Fast IR imaging with sub-wavelength resolution using a transient near-field probe [1]

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Abstract

We present a method for the remote generation of a transient near-field probe using conventional IR microscopy optics. Photo-induced reflectivity generated by picosecond pulses of visible light incident on the surface of a semiconductor substrate is used to create transient mirrors with dimensions determined by the spot size of the visible light. The IR light scattered by such sub-wavelength-size mirror is collected after propagating through the sample. As the sample is located on the semiconductor substrate, no near-field distance control is required, and the image can be taken at the speed of typical laser scanning microscope. And since the near-field probe is generated remotely – using light – the sample to be imaged can be covered by, or encased in, a transparent liquid or solid. The resolution of such an IR microscope is determined by the dimensions of the transient mirror, i.e., by the spot size of the visible light and its penetration depth into the substrate. To prevent resolution degradation due to diffusion of the photo-excited carriers in the substrate, the probe (IR) pulse duration should not exceed a few tens of picoseconds.   © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The mid-infrared vibrational spectrum of materials provides a chemically selective contrast mechanism for imaging. However, the long wavelength of the mid-IR radiation diffraction limits the spatial resolution to no better than a few microns in conventional IR microscopy. (In practice, commercial IR microscopes rarely do as well as 10 μm [1].) This resolution prevents IR microscopy and spectroscopy of single sub-cellular or even cellular features routinely observable with conventional visible light microscopes. It also limits the applicability of IR microscopy in the field of semiconductors as its resolution is far below the standards set by lithographic processing (currently on the order of 0.3 μm).

Scanning near-field optical microscopy can provide sub-wavelength spatial resolution using a

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sub-wavelength source of radiation which is raster scanned over the sample surface at a small (several nanometers) distance [2]. As a light source, very fine tapered fiber tips are generally used, coated with a thin layer of metal to prevent light leakage except at the very end of the tip where there is a small aperture. Strong attenuation of light in the sub-wavelength part of the taper limits the output signal and, consequently, the scanning rate [3,4]. Heating of the fiber coating by light limits the input light power [5]. To overcome these limitations, apertureless schemes have been developed which are based on the detection of light scattered from vibrating tapered metal tips [6,7]. The near-field source must be kept very close to the sample – within a near-field zone (on the order of tip diameter) – to provide a resolution close to the tip diameter. Typically this is accomplished using atomic force-based feedback mechanisms which generally limit the imaging rate to at best a few minutes per image.

In this article we present a method for the remote generation of a transient near-field probe which will allow fast IR imaging and spectroscopy with the resolution typical of conventional visible microscopy.

2. Principle

For samples such as histological sections or thin films fixed to a coverslip or prepared on a substrate, near-field distance control would be unnecessary if the point source of light were generated directly on the surface. In the IR spectral range such a sub-wavelength-size source of light can be generated on the surface of a semiconductor using photo-induced reflectivity [8]. A pulse of visible light absorbed on the surface of a semiconductor can generate a transient electron–hole plasma due to the promotion of electrons from the valence to the conductance band. The plasma carrier density necessary for significant (>70%) mid-IR reflectivity can be obtained with visible pumping levels well below the damage threshold of semiconductor materials [9]. (The lifetime of the photo-induced reflectivity can vary in a ps–ns range depending on the dimensions of the visible

light absorption zone, the IR wavelength, and the properties of the semiconductor material [9].) As the dimensions of such a transient mirror are determined by the size of the *visible* light spot, it can generate a "point" source of IR light on the surface of a semiconductor as shown in Fig. 1.

The IR light is incident on the substrate at Brewster's angle, thus most of the light is transmitted through the substrate, and only about 1% is reflected in a specular direction. This reflected beam misses the Cassegrain objective thus providing "dark-field" illumination of the sample. The visible light focused by the objective on the substrate in the middle of the IR spot generates a transient mirror which reflects the IR light. If the dimensions of this transient mirror are below the wavelength of IR radiation, the reflected IR beam will be highly diverging, and thus can be collected (passing through the sample) by the same objective and focused on a detector. Such a scheme using a conventional IR microscope can provide IR imaging and spectroscopy with the resolution of conventional visible microscopy. As no near-field distance control is required, the sample can be
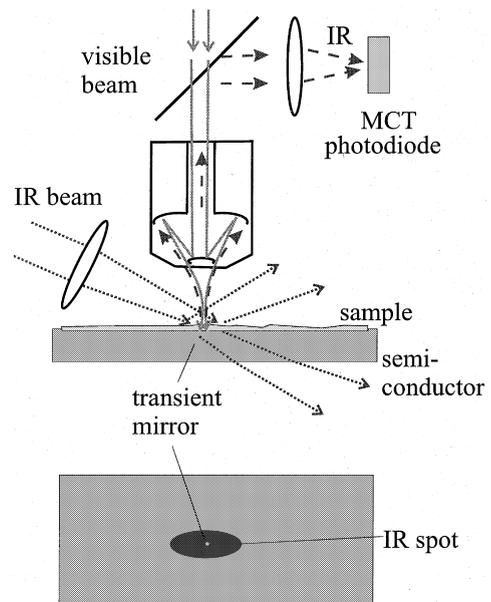

Fig. 1. Simplified side view of the optical layout of the experiment, and a view from above of the optical spots on the substrate.

imaged at the speed of a typical laser scanning microscope. And since the near-field probe is generated remotely – using light – the sample to be imaged can be covered by, or encased in, a transparent liquid or solid.

The photo-induced scattering can be discriminated from the background sample or substrate scattering using gated integration. The details differ depending on whether the IR pulses are longer or shorter than the response time of the detector, but in either case the idea is to subtract a background only level from a background plus signal level. In the case of a short IR pulse, the repetition rate of the train of IR pulses needs to be at least twice that of the visible train. The gate of the one integrator is timed to coincide with the synchronized visible and IR pulses, and thus records a signal which is the sum of a photo-induced component and a scattered component. The gate of the second integrator is timed to overlap an IR pulse in the absence of the visible pulse, so only a scattered signal is recorded. Subtracting the outputs of the two integrators yields the desired photo-induced signal. In the case of a long IR pulse, the repetition rate of the IR and the visible trains can be the same. In this case a portion of the IR pulse preceding the visible pulse is used as a reference for scattering.

3. Experiments

To test the concept we first used a pulsed CO_2 laser ($\lambda = 10.6$ μm, pulse duration ~100 μs, amplitude stability 20%) (F48G-2, Synrad, North Bothell, WA, USA) synchronized with a Ti:Sapphire regenerative amplifier ($\tau \approx 1$ ps, $\lambda = 780$ nm, rep. rate 1 kHz) (Positive Light, Los Gatos, CA, USA). The peak power of the p-polarized CO_2 laser was 10 W, and was focused to a spot about 85×290 μm at about 73° to the substrate (close to Brewster's angle). The spot size of the IR beam at the sample was measured using the specular reflection of the beam. To restrict the average power to 100 mW, the CO_2 repetition rate was kept at 100 Hz. The visible light was focused with a ×25 reflective objective (N.A. 0.4, Ealing Electro-Optics, Herts, UK). Energy fluence in the visible light

spot was about 70 mJ/cm² on the silicon substrate surface, inducing a reflectivity of about 80% at 10.6 μm wavelength [9].

For a resolution test we used the sharp (submicrometer) edge of a gold coating (0.1 μm thick) on a silicon wafer. As the MCT detector was sensitive to both the 780 nm and the IR radiation, we could measure the spot size of the visible beam by scanning the same gold coating edge and using the difference in reflection coefficients of silicon and gold. When the detector was being used for IR, a Si slab was put in front of the detector to block the visible light. The results of the edge scanning test are shown in Fig. 2, on which the resolution has been defined as the width of the signal transition from 10% to 90% of the amplitude variation. The IR spot size was 85 μm wide in these experiments, as mentioned above.

When the Ti:Sapphire laser spot was larger than about 30 μm, the PIR signal transition was about one half the width of the visible spot (see Fig. 2(a)). This sharpening is probably due to the non-linear nature of the photo-induced reflectivity mechanism [9]. When the visible laser was focused to about 7 μm (the smallest visible spot we could obtain with this objective, due to either objective imperfection or misalignment), the PIR transition did not become sharper than about 9 μm (see Fig. 2(b)). This can be explained by carrier diffusion during the plasma relaxation time, or by the deep (10 μm) penetration of the Ti:Sapphire laser in silicon. Diffusion of the non-equilibrium charge carriers during the IR pulse may result in an increase of the effective reflecting spot size. During the recombination time (about 1 ns for silicon substrate with 10^{15} cm^{-3} Boron doping) the reflecting spot will spread by about 5 μm (diffusion coefficient $D \approx 70$ cm²/s), consistent with Fig. 2(b). This limitation can be avoided by using short IR pulses (less than 40 ps for 1 μm resolution). Tunable pulsed IR sources such as optical parametric oscillators or free electron lasers provide pulses on the order of 1 ps and thus will not restrict the resolution by more than ~0.2 μm.

As the entire volume of plasma scatters the IR beam, the resolution may be limited by the penetration depth of the pump beam in the substrate. This can be reduced by using a shorter wavelength,
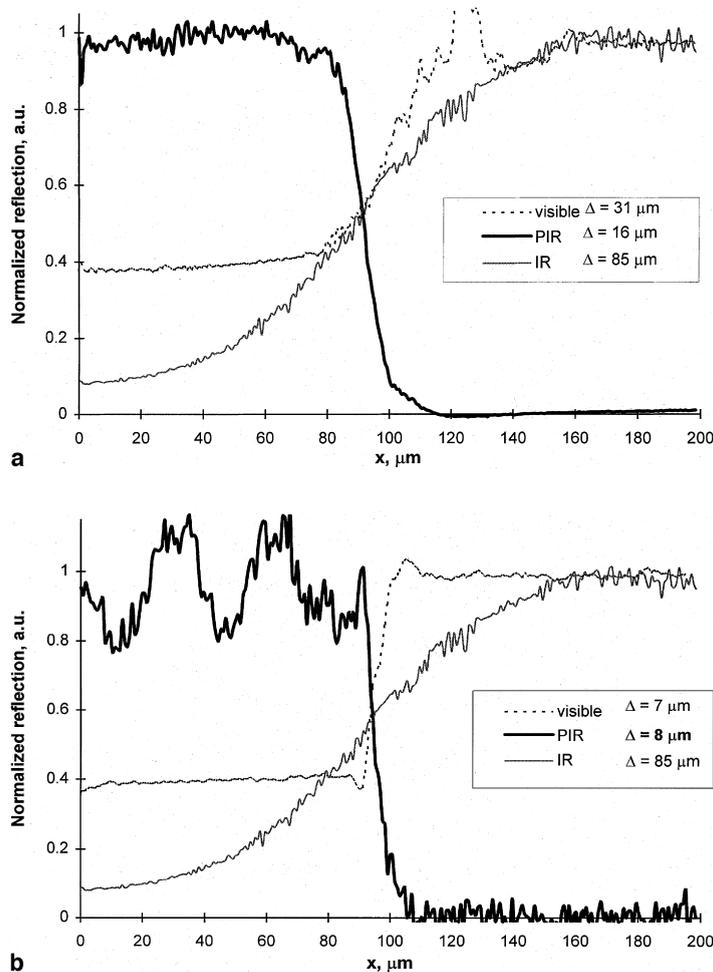
Fig. 2. Scans across a gold coating edge on a silicon slab recorded for all three beams: visible (Ti:Sapphire, $\lambda = 0.8$ μm), CO_2 laser ($\lambda = 10.6$ μm), and photo-induced reflection (PIR). A gold coating is located on the right of the 100 μm mark. The Δ is defined as the width corresponding to the 10–90% variation of the signal. (a) The visible beam spot size is 31 μm. (b) The visible beam is focused to a 7 μm spot.

or a different semiconductor material (penetration depth is about 1 μm at $\lambda = 532$ nm in Si, and 0.2 μm at $\lambda = 780$ nm in Ge).

In a second set of experiments we used a Germanium substrate to avoid possible limitations imposed by the deep penetration of the pumping beam. To prevent the possible degradation of resolution due to the diffusion of the photo-induced carriers, we used 1 ps long IR pulses of the Free Electron Laser (FEL) synchronized with the Ti:Sapphire regenerative amplifier. The energy of the FEL micropulse was about 0.5 μJ on the

sample, and the wavelength was 6.25 μm. The resulting scan across the gold coating edge is shown in Fig. 3. The width of the 10–90% transition in this scan was about 5 μm, whereas the visible spot size was the same as in the previous experiment – about 7 μm.

4. Discussion

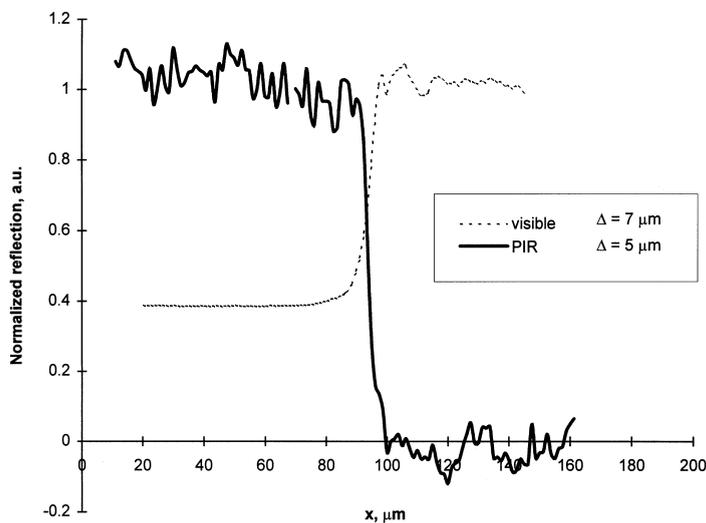Heating of the substrate and the sample by the incident beams are potential problems. First we

Fig. 3. Scan across a gold coating edge on a Ge substrate with the FEL ($\lambda = 6.25$ μm) used as a probe beam. The spot size of the visible beam (Ti:Sapphire, $\lambda = 0.8$ μm) is 7 μm.

estimate substrate heating by the visible pulse. Laser pulses inducing a reflectivity of about 80% (energy density of about 70 J/cm^3) heat the substrate surface layer by about 20 K/pulse. With a spot size of about 1 μm, the heat diffusion time in the substrate is about 5 ns. Pulse repetition rates significantly slower than this diffusion time will lead to no significant cumulative heating of the substrate. Organic samples, for which a 20 K temperature rise might be critical, should not be strongly affected by the substrate heat pulse, as the thermal conductivity of the substrate is by more than 2 orders of magnitude larger than that of water, and even more for biological materials. To estimate the sample heating by the IR pulse, we can assume a sample to be just a layer of water with a thickness below the laser penetration depth and an IR spot size the same as in the present work. In this case a 1 μJ pulse will heat the sample by 1 K. The thermal diffusion time will be on the order of several μs, determined largely by the sample thickness. Thus, if the repetition rate of the IR laser does not exceed several kHz, or the sample is scanned quickly enough to prevent the heat accumulation, IR pulse energies of several μJ should present no heating problems.

Another concern may be the possibility of dielectric breakdown in the sample caused by the intense visible pulse. With the energy density applied to silicon in our experiment – about 70 mJ/cm^2 and 1 ps pulse duration – the peak power fluence will be about 70 MW/cm^2, which is substantially lower than the dielectric breakdown threshold in biological tissue [10] – 1 TW/cm^2. We also measured that plasma generation on silicon surface does not occur until energy levels are at least 10 times higher than those used in our experiment.

In the present experiment we obtained about 3 pJ of detected IR light with a signal-to-noise ratio of 10/1 from a 10 μm spot of visible light. The intensity of IR light scattered from a small (sub-wavelength) probe scales with its diameter d as d^6/λ^4 (dipole approximation). Using this scaling law we can estimate the resolution limit we can obtain optimizing the pulse parameters (ps duration instead of 100 μs, improved amplitude stability, etc.) and optimizing the detection scheme (balanced gated integrators, etc.). We find that we should achieve the same signal-to-noise ratio from a spot size of about $\lambda/6$ with 1 μJ IR pulses. At a wavelength of 6 μm this will provide a resolution of 1 μm, consistent with the desirable goal of focusing the visible light with long working distance objectives (N.A. about 0.6).

Further improvements in resolution and signal-to-noise ratio are possible. To improve the reso-

lution, a scheme based on the use of an inverted microscope can be used. In this arrangement the visible light is focused with a high N.A. objective through a transparent substrate coated with a thin film of semiconductor material. This will improve the visible beam focusing and protect the sample from the visible light. Such protection may be important for samples which could suffer from photo-induced changes induced by high intensity visible light illumination. The coating thickness should be about 0.5 μm – the same as the penetration depth of visible light in the semiconductor substrate. The IR part of the scheme remains the same as in the present setup. However, as the IR objective will be used only for the scattered light collection, it can be replaced with the IR lens and tilted aside to provide space for transmitted light illumination of the sample (the semiconductor coating can be transparent to red light, and be pumped by green or blue light, as for example, GaP).

To increase the signal-to-noise ratio, an interferometric detection scheme that uses a portion of the IR beam as a phase reference can be used. This method of detection is sensitive to the electrical field strength instead of intensity [7], and thus the dipole scaling law is d^3/λ^2. With such an approach signal strength will remain adequate at a resolution of about $\lambda/30$. Thus for the mid-IR the resolution will in practice be determined by the spot size of the visible laser. In our case the interferometric approach would be based on modulation of the reference arm, and thus it is particularly appropriate for use with the high repetition rate IR sources such as an FEL.

In summary, we have proposed a novel type of near-field scanning infrared microscopy based on remote generation of a transient near-field probe. This probe is a photo-induced plasma generated in a semiconductor substrate by a ps pulse of visible light focused to a diffraction limited spot. This plasma scatters the IR light incident on the substrate through the sample and provides a point source of IR radiation with a size determined by the visible laser spot. This approach makes the IR microscopy possible with the resolution of visible microscopy using standard IR microscope optics.

As there is no need for near-field distance control with atomic force based feed-back schemes, fast scanning of the sample becomes possible. In addition, there is no attenuation of the IR beam inside tapered fiber probes and samples can be imaged with high resolution even if covered with transparent material.

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