Characterizing Nanopattern Formation of Polymer Thin Films on Silicon Substrates with Ion Beam Sputtering

Jocelyn Zhang[1,4,5], Grace Pettis[2,5], Benli Jiang[4], Gözde Ozaydin Ince[3], Karl F. Ludwig Jr.[4,5]

Del Norte High School, 16601 Nighthawk Ln, San Diego, CA, 92127[1], Oregon State University, 601 SW 17th Street, Corvallis, OR, 97331[2], Sabanci University IICEC[3], Division of Materials Science and Engineering, Boston University, Boston, MA, 02215[4], Department of Physics, Boston University, Boston, MA, 02215[5]

Introduction

- **Ion Beam Sputtering (IBS)** has previously been observed to create nanopatterns on the surface of materials
  - Formation of patterns on polymer films by ion bombardment is **not yet understood**

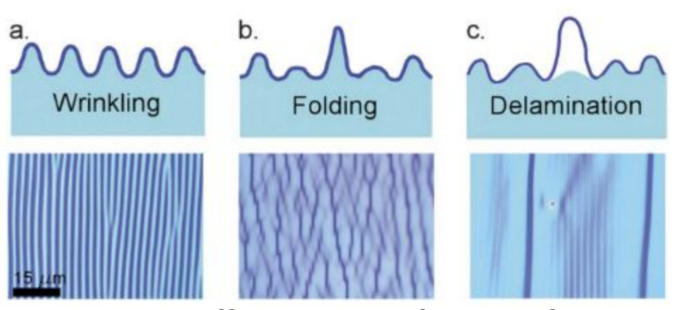


Figure 1. Different types of pattern formation known to be correlated with ion bombardment [1]

- **Poly(4-Vinylpyridine) (4-VP)** and **Polystyrene (PS)** polymer thin films on Silicon substrates were selected
  - Structurally similar
  - **Differ by a single aromatic Nitrogen atom** only present in 4-VP

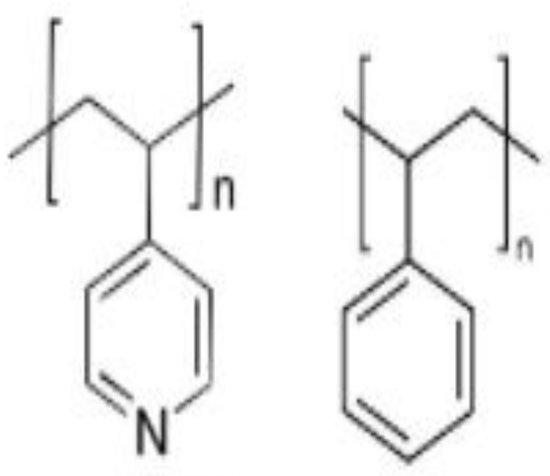


Figure 2. Poly(4-Vinylpyridine) (4-VP) [2]

Figure 3. Polystyrene (PS) [3]

Methods

1. **iCVD (Chemical Vapor Deposition)**

iCVD (performed by Ince's group) was first used to deposit a uniform layer of polymer on top of the Silicon substrate.

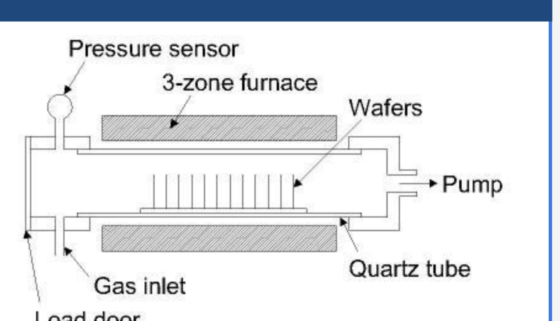
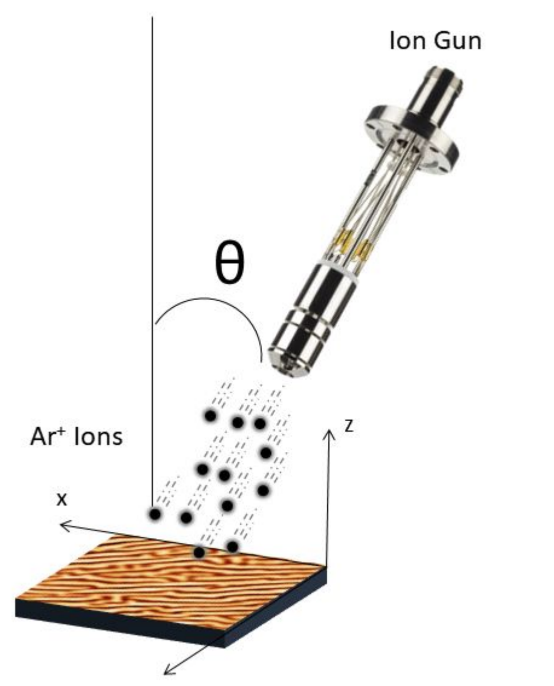


Figure 4. Chemical Vapor Deposition Process [4]



2. **Ion Beam Sputtering (IBS)**

Using an ion gun, samples were bombarded with Ar^+ ions

Incidence Angles (θ):

- normal incidence (0^o)
- off-axis incidence (50^o or 70^o)

Ion Energy: 2000 eV

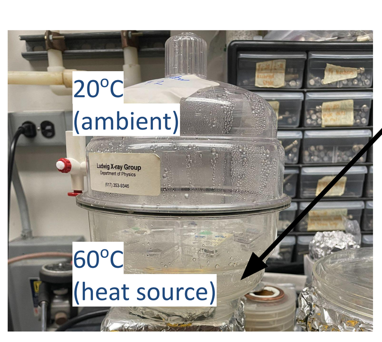
Operating Pressure: 5.00E-05 Torr

Exposure Time: 60 minutes

Flux: ~2.0E+13 Ar+/cm^2*s

3. Humid Environment vs. Dry Desiccator

After bombardment, samples are placed into either a humid environment (left) or a dry desiccator (right)



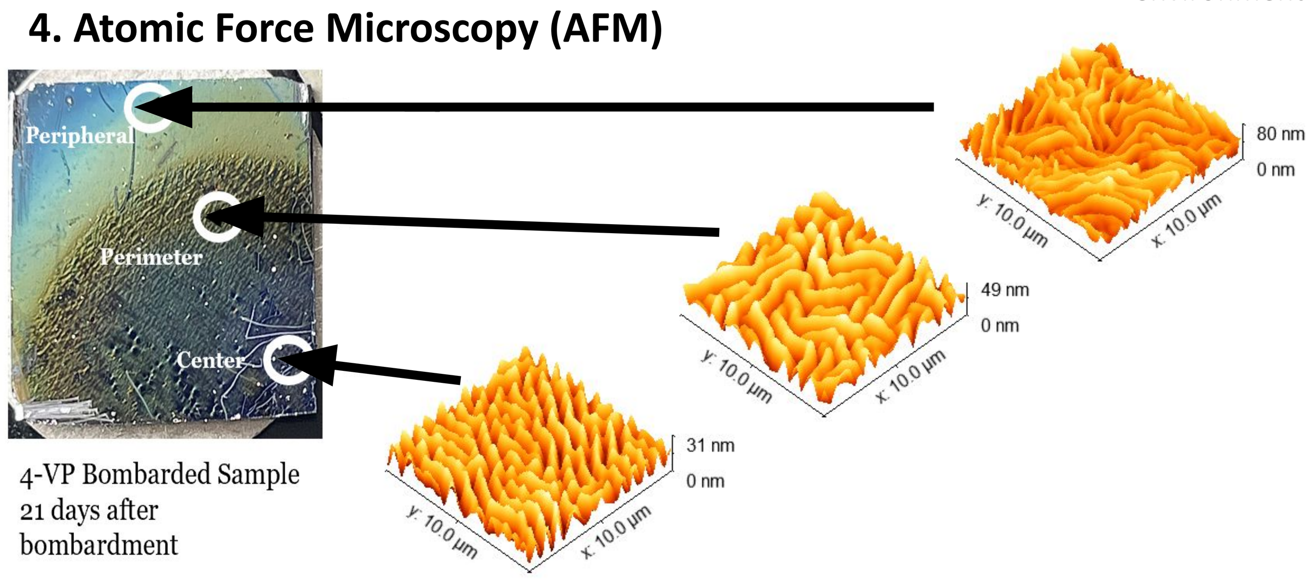
Humid Environment

- Slightly acidic water (pH 4.2) placed in chamber below samples

Dry Desiccator

- Polycarbonate drierite creates dry environment

4. Atomic Force Microscopy (AFM)



4-VP Bombarded Sample 21 days after bombardment

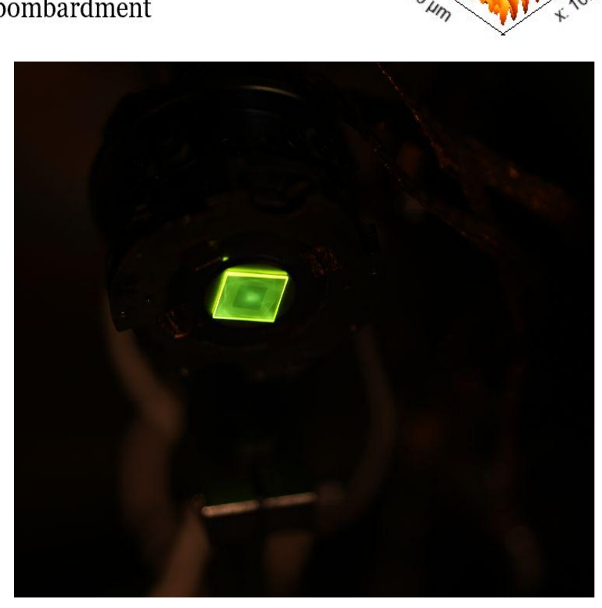


Figure 5. Image of the Ce:YAG crystal with ion beam focus adjust at 2(45) and 0^o bombardment

- **Edges** of the sample received a **lower ion fluence / less concentrated beam**
- Ce:YAG crystal glowing **non-uniformly**
  - **Fluorescence intensity** at **edge** is **low**

5. Optical Microscopy (OM), Raman Microscopy, Contact Angle Measurements

Results

Optical Microscopy (OM) Images (from A. Nikiforov)

- Figures shown are of 4-VP sample placed **in humidity at room temperature**
- **Fluid pockets** formed in conditions with increase in absolute humidity (by increasing temperature)
  - Near these pockets, wrinkles aligned radially *(Fig. 6)*
  - **Delamination** occurs when **fluid pockets popped** *(Fig. 7)*
- **None of these surface features were seen on Polystyrene samples in humidity**

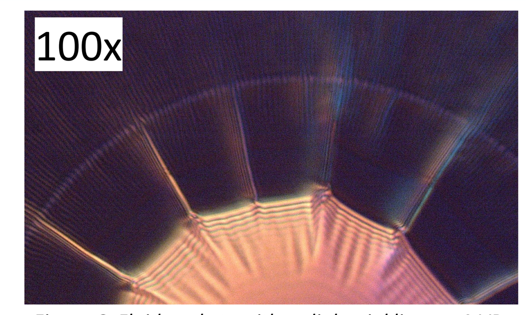


Figure 6. Fluid pockets with radial wrinkling on 4-VP

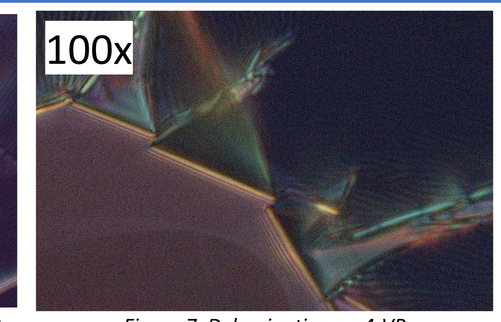
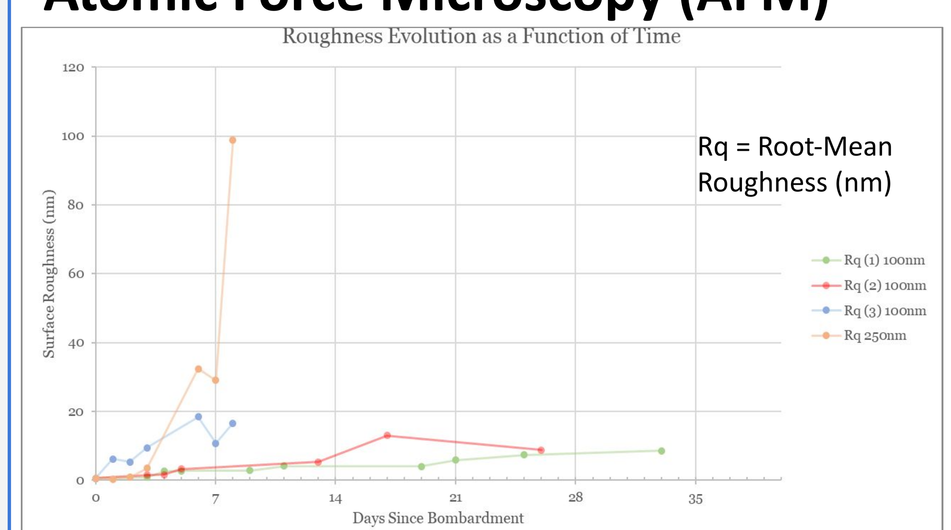
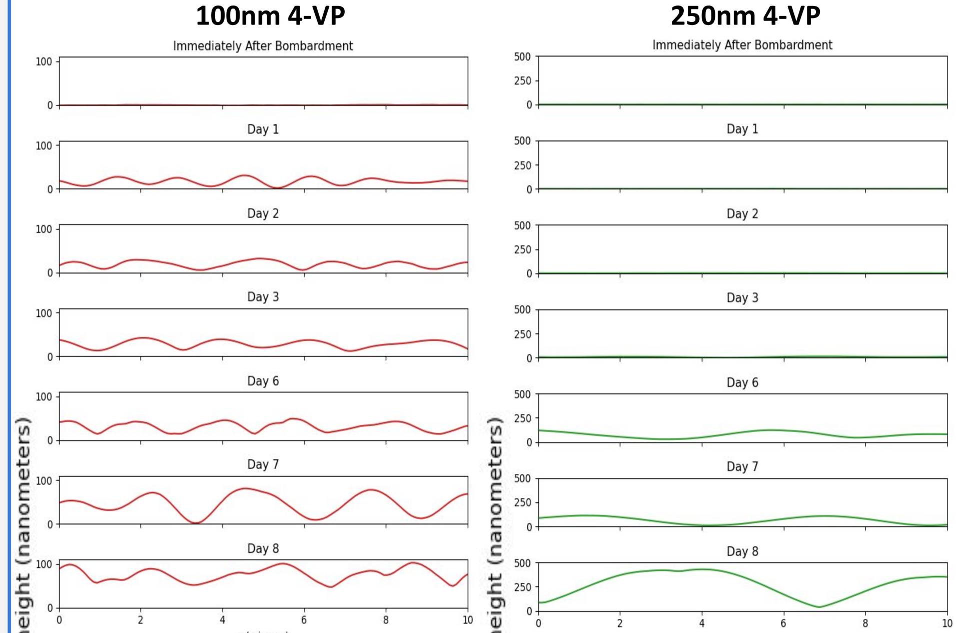


Figure 7. Delamination on 4-VP

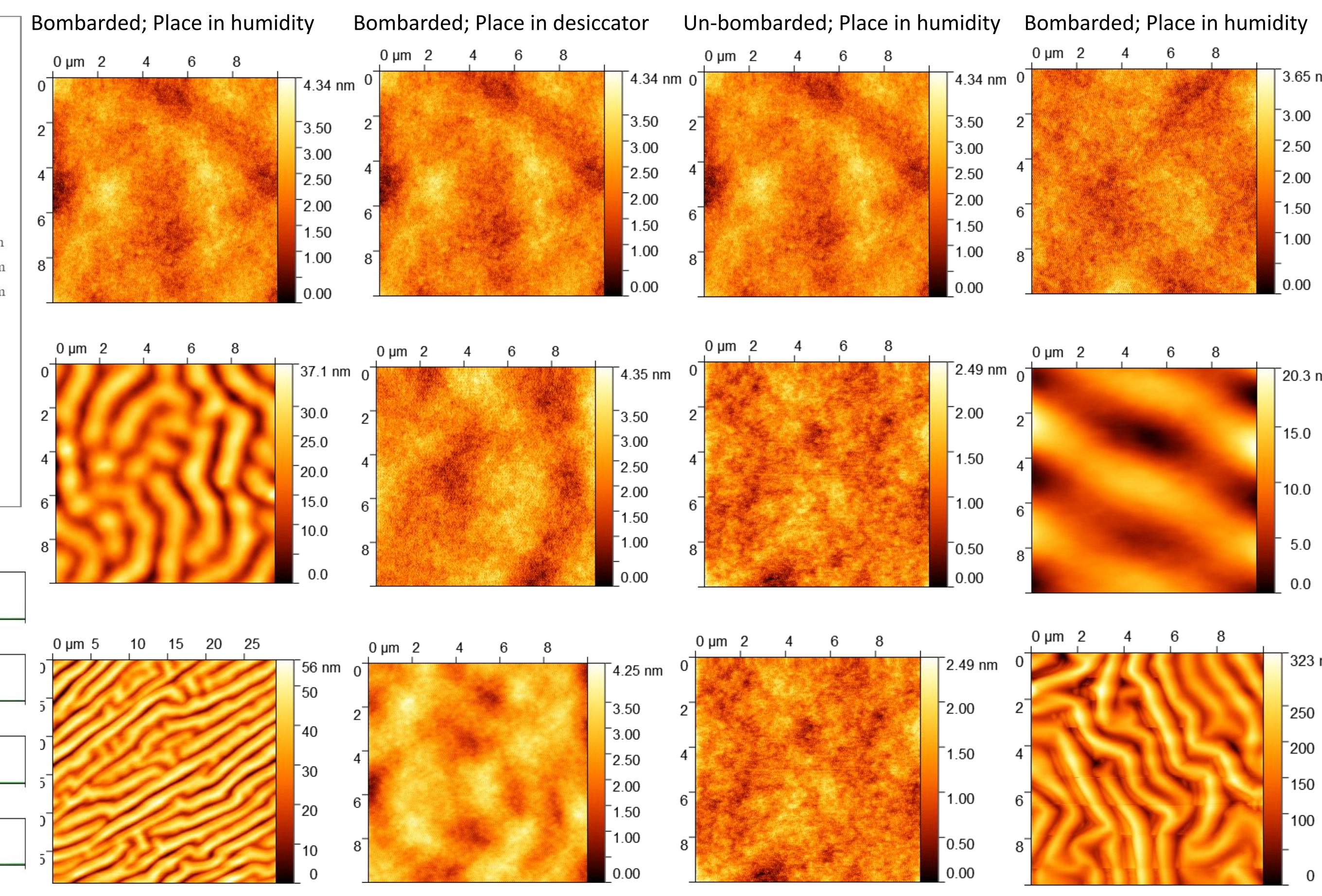
Atomic Force Microscopy (AFM)



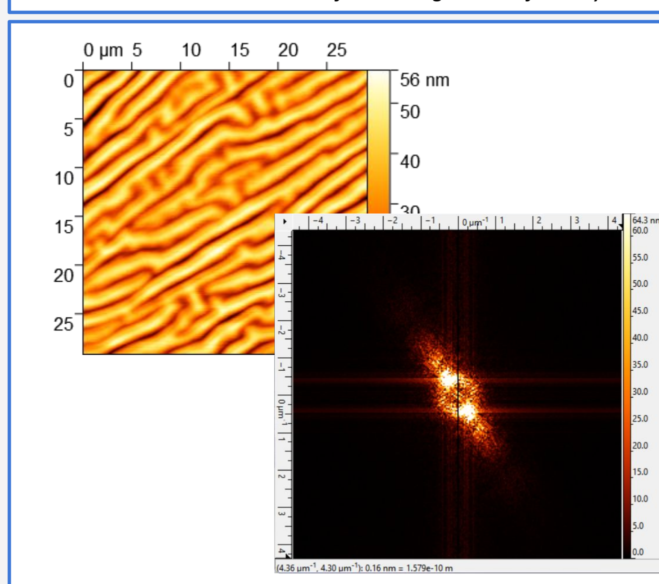


Timeline of wrinkling 1-D Profile Days 1-8

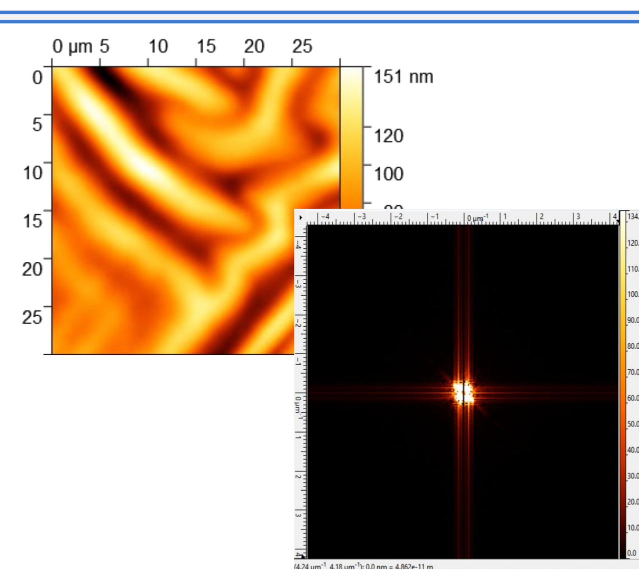
AFM Progression of 4-VP (100nm thickness) Over Time — **250nm thickness Over Time**



- For **both film thicknesses** of 100nm and 250nm, only samples that were **bombarded** and subsequently placed in **humidity** saw **formation of nanopatterns**
- Samples wrinkled faster **after decreasing the absolute humidity of the humid environment** (from roughly 23g/m^3 to 17g/m^3)



*AFM image (left) and 2-D FFT image (right) of **100nm** 4-VP*



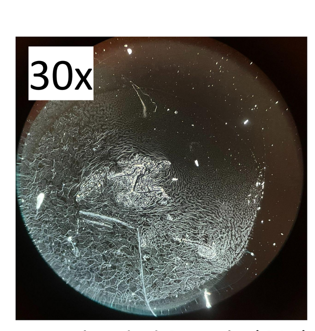
*AFM image (left) and 2-D FFT image (right) of **250nm** 4-VP*

2-D Fast Fourier Transform (FFT)

- **100nm 4-VP** has most frequent wrinkle wavelength of **~1.2 microns**
- **250nm 4-VP** has most frequent wrinkle wavelength of **~4 microns**
- **Increase in polymer film thickness increases wavelength of wrinkles**

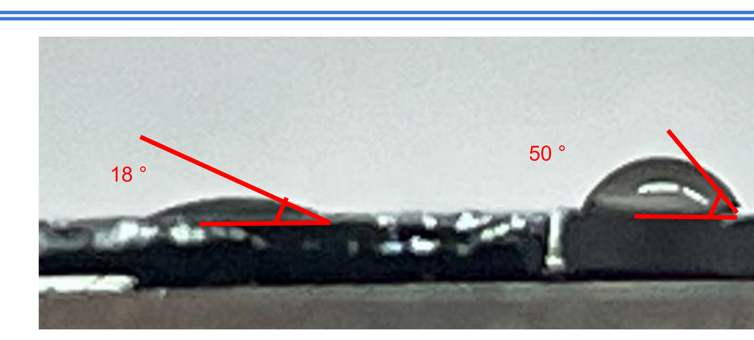
Contact Angle

Un-bombarded Sample (OM)

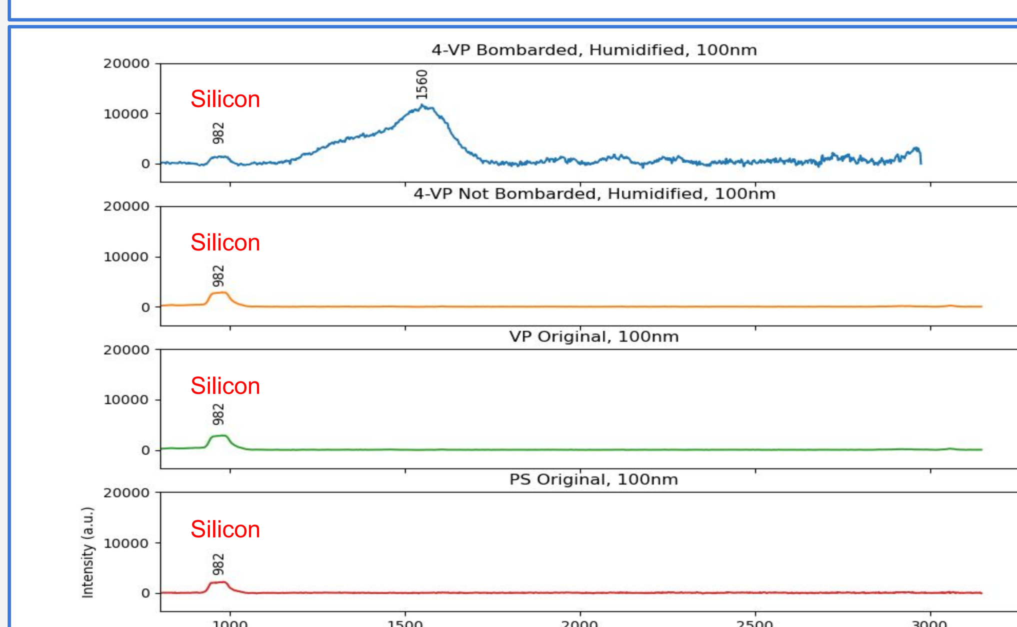


Bombarded Sample (OM)

- Water drop on un-bombarded sample degraded surface, no nanoscale patterns formed
- Water drop on bombarded sample left visible wrinkling, surface features too large to see on AFM



Optical Microscopy (OM) images of bombarded sample (right) consistently had a greater contact angle than the un-bombarded sample (left)



Raman Spectroscopy

- Clear peak change after wrinkling
  - Could be attributed to **absorbance of water**
- Peak at 1560nm similar to **aromatic Nitrogen** and / or **H-O-H bending mode** but isn't conclusively either
- Indeterminate signal above 3000nm **repeatable** in many samples, difficult to capture
  - Could be a **weak O-H stretch signal from water content** as well
- Weak signal from thinness of films reveals little about structure of polymers themselves, leading to flat regions in other spectra

Discussion / Conclusions

- **Water** and **ion exposure** are required for **wrinkling**
  - **Too much ion exposure causes less ordered wrinkling**
  - Areas of **lower ion fluence** have **less ordered wrinkling**
- Ion bombardment is associated with **increase in contact angle, decrease in surface wettability, more hydrophobic**
- Raman peaks likely due to water signal
  - 4-VP is pH responsive
  - Indicates change on the molecular level because they are likely **absorbing slightly acidic water after bombardment and humidification**

References

[1] Ebata, Yuri, et al. "Wrinkling and Strain Localizations in Polymer Thin Films." *Soft Matter*, 26 July 2012, pubs.rsc.org/en/content/articlelanding/2012/SM/c2sm25859e#!divCitation.

[2] "4-Vinylpyridine." *4-Vinylpyridine* -, www.sigmaaldrich.com/US/en/substance/4vinylpyridine10514100436. Accessed 7 Aug. 2023.

[3] "Polystyrene." *Polystyrene - PS*, www.sigmaaldrich.com/US/en/substance/polystyrene123459003536. Accessed 7 Aug. 2023.

[4] "Deposition Processes." *MNX*, www.mems-exchange.org/MEMS/processes/deposition.html. Accessed 5 Aug. 2023.

Acknowledgements

The funding for this work was provided by NSF-2117509. I would like to express my deepest gratitude to my mentor, Professor Ludwig, my lab partner, Grace Pettis, Benli Jiang, Gözde Ozaydin Ince, and the rest of Ludwig Lab; this research would not have been possible without them. I would also like to thank Dr. Nick Fuhr, Dr. Shambhavi Tannir, and Dr. Alexey Nikiforov for their unwavering support and guidance throughout the project.