Measurement of tip-sample interaction forces under infrared irradiation toward high-spatial-resolution infrared spectroscopy using FM-AFM (2)

Yoshihiro Hosokawa[1], Hans-Georg von Ribbeck[2], Rainer Jacob[2], Marc Tabias Wenzel[2], Lukas Eng[2], Kei Kobayashi[1] Kazumi Matsushige[1] and Hirofumi Yamada[1]

1 Department of Electronic Science and Engineering, Kyoto University
2 Institute for Applied Photophysics, Technical University of Dresden, Germany

hosokawa@piezo.kuee.kyoto-u.ac.jp

Infrared (IR) spectroscopy is a superior, analytical technique which is capable of identifying functional groups having characteristic vibration frequencies. However, the spatial resolution in the conventional IR spectroscopy is on the order of micrometers because of the diffraction limit. Recently, several researchers demonstrated high-spatial-resolution IR spectroscopy by detecting thermal expansions on a sample surface using atomic force microscopy (AFM) under IR irradiation[1,2]. They succeeded in detecting a cantilever deflection induced by the thermal expansion by the contact-mode AFM. However the spatial resolution was still limited around 100 nm because of the contact radius of the cantilever tip. Frequency-modulation AFM (FM-AFM) is capable of measuring tip-sample interaction forces with a very high sensitivity. In this technique, we modulated the IR power and detected the AFM signal using a lock-in amplifier (Fig.1). Recently, we succeeded in detecting the modulated frequency shift of the cantilever resonance frequency when the cantilever was brought in close proximity of a polymer film surface irradiated with an IR beam using a free electron laser (Forschungszentrum Dresden-Rossendorf, Germany)[3]. In this experiment a polydimethylsiloxane (PDMS) film spin-coated on a Si surface was used as a sample. The IR beam was modulated using an optical chopper at 530 Hz. The tip, made of Si, was scanned on the same scan line while we changed the wavelength of the IR beam from 6.79 um to 8.22 um for each scan. Figure 2(a) shows an image consisting of one-dimensional topographic data (X) for different IR wavelengths (Y) and Fig. 2(b) shows the wavelength dependence of the modulation components in the frequency shift and energy dissipation signals obtained on the PDMS area. Both signal intensities were normalized to the corresponding values on the Si area. The data were acquired on the dashed lines in Fig. 2(a). We found that some peaks in Fig. 2(b) corresponded to the absorption peaks in a infrared absorption spectrum of the PDMS film, obtained by a conventional FT-IR measurement.

For more precise analysis of the tip-sample interaction forces of FM-AFM on polymer thin films under IR irradiation, a quantum cascade laser (QCL) was used. In this experiment a spin-coated PDMS film deposited on a highly-oriented pyrolytic graphite (HOPG) surface was used, as shown in Fig. 3(a). While the distance between the AFM tip and the sample surface was regulated utilizing the second resonance frequency (420 kHz) of the cantilever, the sample surface was irradiated with an IR beam from the QCL (1050 cm^{-1}) whose intensity was modulated at a frequency close to the first resonance frequency (67 kHz). Figure 3 (b) shows an FM-AFM topographic image, and Figs. 3 (c) and (d) show the magnitude of the cantilever oscillation induced by the IR irradiation at 69 kHz and 65 kHz, respectively. In both Figs. 3(c) and 3(d) the magnitude of the cantilever oscillation on PDMS is clearly different from that on HOPG. The result also shows a remarkable change of the contrast between the PDMS and the HOPG depending on the modulation frequency.

Reference
[1]F. J. Boerio and M. J. Starr, Journal of Adhesion (2008) **84** 874
[2]A. Dazzi, R. Prazeres, F. Glotin and J. M. Ortega, Optics Letters (2005) **30** 18
[3]Y. Hosokawa et al. 18th International Colloquium on Scanning Probe Microscopy, (2010)

Figures

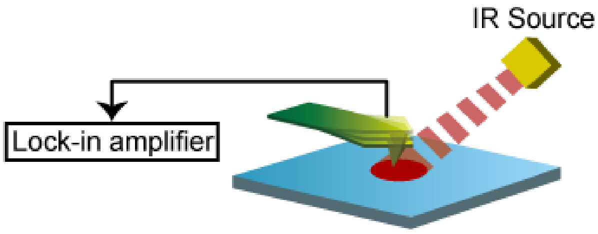

Fig. 1 Schematic of novel infrared spectroscopy using FM-AFM. A tip-sample interaction change caused by a modulated IR beam is detected using lock-in amplifier.

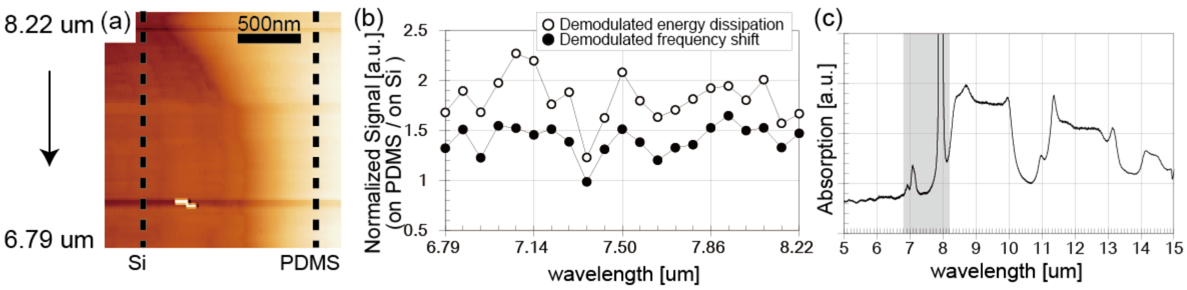

Fig. 2 (a) FM-AFM image consisting of one-dimensional topographic data (X) for different IR wavelengths (Y), obtained on a PDMS film on a Si substrate. (b) Normalized intensities of the modulation components in the frequency shift (●) and energy dissipation signals (○) obtained on the PDMS area, which were normalized to the corresponding values on the Si area. (C) Infrared absorption spectrum of the PDMS film.

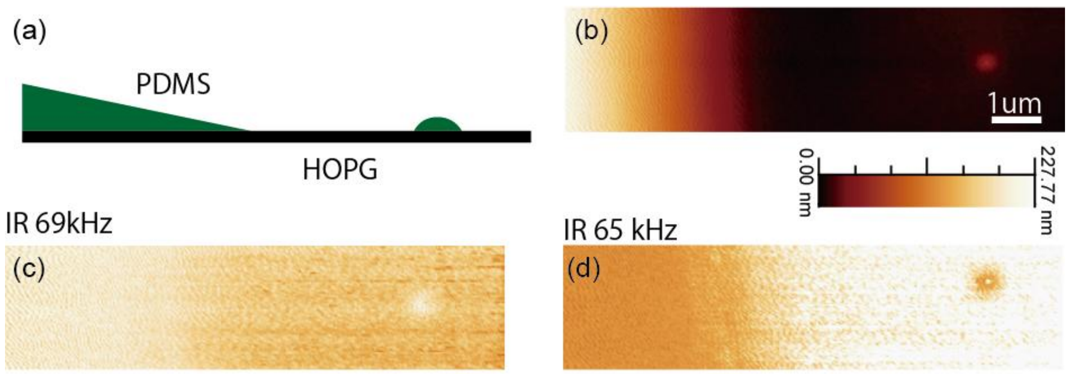

Fig. 3: (a) Illustration of the sample (PDMS film on HOPG). (b) Topographic image of PDMS film on HOPG. (c) and (d) show images of the cantilever oscillation magnitude induced by irradiation of IR laser beam modulated at 69 kHz and 65 kHz, respectively.