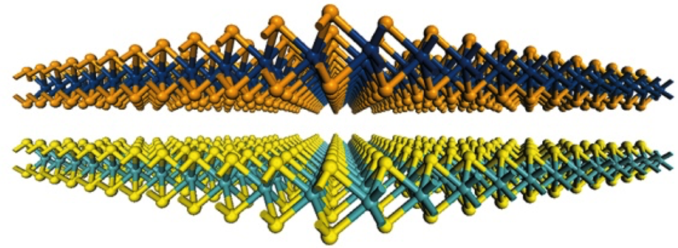
Observation of Interlayer Excitons in Monolayer $\mathrm{MoSe_2} - \mathrm{WSe_2}$ Heterostructures on BN Substrate

Alice Huang, Rutgers University



2015 INT REU, University of Washington
Advisor: Xiaodong Xu

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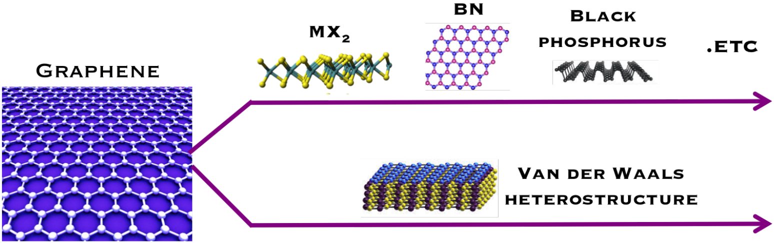
2D Materials [1] [2]

- Graphene is a vast field with more than 10,000 papers published every year → in the recent years, research has expanded to other 2D materials and van der Waals heterostructures



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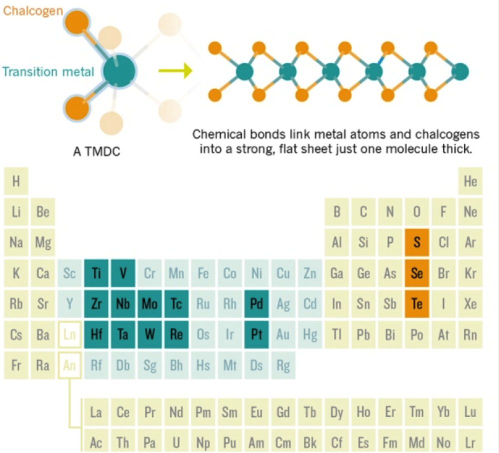
[1] Geim, A. K., et. al, Nature 499, 419-425 (2013)

[2] Gibney, Elizabeth, Nature 522, 7556 (2015)

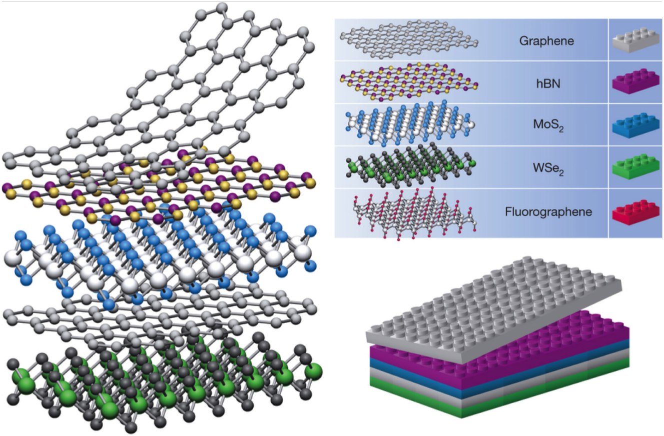
2D Materials [1] [2]

- Transition-Metal Dichalcogenide (TMDC) → chemical formula: $\mathrm{MX_2}$



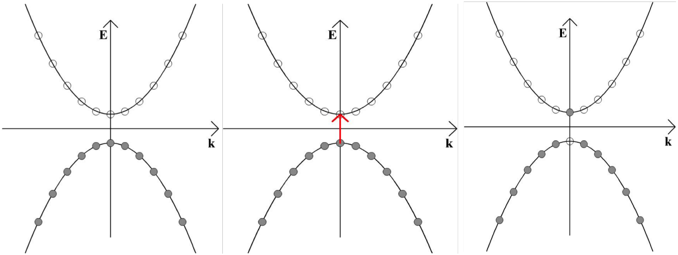
2D Materials [1] [2]

- Building van der Waals heterostructures → Lego block metaphor



What is excitonic physics? [3] [4]

- Absorption of a photon with energy surpassing the bandgap: (1) excites valence band electron into conduction band, (2) creates a 'hole' in the valence band where electron once was



- Given sufficient Coulomb BE, the electron and hole bind together to form an **exciton**, a quasi-particle analogous to the hydrogen atom

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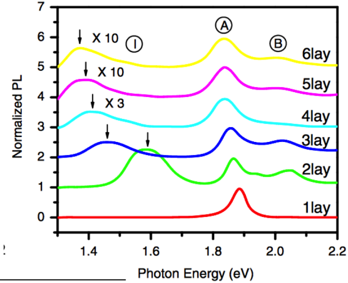
[3] Knowles, Kevin, et. al, "Introduction to Semiconductors," University of Cambridge DoITPoMS (2007)

[4] Miller, D. A. B., "Optical Physics of Quantum Wells" (1996)

Why are monolayer $\mathrm{MX_2}$'s an ideal material for exploring excitonic physics at the 2D limit? [5] [6]

- Characterization of $\mathrm{MoS_2}$ with (a) photoluminescence and (b) optical absorption measurements show crossover from indirect to direct bandgap at the 2D monolayer limit



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[5] Mak, Kin Fai, et. al, Phys. Review Letters 105, 136805 (2010)

[6] Ross, Jason S., Sanfeng Wu, et. al, Nature Communications 4, 1474 (2012)

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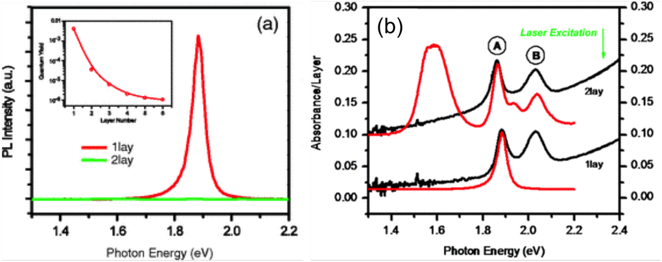

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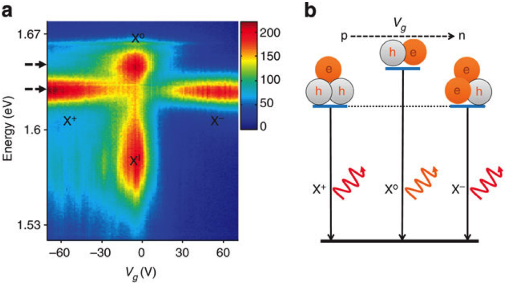
[5] Mak, Kin Fai, et. al, Phys. Review Letters 105, 136805 (2010)

[6] Ross, Jason S., Sanfeng Wu, et. al, Nature Communications 4, 1474 (2012)

Why are monolayer $\mathrm{MX_2}$'s an ideal material for exploring excitonic physics at the 2D limit? [5] [6]

- Because $\mathrm{MX_2}$'s have high Coulomb BE, the neutral exciton (X^0) can bind to an additional electron or hole to become a **trion**, a charged three-body particle (X^- and X^+ respectively)
- Gate dependent PL shows the electric tunability of excitons in $\mathrm{MoSe_2}$



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[5] Mak, Kin Fai, et. al, Phys. Review Letters 105, 136805 (2010)

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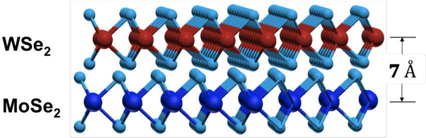
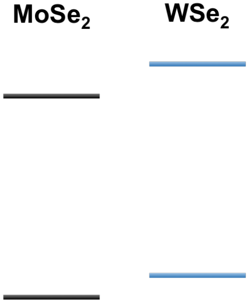
Observation of interlayer excitons in monolayer $\mathrm{MoSe_2} - \mathrm{WSe_2}$ heterostructures [7]

- Type II heterojunction between $\mathrm{MoSe_2}$ and $\mathrm{WSe_2}$





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[7] Rivera, Pasqual, et al., Nature Communications 6, 6242 (2015)

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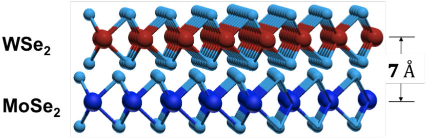

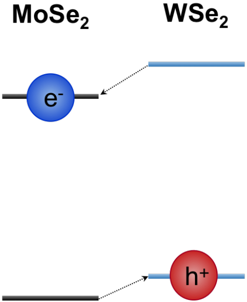

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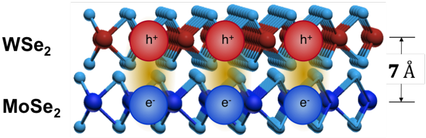

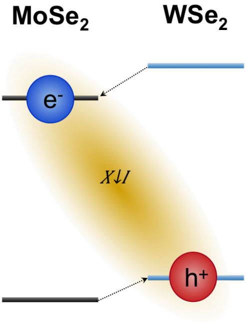

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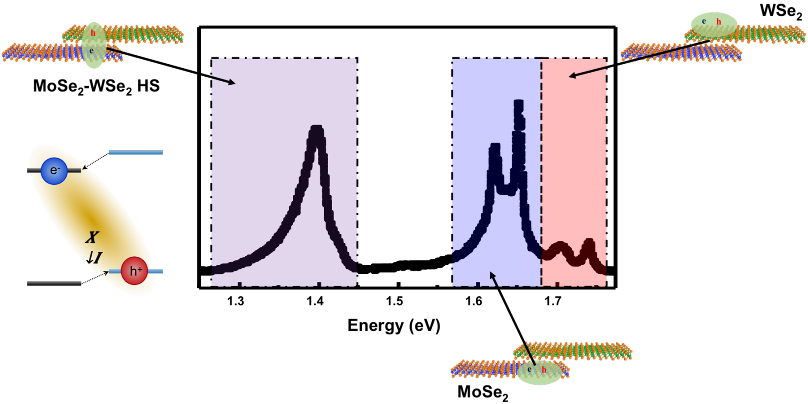
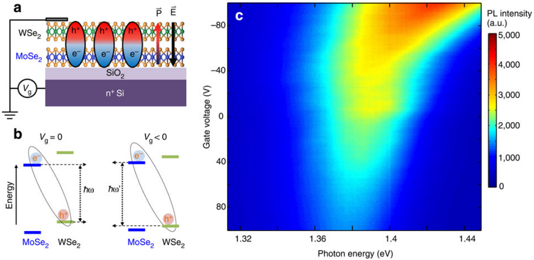
Observation of interlayer excitons in monolayer $\mathrm{MoSe_2} - \mathrm{WSe_2}$ heterostructures [7]

Figure 1: PL measurements reveal distinct interlayer exciton peak



Electrical control of the interlayer exciton [7]

Figure 2: Gate control of the interlayer exciton and band alignment



- Expect a permenant dipole pointing from $\mathrm{MoSe_2}$ to $\mathrm{WSe_2}$

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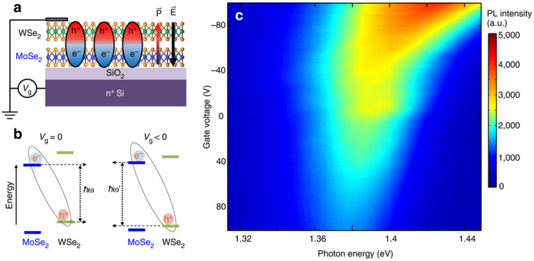

- Expect a permenant dipole pointing from $\mathrm{MoSe_2}$ to $\mathrm{WSe_2}$
- However when stacking order of $\mathrm{MoSe_2}$ and $\mathrm{WSe_2}$ is reversed, the PL intensity with respect to applied voltage does not reverse!

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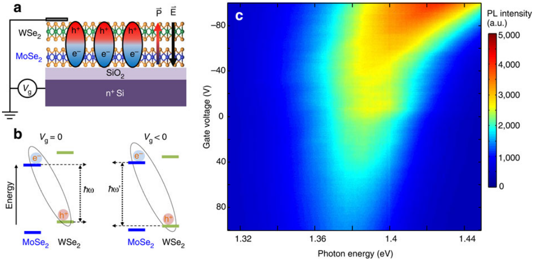
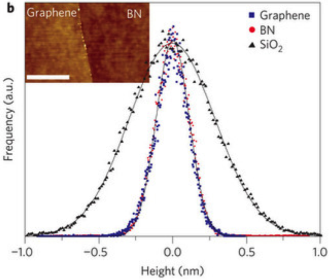


Figure 2: Gate control of the interlayer exciton and band alignment

- Expect a permenant dipole pointing from $\mathrm{MoSe_2}$ to $\mathrm{WSe_2}$
- However when stacking order of $\mathrm{MoSe_2}$ and $\mathrm{WSe_2}$ is reversed, the PL intensity with respect to applied voltage does not reverse!
- Possibly due to charge carrier doping...?

Boron Nitride substrate for ultra-flat high quality electronics [8] [9]

- h-BN is flat and isomorphic with $\mathrm{MX_2}$'s



- AFM measurements show graphene is smoothed by h-BN substrate
- The height distribution for h-BN is nearly identical to that of graphene → graphene adheres to h-BN; distribution width for $\mathrm{SiO_2}$ is 3 times as large

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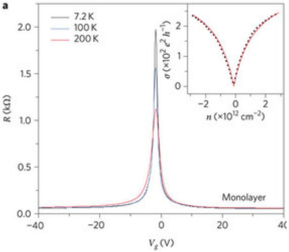
[8] Dean, CR, et al., Nature Nanotech 4, 722-726 (2010)

[9] Xue, Jiamin, et. al., Nature Materials 10, 282-285 (2011)

Boron Nitride substrate for ultra-flat high quality electronics [8] [9]

- h-BN is inert and free of dangling bonds and surface charge traps



- For graphene on h-BN, resistivity peak as a function of backgate (otherwise the charge neutrality point) occurs at $V_g = 0 \rightarrow$ h-BN is already charge neutral without application of external voltage
- From the width of the resistivity peak, carrier inhomogeneity can be determined $\rightarrow \delta_n < 7 * 10^{10} cm^{-2}$, 3 times better than $\mathrm{SiO_2}$ samples

Project Objective, Hypothesis, Questions

Objective

Fabricate and ? a $\mathrm{MoSe_2} - \mathrm{WSe_2}$ heterostructure onto a BN substrate

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Hypothesis

We hypothesize the BN substrate will:

1. smooth the heterostructure surface
2. reduce the heterostructure carrier charge effects

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Fabricate and ? a $\mathrm{MoSe_2 - WSe_2}$ heterostructure onto a BN substrate

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We hypothesize the BN substrate will:

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2. reduce the heterostructure carrier charge effects

Questions

1. Will smoothing of the surface change the band structure and the excitonic behavior of the heterostructure?
2. Will reducing charge carrier effects result in behavior that is consistent with the dipole-electric field model?

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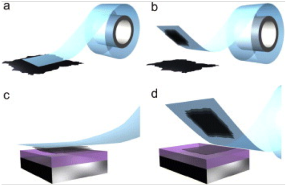
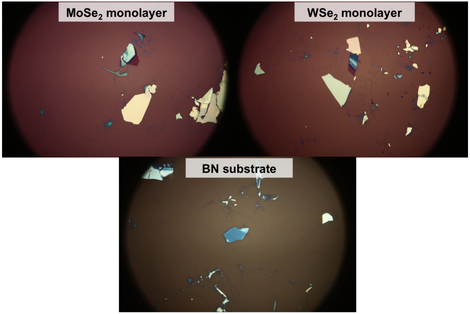
Mechanical Exfoliation [10]

1. Mechanical exfoliation of monolayers using the scotch tape method



2. Identification of monolayers under optical microscope based on color contrast against $SiO_2 \rightarrow$ visible due to thin film interference



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[10] Blake, P., et. al, Appl. Phys. Lett. 91, 063124 (2007)

Atomic Force Spectroscopy (AFM) [11]

- AFM maps the morphology of a sample which is used to determine the cleanliness of sample

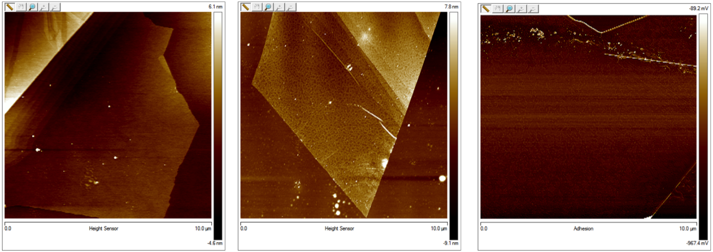

Figure 3: AFM of samples from previous slide

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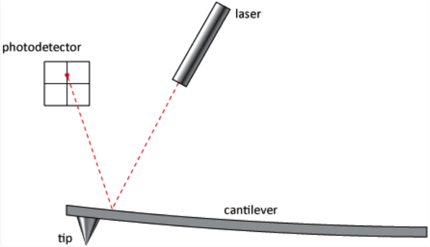
[11]

Atomic Force Spectroscopy (AFM) [11]

- AFM maps the morphology of a sample which is used to determine the cleanliness of sample
- The AFM probe oscillates at resonant frequency which changes in response to electrostatic forces → the sample morphology can be extracted from this difference in frequency



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[11] Knowles, Kevin, et. al, "Atomic Force Spectroscopy," University of Cambridge DoITPoMS (2007)

Cleaning

- Simple experiment to determine best method for cleaning $\mathrm{MX_2}$ monolayers → 10 samples characterized with AFM and/or optical microscope

Cleaning

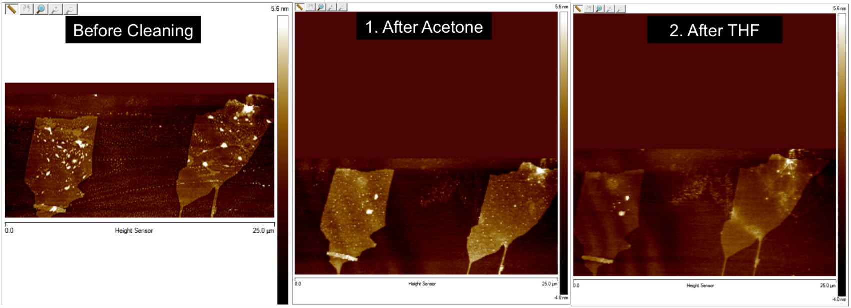
- Simple experiment to determine best method for cleaning $\mathrm{MX_2}$ monolayers → 10 samples characterized with AFM and/or optical microscope
- Here is a summary of results:

Recommended Monolayer $\mathrm{MX_2}$ Cleaning Procedure

1. 15 min bath in tetrahydrofuran (THF) (BP: 66° C) at 50° C with glass cover
2. Immediately wash off with isopropanol and blow with nitrogen

Cleaning summary

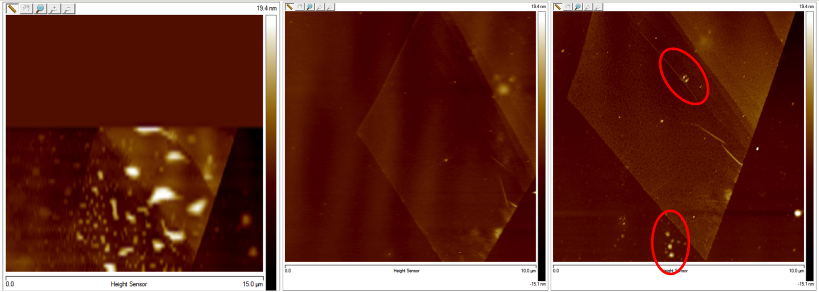
1. The AFM reveals significant improvement after a THF bath but no significant improvement after an acetone bath. In one characterization, the monolayer became dirtier after the acetone bath.



Cleaning summary

1. The AFM reveals significant improvement after a THF bath but no significant improvement after an acetone bath. In one characterization, the monolayer became dirtier after the acetone bath.

There is *more* residue after the acetone bath.



Before Cleaning

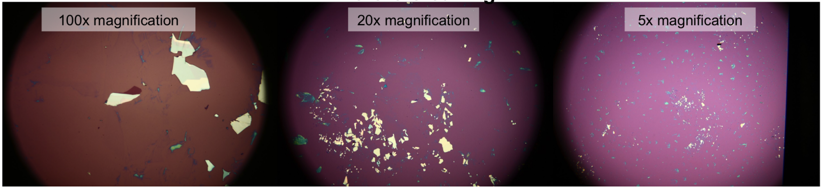
1. After THF

2. After Acetone

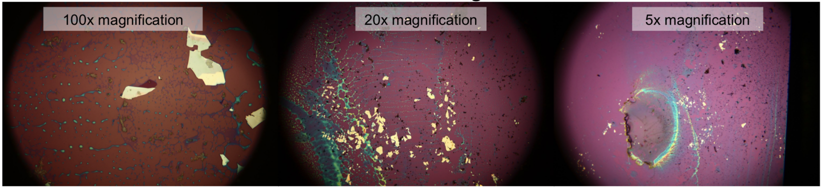
Cleaning summary

2. Immediately wash off with isopropanol after each bath → otherwise the bath will deposit the chip with dirt, rather than remove it

Before Cleaning

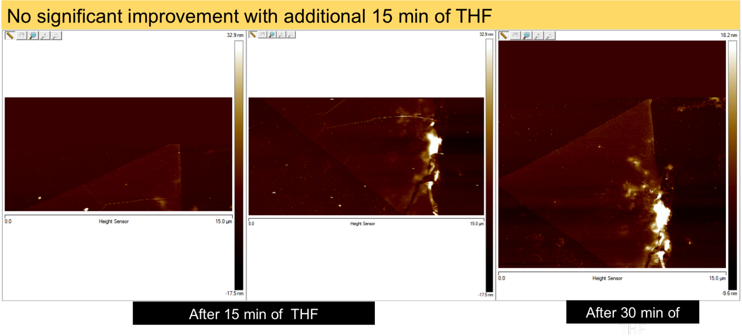


After “Cleaning”



Cleaning summary

3. Time of baths was reduced from 1 hour to 15 min. One characterization showed no significant improvement from 15 min of THF to 30 min of THF. Another characterization showed that the monolayer gets dirtier after more than 15 min in THF.


No significant improvement with additional 15 min of THF

After 15 min of THF

After 30 min of THF

Cleaning summary

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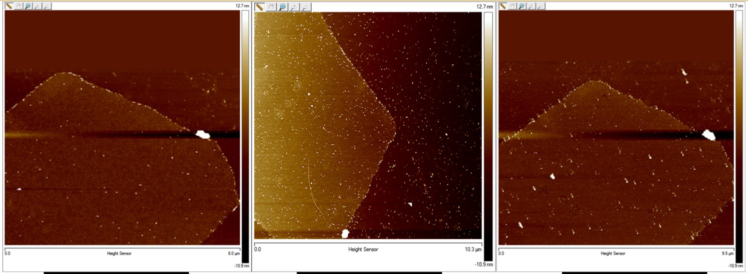
The monolayer is cleanest after 15 min of THF. It actually gets dirtier with increased time



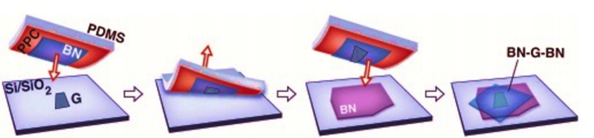
After 15 min of THF

After 30 min of THF

After 1 hour of THF

Heterostructure transfer technique [12]

1. Polymer stamp consisting of PDMS covered with PC film is melted upon the desired sample in the desired orientation
2. The set-up is subsequently cooled → the sample mount contracts, allowing the sample to lift off of the $\mathrm{SiO_2}$ chip onto the stamp



3. The previous two steps are repeated for the desired heterostructure stack
4. For the last transfer, rather than picking up the final layer, the PC layer with the heterostructure is melted onto the $\mathrm{SiO_2}$ chip
5. The $\mathrm{SiO_2}$ chip is bathed in chloroform to clean off the PC film

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[12] Zomer, P. J., et. al, Appl. Phys. Let. 105, 013101 (2014)

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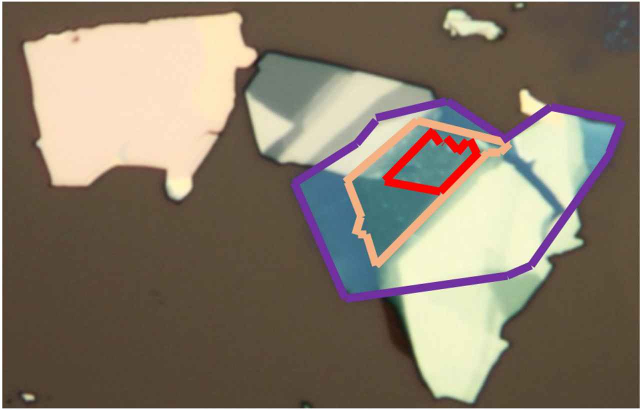
Device 1: $\mathrm{MoSe_2} - \mathrm{WSe_2} - \mathrm{BN}$ heterostructure



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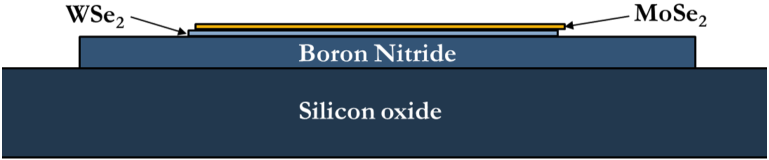
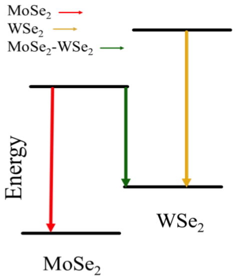
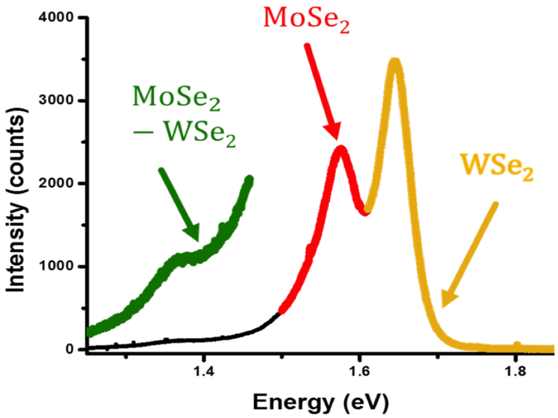


Photoluminescence Characterization





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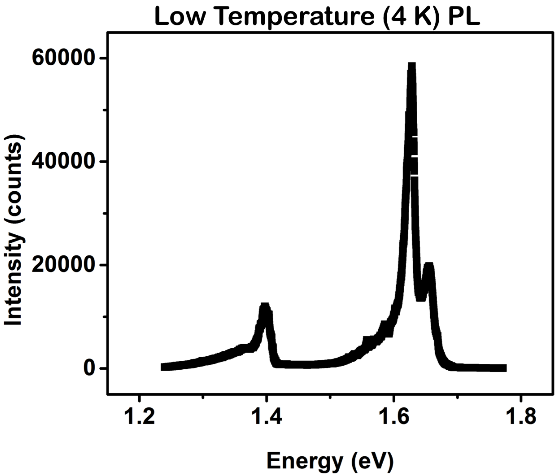

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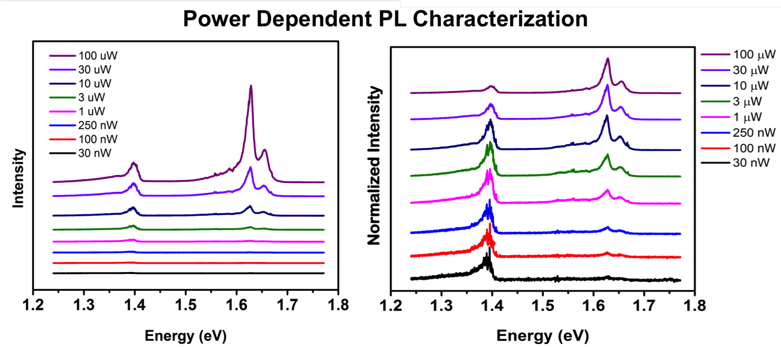

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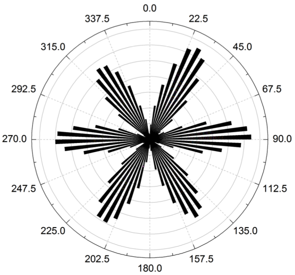
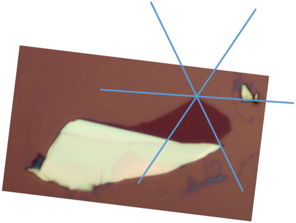
Second Harmonic Generation (SHG) [13]

- Mediums with broken inversion symmetry are capable of generating SHG → non-linear optical process that doubles the frequency of input laser → odd layers of $\mathrm{MX_2}$'s, in particular monolayers





- By sampling SHG intensity at incremental angles, one can determine the crystal axes of an $\mathrm{MX_2}$ monolayer

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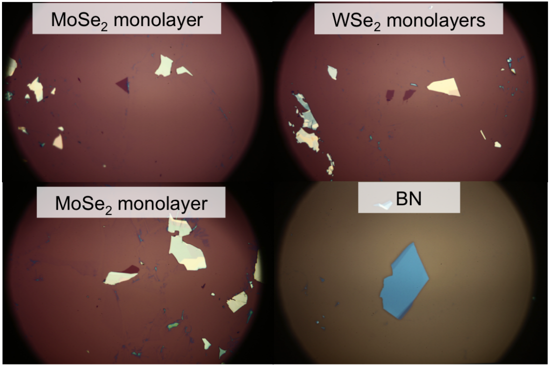
[13] Seyler, Kyle L., et. al, Nature Nano 10, 407-411 (2015)

Device 2



- Match the crystal lattices of the the two monolayers using SHG
- Two hetersotructures on one device with the same BN substrate → $\mathrm{MoSe_2} - \mathrm{WSe_2} - \mathrm{BN}$ and $\mathrm{WSe_2} - \mathrm{MoSe_2} - \mathrm{BN}$ → comparison of stacking order

Future Testing

- Spatial photoluminescnece
- Electrical control of the interlayer exciton
- Power dependence and lifetime of interlayer/intralayer excitons
- Valley polarization of interlayer/intralayer excitons

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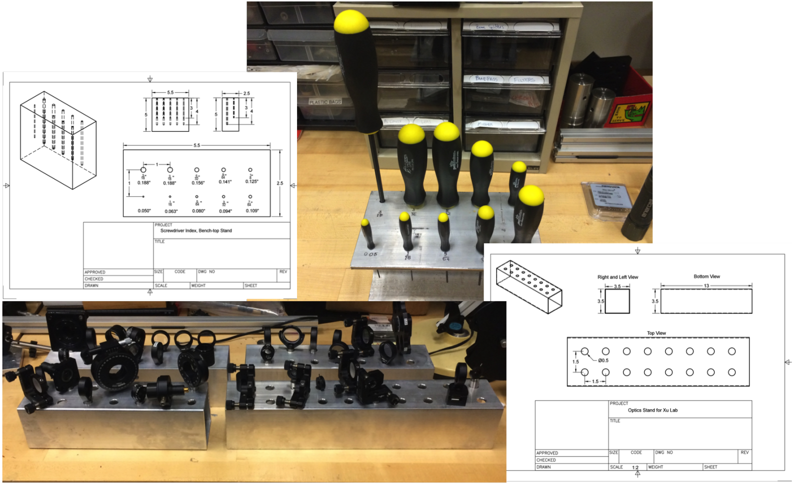
Machine Shop



Acknowledgements

Thank you to Xiaodong Xu for this wonderful summer lab experience.

Special thanks to Pasqual Rivera and Kyle Seyler for being outstanding mentors.

Thank you to Essance Ray, Eric Wong, Paul Nguyen, Genevieve Clark, Jason Ross, Sanfeng Wu, Harold Cai, John Schaibley, Ding Zhong, Jae Hwan Chu, Nathan Wilson, and Bevin Huang who assisted me in lab on a daily basis.

Thank you to Ron Musgrave for the machine shop lessons.

Thank you to the REU coordinators and the NSF.

Questions?