

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

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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 the surface using atomic force microscopy (AFM) during 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 detecting tip-sample interaction forces with a very high sensitivity. While the cantilever is oscillated it at its resonance frequency using a self-oscillation loop, the tip-sample interaction forces induce either a shift in the resonance frequency (conservative interaction) or an change in the oscillation amplitude (dissipative interaction). The conservative and the dissipative force can be independently measured. In this presentation, we show the measurement results of a preliminary experiment on the measurement of the tip-sample interaction forces on polymer thin films under IR irradiation using FM-AFM.

Figure 1 shows a schematic of an experimental setup. We used a commercially available AFM apparatus (JEOL: JSPM-5200) and home-built FM electronics. We used an automatic gain controller (AGC) which kept the oscillation amplitude of the cantilever constant. The energy dissipated by the tip-sample interaction was measured from the output of the AGC quantitatively. We used a Si cantilever (Nanosensors: NCH), whose nominal spring constant and resonance frequency were 40 N/m and 300 kHz, respectively. The quality factor of the cantilever was 10,000 in a vacuum environment (10^{-1} Pa). The typical oscillation amplitude was set at $10 \text{ nm}_{\text{p-p}}$.

We prepared a polyethylene glycol (PEG) film by spin-coating its toluene solution on a silicon surface. We irradiated the sample under the cantilever tip with a collimated quantum cascade laser (QCL) (Hamamatsu Photonics) through a zinc selenide window from outside of the vacuum chamber. The power density on the sample was approximately 1.3 mW/cm^2 . The center wavenumber of the QCL was 1050 cm^{-1} . The temperature of the QCL was controlled by a thermoelectric cooler, which was also used for tuning the wavenumber with a range of $\pm 6 \text{ cm}^{-1}$.

Figure 2 shows a topographic image of the sample. The thickness of the PEG film measured from a step in the image was approximately 200 nm. To measure a relationship between the tip-sample interaction forces and IR irradiation, we modulated the power of the QCL at 750 Hz and detected the modulation component in the frequency shift signal and the energy dissipation of the cantilever using a lock-in amplifier. We measured the relationship between the magnitude of these components and the wavenumber of the QCL. Figure 3 shows plots of the magnitude of the modulated components in the frequency shift (black, thin) and the energy dissipation (red, bold) measured on Si (dotted) and the PEG film (solid) as indicated in Fig. 2. The wavenumber of the QCL was calibrated using a Fourier transform IR spectroscopy of the QCL beam. We found that the magnitude of the modulation component in the energy dissipation induced by IR irradiation was different between those on the PEG film and on the Si surface. In Figure 4, we also show an infrared absorption spectrum of the PEG film using the QCL. We found that two absorption peaks in the absorption spectrum indicated by the arrows, which might be corresponding to the peaks at the same wavenumbers in the dissipative force spectrum in Fig. 2, which are also indicated by the arrows.

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

Figures

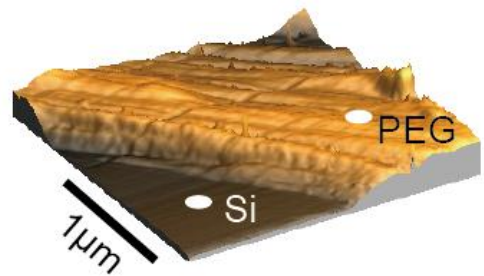
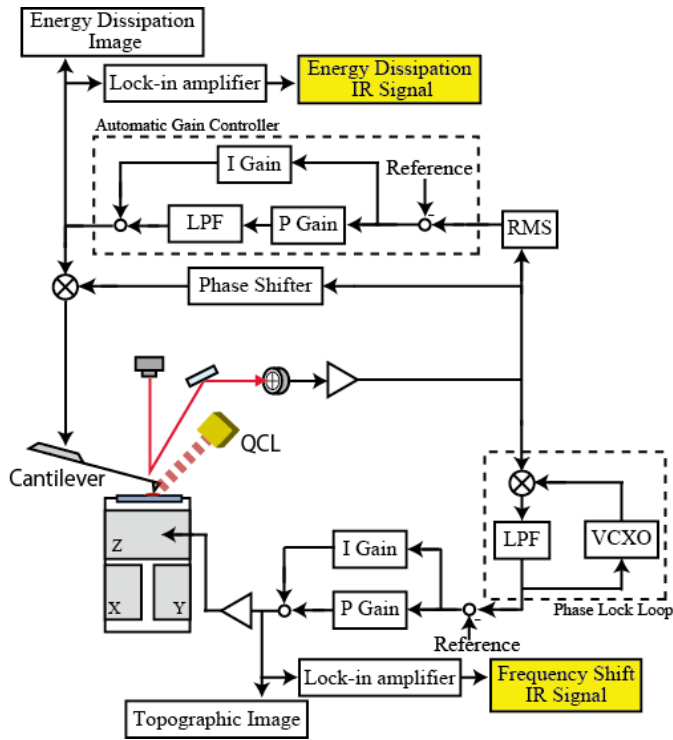


Figure 2: Topographic image of polyethylene glycol (PEG) thin film on the Si surface using FM-AFM.

Figure 1: Experiment setup of FM-AFM combined with irradiate infrared.

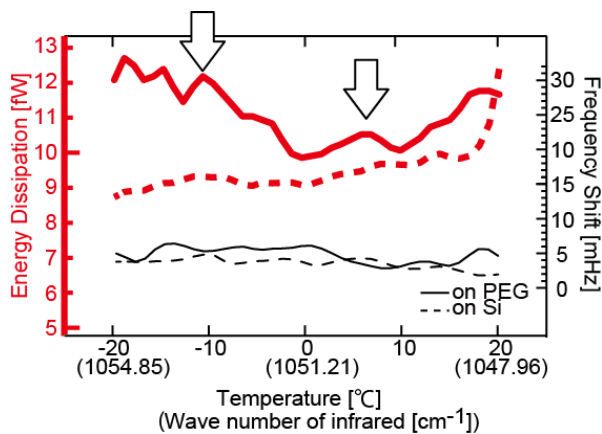


Figure 3: Frequency shift (black, thin) and energy dissipation (red, bold) induced by infrared irradiation measured on Si (dotted) and PEG (solid) as indicated in Fig.2.

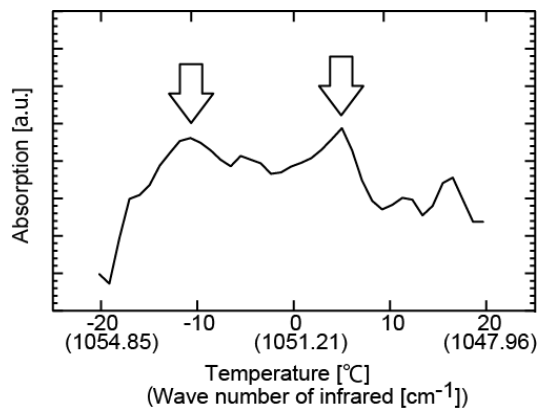


Figure 4: Infrared absorption spectrum of PEG detected by sweeping a temperature of QCL.