Spatial Resolution of PiFM

Nanoscale Chemical Mapping with Sub-10 nm Spatial Resolution

PiFM achieves excellent spatial resolution. Since our Science Advances paper, we have enhanced the spatial resolution of PiFM to the point where we are now able to resolve the different chemical blocks of a PS-b-PMMA sample with a pitch of about 22 nm. Figure 1 shows the PS and PMMA molecules in red and green colors respectively. Cross-sections of the PiFM images for PS and PMMA anti-correlate with each other as they should and show the measured pitch to be about 21 nm (in the cross-section, two pitches are measured). Each polymer molecular block with width of about 11 nm is imaged clearly, and the rise of the signal measures less than 6 nm, which is used by many as the instrument's spatial resolution.

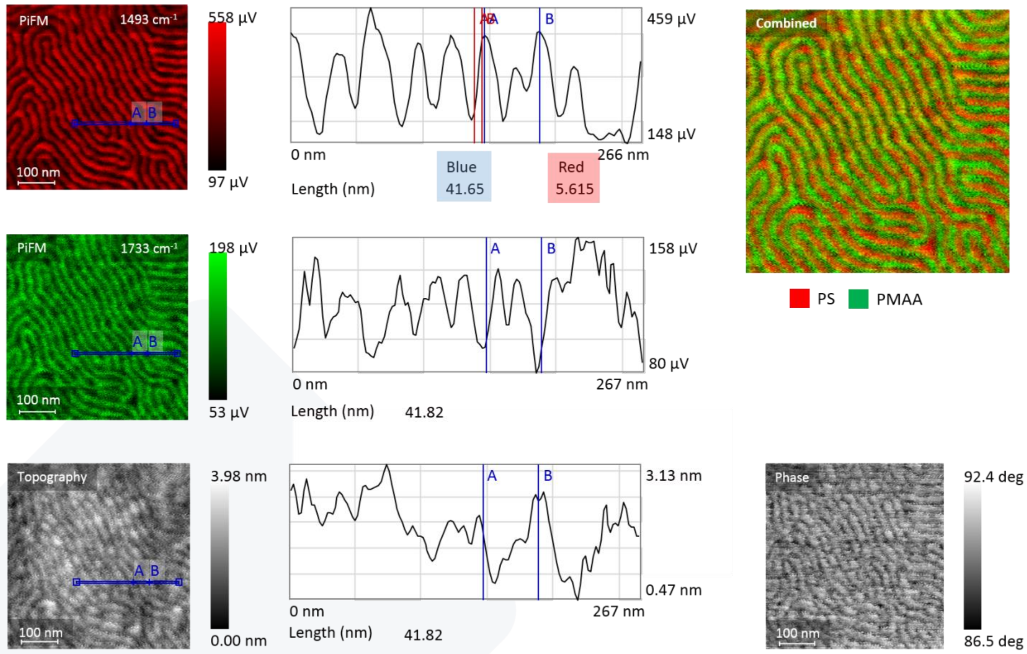

Figure 1: PiFM images at 1493 cm^{-1} (for PS in red) and at 1733 cm^{-1} (for PMMA in green) along with AFM topography (bottom left) and phase image (bottom right) with cross-section profiles along the line shown in the images; the lines are drawn at the same location of the sample. Note that the PS and PMMA line profiles anti-correlate as they should for BCP. The combined chemical image (top right) confirm the lamellar nature of the BCP. The measured full pitch is 21 nm (the cross-section measures two full pitch).

The spatial resolution of AFM IR instrument is determined by several criteria: (1) effective volumes of the tip and sample that are interacting; (2) sensitivity of the detection technique; and (3) background signal that will determine the signal-to-noise. The table below shows how PiFM compares with the competing techniques in these areas:

Technique	Interaction Volume	Sensitivity	Background Signal
PiFM	Smaller than tip radius; independent of film thickness	Excellent on all sample thickness (depends on Q of cantilever)	No competing background signal
Photo-thermal	Larger than tip radius; grows with film thickness	Good on thicker samples (> ~ 100 nm)	Thermal expansion from neighboring material
Scattering SNOM	Smaller than tip radius; independent of film thickness	Depends on quality of optics	Strong far-field scattered signal

As can be seen, compared to alternative AFM IR techniques, PiFM enjoys favorable operating conditions on all of the above criteria, which provides the basis for its superior performance, both in spatial resolution and surface sensitivity.

Interaction Volume

Generally, the effective volumes of the tip and sample that are interacting in a scanning probe microscopy technique will depend on the following parameters (see Figure 2): tip radius, t_r; the gap spacing between the tip and the sample, z_{ts}; and the tip-sample interaction as a function of z_{ts}, $f_i(z_{ts})$. These parameters along with the field enhancements that result from the shape and metal coating of the tip and the nature of substrate will determine the lower limit of the spatial resolution. In the special case where $f_i(z_{ts})$ is a step function, i.e., the tip-sample interaction is zero until it comes into contact with the sample surface as in PTIR, the sample volume will mostly determine the spatial resolution.

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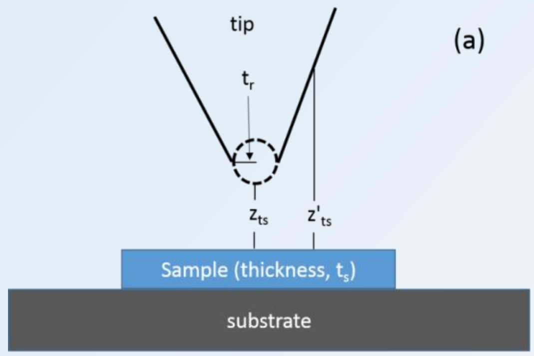
Spatial Resolution of PiFM

Highest Spatial Resolution of all AFM + IR Techniques

In PiFM, where the dipole-dipole attractive force determines the spatial resolution, the governing $f_i(z_{ts})$ varies with $1/z_{ts}^4$, whose magnitude falls off extremely fast with increasing z_{ts}. The consequence of the fast fall-off is that, referring to figure 2, $f_i(z'_{ts})$ will be much smaller than $f_i(z_{ts})$, thus keeping the interaction volume of tip and sample to be quite small on the order of tip radius. It is also easy to see from the geometry that it is important to keep z_{ts} as small as possible to keep the ratio between z_{ts} and z'_{ts} be as large as possible since that will determine the ratio between $f_i(z_{ts})$ and $f_i(z'_{ts})$. In practice, we achieve small z_{ts} by feedback controlling the AFM on the second mechanical mode of the cantilever where the force constant is about 40 times larger than the first mode and can support amplitude oscillation of less 1 nm. In the case of PiFM, the metal coated tip has a tip radius of 20 ~ 30 nm while PiFM achieves a practical spatial resolution of less than 10 nm. The reason for the spatial resolution that is smaller than the tip radius is that the field enhancement of the electromagnetic field reduces the value of the effective tip radius; see figure 2b where the field enhancement creates a much sharper radius compared to the physical radius of the gold tip; compare the two red circles drawn on the electromagnetic shape and the physical gold tip shape



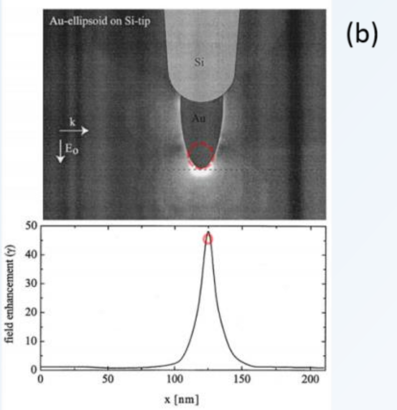


Figure 2: (a) Definition of parameters that determine the spatial resolution of PiFM; and (b) field enhancement creates a smaller effective radius (shown below)for PiFM compared to the physical radius of the gold particle (shown above).

[from J. Appl. Phys. 89, 5774 (2001)].

The exceptional spatial resolution of PiFM due to rapid fall-off and small tip-sample spacing is depicted in figure 3(a) and compared to two cases of electrostatic force microscopy (EFM): one operated in a similar bi-modal manner as in PiFM ([3(b)] and the standard EFM on one cantilever mode [3(c)]. $f_i(z)$ for EFM varies with $1/z_{ts}^2$, a slower fall-off than PiFM, resulting in poorer spatial resolution.

In photo-thermal measurements, the tip radius has little impact on the resolution since in the time scale of measurements, thermal diffusion takes place to affect the sample region much larger than the tip radius. Thus the affected sample volume will determine the practical spatial resolution. Typically samples are deposited onto substrates with higher thermal conductivity so that once the thermal front reaches the substrate, the heat will stop spreading, which puts the film thickness as a good estimate for spatial resolution of photo-thermal technique, provided it is thick enough (> ~ 100 nm) to produce measurable expansion. This is shown in Figure 3(d) schematically. For samples that can withstand high field strengths, PTIR can achieve higher spatial resolution by depositing a thin sample on top of a gold substrate to produce a strong gap field between the tip and the substrate. However, the special substrate requirement may change the nature of the sample from its natural state. In summary, PiFM today offers the highest spatial resolution of all AFM + IR techniques.

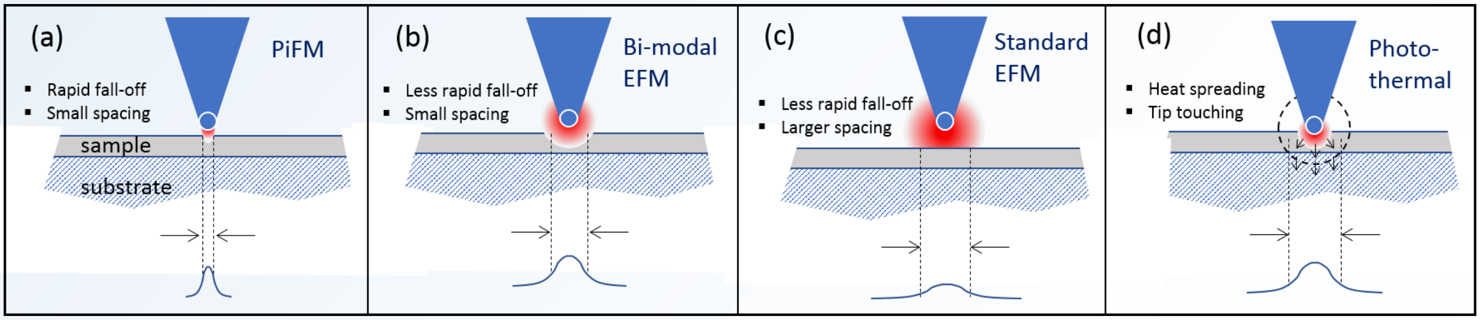


Figure 3: Spatial resolution expected for different interaction mechanisms (with different fall-offs) and tip-sample spacing.