Midinfrared absorption measured at a $\lambda/400$ resolution with an atomic force microscope

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Abstract: Midinfrared absorption can be locally measured using a detection combining an atomic force microscope and a pulsed excitation. This is illustrated for the midinfrared bulk GaAs phonon absorption and for the midinfrared absorption of thin SiO_2 microdisks. We show that the signal given by the cantilever oscillation amplitude of the atomic force microscope follows the spectral dependence of the bulk material absorption. The absorption spatial resolution achieved with microdisks is around 50 nanometer for an optical excitation around 22 micrometer wavelength.

OCIS codes: (180.5810) Scanning microscopy; (300.6430) Spectroscopy, photothermal; (300.6470) Spectroscopy, semiconductors; (300.6270) Spectroscopy, far infrared

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1. Introduction

The local measurement of midinfrared absorption with a nanometer scale resolution is a challenging issue. Several approaches have been developed over the last years to perform two-dimensional absorption imaging with a high spatial resolution in the midinfrared. Apertureless scattering scanning near-field microscopy has been demonstrated on various type of samples using an optical excitation delivered by a CO_2 laser around 10.6 μm.[1, 2] The apertureless near-field microscope is based on the scattering of the electromagnetic field induced by the tip of an atomic force microscope (AFM) in tapping mode. This scattering is dependent on the local value of the complex dielectric function. This technique was recently extended to far-infrared using free-electron laser pulses to image ferroelectric domains.[3] Midinfrared absorption can also be measured using an atomic force microscope tip in contact mode as a sensor. This approach was first demonstrated by Dazzi *et al.* using bacteria or viruses as midinfrared absorbing media.[4, 5] The principle of operation for this measurement is the following and summarized in Fig. 1: the absorption of the pulsed exciting laser generates a local displacement of the sample surface. The displacement is transferred to the vibration modes of an atomic force microscope cantilever. The amplitude of the cantilever oscillation is a signature of the absorption and its measurement allows to perform a two-dimensional absorption imaging with high sensitivity and high lateral resolution. We have recently shown that this technique can be used to measure at room temperature the intersublevel ultrasmall absorption of single self-assembled InGaAs quantum dots around 10 μm wavelength.[6] The lateral resolution in the quantum dot experiment was found to be around 60 nm. The homogeneous linewidth of the intersublevel absorption was measured at room temperature by this way.

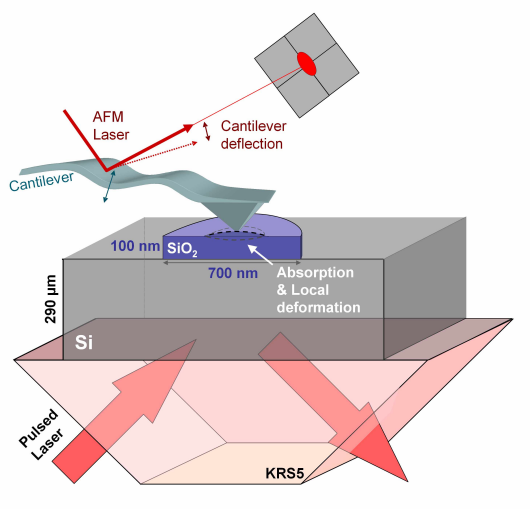

Fig. 1. Schematic view of the experimental setup for the local measurement of the absorption as described in the text.

In this work, we have investigated the measurement of midinfrared absorption at long wavelengths around 20 μm on solid-state semiconductor samples using the atomic force microscope

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in contact mode. We show that the oscillation amplitude of the atomic force microscope cantilever is directly correlated to the spectral dependence of the absorption. This is illustrated in the case of phonon absorption of bulk GaAs and in the case of SiO_2 microdisk absorption. Different contributions to the signal are observed coming either from the surface or from the bulk. A qualitative framework based on percutionnal mechanical excitation is proposed as a base for the discussion of the observed signal features.

2. Samples

Two types of sample have been investigated. The first sample is a bulk GaAs substrate with a 72 μm thickness. The second sample is a 290 μm thick silicon substrate on top of which SiO_2 microdisks have been deposited. In the latter case, a 100 nm thick oxide was first deposited by plasma-enhanced chemical vapor deposition on the silicon substrate. The microdisks were patterned by e-beam lithography with a negative photoresist followed by wet etching with fluorydric acid. Microdisks with 0.7 μm diameter were fabricated, each disk being separated from its neighbour by a 8 μm distance. The optical excitation was provided by the optical pulses of the free-electron laser CLIO. The free-electron laser delivers 8 μs long macropulses at the 25 Hz repetition frequency, each macropulse being composed of picosecond micropulses at a repetition rate of 32 MHz. The samples were deposited on top of a KRS5 prism following the set-up described in [4] and [6].

As illustrated schematically in Fig. 1 the GaAs and silicon samples have an higher index of refraction than KRS5. Light is thus coupled to the samples by refraction and experiences a total internal reflection at the upper sample-air interface. We have used silicon cantilevers equally metallized on both faces as the absorption sensor. In contact mode, the cantilevers have a main vibration frequency around 50 kHz. In the experiment, the time-dependent oscillation of the cantilever with its tip in contact mode is recorded as a function of time and then Fourier-transformed. The amplitude of the integrated signal around the resonance frequency provides a local measurement of the surface displacement and consequently is the signature of the absorption. In a simplified approach, the tip+cantilever can be viewed as a mechanical oscillator with mass m and and stiffness k and a natural frequency $\omega = \sqrt{k/m}$. The mechanical oscillator is subject to a displacement associated with the sample surface deformation and obeys the equation of motion $\ddot{y} + \omega^2 y = \omega^2 u(t)$ where the surface displacement u(t) is a short impulse which results from the free-electron laser induced deformation. The displacement response of the mechanical oscillator is given by the convolution integral $y(t) = \omega \int_{-\infty}^{\infty} u(\tau) \sin \omega(t-\tau) d\tau$.[7] Following the shock impulse, the mechanical oscillator oscillates at its natural frequency with an amplitude which depends on the displacement induced by the deformation associated with the laser absorption. The convolution integral implies that the amplitude of the displacement response is ruled by the Fourier frequency component of u at the natural frequency of the mechanical oscillator.

3. Spectral dependence for a GaAs substrate

The upper part of Fig. 2 shows the transmission of a bulk 72 μm thick GaAs sample as measured by standard Fourier-transform infrared spectroscopy. The oscillations correspond to Fabry-Perot interferences due to the 72 μm sample thickness. The transmission is modulated by the multiphonon absorption of the sample. Following [8], the peak absorptions at 65 meV and 55 meV correspond to a 2 TO and 1 TO + 1 LA phonon absorptions where TO stands for transverse optical and LO for longitudinal optical phonons. The absorption amplitude is 55 cm^{-1} and 30 cm^{-1} for 2 TO and 1 TO + LA resonances respectively. At 50 meV, the absorption amplitude is around 10 cm^{-1} at room temperature. The lower part of Fig. 2 shows the spectral dependence of the atomic force microscope cantilever oscillation amplitude integrated around

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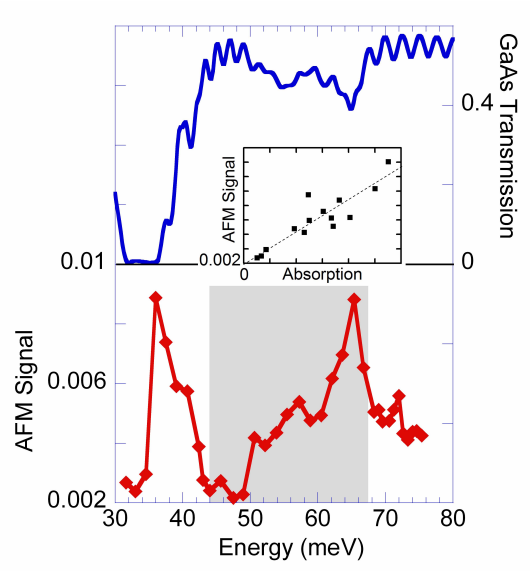

Fig. 2. Top: transmission of a 72 μm thick GaAs bulk substrate. Bottom: integrated oscillation amplitude the atomic force microscope cantilever in contact mode on the surface of the bulk GaAs substrate. The squares in the inset depict the oscillation amplitude as a function of the absorption (arbitrary units) deduced from the smoothed transmission in the 44-68 meV grayed energy range. The dotted line in the inset is a guide to the eye.

48 kHz which corresponds to the natural frequency of the cantilever in contact mode. Between 44 and 68 meV, the signal follows the GaAs phonon absorption and exhibits roughly a linear dependence versus the phonon absorption magnitude as depicted in the inset. At higher energy an increased background signal is observed and attributed to the continuous change over large spectral range of the Fabry-Perrot effect and tunnel coupling of the pulses into the sample, as well as an increase of the diffusion at short wavelength which perturbates the cantilever oscillation. We note that whereas in [6] the electronic absorption is followed by phonon emission and surface deformation, we use in the present experiment the phonon absorption to generate a surface displacement which is transferred into cantilever vibration.

The situation is quite different below 50 meV in the Reststrahlen region. The AFM signal increases up to 36 meV and drops sharply when the sample becomes non transparent. The signal amplitude at 36 meV is however not larger than the signal amplitude at 65 meV whereas the absorption coefficient is 200 times larger. It indicates that the response is not linear for strongly absorbing samples. Several features may explain this deviation. A first factor is associated with the change of reflectivity of GaAs in the Reststrahlen region. The reflectance increases up to $\sim$93 % at room temperature and normal incidence around the LO an TO phonon absorption. Because of this high reflectivity, the pulse energy which can be transferred to the lattice is decreased accordingly. Other factors may be associated with the propagation and diffusion of the lattice deformation through the sample, in particular related to the acoustic and thermal dynamics accounting for the limit conditions. The detailed analysis of these factors are beyond the scope of this article and needs to be further investigated. Here we provide key typical figures on the experiment configuration.

Around 34 meV, the absorption coefficient of GaAs is larger than $10^4\,\mathrm{cm}^{-1}$ which means that all the incident light is absorbed within the first micrometer at the rear surface of the

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sample. Acoustic waves generated by the absorption of the incident laser pulses propagate over micrometer distances on a nanosecond time scale before attenuation. However the resonant frequency of the cantilever being around 50 kHz, the characteristic time of the measurement for the signal detection is around 20 microseconds. If we consider a thermal heat pulse, the thermal diffusion length L_d is $2\sqrt{at}$ where a is the thermal diffusivity of GaAs (0.31 cm^2/s) and t the characteristic time of the measurement.[9, 10] At room temperature, the thermal diffusion is thus around 50 micrometers, i.e. a length of the order of the sample thickness.

4. Spatial resolution with SiO_2 microdisks

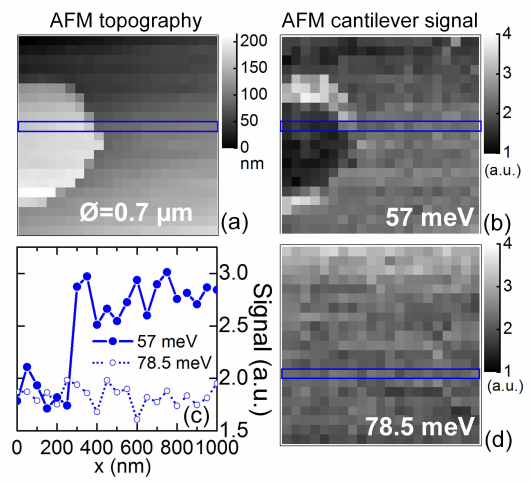

Fig. 3. Two-dimensional imaging of a 100 nm thick, 700 nm in diameter, SiO_2 microdisk deposited on a silicon substrate. (a) Topography signal of the microdisk measured simultaneously with the signal in (b). The size of a pixel is 50 nm. (b) Frequency integrated amplitude of cantilever oscillation signal depicted as a gray level. The laser wavelength is 21.8 μm. (c) Signal extracted from the scan line highlithed in (b) and (d) by a blue rectangle at 57 meV and 78.5 meV respectively. At 78.5 meV the signal values (in arbitrary units) have been multiplied by a constant factor (0.825) to ease comparison. (d) Frequency integrated amplitude of cantilever oscillation signal at a laser wavelength of 15.8 μm, out of resonance of the SiO_2 microdisk absorption.

We have investigated the spatial resolution that can be achieved with bulk absorption with SiO_2 microdisks deposited on a silicon substrate. The spatial resolution is by definition related to the intrinsic capability of the measurement to distinguish two spatially close different absorptions. Note that due to the measurement configuration schematically described in Fig. 1, it is the local deformation that is measured as a signature of the absorption. The resolution therefore amounts to the ability to separate two different local deformations generated by different absorption sources.

Figure 3 (a) shows the topography signal of a 0.7 μm diameter SiO_2 microdisk as measured during the surface scan. The topography signal is not corrected from the drift of the piezoelectric z-scanner. The pixel size is 50 nm. Figure 3(b) shows the amplitude of the cantilever oscillation, during the same scan, spectrally integrated around 48 kHz for an optical excitation at 57 meV. The AFM signal decreases on top of the microdisk as compared to the signal recorded on the silicon surface. This change of signal is better observed in Fig. 3(c) full line on the line scan highlighted in Fig. 3(a), 3(b) and 3(c) going though the middle of the microdisk.

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A signal decrease of ∼1.7 dB is measured when the AFM is on top of the microdisk. As shown below, the signal decrease follows the spectral dependence of the SiO_2 absorption. At 78.5 meV, out of the SiO_2 absorption resonance, the signal is spatially uniform as observed in Fig. 3(d) and as observed along the highlighted scan line plotted as a dotted line in Fig. 3(c). Without absorption there is therefore no topography signature in the recorded signal. The cantilever vibration amplitude is a signature of the midinfrared absorption of the microdisk and not an artifact associated with the difference of material parameters and the local contact change of the AFM tip. We note that the topography of the sample can modify the contact and the signal amplitude on the upper and lower edge of the microdisks which are along the AFM tip path (from left to right in the present experiment). We also note that there is a small regular increase of the signal amplitude from top to bottom which is associated with the change of the load applied on the cantilever during the scan, as it can be observed on the topography signal.

In Fig. 3(c) the transition between Si and SiO_2 is very abrupt and occurs over a single pixel, i.e. 50 nm. As compared to the 21.8 μm excitation wavelength, the absorption spatial resolution is a factor of 400 smaller than the wavelength. A resolution better than 100 nm and around 60 nm were previously reported with cells immersed in liquid water[11] or semiconductor quantum dots.[6] It indicates that this atomic force microscopy is a very suitable tool for high resolution midinfrared absorption imaging. Note that if the microdisk was embedded into silicon, the thermal diffusion and acoustic propagation would occur on larger distances and the observed resolution would be therefore a distance larger than 50 nm for the same microdisk. This last configuration would be less favorable to probe and get closer to the ultimate resolution of the instrument. The measurement is related to the surface deformation. We expect the resolution to be limited by the contact radius between the tip and the surface, estimated around 2 nm from a Hertz contact approach.

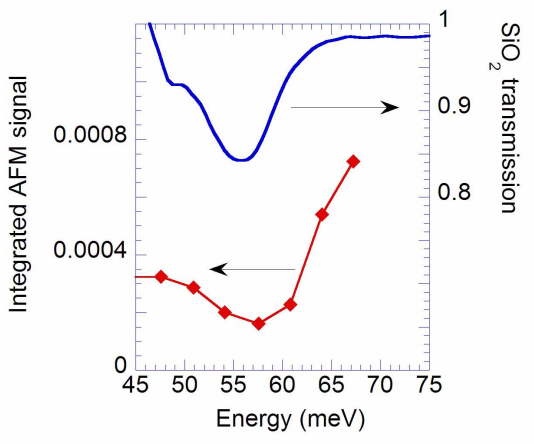

Fig. 4. Top: Transmission of a 200 nm thick SiO_2 film measured by standard Fourier transform spectroscopy. The SiO_2 is deposited on a silicon substrate and the transmission has been *normalized* by the transmission of the silicon substrate. The Si absorption bands around 70 meV are therefore not observed in this normalized transmission. Note that the thickness of the layer is twice as large as the 100 nm thickness of the microdisk. Bottom: Spectral dependence of the integrated cantilever oscillation amplitude on top of the SiO_2 microdisk.

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5. Spectral dependence for a SiO_2 microdisk and discussion

Figure 4 shows the spectral dependence of the AFM signal measured in the middle of the 100 nm thick microdisk as compared to the absorption of a 200 nm thick SiO_2 film measured with a Fourier transform spectrometer. A strong absorption maximum at 57 meV is observed by transmission. The absorption coefficient extracted from this resonance amplitude is around 10^4 cm^{-1}, in agreement with the data reported in [12]. The integrated AFM signal follows the spectral dependence of the absorption. The striking feature shown in Fig. 3(b) and Fig. 4 is the decrease of the signal on top of the nano-object. Several contributions to the signal exist and are associated with two different absorptions: the absorption of the oxide of the microdisk on top of the sample and the deep residual absorption of the silicon substrate.

The relevant description of the interplay of these contributions would require a detailed nanothermal and nanoacoustical analysis at the ps, ns and μs time scales, beyond the scope of this article. Several features can nonetheless be emphasized. Separate transmission measurements performed with the silicon substrate show that its absorption increases regularly from 50 to 65 meV because of the LO + TA and TO + TA lattice absorption. The absorption amounts to a few % (3 % at 60 meV), i.e. an amplitude of the same order of magnitude than the oxide absorption. The substrate lattice absorption explains the increase of the signal at high energy in Fig. 4 as observed with the GaAs substrate. A striking difference exists however between both oxide and substrate absorptions: the oxide absorption is localized very close to the AFM tip and the acoustic and thermal deformation is instantaneously transmitted to the cantilever. The bulk absorption occurs deeper in the whole substrate. For each picosecond pulses, acoustic deformation propagates at the sound velocity in a few tens of nanoseconds over the thickness of the substrate. However the thermal diffusion occurs on a much longer time scale in the μs range and heat will diffuse outside of the substrate. If we consider a 0.8 cm^2/s thermal diffusivity for silicon, the thermal diffusion length is 80 μm for a time delay of 20 μs which corresponds to the time-scale of the measurement. In a simplified view, the signal which triggers the oscillation of the cantilever has thus two components: instantaneous components and a longer thermal component corresponding to the bulk substrate heat diffusion. The displacement response of the cantilever can be qualitatively understood and described in a first approximation neglecting oscillation damping by: $y(t) = \omega \int_{-\infty}^{\infty} (u_1(\tau) + u_2(\tau - t_d)) \sin \omega(t-\tau) d\tau$ where u_1 and u_2 are the displacement temporal profiles corresponding to these components and t_d is an effective time delay between these two deformation components which modify the surface displacement. If the diffusion delay is of the order of the natural frequency of the cantilever (the phase delay is of the order of π) the two u_1 and u_2 components can compensate each other in the same way that the oscillation amplitude of a mechanical oscillator can be decreased when subjected to one out-of phase shock impulse. Qualitatively both contributions are thus not necessarily additive.

Another mechanism, different from the percutionnal mechanical excitation, could possibly contribute to the observed signal. Heat may diffuse into the tip and subsequently into the cantilever. Temperature actuation of cantilevers by e.g. electrothermal heating has already been reported.[14] We confirm that in our case, if the tip is not gold covered, an oscillation of the cantilever is triggered due to the absorption of the incident evanescent electromagnetic pulse and subsequent heating of the cantilever. In the present experiment the cantilever is gold covered on both faces but still there is a contact area between the gold covered tip and the sample surface enabling in principle heat flow from the sample to the tip. The heating of the cantilever is thus a relevant process that cannot be formally excluded, nor the dilation of the heated material. This process is formally identical to the photoacoustic 1880 Bell experiment in which the illuminated material heats the air and launch a sound wave (here the cantilever signal medium plays the role of the air).[13] In the later case the recorded signal originates from air heating rather than material dilation.[15] In our case the contact radius between the tip and the surface

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is however small ($\sim$2 nm). This figure strongly limits the heat flux from the surface to the tip as compared to the free thermal diffusion and dilation in the material volume beneath the tip. Note that at the present stage we cannot provide experimental data excluding this specific heat transfer mechanism.

6. Conclusion

In conclusion, we have shown that midinfrared absorption of bulk samples can be measured through the oscillation amplitude of an atomic force microscope cantilever in contact mode on the surface. The oscillations are triggered by the surface displacement resulting from the absorption. The oscillation amplitude follows the spectral dependence of the bulk absorption. A spatial resolution around 50 nm is achieved as evidenced with the measurements on SiO_2 microdisks. The measurements on bulk GaAs and on SiO_2 microdisks deposited on silicon have shown that both surface and bulk can contribute to the signal. These measurements suggest that the acoustic and thermal propagation of the deformation plays an important role which can lead to phase delays and can induce a decrease of the oscillation amplitude of the cantilever.

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