

# Chemical Mapping at the Nanoscale by Photo-induced Force Microscopy

Thomas R. Albrecht<sup>1</sup>, Derek Nowak<sup>1</sup>, Will Morrison<sup>1</sup> and Sung Park<sup>1</sup>

<sup>1</sup> Molecular Vista, Inc., San Jose, CA, USA.

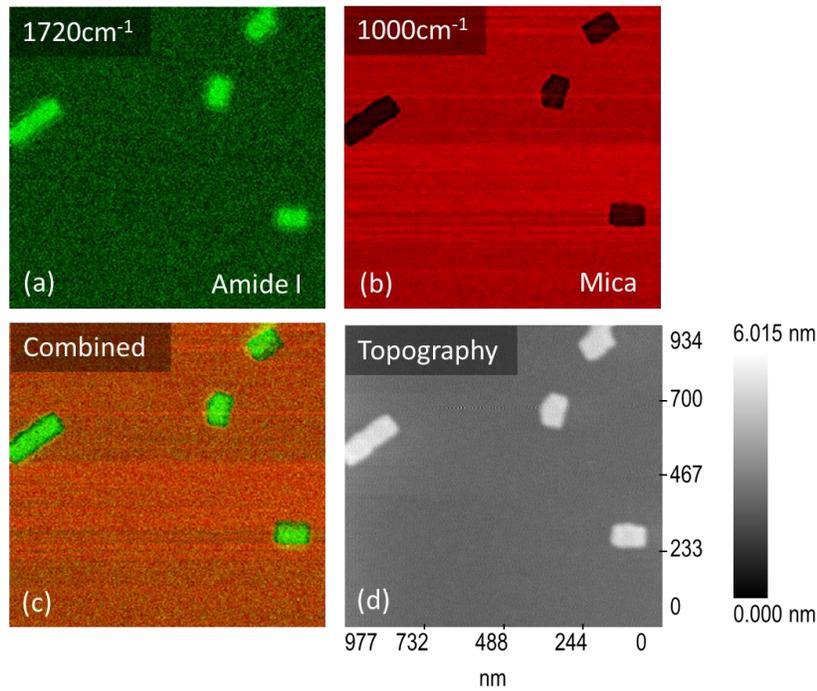
Several recently developed techniques based on a combination of infrared (IR) spectroscopy and atomic force microscopy (AFM) have demonstrated the ability to perform chemical mapping far below the diffraction limit of light. These include scanning scattering near-field microscopy (sSNOM) [1], photothermal induced resonance (PTIR) [2], and the subject of this paper, which is Photo-induced Force Microscopy (PiFM) [3,4]. These techniques are complementary, and are based on physically distinct sensing mechanisms. While sSNOM relies on collection of scattered light, PTIR and PiFM exploit mechanical detection of IR absorption in the sample. PTIR detects cantilever vibrations arising from rapid thermal expansion of the sample in response to absorption of pulsed IR light. Although PiFM also detects cantilever vibrations in response to pulsed IR, the experimental setup and behavior of the system show clear differences between PiFM and PTIR, which indicates that thermal expansion is not the dominant mechanism behind PiFM.

In PiFM, a metal-coated AFM tip is operated in a noncontact or light tapping mode at one resonant frequency of the cantilever (used for topographic imaging), while a tunable IR light source is pulsed at the difference frequency between the topographic mode and a second vibrational mode of the cantilever. Force gradients generated between the tip and sample at the laser pulsing frequency then mix with the first mode to generate vibrations at the second mode used for PiFM sensing. Such force gradients may arise from polarization of the sample, which in turn act on the tip via image force generation in the electrically conducting tip material. Since PiFM signals correlate with IR absorption in the sample, PiFM can be used to generate local IR absorption spectra, useful for identification of the material under the tip. Sensitivity and resolution are such that usable signals are generated from samples as thin as 1 nm, and lateral resolution is better than 10 nm. Penetration depth into the sample appears to be around 10 nm or less.

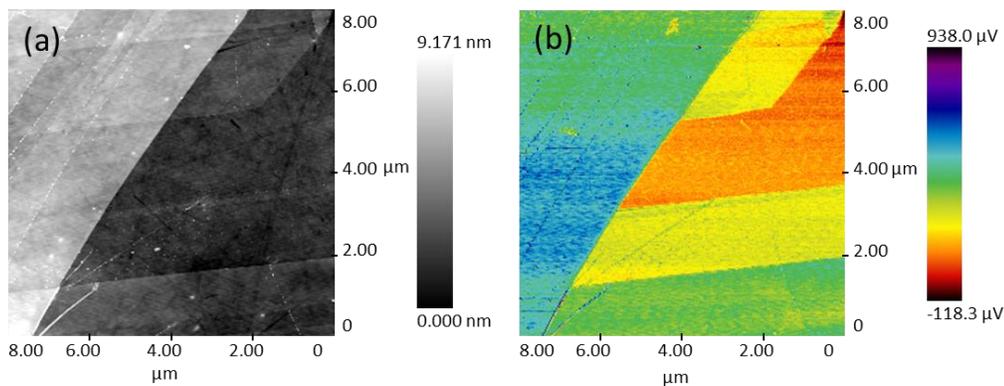
Unlike PTIR, which shows the expected dependence on gauge length (i.e., sample thickness) and coefficient of thermal expansion, PiFM generates signals which are relatively independent of sample thickness beyond a few tens of nm. Likewise, materials with low thermal expansion, such as thin inorganic samples, generate clearly detectable PiFM signals. Even very thin samples on nonconducting substrates (where tip field enhancement is reduced) generate PiFM signals useful for chemical mapping.

An example of a PiFM spectroscopic image on very thin sample is shown in Fig. 1. The sample is a DNA origami structure on a nonconducting mica substrate [5]. PiFM images at two different wavenumbers can clearly distinguish between the two materials and can generate a precise map of the two chemical species present as shown in Fig. 1(c). Figure 2 shows a PiFM image of a graphene sample, with monolayer changes in thickness revealing differing PiFM signal amplitude. This sample is an example of an inorganic material with low thermal expansion. Both figures demonstrate PiFM signals on samples where thermal expansion alone would not be expected to generate a usable signal level.

- [1] N. Ocelic, A. Huber and R. Hillenbrand, *Appl. Phys. Lett.* **89** (2006), p. 101124.  
 [2] A. Dazzi, R. Prazeres, F. Glotin and J.M. Ortega, *Infrared Phys. Technol.* **49** (2006), p. 113.  
 [3] I. Rajapaksa, K. Uenal and H.K. Wickramasinghe, *Appl. Phys. Lett.* **97** (2010), p. 073121.  
 [4] D. Nowak *et al.*, *Sci. Adv.* **2** (2016), p. e1501571.  
 [5] Sample provided by R. Berger, Max Planck Institute, Germany.



**Figure 1.** PiFM mapping of DNA origami structures (2-3 nm thick) on mica.[1] (a) PiFM response with sample illumination at  $1720\text{ cm}^{-1}$  (amide I peak) highlights DNA, while (b) PiFM at  $1000\text{ cm}^{-1}$  responds to the mica substrate. (c) Combined responses show complete chemical map. (d) AFM topography acquired simultaneously.



**Figure 2.** (a) AFM topography and (b) PiFM response to monolayer thickness variations on graphene.