Role of Thin Film Morphology on Organic Photovoltaic Performance

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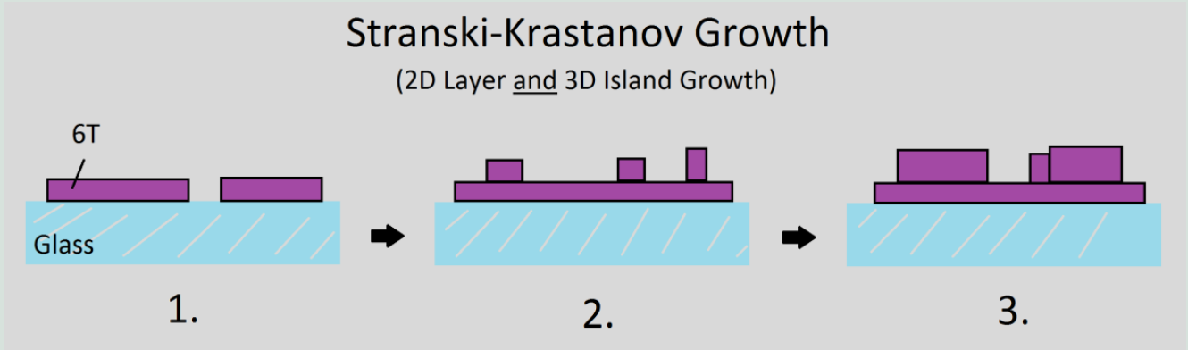
Abstract

As the necessity for smaller, more efficient electronic devices and the drive to harness alternative sources of energy develops, understanding organic semiconductors has become a prevalent cornerstone of technology in many facets of research and industry. Atomic Force Microscopy (AFM) is a type of scanning probe microscope that analyzes surface specific properties such as height, friction, and roughness of samples. In this project, sexithiophene (6T), an organic semiconductor, is studied using AFM to characterize its morphology relative to its electrical properties. In identifying growth patterns of crystallites in thin films, organic photovoltaic devices may be optimized with increased efficiency and reduced costs[3].

Objectives

- Explore AC mode and Contact mode AFM techniques that can be used to extract information on the morphology of 6T.
- Analyze the topography, phase, friction, and roughness of the materials - indicative of changes in morphology of the sexithiophene films.
- Evaluate which thickness a monolayer is formed, and confirm a Stranksi-Krastanov growth mechanism of the material.

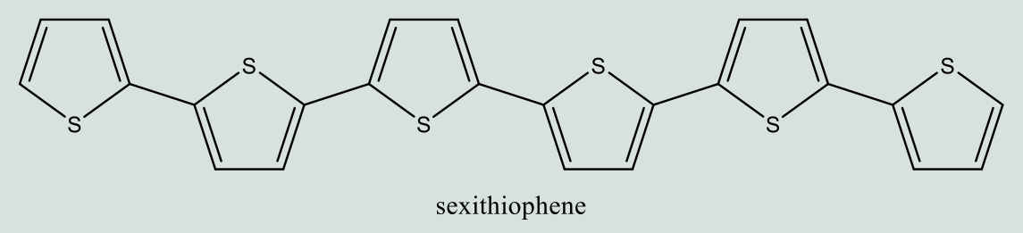


Materials and Methodology

Sample Preparation:

- 6T is deposited using a chemical vapor deposition chamber, monitoring the thickness with a quartz crystal microbalance.

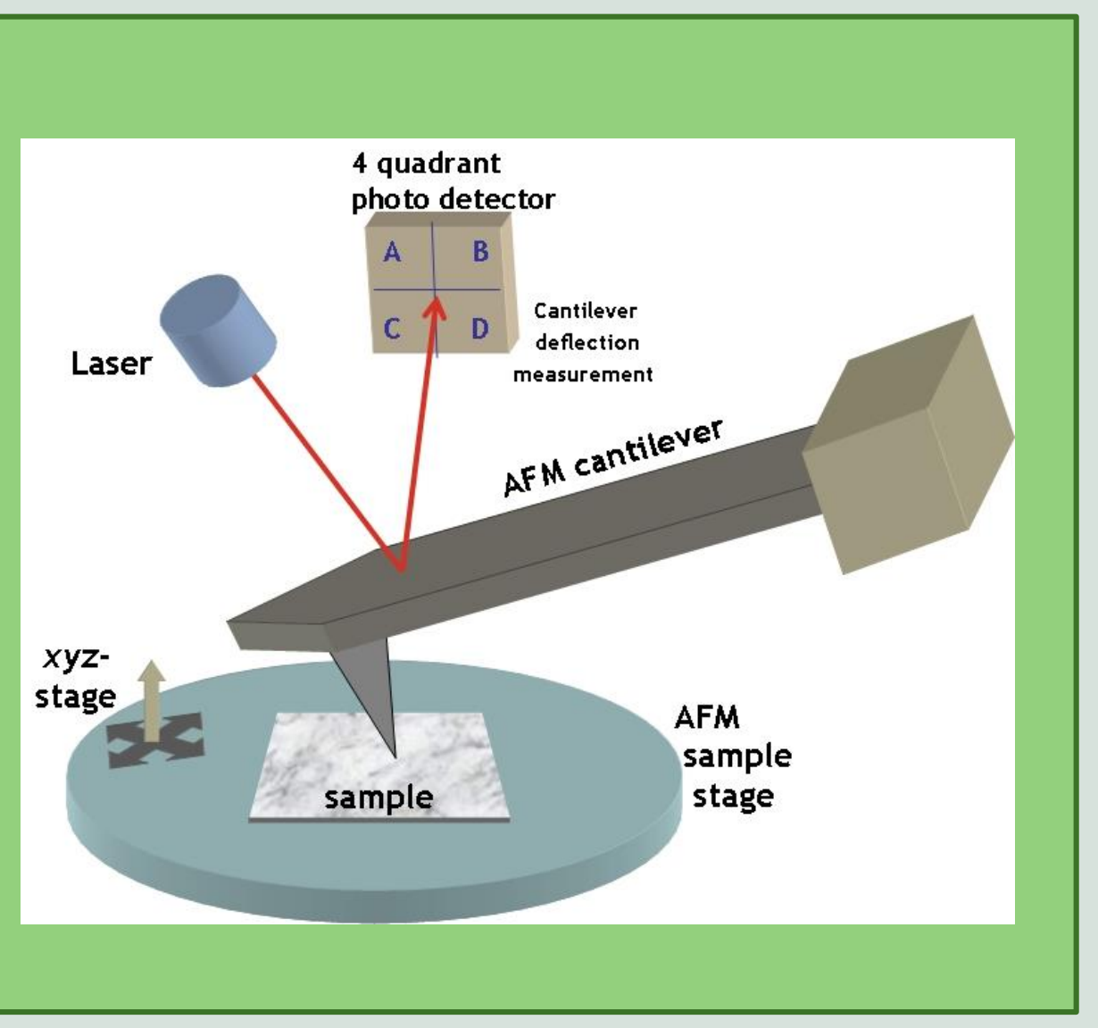
AFM Technique:


sexithiophene

- Both AC and Contact modes are used to examine the films properties. Contact mode is used for a scraping technique to remove the top layer of 6T on the 1 nm thick sample. This is done with a force of about 10nN at a scan rate of 24 lines/sec over an area of 3x3 micrometers.

How AFM is Used:

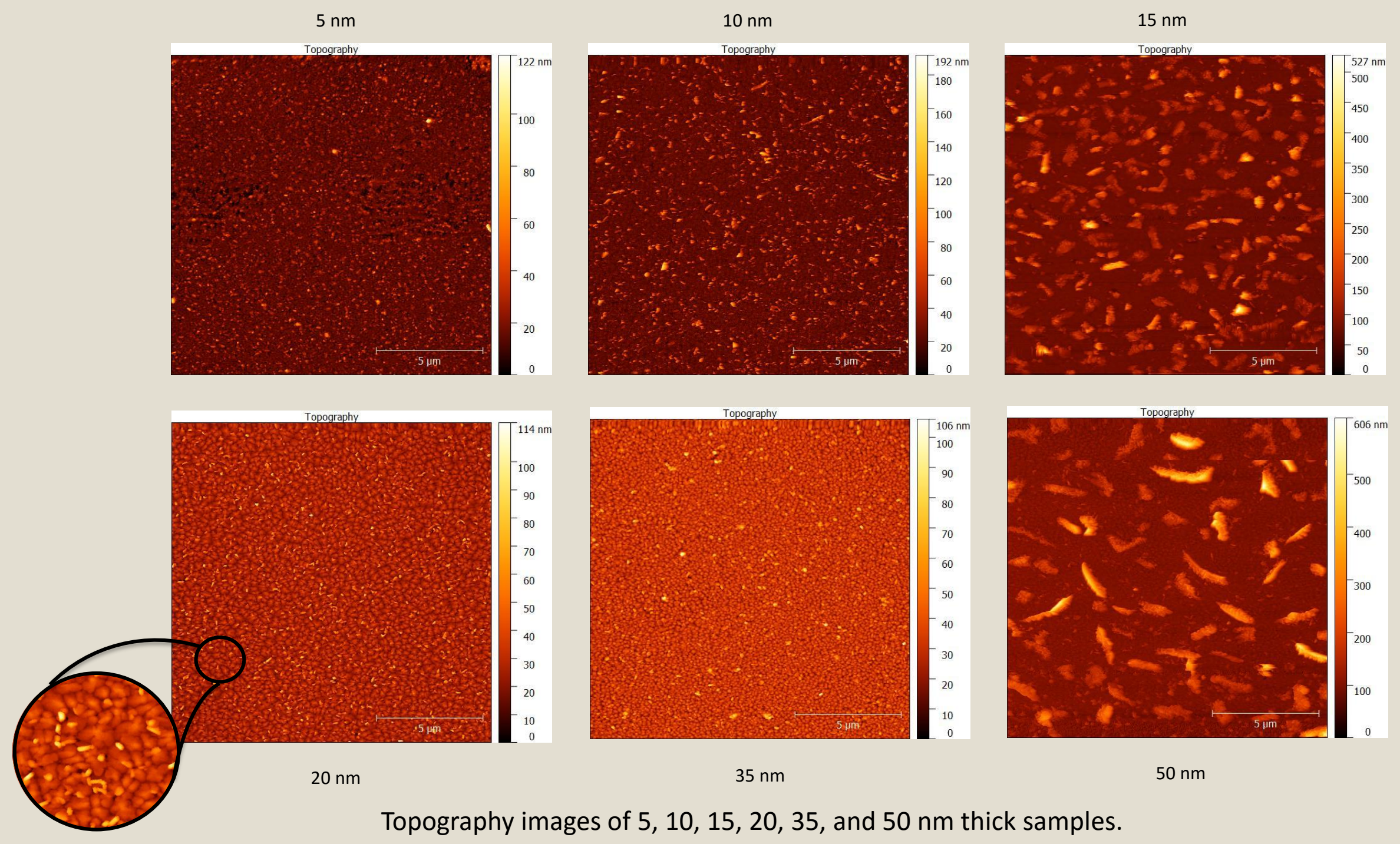
A laser is used to measure the deflection of the AFM cantilever as the cantilever moves up and down, scanning across the surface of a sample. The deflected laser is measured with a photodiode (photo detector in this image) mapping the position of the tip and resulting in an image of the topography of the sample[1].



Results

Topographical Changes:

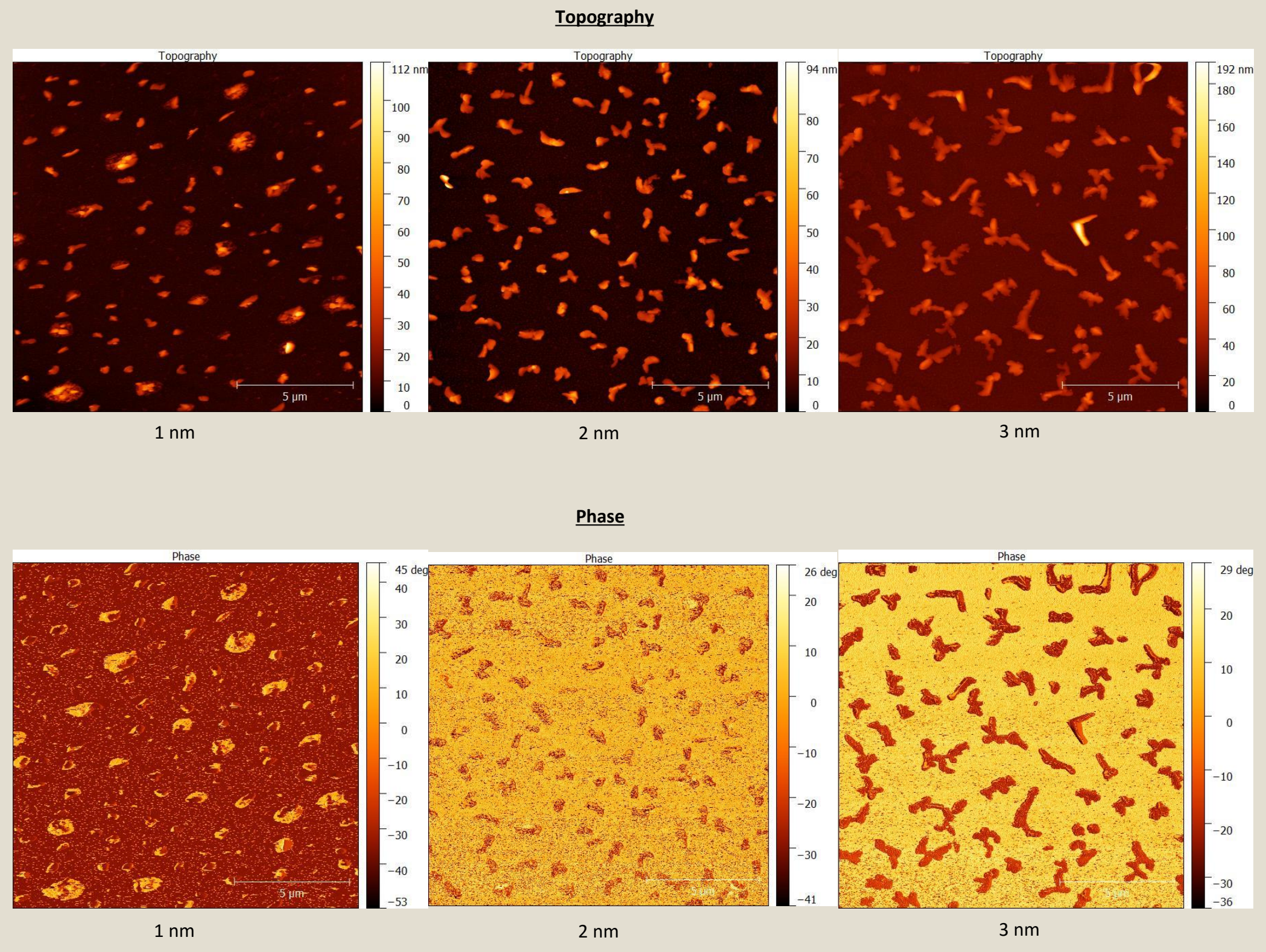
- 5, 10, 15, 20, 35, and 50 nm thick films are characterized using AFM and their respective topographies are analyzed.
- From these images, a glimpse at how crystallites of 6T form as more material is deposited on the substrate is revealed.
- These samples indicate that the small islands or crystallites of 6T can form layers between 1 and 5 nm. Multiple sublayers are evident beneath the top crystallites.



Topography images of 5, 10, 15, 20, 35, and 50 nm thick samples.

Observing Phase Differences:

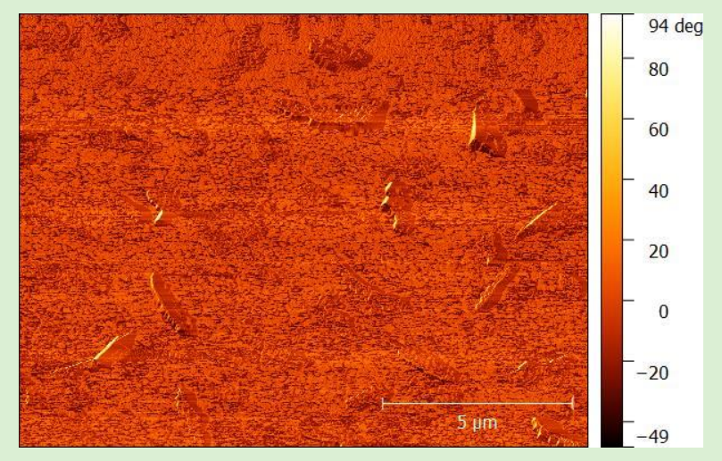
- The growth of the 6T crystallites are illustrated increasing in size and density from 1 nm to 3 nm.
- The phase of these images indicate differences between attractive and repulsive regimes during the scan. Different phases are clearly visible going between the crystallites and their background – demonstrating different interactions with the AFM tip.
- This data suggests that material in the background of the crystallites is glass.



Topography and Phase images if the 1, 2, and 3 nm thick samples.

Phase Image of 50 nm Sample:

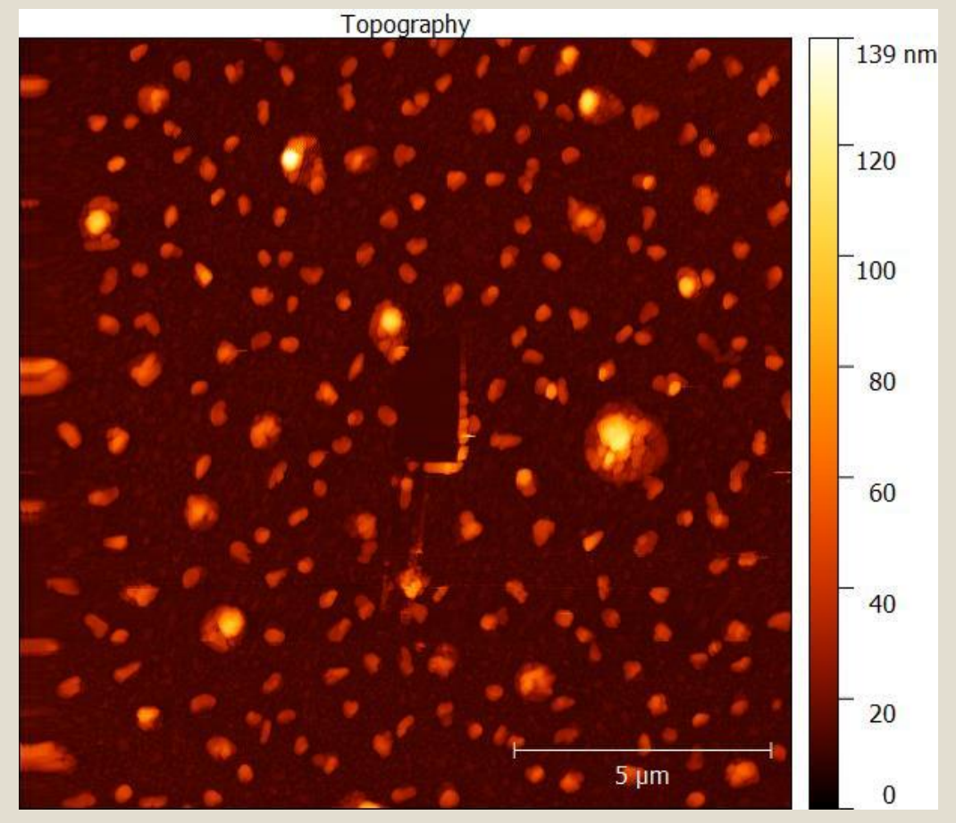
With the thicker samples that have crystallites on sublayers of 6T, the contrast in the phases are not as apparent compared to the 1, 2 and 3 nanometer samples.



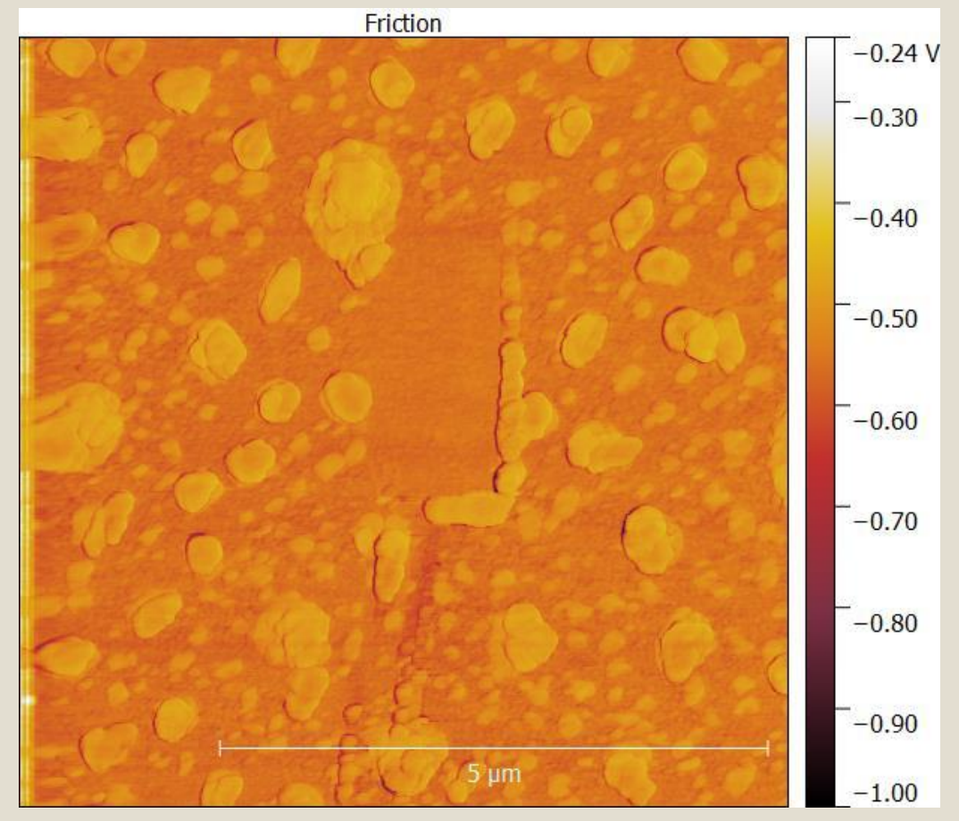
50 nm Phase Image

At What Thickness Do We Detect A Monolayer?

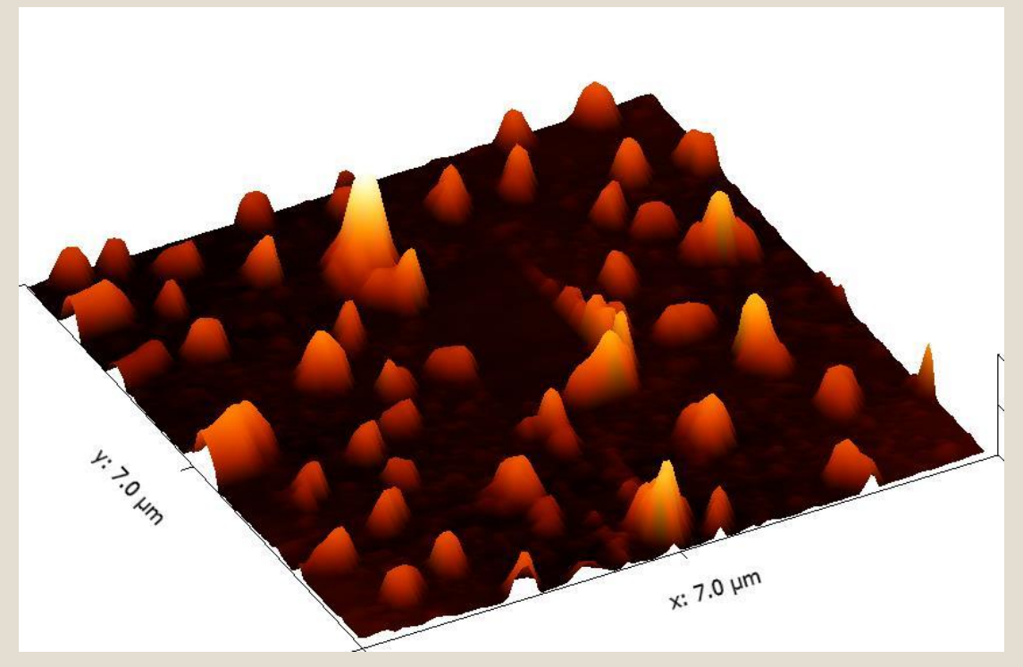
- In an attempt to understand if the crystallites seen at the 1 - 3 nm thicknesses are on top of 6T or glass, an excavation method using contact mode AFM is used to scrape at the sample to see if any 6T can be removed.



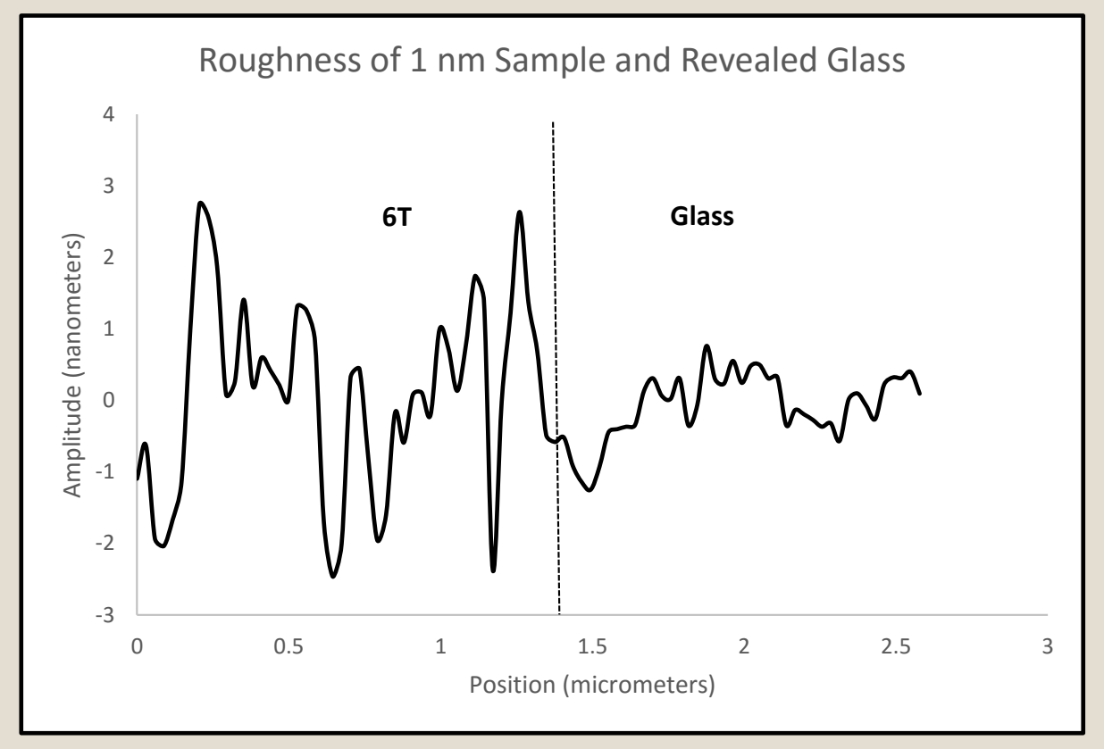
Topography Image of 1 nm sample with rectangle of 6T excavated.



Friction Image of 1 nm sample with rectangle of 6T excavated.



3D rendering of the removed 6T layer on the 1 nm thick sample.



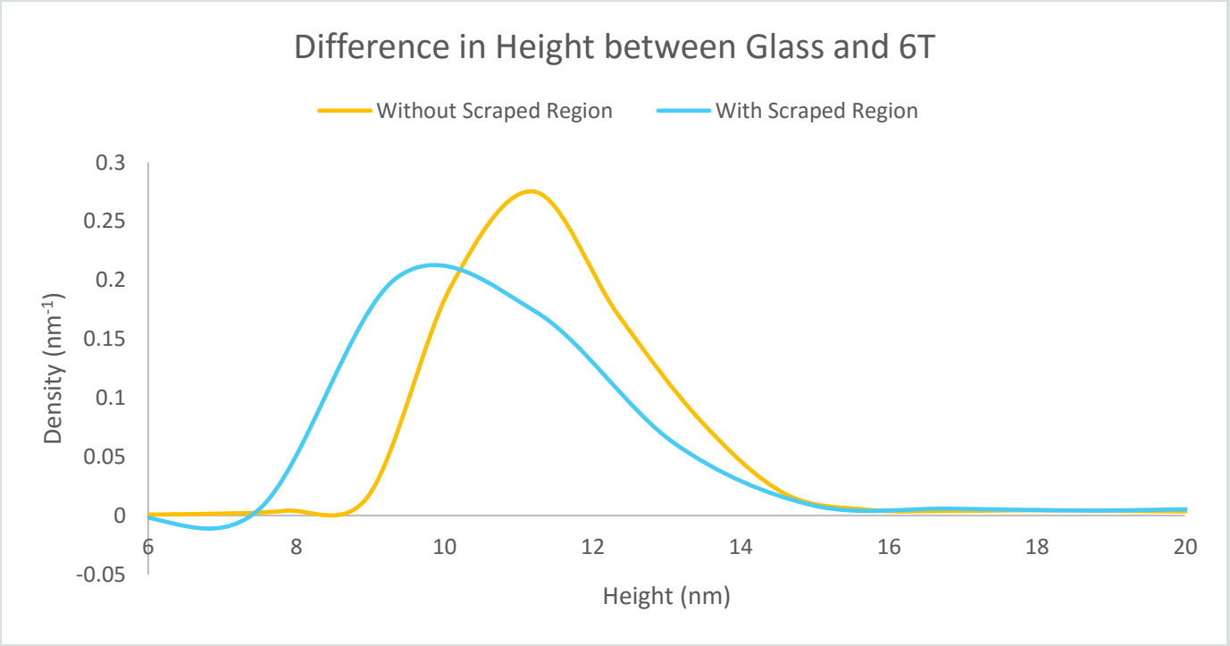
This figure demonstrates the difference in roughness between the excavated glass and the layer of 6T.

Conclusion

- The apparent thickness of the films are an average of a multitude of varying topographical features, as opposed to a single height measured by the quartz crystal microbalance that monitors their growth in the deposition chamber. The images of the 1, 2, and 3 nm thick samples support the model of Stranski-Krastanov growth as a result of both a sub-layer formation in addition to simultaneous islands of 6T developing. The following data also exemplifies the wide distribution of heights inherent in the samples.

Sample	Range in Height	Median Height	Average Height
1 nm	112.17 nm	5.50 nm	7.38 nm
2 nm	75.47 nm	4.01 nm	7.24 nm
3 nm	191.65 nm	20.23 nm	24.62 nm

The scraping technique demonstrates both the variety of heights in the 6T layer topography, and a shift in height as a result of the removal of the material from the glass.



Future Work

- Future work on this project includes studying the vibrational sum frequency generation data acquired on the samples, and pairing this data which provides information on the orientation of the molecules at the surface, with the topography of the 6T to fully capture the structured layering of the material.
- Additionally, it would be beneficial to manufacture complete organic photovoltaics to test the potential of the cells with regards to the different morphologies. Then, the predictions in performance based on the data obtained from the AFM of the 6T could be compared to experimental data, seeing if the morphology has a significant difference on the efficiency of the cell.

References

1. David Nečas, Petr Klapetek, Gwyddion: an open-source software for SPM data analysis, *Cent. Eur. J. Phys.* **10**(1) (2012) 181-188
2. "Typical atomic force microscope (AFM) setup" by yashvant is licensedunder CC BY 2.5
3. Gunes S.; Neugebauer H.; Sariciftci S.S. Conjugated Polymer-Based Solar Cells. *Chem. Rev.* **2007,** 107, 1324-1338

Acknowledgement

Funding for this project was graciously provided by the University of Minnesota's Undergraduate Research Opportunities Program.