Penetration Depth of PiFM
Nanoscale Chemical Mapping with Extreme Surface Sensitivity

Since the dipole-dipole interaction between the induced sample dipole and the image tip dipole will vary with \( \frac{1}{z^4} \) dependence where \( z \) is the tip-sample spacing, PiFM is expected to provide extreme surface sensitivity. PiFM is expected to provide extreme surface sensitivity. PS-polystyrene)-b-PTMSS[poly(4-trimethylsilylstyrene)] block copolymer (PS-PTMSS BCP) with horizontal lamellae is used to demonstrate the surface sensitivity. BCP is an excellent sample to demonstrate both spatial and depth resolution since the thickness of each component can be controlled precisely by adjusting the molecular weights of the components. In this case, the pitch \( L_0 \) of the BCP is \( \sim 22 \) nm as shown in figure 1a. One sample with island features with PTMSS at the top (Sample-I shown in Fig. 1b) and another sample with holes with PS at the bottom (Sample-H shown in Fig. 1c) were prepared on silicon substrate.

Figure 2 shows what typical topography and phase images a standard AFM would produce on these two samples. Note that the height of the island feature and the depth of the hole feature measure about 11 nm, as expected from the cartoons in Fig 1b and 1c. Even though the height (or depth) can be confirmed, AFM topography and phase cannot determine whether the top of the island structure is composed of PTMSS. Similarly, there is no way to determine from AFM measurements whether the bottom of the hole structure is PS. In fact, it will be difficult to find an analytical technique that combines the surface chemical sensitivity and the nanoscale spatial resolution that are required to shed light on the chemical nature of the molecules associated with this type of structures.

Figure 3a and 3b show the PiFM spectra associated with PTMSS and PS Homopolymer films on silicon substrate respectively. We can see that PiFM should be able to highlight the two different polymer molecules by using 1599 cm\(^{-1}\) for PTMSS and 1493 cm\(^{-1}\) for PS as our IR excitation light.
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Surface Sensitivity & Nanoscale Spatial Resolution

Figure 4 shows PiFM images acquired at 1599 cm\(^{-1}\) and 1493 cm\(^{-1}\) along with topography for both Sample-I (top row) and Sample-H (bottom row). We used the red color to denote the PS molecules (imaged at 1493 cm\(^{-1}\)) and the blue color to denote the PTMSS molecules (imaged at 1599 cm\(^{-1}\)), consistent with the colors used for the cartoons in Figure 1. One can see that for Sample-I, PS molecules cover regions surrounding the island features (identifiable by taller features in topography) while PTMSS molecules cover the island. One can also see that for Sample-H, PS molecules “cover” the hole features (identifiable as depressions in topography) while PTMSS molecules cover regions surrounding the hole features. Thus PiFM is capable of identifying which molecules cover the different regions even though the layer that we are measuring is only 5.5 nm thick. Even though the PiFM images of Sample-I seem that there is no PS molecules associated with the island features, we know that there are PS molecules underneath the top PTMSS molecules. From other experiments where thickness dependence of PiFM was measured, we know that PiFM can probe down to about ~ 15 nm of the sample depth. Therefore, even though the images seem to indicate absence of PS molecules, we know that it is only due to the contrast based on relative signal strength.

Figure 5 shows PiFM spectra associated with two different bi-layer samples, one with PS on top of PTMSS and another with PTMSS on top of PS. One can see that even in the case of PTMSS on top of PS, the two PS absorption bands are clearly seen in the spectrum albeit greatly reduced from that of PS on top of PTMSS. The rapid reduction in the PiFM signal is due to the dipole-dipole nature of PiFM, which results in its extreme surface sensitivity.

Since topographically data are collected concurrently with PiFM images, we can overlay the chemical map (with the color designation of molecules) on top of 3D topography of the sample. Such renderings are shown in Figure 6 for both Sample-I and Sample-H, clearing confirming the 3D structure of the samples.

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![Figure 4: Topography and PiFM images at 1493 cm\(^{-1}\) and 1599 cm\(^{-1}\) to identify PS and PTMSS molecules. PS and PTMSS molecules are colored artificially red and blue respectively, to be consistent with the cartoon colors.](image)

![Figure 5: PiFM spectra of bilayer samples showing the precipitous drop in PiFM signal at a depth of 5.5 nm.](image)

![Figure 6: Chemical map data overlaid on 3D topography renderings of both sample types.](image)