Mid-infrared absorption microscopy with λ/100 spatial resolution using tunable quantum cascade lasers

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Abstract: Highly-sensitive mid-infrared microscopy is reported. Subwavelength resolution is achieved by detecting absorption through local sample expansion. High sensitivity is obtained by moving laser pulses repetition rate in resonance with the atomic force microscope cantilever eigenfrequency.

1. Introduction

Mid-infrared (mid-IR) vibrational spectroscopy in the "molecular fingerprint" region (λ=3-15μm) is a powerful method for determining the chemical composition of samples. It may also be used to determine molecular orientation through comparing absorption spectra for different light polarizations. A mid-IR spectroscopy with nanoscale spatial resolution is highly desired for understanding chemical composition and molecular orientation of samples at nanoscale. Light diffraction limits the spatial resolution of traditional optical microscopes to ~1.5μm in mid-IR. Aperture and apertureless near-field scanning optical microscopy (NSOM) techniques have been developed to overcome these limitations. However, aperture-based NSOM can only provide spatial resolutions ~λ/10 in mid-IR and apertureless NSOM can provide spatial resolution better than λ/100 in mid-IR but it requires a very complex setup [1,2] which is subject to numerous experimental artifacts. In addition, the information obtained by apertureless NSOM is related to the sample refractive index variation and requires post-processing to obtain absorption data.

An alternative method of measuring mid-IR absorption spectra at nanoscale has been demonstrated recently [3]. The optical absorption is detected through measuring local thermal expansion of samples induced by the light absorption (we refer to this method as 'photoexpansion microscopy'). The sample expansion is detected by observing a deflection of a standard atomic force microscope (AFM) cantilever in contact with the sample surface. This approach results in a very simple experimental setup with no optical detectors. The cantilever deflection is directly proportional to sample absorption. The spatial resolution of this method is determined by thermal diffusion length (*l*), which is given as $l \approx (\tau \kappa / \rho C)^{1/2}$, where τ is the duration of the laser pulse and κ, ρ, and C are the thermal conductance, the volume density, and the heat capacity of a sample, respectively. This expression results in *l<100nm* for typical chem/bio samples excited with short (<100ns) light pulses.

To produce detectable AFM signal, previous experimental reports utilized high-power mid-infrared lasers or optical parametric oscillators to induce sample heating of 5-50K during the laser pulse. This approach results in bulky optical setups and potential sample damage. In this paper, we report a novel method of photoexpansion microscopy that benefits from the resonant enhancement of the AFM cantilever oscillations when the repetition rate of the laser pulses coincide with the AMF cantilever mechanical resonant frequency. Much smaller laser pulse power and sample heating are needed with this technique to perform spectroscopy. As a result we can utilize compact room-temperature tunable mid-IR quantum cascade laser (QCL) and obtain high-quality absorption spectra of thin-film samples with spatial resolution $\approx\lambda$/100.

2. Experimental approach

The sudden photoexpansion induced by a nanosecond laser pulse exerts 'photoexpansion' force on the AFM cantilever. If this force has a periodicity in resonance with the mechanical frequency of a bending mode of the AFM cantilever, we expect the cantilever bending amplitude to increase proportionally to the quality factor (Q-factor) of this mechanical oscillation. We note that AFM cantilevers with Q-factor as high as 5000 in air exist [4]. The resonant frequencies of cantilevers in contact mode are typically higher than 30kHz. The exact values of the resonant frequency are affected by cantilever parameters and sample properties. A short-pulse tunable mid-IR laser source with controllable pulse repletion frequency is required to implement the proposed spectroscopic method. Quantum cascade lasers (QCLs) [5] are uniquely suited for this task.

3. Experimental setup and results

Two QCL sources (Daylight Solutions, Inc.) tunable in 1580-1700cm^{-1} and 1120-1200cm^{-1} spectral range were used in our experiments. Samples were 300nm-thick SU-8 and LOR-3A polymers deposited on undoped Si and GaAs substrates. Samples were illuminated from the substrate side with 60ns 100mW-peak-power laser pulses. The AFM cantilever deflection (XE-70 AFM from Park systems) signal was sent to a lock-in amplifier with the QCL repetition frequency serving as a reference. The lock-in output is referred to as 'photoexpansion signal' in the figures below.
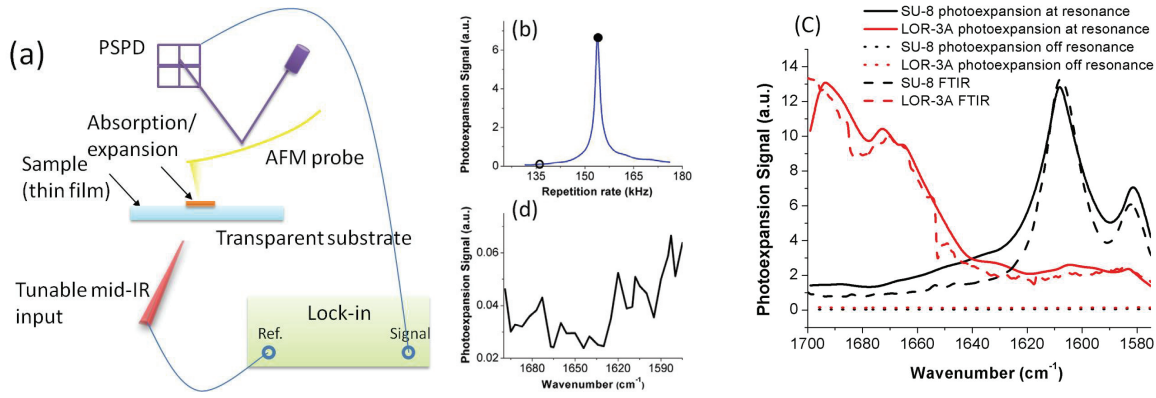

Fig.1. (a) Experimental setup of photoexpansion microscopy; (b) Demonstration of photoexpansion signal enhancement by cantilever resonance for a 300nm-thick SU8 film on Si substrate; (c) Comparison of photoexpansion spectra of SU-8 and LOR-3A polymers with optical spectra obtained by a Fourier transform infrared spectrometer. Photoexpansion spectra obtained with laser pulses repetition frequency being in resonance (solid lines, filler circle in (b)) and off resonance (dotted lines, open circle in (b)) with the cantilever mechanical frequency are shown there. In the latter case, the spectroscopic data is indistinguishable from noise. (d) Zoom-in of the black dotted line in (c).
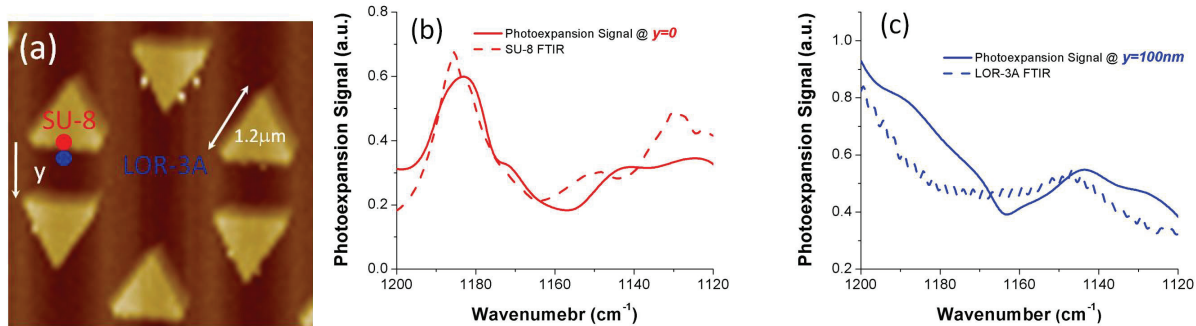

Fig 2. (a) Topographic image of patterned 300nm-thick SU-8 on top of 300nm-thick LOR-3A film on GaAs. (b) Photoexpansion spectrum at the position indicated by the red spot in (a) compared with SU-8 absorption spectrum. (c) Photoexpansion spectrum at a position 100nm away from that in (b) (the position is indicated by the blue spot in (a)), compared to the absorption spectrum of LOR-3A.

The AFM tip was gold-coated to prevent light absorption by the tip. Figure 1(a) shows the experimental setup. Figure 1(b) shows the photoexpansion signal enhancement as the laser pulses repetition frequency approaches the AFM cantilever mechanical resonance. Figure 1(c) demonstrates a good agreement between photoexpansion and optical spectra. Figure 1(d) emphasizes the importance of resonant enhancement in our technique.

High resolution of our technique is demonstrated by the data in Fig. 2. The sample is composed of 300nm-thick SU-8 triangles on top of a 300nm-thick LOR-3A film. The photoexpansion spectra were measured at two positions 100nm away from each other and are shown in Fig. 2(b) and 2(c). We can clearly distinguish the sample chemical composition at the two spots.

3. References
[1] B. Knoll and F. Keilmann, Nature **399,** 134 (1999).
[2] A. J. Huber, A. Ziegler, T. Kock and R. Hillenbrand, Nat. Nanotech. **4,** 153 (2008).
[3] A Dazzi, R. Prazeres, F. Glotin, and J. M. Ortega, Opt. Lett. **30,** 2388 (2005).
[4] H. Hida, M. Shikida, K. Fukuzawa, S. Murakami, Ke. Sato, K. Asaumi, Y. Iriye and Ka. Sato, Sensors Actuators A, **148,** 311 (2008).
[5] Andreas Hugi, Romain Terazzi, Yargo Bonetti, Andreas Wittmann, Milan Fischer, Mattias Beck, Jerome Faist, and Emilio Gini, Appl. Phys. Lett. **95,** 061103 (2009).