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IR microscopy with a transient photo-induced near-field probe (tipless near-field microscopy)

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Abstract

Photo-induced reflectivity generated by picosecond pulses of light incident on the surface of semiconductors has been used to create transient mirrors with dimensions determined by the spot size of the visible light. These mirrors were used as near-field probes for scattering of the infrared (IR) laser beam. It has been verified that the IR light reflected from this transient mirror has a spatial resolution determined by the spot size of the visible light. This methodology enables IR microscopy of thin samples with the resolution of a visible microscope. Advantages of this approach are: (i) no need for near-field distance control, (ii) possibility of fast sample scanning, (iii) no attenuation of the IR beam in a tapered fiber probe, and (iv) the sample to be imaged can be covered by or encased in a transparent liquid or solid. Preliminary results, prospects and limitations are discussed. © 1998 Elsevier Science B.V.

Keywords: Near-field microscopy; IR microscopy; Photo-induced reflectivity

1. Introduction

Scanning near-field optical microscopy is attracting growing interest as a method for imaging [1–4], spectroscopy [5,6], and material processing [7,8] as it can provide sub-wavelength spatial resolution over a broad range of the electromagnetic spectrum – from ultraviolet to microwave frequencies. This technique is based on a source of radiation which is sub-wavelength in size and which is raster scanned over the sample surface at a small (several nanometers) distance. For microscopy the most common light source is a very fine tapered tip at the end of a single mode optical fiber. The tip is generally coated with a thin layer of metal to prevent light leakage except the very end of the tip, where there is a small aperture. The transmission of such a tip depends on both the aperture size and the taper angle [9], and is typically on the order of 10^{-4}–10^{-7} for aperture sizes $\lambda/5$–$\lambda/10$ [10]. Such a low transmission limits the scanning rate and makes it very difficult to use smaller apertures. Much of the untransmitted light is reflected back into the fiber by the metal coating and can cause considerable heating and damage, thus limiting the input light power [11]. To overcome these limitations, apertureless schemes have been developed which are based on the detection of light scattered from vibrating tapered metallic tips [12,13]. In all cases 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 an atomic force based feedback mechanism detecting either the deflection of the tip cantilever touching the sample (contact mode), or the change of the amplitude or phase of the vibrating tip as it approaches the sample surface (tapping mode). The need for near-field distance control generally limits the imaging rate to at least a few minutes per image.

Infrared (IR) spectroscopy is a widely used and sensitive technique for the detection and characterization of molecules. It finds application in a variety of fields ranging from biology to material science. However, in conventional IR microscopy, diffraction of the long wavelength

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radiation (5–12 μm) limits the spatial resolution to no better than a few micrometers. In practice, commercial IR microscopes rarely do as well as 10 μm [14] in this spectral range. This resolution prevents the IR 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). In this article we present what we believe to be the first 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 and experiment

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 subwavelength-size source of light can be generated on the surface of a semiconductor using photo-induced reflectivity [15]. A pulse of visible light absorbed in the surface layer of a semiconductor can generate a transient electron-hole plasma due to the promotion of electrons from the valence to the conduction band.

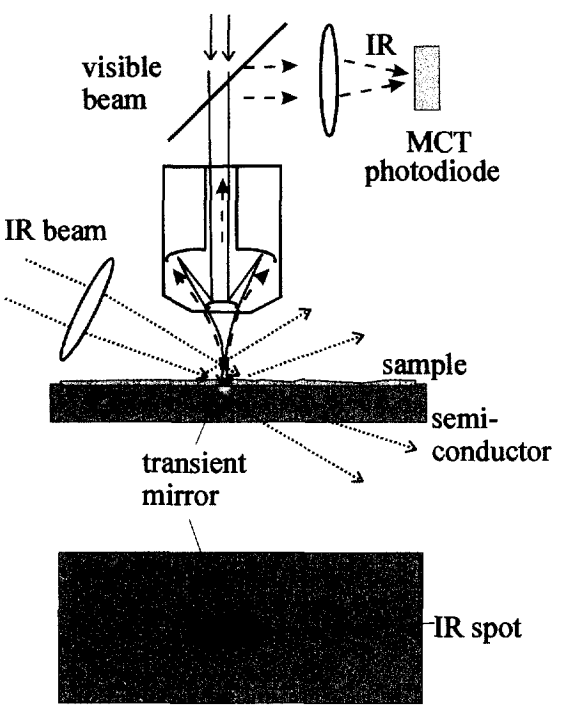

Fig. 1. Simplified side view of the optical layout of the experiment, and a view from above of the optical spots on the substrate.

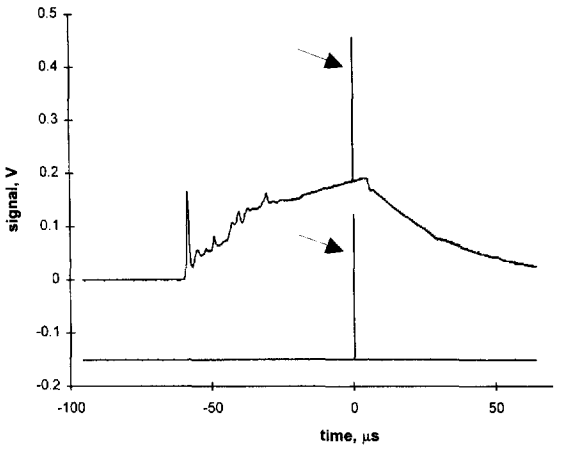

Fig. 2. Traces of single shots of the CO_2 laser detected by a MCT photodiode on a scattering (upper curve) and non-scattering (lower curve) part of a silicon wafer. The sharp peaks indicated by the arrows result from photo-induced reflectivity. The curves are offset for convenience.

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 [16–18]. (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 [16–18].) 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 surface of a semiconductor as shown in Fig. 1. The IR light is incident on the surface at such an angle that its specular reflection 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 scatters the IR light as if from a point (subwavelength) source. The scattered IR radiation coming through the sample is collected by the same objective and is 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 imaged at the speed of any 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 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.

To test the concept we 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, repetition rate 1 kHz), (Positive Light Inc., 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 (NA 0.4, Ealing Electro-Optics Inc., Herts, UK). Energy fluence in the visible light spot was about 70 mJ/cm^2 on the silicon substrate surface, inducing a reflectivity of about 80% at 10.6 μm wavelength [16–18].

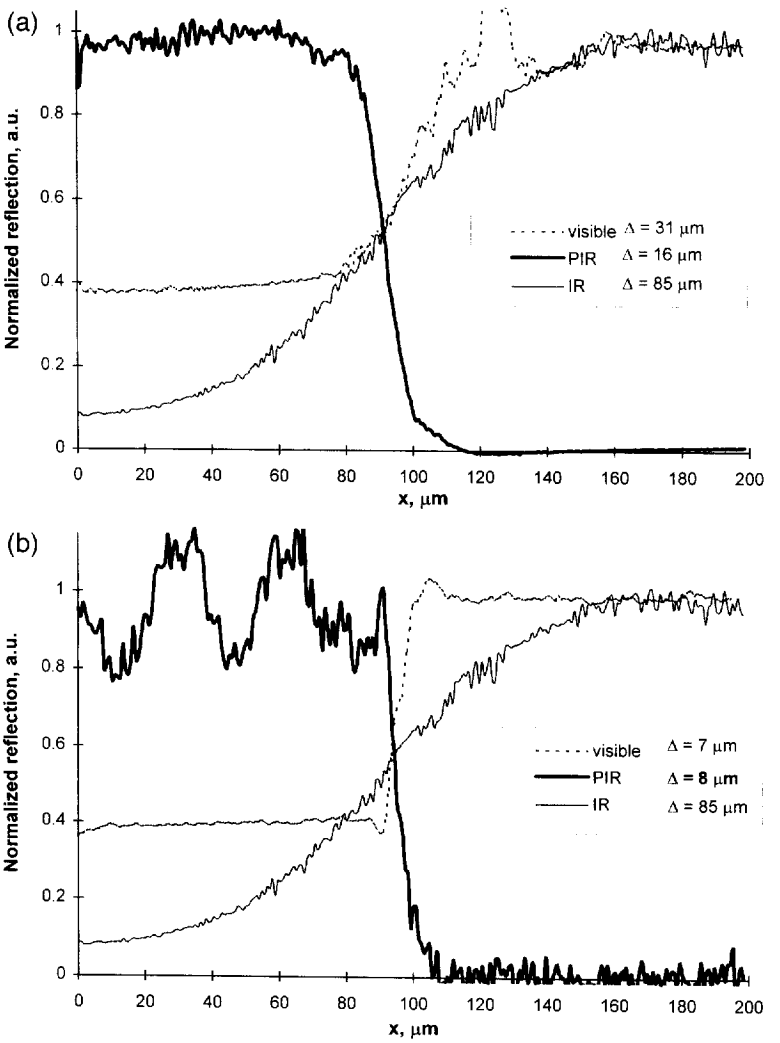

Fig. 3. Edge scanning test for all three beams: visible, IR and photo-induced reflection (PIR). A gold coating is located on the right of the 100 μm mark. The width Δ is defined as the 10–90% transition. (a) The visible beam spot size is 31 μm. (b) The visible beam is focused to a 7 μm spot.

The resulting trace of a single pulse detected by the HgCdTe (MCT) photodiode (KMPV50-0.5-J2, Kolmar Technologies, Inc., Conyers, GA, USA) is shown in Fig. 2. The upper curve corresponds to a sample region with strong scattering (dust, scratches, etc.). Consequently, the CO_2 laser pulse shape is easily seen. The short, intense spike indicated by the arrow is due to the photo-induced scattering of the CO_2 laser obtained with a visible spot size of about 20 μm in diameter. The duration of the detected signal was determined by the response time of the detector (20 ns), as the lifetime of the transient mirror was below 3 ns [16–18]. The lower curve represents a signal obtained with the same conditions as above, but with a clean wafer. No scattering was observed. (The curves are offset for convenience.)

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 used as a visible light filter. The results of the edge scanning test are shown in Fig. 3, on which the resolutions have been defined as the width corresponding to a 10–90% transition. 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. 3a). This sharpening is probably due to the non-linear nature of the photo-induced reflectivity mechanism [16–18]. 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 8 μm (see Fig. 3b). 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) [16–18] the reflecting spot will spread by about 5 μm (diffusion coefficient $D \approx 70$ cm^2/s), consistent with Fig. 3b. 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 plasma volume 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, 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).

Signal oscillations seen on the left of the edge transition in Fig. 3b probably result from interference of the light scattered by the photo-induced mirror with the light scattered by the gold edge. The period of the oscillations (36 μm) equals to the IR wavelength (10.6 μm) divided by the cosine of the incidence angle (73°). No interference was observed in the case of large visible spot due to the averaging of the light phase coming from the mirror surface of the same width as the period of oscillations (Fig. 3a). In a more homogeneous or less contrast sample than the single metal edge applied in the present experiment, the amplitude of the interference pattern would be substantially lower.

3. Prospects and limitations

Heating of the substrate and the sample by the incident beams are potential problems. First we 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 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, assume a water sample 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 IR laser does not exceed several kHz, or the sample is scanned quickly enough that there is no 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 an energy density applied in our experiment of 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, 1 TW/cm^2 [19]. 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 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 (subwavelength) 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

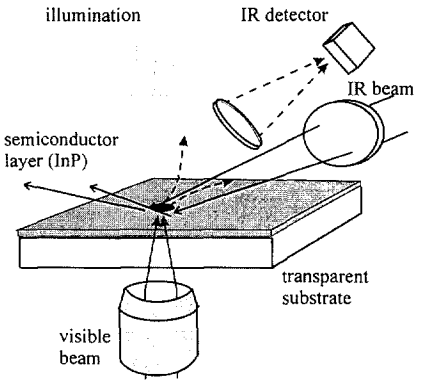

Fig. 4. Schematic optical layout of the inverted microscope-based design of the PIR near-field microscope.

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 (NA about 0.7).

Further improvements in resolution and signal-to-noise ratio are possible. To improve the resolution, a scheme based on the use of an inverted microscope can be used (see Fig. 4). In this arrangement the visible light is focused with a high NA 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 due to high intensity visible light illumination. The coating thickness should be about 0.5 μm – the same as the penetration depth of visible light. The IR part of the scheme remains the same as in the present setup. However, as the IR objective will be used only for scattered light collection, it can be replace with IR lens and tilted aside to provide space for transmitted light illumination of the sample (the semiconductor coating can be transparent to red 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 electromagnetic field strength instead of intensity [13], 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 interferometric approach would be based on modulation of the reference arm, and thus it is particularly appropriate for use with 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 possible IR microscopy 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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