Featuring Vista Series microscopes

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MOLECULAR VISTA

Application Note

Spatial Resolution of PiFM

PiFM achieves excellent spatial resolution. Since our Science Advances paper [1], 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 10% - 90% rise of the signal measures 5.6 nm, which is used by many as the instrument's spatial resolution.

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

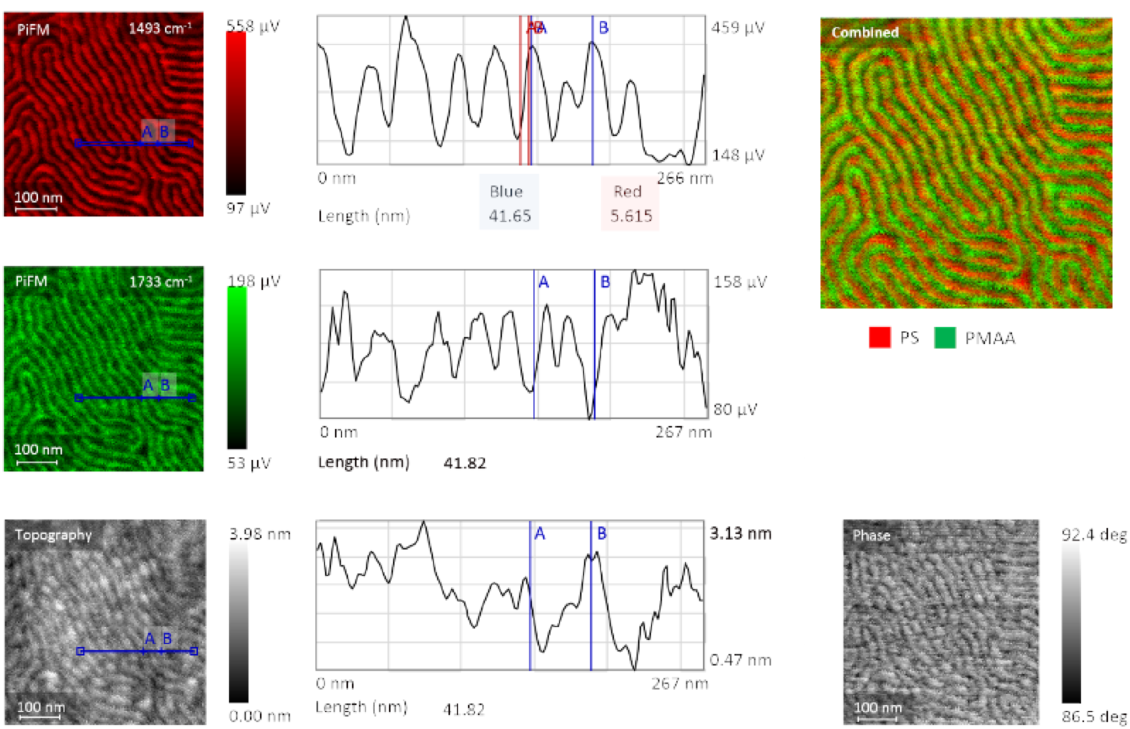

FIGURE 1: PiFM images at 1493 cm^{-1} (for PS in red) and at 1733 cm^{-1} (for PMMA in green) along with AFM topography (bottom left) and phase image (bottom right) with cross-section profiles along the line shown in the images; the lines are drawn at the same location of the sample. Note that the PS 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 10% - 90% rise measures 5.6 nm, demonstrating exceptional spatial resolution of PiFM.

detection technique; and (3) background signal that will determine the signal-to-noise. The table above shows how PiFM compares with the competing techniques in these areas. As can be seen, compared to alternative AFM IR techniques, PiFM enjoys favorable operating conditions on all criteria, which provides the basis for its superior performance, both in spatial resolution and surface sensitivity.

Technique	Interaction Volume	Sensitivity	Background Signal
PiFM	Smaller than tip radius; independent of film thickness	Monolayer	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	Comparable to tip radius; independent of film thickness	Monolayer	Strong far-field scattered signal

TABLE 1: A comparison of the three most popular nano-IR microscopy techniques available.

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.

In PiFM, where the photo-induced attractive force determines the spatial resolution, the governing $f_i(z_{ts})$ varies with $1/z_{ts}^4$ (or $1/z_{ts}^2$ depending on the nature of the force [2]) so that its 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 the 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} as large as possible since that will determine the ratio between $f_i(z_{ts})$ and $f_i(z'_{ts})$. In order to achieve the smallest practical z_{ts} (~ 1 nm), the photo-induced force (PiF) is measured by maintaining a constant and small (~ 1 nm) gap between the AFM tip and the sample surface by feedbacking on the 2nd mechanical mode of the cantilever (whose force constant is ~ 1000 N/m and prevents snap-in) while modulating the excitation laser at a frequency such

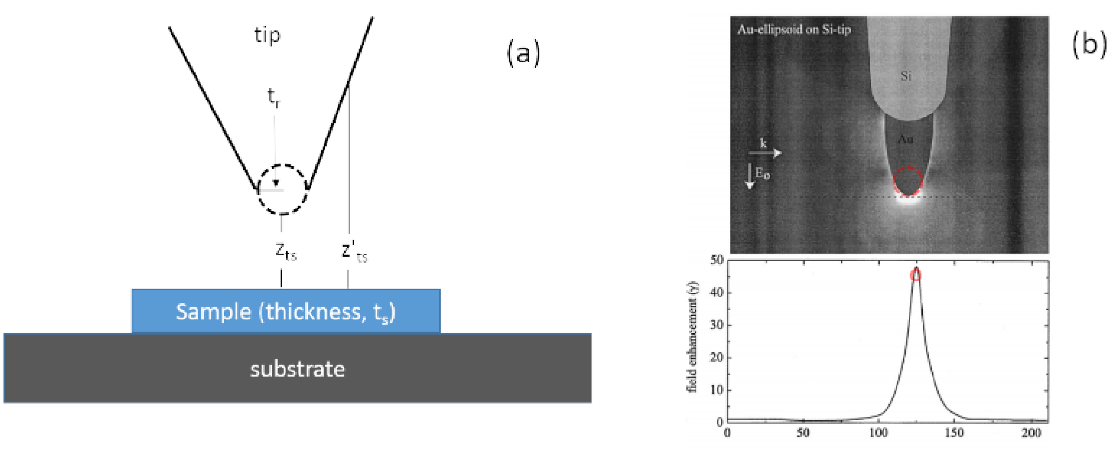

FIGURE 2: (a) Definition of parameters that determine the spatial resolution of PiFM; and (b) field enhancement creates a smaller effective radius (shown below) for PiFM compared to the physical radius of the gold particle (shown above).

that the resulting modulated PiF drives the 1st mechanical mode of the AFM cantilever.

The metal coated tips used for PiFM have a tip radius of 20 ~ 30 nm while PiFM achieves a practical spatial resolution of ~ 5 nm. This enhanced spatial resolution arises from the fact that the tip-enhanced field profile is much smaller than the physical tip profile. Figure 2b compares the profiles of the physical tip (upper image) and the tip-enhanced field profile (lower image); two red circles highlight the two different effective "tip radius", which would determine the spatial resolution [from J. Appl. Phys. 89, 5774 (2001)].

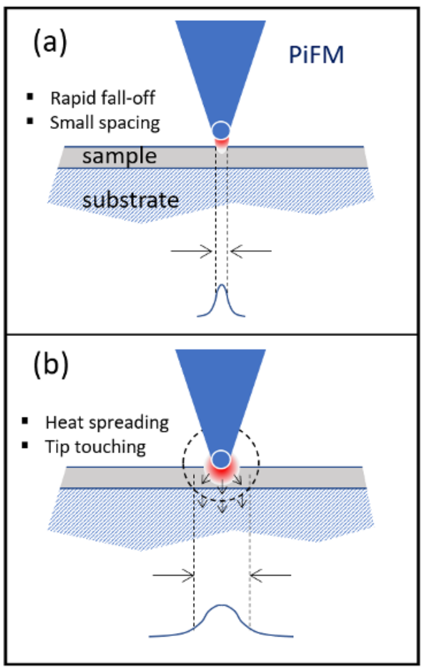

FIGURE 3: Spatial resolution expected for different interaction mechanisms (with different fall-offs) and tip-sample spacing.

The exceptional spatial resolution of PiFM due to rapid fall-off and small tip-sample spacing is depicted in figure 3a and compared to the photo-thermal measurements (figure 3b).

In photo-thermal measurements, the tip radius has less impact on the resolution since in the time scale of measurements, thermal diffusion takes place to affect the sample region that is 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 expansion measurable by contact AFM. This is shown in Figure 3b schematically. For samples that can withstand high field strengths, PTIR can achieve higher spatial resolution (~ 20 nm) 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 among AFM + IR techniques.

References

[1] D. Nowak et al., Sci. Adv. 2, e150157 (2016).
[2] J. Jahng et al., PNAS 116 (52), 26359 (2019)