

RHK Technology Brief

Application * Tutorial * Technology

Scanning Polarization Force Microscopy

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The development of new scanned probe microscope (SPM) techniques has allowed a great deal of knowledge to be gained in the microscopic structure and properties of materials. A particularly unique problem has been the investigation of liquid-solid interactions. Non-perturbative observation techniques are required due to the sensitive nature of a liquid, they are easily influenced by external forces. The field has been revolutionized by the development of scanning polarization force microscopy (SPFM). All problems related to contact AFM tip-liquid surface interactions are avoided using SPFM by holding the tip a fixed distance above the surface, usually a few hundred angstroms. The increased separation leads to a decrease in effective resolution in the xy plane, while it remains in the angstrom level in the z-direction. However, the technique still produces higher resolution than any other present techniques available to study a liquid-solid interface.

The SPFM technique is illustrated in Figure 1. A conducting tip (doped silicon or metal coated Si_3N_4) is placed $\sim 200 \text{ \AA}$ above the surface. A voltage (either AC or DC) is applied to the tip which induces an image charge in the surface. The tip will deflect towards the surface due to the attractive nature of the image charge. This deflection can be recorded as a change in the voltage output from a position sensitive detector in the AFM head. The signal from the PSD can be used as a feedback mechanism and the sample moved vertically to maintain a constant cantilever deflection. Therefore, as the sample is scanned across the surface, an image is formed that is related to the deflection of the cantilever as a function of surface position.

If a DC voltage is applied, the resulting image will be a convolution of surface potential,

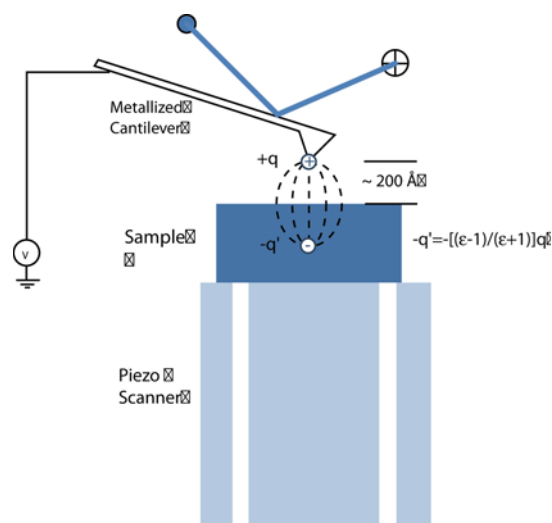


Figure 1. Diagram of SPFM operation, showing biased AFM cantilever and resulting image charge on surface.

dielectric, and topographic effects. The attractive force will change over areas where the dielectric constant or the surface potential changes since the magnitude of the image charge will be different. The force also will change wherever the surface height increases (decreases) because this will make the image charge closer to (further from) the tip and subsequently increase(decrease) the attractive force. It is difficult, though possible, to separate the two effects; one way to do this is to rescan the same area with a different bias applied to the tip. Topographic effects will look the same, whereas electronic artifacts will look much different in the image.

The difficulty of deconvolving electronic and topographic effects can be circumvented by applying an AC voltage (usually a few kHz up to 10 kHz). The force on the cantilever will be given by:

$$\begin{aligned}
 F &= B * f\left(\frac{R}{z}\right) \left[-\frac{1}{2} V_{tip}^2 \cos(2\omega t) - 2V_{tip} \phi \sin(\omega t) + \frac{1}{2} V_{tip}^2 + \phi^2 \right] \\
 &= F(2\omega) + F(1\omega) + F(0\omega) \\
 B &= -4\pi\epsilon_0 \frac{\epsilon - 1}{\epsilon + 1}
 \end{aligned}$$

The amplitudes of the 2ω and ω signals can be measured through the use of two lock-in amplifiers. If the force at 2ω is used as the feedback signal and therefore kept constant, the image of the z piezo correction signal will be the topography only. The output of the lock-in amplifier tuned to ω can be applied to an auxiliary channel and the image formed by this channel will be a map of the dielectric constant over the surface¹.

A complete SPFM system can be constructed utilizing the SPM 1000 control system, an AFM head from Molecular Imaging, and the AIM-MI interface unit. The SPM 1000 is the perfect choice for control electronics as it offers maximum flexibility both in terms of the data acquisition capabilities of the control software and easy access to the required control signals.

It is the only commercial electronics that does not require complicated, customized changes required for SPFM.

The additional connections needed for SPFM are illustrated in Figure 2. All cables related to conventional AFM have been removed for clarity. The oscillating voltage output from the lock-in amplifier (LIA) is connected to the AIM-MI where it is subsequently applied to the conductive cantilever. The PSD signal out of the head is intercepted inside the AIM-MI and routed to the input of each LIA. The output of the LIA tuned to

2ω is sent to the rear panel feedback input BNC on the SPM100 to be used as the feedback signal. This output amplitude is maintained at constant value by continually adjusting the Z piezo height. The output of the second LIA tuned to ω is applied to one of the rear panel auxiliary channels and sampled while imaging.

A fundamental problem that has been investigated by SPFM is the microscopic nature of wetting. Ultimately it would be advantageous to study the edge of a droplet with molecular resolution, however this is not possible with existing technology. Microscopic droplets can be prepared in a number of ways. One simple method is to place a macroscopic drop on a surface and then “wick” off the majority of the liquid via contact with filter paper. Alternatively

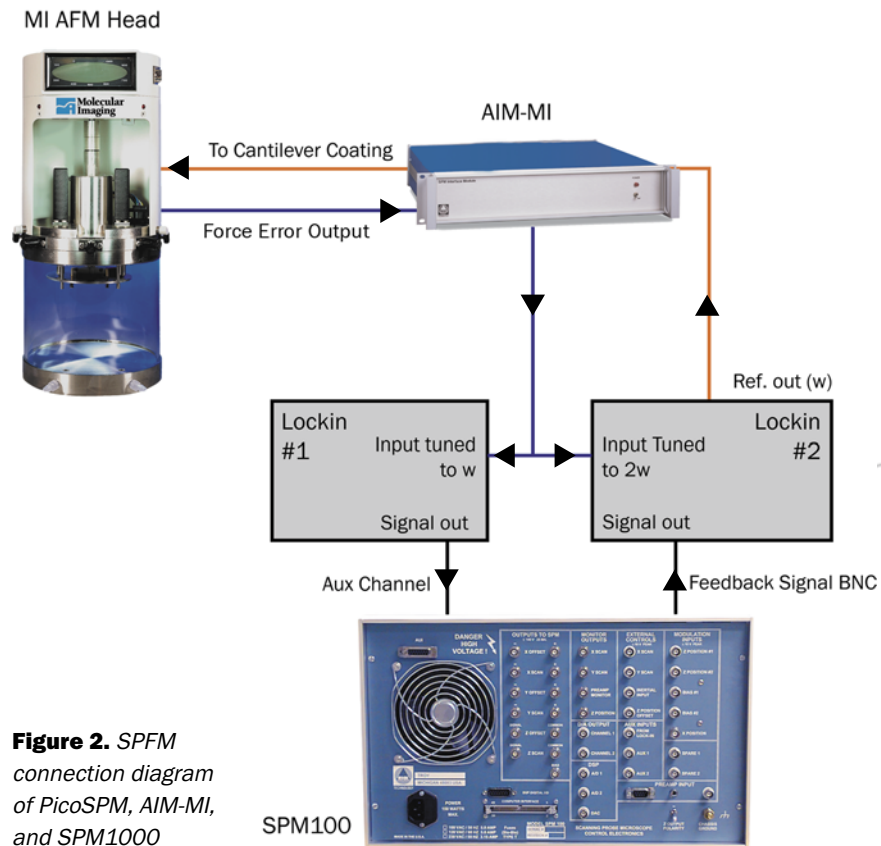


Figure 2. SPFM connection diagram of PicoSPM, AIM-MI, and SPM1000

the surface could be blown with high pressure nitrogen gas. The surface will appear completely dry to the eye, but microscopic droplets can still be found.

Figure 3 is a 10 micron x 10 micron image of aqueous KOH on highly oriented pyrolytic graphite (HOPG). The droplets are predominantly trapped at the atomic steps present on the surface and the terraces are almost devoid of liquid. The image was acquired at room temperature with a relative humidity of 35%-40%. The droplets range in lateral extent from a few hundred angstroms to a maximum of a few microns with a height from tens to 100's Å. It is interesting to note that a step only a few atomic layers high can capture a large drop with millions of molecules. It is also apparent that the largest droplets are found at the edge of the largest terraces.

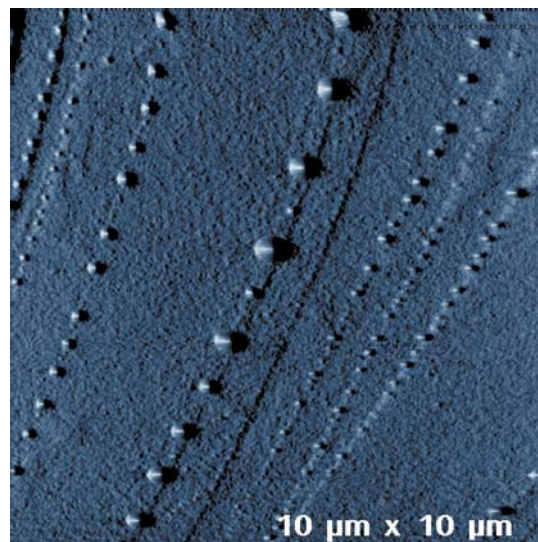


Figure 3. Aqueous KOH on HOPG. Image size: 10μm x 10μm. J Hu, RW Carpick, M Salmeron, XD Xiao. *J Vac Sci Technol B (14) 1996*

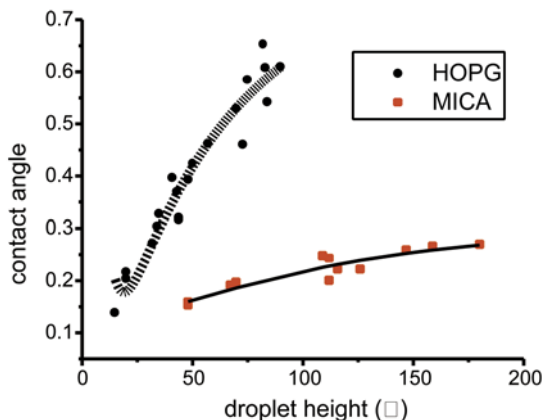


Figure 4. Relationship between contact angle and droplet size of KOH on mica and KOH on HOPG. From "Studies of wetting and Capillary Phenomena at Nanometer Scale with Scanning Polarization Force Microscopy", by Lei Xu and Miquel Salmeron. Chapter in *NANO-SURFACE CHEMISTRY*, ed. Morton Rosoff (Marcel Dekker, New York), 2001.

The height and curvature of the droplets can be measured accurately and a contact angle calculated. The graph displayed in the lower part of Figure 4 displays the relationship between the contact angle and droplet size for two systems. The KOH:mica and KOH:HOPG systems both exhibit an increase in contact angle as droplet height increases. Also apparent is the KOH:mica system displays much lower angles for equivalent droplet sizes compared to KOH:HOPG. The conclusion from the data is the hydrophobic action of this system is much weaker compared to the KOH:HOPG.

The wetting properties of liquid crystals has a great deal of technological interest, particularly in the field of display devices. One particular system designated 8CB (4'-n-octyl-4-cyanobiphenyl) has undergone a great deal of scrutiny when placed on silicon. The material exists in three phases. A transition from a crystal to a smectic-A phase occurs at 21.5° C, and at 40.5° C the material undergoes a weak

first order transition to an isotropic liquid. At 335° C, a second order transition to a nematic phase takes place. In bulk 8CB, the molecules are paired into dimers that are 1.4 times the length of a free molecule. In the smectic phase the dimers form layers spaced 31.7 Å apart with the dimers aligned perpendicular to the layer. The liquid was placed on the clean silicon and a single height layer immediately covered the entire surface with large droplets dispersed on top of the single 8CB layer. The edge of an

The exciting SPFM technique has a great deal of potential to unravel problems with its unique capability to acquire real space images of liquids with a resolution better than a few hundred angstroms. Another very exciting application would be using an AC voltage in the MHz range or higher. Then the exciting signal will have the same frequency range as typical molecular bond frequencies and this could open the possibility of performing chemical identity imaging and spectroscopy at a very high resolution. The unique flexibility offered by the RHK SPM1000 system coupled with an ambient AFM permits the routine application of this new technique.

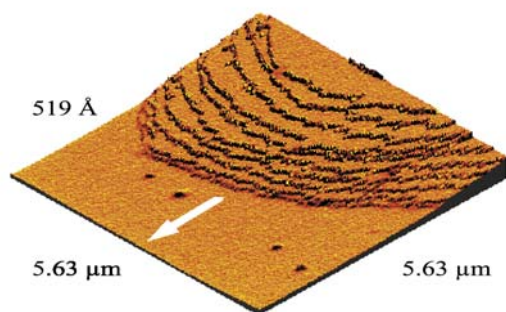


Figure 5. Edge of isolated 8CB droplet on silicon, showing single dimer layers. L Xu, M Slameron, S Bardon. *Phys Rev Lett* (84) 2000

isolated droplet is displayed in Figure 5. Very well resolved single height dimer layers are observed with rather large terraces between each step edge. This dramatically demonstrates that the curvature of the droplets is determined by the ratio between the average terrace width and the height of the single dimer layer as the droplet itself is composed of individual layers of liquid with successively smaller lateral extent. The spreading of the drop across the surface can also be measured by acquiring successive images and comparing the location of step edges in subsequent scans. This method yields a value for 20-30 Å/s. No other technique available offers the type of resolution displayed here to resolve the individual layers of the liquid at the edge of the droplet.



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