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(54) Title: NON-CONTACT PHOTOTHERMAL RADIOMETRIC METROLOGIES AND INSTRUMENTATION FOR CHARACTERIZATION OF SEMICONDUCTOR WAFERS, OPTICAL MATERIALS AND DEVICES

(57) Abstract: There is provided a metrologic methodology, useful for in-situ, non-destructive monitoring, comprising a combination of novel signal and laser infrared radiometric instrumental configurations for measuring thermal and electronic properties of industrial semiconductor wafers. This methodology includes: The common-mode rejection demodulation (CMRD; or bi-modal pulse) method for detection of very weak inhomogeneities in semiconductor materials, based on generating a real time periodic waveform consisting of two incident pulses with a certain lineshape and pulse width (i.e. square-wave pulses). The foregoing common-mode rejection demodulation method is a very general signal generation and detection methodology and is not limited to photothermal or photoacoustic phenomena, but rather encompasses any and all methodologies that utilize signal modulation.
NON-CONTACT PHOTOTHERMAL RADIOMETRIC METROLOGIES AND INSTRUMENTATION FOR CHARACTERIZATION OF SEMICONDUCTOR WAFERS, OPTICAL MATERIALS AND DEVICES

FIELD OF INVENTION

The present invention relates to metrologic methodologies and instrumentation for measuring electronic, optical, transport and other physical or solid state properties in materials such as semiconductors or semiconductor wafers, devices and other semiconductor based devices or materials. In particular, the present invention relates to the metrologic application to ion implanted, epitaxial semiconductor wafers, contaminated wafers with heavy metals, surface handled or damaged wafers and electronic transport properties in semiconductor wafers.

BACKGROUND OF THE INVENTION

There are essentially two dynamic or time-dependent methods for measuring thermal and electronic properties of solids. Regarding thermal (or thermophysical) properties, the first is the periodic heat flow method (see for example L. Qian and P. Li, Appl. Opt. 29, 4241, 1990) and the second one is the transient method (see W. P. Leung and C. A. Tam, J. Appl. Phys. 56, 153, 1984), including the spectral analysis and cross-correlation (multi-frequency) method (S. Peralta, S. C. Ellis, C. Christofides and A. Mandelis, J. Res. Non-Destructive Eval., 3, 69, 1991).

In the periodic heat flow case of non-electronic materials, a solid sample is irradiated with a harmonically modulated laser beam thereby launching a thermal wave through the sample. The resulting periodic temperature profile at the front or back of the surface of the sample is monitored at several modulation frequencies $f$, also known as the frequency scan method. The frequency dependent thermal diffusion length $\mu$ is given by:

$$\mu = \sqrt{\frac{\alpha}{\pi f}}$$

and is related to the phase-lag of the detected temperature wave with respect to the heating source and may be monitored using a lock-in amplifier.

In transient measurement techniques such as pulsed or multi-frequency spectral excitation, a sample is irradiated on one side with a laser pulse and the time evolution of
the temperature is monitored and the rate of decay of the temperature is related to thermal diffusivity of the solid.


Conventional Photothermal Electronic Lifetime Measurement Methods

For sometime now several laser-based photothermal techniques have been developed to monitor photoexited carrier kinetics and transport properties in semiconductors, the advantage over other, mainly electrical, methods being that electronic effects can thus be monitored in a non-contacting and non-destructive manner, therefore

\[
\Delta R(\omega) = \left( \frac{\partial R}{\partial T} \right) \Delta T(\omega) + \left( \frac{\partial R}{\partial N} \right) \Delta N(\omega)
\]

(1)

Very tightly focused (∼1 μm²) pump beams can, in principle, lead to the domination of PMOR by the plasma response, yet this constraint almost invariably gives rise to unwanted non-linear phenomena, such as Auger recombination, which further complicate the quantitative aspects of the technique [R. E. Wagner and A. Mandelis, Semicond. Sci. Technol. 11, 289 (1996); and 300 (1996)]. Therefore, very tight laser focusing can be detrimental to the study of electronic defects, since the exceedingly high fluence may greatly perturb the experimental behavior of an electronic material or even anneal the semiconductor.
Regarding laser infrared photothermal radiometry (PTR) of semiconductors, the pulsed time-domain mode may exhibit severe overlap of free-carrier density and thermal effects [K. Cho and C. Davis, IEEE J. Quantum Electron. QE-25, 1112 (1989)] and non-optimized signal-to-noise ratio, SNR [A. Mandelis, Rev. Sci. Instrum. 65, 3309 (1994)]. Unlike the PMOR technique, two key studies have shown that the electronic (plasma-wave) component of the spectrally cross-correlated infrared emissivity PTR signal fully (or nearly so) dominates the thermal-wave component in typical industrial Si wafers [A. Mandelis, R. Bleiss and F. Shimura, J. Appl. Phys. 74, 3431 (1993)]; similar results were obtained with frequency-scanned PTR signal generation studies and comparisons with PMOR signal generation [A. Salnick, A. Mandelis, H. Ruda and C. Jean, J. Appl. Phys. 82, 1853 (1997)], thus making PTR the preferred method for industrial semiconductor metrologic technology development. In terms of physical interpretation of signals, the time-domain technique is considered preferable to the frequency-domain counterpart [S. J. Sheard M. G. Somekh and T. Hiller, Mater. Sci. Eng. B5, 101, (1990); Z. H. Chen, R. Bleiss, A. Mandelis and F. Shimura, J. Appl. Phys. 73, 5043 (1993)] due to the inherent ability of transient-response techniques to be interpretable in terms of simple system time-delay constants. The same information can be obtained, in principle, from the frequency-scanned data; however, this method requires the de-multiplexing of data over broad frequency ranges, typical of the existing relationship between Fourier transform pairs (i.e. time and frequency domains). Nevertheless, the superior frequency-domain SNR, which is achievable via lock-in filtering and demodulation, coupled with further improvements regarding either the substantial acceleration of the measurement process by use of transfer function measurements via spectral analysis and cross-correlation methods [A. Mandelis et al., Rev. Sci. Instrum. 57, 617 (1986); and 622 (1986); and 630 91986)], or the SNR of the signal generation and processing techniques introduced in the present invention, renders the frequency-domain (FD) PTR mode the measurement method of choice for the development of novel industrial-level semiconductor metrologic technologies.
SUMMARY OF THE INVENTION

The present invention provides a general instrumental method for detection of very weak inhomogeneities in materials such as semiconductor materials that are not possible to detect with conventional signal generation techniques.

In one aspect of the invention there is provided a non-destructive method for measuring physical, optical, electronic or transport properties of a material having a valence energy band separated from a conduction energy band by a bandgap energy, comprising the steps of:

a) irradiating a material with a modulated excitation energy beam, said modulated excitation energy beam being modulated to produce a periodic waveform of period T, said periodic waveform including within each period T first and second pulses of pre-selected line-shape, said first pulse having a line-width width $\tau_1$ and said second pulse having a line-width $\tau_2$, said first and second pulses being separated by a center-to-center time delay $\Delta$ between a center of each of said first and second pulses, wherein $\tau_1$ and $\tau_2$ are not equal and $T > \Delta > (\tau_1 + \tau_2)/2$;

b) detecting signals emitted from said material responsive to being irradiated by said modulated excitation energy beam;

c) demodulating said signals emitted from said material; and

d) outputting said demodulated signals and storing said demodulated signals or displaying said demodulated signals.

The modulated excitation beam may be a laser beam having an energy sufficient to excite carriers from defects, dopants, impurities within the bandgap into the conduction band or it may have an energy sufficient to excite carriers across the bandgap from the valence band to the conduction band.

The steps of detecting and demodulating the signals may include detecting the signals using a detection means connected to a signal analyzing means, the signal analyzing means and the detection means being synchronized using a waveform generator which produces the periodic waveform. The signal analyzing means may be a lock-in amplifier.
The material may be a semiconductor, semiconductor wafer or semiconductor device and the method may be performed as part of a wafer, chip or device fabrication step.

The present invention is by no means confined to thermal-wave signal generation, but encompasses all manner of modulated signals, such as acoustic, optical, ultrasonic, X-rays and any other signal generation method accessible to those skilled in the art.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The method of the present invention will now be described by way of example only, reference being had to the accompanying drawings in which:

Figure 1 illustrates a schematic block diagram of one embodiment of an apparatus used for measuring transport, optical, physical and electronic properties according to the present invention;

Figure 2 shows the (a) optical excitation pulse train \( i(t) \); (b) radiometric repetitive transient signal \( s(t) \) due to \( i(t) \); and (c) lock-in weighting function \( w(t) \);

Figure 3 shows the amplitude of the in-phase (IP) and quadrature (Q) component of the lock-in analyzer (LIA) radiometric response, as function of the separation between two pulses \( \tau_i/T \) values reported in the inset, the sample has been assumed homogeneous, i.e. \( \text{Re}[S(f)]/|\text{Im}[S(f)]| \) and \( \tau_2/T = 25\% \), where \( S(f) \) is the system frequency response; \( T \) is the period; \( \tau_i \) is the duration of pulse 1; and \( \tau_2 \) is the duration of pulse 2;

Figure 4 shows the IP and Q components of the LIA response, as functions of the pulse separation, \( \Delta \), for various arguments of \( S(f) \) reported in the inset. \( \tau_i/T \) and \( \tau_2/T \) have been assumed equal to 5 and 25\%, respectively;

Figure 5 shows the dependence of the zero crossing values \( \Delta_{0,IP} \) and \( \Delta_{0,Q} \) on the duration of the first pulse for the \( \text{arg}[S(f)] \) values reported in the inset. \( \tau_2/T \) has been assumed equal to 25\%;

Figure 6 shows the PTR amplitude frequency scans of \( P^+ \) ion-implanted Si wafers at 100 keV, doses (ions/cm\(^2\)): (□) \( 1 \times 10^{11} \); (O) \( 4 \times 10^{11} \); (△) \( 4 \times 10^{12} \); (▽) \( 4 \times 10^{12} \); (◇) \( 1 \times 10^{13} \);
Figure 7 shows PTR frequency-scan amplitude dependencies on implantation dose at 4 kHz. (◇): B⁺; (△): P⁺; (◯): As⁺ (unoxidized); (□): As⁺ (with 100-Å thick oxide layer);

Figure 8 shows a conventional 50%-duty-cycle square-wave modulated PTR traces from the four overlapped P⁺-implanted Si wafers at 4 kHz, as a function of time upon initial exposure to the laser beam. Doses (ions/cm²): (◯) 4×10¹¹; (△) 1×10¹²; (◇) 4×10¹²; (□) 1×10¹³;

Figure 9 shows the amplitude of the PTR-CMRD signal output of P⁺ ion-implanted Si wafers. Doses (ions/cm²): (□) 1×10¹¹; (△) 4×10¹¹; (◇) 1×10¹²; (◯) 4×10¹²;

Figure 10 shows high-resolution PTR-CMRD amplitude signals from the P⁺-implanted wafers vs. center-to-center pulse separation Δ (%). Doses (ions/cm²): (◯) 4×10¹¹; (△) 1×10¹²; (◇) 4×10¹²; (□) 1×10¹³ Pulse separation increment δΔ=1%; and

Figure 11 illustrates 4-kHz frequency-scans using a 50% duty-cycle square waveform and CMRD amplitude signals from B⁺-implanted Si wafers, for direct comparison, both sets of data points are normalized to the first datum. (□) frequency scan; (◯) CMRD scan.

DETAILED DESCRIPTION OF THE INVENTION

1) APPARATUS FOR NON-DESTRUCTIVELY MEASURING PHYSICAL, OPTICAL, TRANSPORT AND ELECTRONIC PARAMETERS OF SEMICONDUCTOR AND OPTICAL MATERIALS

The instrumentation system (apparatus) using laser PTR as the preferred (but not sole) embodiment of the present invention for measuring the physical, optical, transport and electronic properties of semiconductors using a dual pulse excitation waveform, as well as by parallel or sequential scanning wafer imaging at a fixed frequency, will now be described.
A schematic diagram of the apparatus for non-destructive measurement of the properties of semiconductor wafers or chips is shown generally at 10 in Figure 1. Apparatus 10 includes an excitation energy beam source 12 which is preferably a laser with modulated power up to a few watts and super-bandgap wavelength (<1000 nm for Si or <600 nm for very-near-surface probing). The excitation energy beam is modulated using an acousto-optic (AOM) or electro-optic modulator 14, the digital driver of which is connected to a four-channel delay digital generator 16 (Stanford Research Model DG535). The digital delay generator 16 allows the construction of the preferred variable-width two-square-pulse waveform of Figure 2a through appropriate computer-controlled software and is used to drive the AOM 14 through the driver which is connected to the waveform generator 16 which produces the dual-pulse waveform.

The modulated excitation energy beam is directed onto the surface of a sample 38 using focusing optics including reflecting mirrors 18 and 20 which direct the excitation beam through a beam expander 22. The expanded beam is reflected from mirror 24 through a gradiun lens 26 onto the surface of sample 38. The radiation emitted from the surface of the sample 38 is collected and focused onto a detector 28 using a pair of reflecting objectives 30 (two off-axis paraboloidal mirrors or one elliptical mirror can also be used). Preferably detector 28 is a liquid-N2 cooled HgCdTe (EG & G Judson model J15D16-M204) with an active area of 1 mm² or less and a spectrally sensitive range of 2-10 μm. Other non-cryogenic IR detectors such as pyroelectric sensors or Golay cells can be substituted for the LN2 detector, as required. An anti-reflection (AR)-coated Ge window 32 with a transmission bandwidth of 2-13 μm is mounted in front of detector 28 to block any visible radiation from the excitation beam source 12.

The pump spot diameter on sample 38 is typically ca. 1 to 5 μm. The photothermal signal, which is proportional to the change of the IR radiation emitted from an area viewed by detector 28, is amplified by a preamplifier 34 (EG & G Judson model PA-101) before being sent to a digital lock-in amplifier 36 (e.g. Stanford Research Systems, Model SR 850). The PTR signal from the detector is pre-amplified (EG&G Judson Model PA 350) and fed to an analog lock-in amplifier (LIA) (e.g. EG&G Model 5210), which is connected to digital delay generator 16 to provide the latter with the external triggering.
signal. The lock-in amplifier is referenced to a frequency of 1/T where T is the period of
the bi-modal waveform discussed herein after.

Lock-in amplifier 36 is interfaced with a computer 40 used to control the
modulation waveform and to store the LIA signal components so that the frequency scan
and data acquisition and storage are automated. The laser can also be modulated by a FFT
dynamic signal analyzer 46 or the dual pulse generator 16. The sample 38 is mounted on
an automated sample holder 39 with X-Y scanning capability for sample mapping
applications through fast point-by-point image construction. In order to do real-time
normalization of the signal, a beam splitter 42 is placed in front of the laser source which
directs a portion of the laser beam to the photodiode 44. The signal response from the
photodiode 44 is then fed to the lock-in amplifier 36. The signal coming from the infrared
detector 28 is then divided by the signal coming from the photodiode 44 by using the
“ratio” option of the lock-in amplifier 36.

As mentioned above the preferred method of detecting and demodulating signals
includes detecting the signals using a detection means connected to a signal analyzing
means with the signal analyzing means and the detection means being synchronized using
a waveform generator. Most preferably the signal analyzing means is a lock-in amplifier
which is referenced to a frequency of 1/T. The lock-in amplifier can operate under
normal input signal-level conditions in both channels (in-phase and quadrature, or
amplitude and phase), or with one channel overloaded, in order to maximize the
sensitivity and dynamic range of the other, non-overloaded, channel. If under overloaded
channel operation, the conventional square or sinusoidal-wave operation are also claimed
as natural limiting cases when $\tau_2 = 0$ and $\tau_1 = T/2$.

The excitation energy source 12 is preferably a laser and the wavelength must be
selected so the photons have sufficient energy to promote carriers either in the bandgap or
between bands. For example, in order to raise free electrons (holes) into the conduction
band from the valence band the energy must be greater than or equal to the bandgap
energy. The energy of the excitation energy beam may also be less than the bandgap
energy when exciting carriers from defect, dopant or impurity states within the bandgap
of the semiconductor. This also applies to optical (laser) materials. When the modulated
energy beam is incident on the semiconductor, carriers are excited across the bandgap.
For these electronic materials, the physical response giving rise to the emitted signals that
are detected by the detector is due to the recombination of photo-excited free carriers
resulting in the emission of photons which are captured by a detector; or a change in the
current measured across the material upon the application of a voltage due to the same
mechanism, or a change in the infrared absorption coefficient of a probe laser beam due
to the excess photo-excited free carrier "cloud". For optical materials, such as laser
crystals, the said physical response is due to decaying excited state particles emitting
radiation (radiative decay) or heat/thermal photons (non-radiative decay).

Owing to very-close signal levels in semiconductors following some processing
steps, such as junction formation (diffusion) and ion implantation in the (so-far difficult-
to-measure with any other optical techniques) $10^{12} - 10^{13}$ cm$^{-2}$ dose range with B+ and P+
ions, real-time signal normalization must be effected to compensate for laser source
fluctuations. This is done using a beam-splitter and photodiode set-up as shown in Figure
1, where a small portion of the laser intensity is directed to the photodiode, the output of
which is directed into the same lock-in amplifier as the signal output from the wafer. The
in-phase and quadrature channels are monitored under the ratio-option. Amplitude and
phase are calculated by the software in the computer from these two normalized channels.

For semiconductors it is preferred to be in a signal frequency range where the
recombination rate of the free photo-excited carriers is of the same order as the
modulation rate. This means frequencies 1 - 100 kHz for Si and even higher for direct
gap semiconductors, such as GaAs and InP (in the MHz range). With semiconductors
preferred detectors are a (high-frequency) photovoltaic HgCdTe and/or a (lower
frequency) photoconductive HgCdTe. Eventually, for best signal resolution, say between
two very closely ion-implanted Si wafers, an optimal frequency range is chosen by a)
scanning laser beam modulation frequencies with a conventional square-wave form so as
to reach the characteristic flat portion of the amplitude curve (plateau) but not higher than
the onset of the downward slope of the curve ("knee"); such that the product of the
angular modulation frequency, $\omega$; and the photo-excited carrier recombination lifetime, $\tau$
is equal to 1; b) estimating the photoexcited carrier lifetime, $\tau$, from the frequency, $f_0$,
position of the aformentioned "knee", so that $\tau \sim 1/\pi f_0$; and c) fixing the CMRD
frequency so that $f_0 \sim 1/2\pi \tau$, at which frequency a CMRD pulse scan is effected. Similar
range finding procedures must be followed with an optical material, in which excited ions or molecules ("optically active particles") undergo radiative or non-radiative deexcitations.

The inventors have found that for characterizing semiconductors it is the nearly-flat portion of the amplitude and the quadrature signal channels vs. center-to-center pulse separation distance of the lock-in signal output under the CMRD scheme that yield the optimal resolution (at least with respect to ion implantation); the zero of the in-phase signal can also be adjusted to be most sensitive.

It will be understood that besides using a lock-in amplifier as the signal processor, other signal processing means may be used. For example, if a pulsed laser is used for PTR measurements of a semiconductor, the PTR response of the material can be inserted into a boxcar integrator, which is triggered by the laser pulse and its electrical imprint registered by a photodiode using a beam-splitter arrangement. The single or double gate of the boxcar can be scanned and set (fixed) so as to monitor the, say, peak signal and its changes as a function of the coordinate on the same sample or as a function of processing parameters on different samples. Alternatively, for harmonically modulated signals, the boxcar integrator time gates can be set at a fixed time delay, fixed widths and at the desired repetition period, and yield a demodulated output reasonably similar to the LIA CMRD output.

i) Lock-in Common-Mode Rejection Method

a) Description of the method

Electronic transport properties are, in general, an indicator of the degree of homogeneity of a given semiconductor sample because they are strongly affected by variations occurring in the sample crystal lattice. An introduction to carrier plasma-wave non-destructive detection has been discussed in the "Background of the Invention". Briefly, the common working principle of conventional photothermal techniques monitoring electronic plasmas is based on the study of the periodic carrier density distribution, i.e. the plasma wave, produced in a given sample as a result of optical excitation due to an intensity modulated pump laser source impinging on the surface. Thermal and plasma waves inside a homogeneous sample diffuse over a characteristic
distance, which is given by the diffusion length \( \mu(f) = (D \tau)^{1/2}(1+2\pi i f \tau) \), where \( D \) is the carrier diffusivity, \( \tau \) is the recombination lifetime, and \( f \) the modulation frequency. By changing the modulation frequency, the plasma wave propagates over different distances and probes the presence of electronic inhomogeneities located at various depths beneath the surface. In fact, trap and defect features inside the sample alter the free-carrier transport rate and density, thus affecting the resulting density distribution which is detected by various techniques. When PTR is used, the inventors have found that the signal is the result of infrared photon emission from free photoexcited carriers recombining in the bulk and on the surfaces of a semiconductor, with the signal being weighed by photon re-absorption across the thickness of the laser-excited sample. Finally, by analyzing the dependence of the photothermal signal from electronic materials on the modulation frequency, it is possible to derive some material parameters (carrier diffusivity, lifetime, surface recombination velocity) and/or obtain information on inhomogeneities, such as position, size, depth profile, etc. This is the basic principle of all plasma wave inspection methods. Conventional frequency domain photothermal methods probing electronic plasmas are basically single-ended techniques using an intensity-modulated laser beam (either a 50% duty-cycle square wave, or a sinusoidal wave), and a lock-in amplifier (LIA) for signal processing. The limitations of single-ended detection are that, if the signal contributions from sample traps and defects are much smaller than that from the homogeneous bulk of the material (background signal), then they cannot be easily detected. In a single-ended technique the sensitivity of the experiment is determined by the magnitude of the background signal. Without further conditioning, the signal level is simply too high to probe variations of amplitude much smaller than this background. For the purposes of this invention, these very small variations will be called “contrast signals”.

As also discussed in the Background, in order to obtain quantitative information about the sample properties, the photothermal signal must be normalized, i.e. compared to that obtained from a homogenous reference sample in order to account for the instrumental transfer function. Properly normalized signal amplitude ratios and phase differences must be collected as a function of the modulation frequency. This procedure introduces several problems especially when one intends to probe slightly defective
semiconductor samples with theoretical contrast signals approaching the noise level of the experiment. In fact, the effect of normalization is, in general, to add some more noise to the measurement, thus resulting in poor signal-to-noise ratio (SNR), which usually masks contrast signals. A strong noise reduction is required for these kinds of applications and conventional photothermal techniques do not compensate against slowly varying drift phenomena, which can occur during a measurement, because of their single-ended nature [C. H. Wang and A. Mandelis, Rev. Sci. Instrum., 70, 2372(1999)]. All this despite the advantage of the narrow-bandwidth filtering action of the demodulating lock-in amplifier, since the noise frequency components within the filter bandwidth are not rejected and are still present and become enhanced during the normalization procedure.

The new lock-in common-mode-rejection demodulation (CMRD) scheme disclosed herein provides a high-resolution carrier plasma-wave non-destructive material evaluation (NDE) methodology. If the sample is irradiated with a periodic optical waveform consisting of two pulses, then the LIA output is basically given by the difference of the physical response waveforms produced by each of the two pulses. This fact is of fundamental importance toward the improvement of low-dynamic range techniques, such as plasma-wave NDE, in their ability to detect relatively small signal variations from slightly different materials. In practice, the differential action has the effect of suppressing the signal baseline, which leads to an enhanced detectivity when compared to conventional single-ended techniques. Thus, the instrumental sensitivity is not compromised by the high-level signal baseline and can easily match the level of small signal variations introduced by slightly different materials or by very weak electronic defect structures in a given material. The principle of the invention can be broadly applied to any technique utilizing a lock-in analyzer demodulation scheme of periodic signal waveforms, such as in thermal-and acoustic/ultrasonic-wave NDE.

In order to achieve a differential input with a single excitation source and demodulation instrument, a new periodic optical excitation waveform, Fig. 2(a), has been designed, which exploits advantages due to the built-in weighing-function waveform of the LIA [G. L. Miller, J. V. Ramirez and H. A. Robinson, J. Appl. Phys. 46, 2638 (1975); A. Mandelis, Rev. Sci. Instrum. 65, 3309 (1994)]. As shown in Fig. 2(a), in a given period T the sample is excited by preferably two square-wave pulses (or any other pulses with
certain lineshape and pulse width) with center-to-center separation by a time interval $\Delta$.

As a consequence of the asymmetric periodic excitation, the transient (photothermal) response $s(t)$ of the sample, Fig. 2(b), rises and decays twice during a period, also with a certain degree of asymmetry. The in-phase or quadrature component of the LIA response to the incoming signal $s(t)$ with a long integration time constant may be written as [A. Mandelis, Rev. Sci. Instrum. 65, 3309 (1994)]

$$y(t) = \int_{0}^{\tau} s(t) w(t) dt = \int_{0}^{\tau/2} (+) s(t) dt + \int_{\tau/2}^{\tau} (-) s(t) dt$$  \hspace{1cm} (2)

where $w(t)$ is the square weighing function shown in Fig. 2(c) and assumed to have a zero-delay rising edge. Owing to the opposite signs of $w(t)$ across the mid-period point $T/2$ for zero phase delay at $t=0$, the LIA acts like a real-time differential comparator whose output level is a measure of the degree of asymmetry of the two $s(t)$ lineshapes in the two half periods. Therefore, with this waveform design, a differential input configuration is achieved, which suppresses the signal baseline and takes full advantage of the highly efficient noise suppression by the LIA due to its extremely narrow filtering.

The difference between analog and digital LIAs, which use square-wave and synthesized sine-wave reference signals, respectively, has been extensively treated elsewhere [A. Mandelis, Rev. Sci. Instrum. 65, 3309 (1994)]. The output is quantitatively the same for the two types of LIA, provided that a tracking filter is inserted into the input of the analog version, in order to reject the odd harmonics of the input signal.

As mentioned above, while an excitation beam having a dual pulse square waveform is preferred, in principle, arbitrary waveform line-shapes $s(t)$ may be used with the foregoing waveform design, provided a double energy distribution is injected into the detector during each repetition period. Preferably the line-shape is of the square-wave type, because with square-wave forms the control of the onset and end of each pulse is optimal, which allows the clearest determination of the characteristic time constants in the sample response. Furthermore, square-wave pulses possess uniform pulse widths with clear separation between the first and second pulse.
b) Theory of output signal

In this section a theoretical description of the signal generation due to the new waveform of Fig. 2 will be given, providing analytical expressions for both the in-phase (IP) and quadrature (Q) components of the lock-in response. In particular, we are interested in pointing out how the signal output is influenced by the parameters of the composite optical waveform ($\tau_1$, $\tau_2$ and $\Delta$). We will also demonstrate signal sensitivity to the response of the system under investigation. In the analysis, we assume that the system is excited with a repetitive waveform consisting of two pulses of given lineshape and width (i.e. square pulses) within one period T having the same amplitude $I_0$, durations $\tau_1$ and $\tau_2$, and separation $\Delta$. For periodic waveforms it is convenient to consider the Fourier series representation of $i(t)$.

$$i(t) = \sum_{k=-\infty}^{\infty} c_k \exp\left(\frac{j2\pi kt}{T}\right)$$  \hspace{1cm} (3)

in complex form, or,

$$i(t) = \frac{a_0}{2} + \sum_{k=1}^{\infty} \left[ a_k \cos\left(\frac{2\pi kt}{T}\right) + b_k \sin\left(\frac{2\pi kt}{T}\right) \right]$$  \hspace{1cm} (4)

with

$$c_k = \frac{a_k - jb_k}{2} = \frac{1}{T} \int_{-\frac{T}{2}}^{\frac{T}{2}} i(t) \exp\left(-\frac{j2\pi kt}{T}\right) dt = \frac{1}{T} I\left(\frac{k}{T}\right)$$  \hspace{1cm} (5)

where $I(f)$ is the Fourier transform of $i(t)$ calculated over one period. By applying the time shift property to the two-square-pulse Fourier transform, it is easy to show that
\[ c_k = \left\{ \frac{I_0}{T} \tau_1 \frac{\sin(\frac{\pi k \tau_1}{T})}{\pi k \tau_1} \right\} \exp[-j2\pi \frac{k}{T} (\frac{T}{2} - \frac{\Delta}{2})] + \left\{ \frac{I_0}{T} \tau_2 \frac{\sin(\frac{\pi k \tau_2}{T})}{\pi k \tau_2} \right\} \exp[-j2\pi \frac{k}{T} (\frac{T}{2} + \frac{\Delta}{2})] \] (6)

and, after some manipulation,

\[ c_k = \left( -1 \right)^k \frac{I_0}{\pi k} \right\{ \cos(\frac{\pi k \Delta}{T})[\sin(\frac{\pi k \tau_1}{T}) + \sin(\frac{\pi k \tau_2}{T})] + j\sin(\frac{\pi k \Delta}{T})[\sin(\frac{\pi k \tau_1}{T}) - \sin(\frac{\pi k \tau_2}{T})] \} \] (7)

The LIA monitors only the fundamental component of the harmonic signal, so we can limit our attention to the first term of the Fourier series, the coefficients of which are given by

\[ c_1 = -\frac{I_0}{\pi} \right\{ \cos(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) + \sin(\frac{\pi \tau_2}{T})] + j\sin(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) - \sin(\frac{\pi \tau_2}{T})] \} \] (8)

\[ a_1 = 2 \Re(c_1) = -\frac{2I_0}{\pi} \cos(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) + \sin(\frac{\pi \tau_2}{T})] \] (9)

\[ b_1 = -2 \Im(c_1) = \frac{2I_0}{\pi} \sin(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) - \sin(\frac{\pi \tau_2}{T})] \] (10)

In order to calculate the LIA response to the excitation pulse train, we introduce the system frequency response \( S(f) = \Re[S(f)] + j\Im[S(f)] \) which can be unambiguously defined for each sample as the Fourier transform of the transient impulse response. In so doing, the LIA output may be written as:

\[ Y(f) = \{ \Re[S(f)] + j\Im[S(f)] \} (a_1 + jb_1), \] (11)
which can be eventually decomposed into in-phase (IP) and quadrature (Q) components
given by:

\[ Y_{IP} = \text{Re}[Y(f)] = \]
\[ -\frac{2I_0}{\pi} \{ \cos(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) + \sin(\frac{\pi \tau_2}{T})] \text{Re}[S(f)] + \sin(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) - \sin(\frac{\pi \tau_2}{T})] \text{Im}[S(f)] \} \]

(12)

and

\[ Y_{Q} = \text{Im}[Y(f)] = \]
\[ \frac{2I_0}{\pi} \{ \sin(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) - \sin(\frac{\pi \tau_2}{T})] \text{Re}[S(f)] - \cos(\frac{\pi \Delta}{T})[\sin(\frac{\pi \tau_1}{T}) + \sin(\frac{\pi \tau_2}{T})] \text{Im}[S(f)] \} \]

(13)

It can be seen that, in order to obtain a true differential output, the pulse widths

must be different. Otherwise, the effect of the new optical waveform is only to generate a
signal equivalent to that obtained from the conventional frequency scan method, from
which it differs only by a multiplicative (amplitude) factor. This is physically reasonable,
because the effect of two equal-width pulses is the same in the two half periods, Fig. 2,
and as a result it does not reveal the asymmetric behavior of the response s(t). If \( \tau_1 \) is
different from \( \tau_2 \), then the mixer – low-pass filter action of the LIA mixes the IP- and Q-
channel signals created by the single-ended or by the equal-width two-pulse waveform. It
is most interesting that the demodulated signal output multiplication factors are the real
and the imaginary part of the response \( S(f) \). In fact, by choosing suitable values of
\( \tau_1, \tau_2, \Delta \), it is possible to balance the two terms of the IP and Q components so as to obtain
zero magnitude for either the IP or the Q signal channel.

Therefore, the present includes irradiating a semiconductor with a modulated
excitation energy beam of suitable energy and scanning \( \Delta \) through a selected range of \( \Delta/T \)
by varying $\Delta$ by an increment $\delta \Delta$ after a preselected number of periods $T$ while keeping $\tau_1$ and $\tau_2$ fixed. The pre-selected number of periods is sufficient so that statistically meaningful data is collected.

Alternatively, one may scan $\tau_1$ through a selected range of times by varying $\tau_1$ after a preselected number of periods $T$ while keeping $\Delta$ and $\tau_2$ fixed, or, scanning $\tau_2$ through a selected range of times by varying $\tau_2$ after a preselected number of periods $T$ while keeping $\Delta$ and $\tau_1$ fixed.

Figure 3 shows the theoretical behavior of the IP and Q channel outputs obtained for $\text{Re}[S(f)]/\text{Im}[S(f)] = -1$ (as will be shown in the next paragraph, in the thermal-wave case this condition corresponds to having a thermally homogeneous sample) as a function of the pulse separation $\Delta$ for different $\tau_1/T$ values. The plots clearly show the existence of particular pulse separation values $\Delta_{0,\text{IP}}$ and $\Delta_{0,\text{Q}}$ for which the IP or the Q component is equal to zero. Modifying the properties of the system leads to different values of the ratio $\text{Re}[S(f)]/\text{Im}[S(f)]$, thus shifting the output zero to a new position along the $\Delta$ axis provided that $\tau_1$ and $\tau_2$ are fixed. The IP and Q loci of the zero crossing points can be derived from Eqs. (12) and (13), and are given by the following expressions:

$$\tan\left(\frac{\pi \Delta_{0,\text{IP}}}{T}\right) = \left\{ \frac{\text{Re}[S(f)]}{\text{Im}[S(f)]} \frac{\sin\left(\frac{\pi \tau_1}{T}\right) + \sin\left(\frac{\pi \tau_2}{T}\right)}{\sin\left(\frac{\pi \tau_2}{T}\right) - \sin\left(\frac{\pi \tau_1}{T}\right)} \right\}$$

(14)

and

$$\tan\left(\frac{\pi \Delta_{0,\text{Q}}}{T}\right) = \left\{ \frac{\text{Im}[S(f)]}{\text{Re}[S(f)]} \frac{\sin\left(\frac{\pi \tau_1}{T}\right) + \sin\left(\frac{\pi \tau_2}{T}\right)}{\sin\left(\frac{\pi \tau_2}{T}\right) - \sin\left(\frac{\pi \tau_1}{T}\right)} \right\}$$

(15)

The existence of zeros in the outputs appears promising, because relatively small variations in the response of a physical system can be readily obtained from the position of the zero on the $\Delta$ axis for different values of $\tau_1$ or $\tau_2$. Moreover random fluctuations of the signal amplitude, which normally are not suppressed by LIA filtering [C. H. Wang and A.
Mandelis, Rev. Sci. Instrum., 70, 2372(1999), affect less the response of the experiment. Of course, an additional noise suppression factor in this technique is the constant, single-frequency bandwidth used for the entire measurement [J. Shen, A. Mandelis, and B. D. Aloysius, Int. J. Thermophys. 17, 1241 (1996)]. This substantially limits the noise output compared to the variable bandwidth of a conventional frequency- or time-scan [M. Munidasa and A. Mandelis, Rev. Sci. Instrum. 65, 2344 (1994)] and is an instrumental feature commonly shared with the single pulsewidth-scan LIA method [A. Mandelis and M. Munidasa, U.S. Patent 5,667,300 (Sept. 16, 1997)]

In Figure 4 both the IP and Q amplitude, calculated according to Eqs. (12) and (13), are shown as functions of the pulse separation for \(\tau_1/T = 5\%\), \(\tau_2/T = 25\%\) and for different \(\text{Im}[S(f)]/\text{Re}[S(f)]\) ratios corresponding to the \(\text{arg}[S(f)]\) values reported in the inset. The Q component crosses the zero magnitude axis at lower values of \(\Delta\) than the IP component. This can be understood in terms of the fact that the \textit{odd} \(w(t)\) weighting function used at the mixing stage to obtain the Q component is the one actually shown in Fig. 2(c). The \textit{even} weighing function used to obtain the IP component is shifted by \(T/2\), which implies an equivalent shift of the zero positions close to the upper edge of the \(\Delta/T\) axis. Figure 5 shows the locus of zeroes as a function of \(\tau_1\) for \(\tau_2/T = 25\%\) and for the \(\text{arg}[S(f)]\) values shown in the inset. It is seen that the greater the difference in value between pulsewidths \(\tau_1\) and \(\tau_2\), the better the loci positions are resolved. This reflects, again, the fact that the use of two different pulse widths forces the response to show a measurably different behavior in the two half periods. These facts corroborate the use of narrow pulsewidths. Long pulsewidths limit the available \(\Delta\) scan range and hence the resolution of the experiment. In some experimental situations, such as photothermal measurements in transmission across the thickness of a material, the magnitude of one of the two LIA channels is much greater than that of the other, zero-crossing, channel. This may adversely affect the effectiveness of the technique by forcing the LIA baseline to remain high for both channels. In those situations the baseline can be lowered and the effectiveness of the technique can be restored by e.g. using an appropriate lock-in analyzer, such as the EG&G models 7220, 7260 or 7265 with the availability of a synchronous oscillator signal to produce an offsetting voltage or current signal into the differential input amplifier. The offsetting method is described in the EG&G Application
Note AN 1001, "Input Offset Reduction using the model 7265/7260/7220 Synchronous Oscillator/Demodulator Monitor Output" and must be used in combination with the lock-in common-mode rejection method as an integral part of the present invention.

c) Application of the lock-in common-mode-rejection method using laser PTR diagnostics for high resolution monitoring of ion implanted Si wafers.

A simple PTR embodiment of the common-mode-rejection LIA methodology was constructed. A schematic diagram of the experimental setup used to perform the PTR measurements is shown in Figure 1. An Ar-ion laser (514 nm) from Coherent, model Innova 100, was used as a 250-mW pump beam with a 2-mm spot size impinging on the sample surface. The beam was intensity modulated by an acousto-optic modulator (AOM), the digital driver of which was connected to a four-channel delay digital generator (Stanford Research Model DG535). The digital delay generator allows the construction of the variable-width two-square-pulse waveform through appropriate computer-controlled software and is used to drive the AOM through the driver. The emitted IR radiation from the sample was collected and focused onto the detector using two Ag coated off-axis paraboloidal mirrors. The PTR optical detection circuit was as described in Figure 1. The PTR signal from the detector was pre-amplified (EG&G Judson Model PA 350) and fed to an analog LIA (EG&G Model 5210), which also provided the external triggering signal for the digital delay generator. A personal computer was used to control the modulation waveform and to store the LIA signal components.

A comparative dose-resolution study of conventional frequency-domain PTR and CMRD PTR using 100-keV B⁺, P⁺, and As⁺ ion-implanted industrial Si wafers in the dose range $1 \times 10^{11} - 1 \times 10^{13}$ ions/cm² was done. As a result of this study, details of dose-resolution advantages of CMRD-PTR have been quantified.

Three sets of five polished 4" Si wafers, 10-14 Ωcm, were ion implanted with B⁺, P⁺, and As⁺. One set of five wafers with a grown 100-Å thick oxide was also implanted with As⁺. The details of the wafer matrix are shown in Table I.
**Table I.** Si-wafer ion-implantation matrix. Implantation energy for all wafers: 100 keV.

<table>
<thead>
<tr>
<th>Ion-implant species</th>
<th>Oxide</th>
<th>Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>100 A</td>
<td>$1\times10^{11}$</td>
</tr>
<tr>
<td>As</td>
<td>100 A</td>
<td>$4\times10^{11}$</td>
</tr>
<tr>
<td>As</td>
<td>100 A</td>
<td>$1\times10^{12}$</td>
</tr>
<tr>
<td>As</td>
<td>100 A</td>
<td>$4\times10^{12}$</td>
</tr>
<tr>
<td>As</td>
<td>native</td>
<td>$1\times10^{11}$</td>
</tr>
<tr>
<td>As</td>
<td>&quot;</td>
<td>$4\times10^{11}$</td>
</tr>
<tr>
<td>As</td>
<td>&quot;</td>
<td>$1\times10^{12}$</td>
</tr>
<tr>
<td>As</td>
<td>&quot;</td>
<td>$4\times10^{12}$</td>
</tr>
<tr>
<td>As</td>
<td>&quot;</td>
<td>$1\times10^{13}$</td>
</tr>
<tr>
<td>P</td>
<td>&quot;</td>
<td>$1\times10^{11}$</td>
</tr>
<tr>
<td>P</td>
<td>&quot;</td>
<td>$4\times10^{11}$</td>
</tr>
<tr>
<td>P</td>
<td>&quot;</td>
<td>$1\times10^{12}$</td>
</tr>
<tr>
<td>P</td>
<td>&quot;</td>
<td>$4\times10^{12}$</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>$1\times10^{13}$</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>$1\times10^{11}$</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>$4\times10^{11}$</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>$1\times10^{12}$</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>$4\times10^{12}$</td>
</tr>
<tr>
<td>B</td>
<td>&quot;</td>
<td>$1\times10^{13}$</td>
</tr>
</tbody>
</table>

Using the standard PTR experimental set-up for semiconductor metrology, frequency scans were performed in the range 10 Hz – 100 kHz. Furthermore, CMRD scans at a fixed frequency (4 kHz) were performed by replacing the square-waveform generator connected to the acousto-optic modulator by a programmable waveform synthesizer (4-channel delay digital generator, Stanford Research Systems Model DG535) and
appropriate software. The Ar-ion laser beam (515 nm) was focused to a spotsize of ~50 µm at an average power of 50 mW. In anticipation of very small signal variations for some wafers, stringent measures were taken to continuously monitor and record laser power for unwanted drifts simultaneously with the PTR measurements. For implantation doses which yielded well-resolved, frequency-scanned PTR signals (e.g. As⁺ implants) a beam-splitter - photodiode assembly was used for this purpose. For the P⁺-implanted wafers in the range 4×10¹¹ - 4×10¹³ cm⁻² which exhibited highly overlapped frequency scans, real-time lock-in in-phase (IP) and quadrature (Q) ratios with a beam-splitted fraction of the output power of the laser were monitored. Amplitudes and phases were subsequently calculated from the laser-power-normalized IP and Q signals. The lock-in amplifier filter time constant was set at 3 s in all our experiments. PTR signal transients were also monitored by performing fixed-frequency 2600-s duration time scans immediately before each frequency scan and each CMRD scan for every wafer. PTR transients are known to occur upon the interaction of laser beams with unoxidized Si wafers and they constitute a form of low-activation-energy laser annealing [M. E. Rodriguez, J. A. Garcia, A. Mandelis, C. Jean and Y. Riopel, Appl. Phys. Lett. 74, 2429 (1999)]. Every wafer was probed at, or near, the center-point. Each frequency scan was immediately followed by a CMRD pulse-separation, Δ, scan at the same coordinate point without disturbing the wafer. The surface reflectivity was also monitored in a separate experiment but no measurable changes were found across the entire wafer set.

**PTR frequency and time scans.** A typical set of frequency-response curves from near the center of the five unoxidized P⁺-implanted wafers examined in this work is shown in Figure 6. PTR phase curves have not been used in the quantitative aspects of this comparative study because they are more poorly resolved with respect to implantation dose than the associated amplitudes. Similar shape curves were obtained from all wafer implantation groups. The low-frequency slopes in Figure 6 are due to thermal-wave domination of the signal as a result of lattice damage by the implantation process. In the 1 – 100 kHz range, the photo-excited carrier plasma-wave dominates the PTR signal. The amplitude depends on the depth integral of the free-carrier-density wave and, in principle, it decreases monotonically with increasing implantation dose, as a result of enhanced recombination and trapping of photo-excited carriers at electronic defect
states and traps, the density of which also increases with ion implantation dose. Polishing
damage, chemical clean contamination, and implant dose non-uniformity however, are
potentially superposed mechanisms, which can generate non-uniform signal distributions
across a wafer when PTR and MTR, diffusion-wave techniques sensitive to these
variations, are employed.

In Figure 6 it is clearly seen that signal resolution is severely compromised for
doses at and above $4 \times 10^{11}$ cm$^{-2}$. Furthermore, for the particular probe coordinate point
near the wafer center used in these measurements, the signal amplitude for the wafer
nominally implanted with $1 \times 10^{13}$ cm$^{-2}$ is higher than that from the wafers implanted with
the next two lower doses. This trend was consistent with signals obtained from other
coordinate points on these wafers. The size of experimental error bars is that of the data
points in Figure 6. The precise origin of the $1 \times 10^{13}$ cm$^{-2}$ dose anomaly for P$^+$
implantation is not clear, however, in view of its consistency across a few points probed
on the wafer surface, it is likely to be due to variations in non-implantation parameters of
the wafer, such as chemopolishing damage. Variations in the PTR signal are not likely to
be affected by this type of damage if dose increments (and thus signal change increments)
are large, but in the narrow, low-signal-sensitivity dose range considered here, wafer
history and processing damage could be important and even dominate the relative size of
PTR signals.

Monotonic amplitude decreases with increasing dose were found, as expected, for
the remaining wafers, with the exception of the B$^+$ wafer implanted with $4 \times 10^{12}$ cm$^{-2}$,
which consistently exhibited significant amplitude increase over the $1 \times 10^{12}$ cm$^{-2}$ B$^+$-
implanted wafer at several coordinate points across the wafer surface. Again, the precise
origin of this anomaly is unknown, but comments similar to those pertaining to the
$1 \times 10^{13}$ cm$^{-2}$ P$^+$ case above can also be made here. The signals from the $1 \times 10^{12}$ cm$^{-2}$ and
$1 \times 10^{13}$ cm$^{-2}$ B$^+$-implanted wafers (center points) were very close to each other, but not
totally overlapped. Figure 7 is a summary of the experimental results from the entire set
of wafers at 4 kHz, a frequency at which implant dose resolution was found to be optimal
for all PTR frequency scans such as those of Figure 6. In Figure 7, with the exception of
the anomalous $4 \times 10^{12}$ cm$^{-2}$ B$^+$ and $1 \times 10^{13}$ cm$^{-2}$ P$^+$ ion implants, the decreasing order of
PTR amplitudes with increasing dose and with increasing ionic mass (B$^+$, P$^+$, As$^+$) for the
unoxidized wafers is consistent with the increasing degree of damage incurred to the Si lattice by the progressively larger doses and ions.

It is interesting to note the relatively large restoration of PTR amplitude exhibited by the oxidized, As⁺-implanted wafers, as expected from the decreased defect density at the SiO₂-Si interface. Figure 8 shows time scans of the 4-kHz conventional PTR signal amplitudes from the four P⁺-implanted wafers (4×10¹¹ - 1×10¹³ cm⁻²) with nearly overlapped signal amplitudes. The data curve from the 1×10¹¹ cm⁻² implanted wafer was well separated from the rest of the curves (Figure 6) and is not shown here. The relative levels of these traces are consistent with the amplitudes shown in Figure 6 at the same frequency.

**PTR CMRD scans.** The CMRD technique was applied to our wafers. The repetition frequency of 4 kHz was chosen because the PTR signal there is dominated by the carrier diffusion wave; it was further chosen for direct comparisons with the conventional square-wave modulation curves of Figure 7. Waveform center-to-center scans (separation Δ) were performed with τ₁=5 ms and τ₂=25 ms. These pulse durations were chosen because they yielded maximum signal resolution with respect to implant dose. Each CMRD scan was preceded by a time-scan and by a complete frequency scan such as those in Figure 6 at the same coordinate point without moving the wafer. Figure 8 shows the Conventional 50%-duty-cycle square-wave modulated PTR traces from the four overlapped P⁺-implanted Si wafers at 4 kHz, as a function of time upon initial exposure to the laser beam.

Figure 9 shows the amplitude of the PTR-CMRD signal output of P⁺ ion-implanted Si wafers. Figure 9 exhibits better resolution of the P⁺-implant signals than Figure 6 primarily due to noise suppression, yet the overlap between the 1×10¹² cm⁻² and 4×10¹² cm⁻² remains essentially unresolved. According to Fig. 7, the signals for the various doses of As⁺-implanted wafers are well separated. No discernible advantage to using the CMRD for well-resolved frequency-scanned PTR signals as functions of dose was found. This sensitivity correlation between frequency-domain and CMRD PTR is reasonable, because for large, dose-generated, PTR signal changes the baseline suppression ability of the CMRD is limited by the natural signal differences among PTR curves.
Based on this argument, it is expected that the size of the increments $\delta \Delta$ may control the dose resolution of the technique, as the degree of lock-in signal baseline and noise suppression depends on $\delta \Delta$ for minimizing the area difference between the [0, T/2]-range and the [T/2, T]-range pulses. Therefore, the $\delta \Delta=5\%$ increment scans of Fig. 9 for P$^+$ implants were followed by $\delta \Delta=1\%$ increment scans in the “flat” separation range between 40 – 49%. The resulting curves are shown in Figure 10. In comparison with the $\delta \Delta=5\%$ increment CMRD amplitude scan, Figure 9, the narrower-range $\delta \Delta=1\%$ increment scan is shown to be capable of superior and complete resolution of the $1 \times 10^{12}$ cm$^{-2}$ and $4 \times 10^{12}$ cm$^{-2}$ dose curves.

The amplitude and Q channels are very well resolved with respect to all four curves, whereas the $4 \times 10^{11}$ and $1 \times 10^{13}$ cm$^{-2}$ curves remain essentially unresolved in both phase and IP channels. These trends are consistent with Figure 9. Furthermore, direct amplitude comparison of Fig. 10 with the 4-kHz square-wave-modulated time scans of Fig. 8 shows that, in terms of relative positions, both groups of curves share similarities, with the pair of $4 \times 10^{11}$ and $1 \times 10^{13}$ cm$^{-2}$ close together and well separated from the lower-amplitude pair $1 \times 10^{12}$ and $4 \times 10^{12}$ cm$^{-2}$. Intra-pair resolution and noise level are, however, much poorer under square-wave modulation, Figure 8, than under CMRD modulation, Figure 10. The percent fractional-amplitude-difference comparison (signal and noise) of the relative variations of a) the time-averaged 4-kHz square-wave PTR signal, Figure 8; and b) and CMRD signal, Figure 10, from P$^+$-implanted wafers is given in Table II.

Table II shows a comparison between fixed-frequency time-scanned and CMRD PTR amplitudes in dose low-resolution ranges for the P$^+$ ion-implanted Si wafers in Table I. $\Delta D$: successive dose differences between which % signal changes, $\Delta S/S$, are calculated. $\Delta S_{/S_1}$: percent square-wave-modulation time-averaged trace change over the $\Delta D$ shown in column #1 at 4 kHz, Figure 8. $\Delta S_{CMRD}/S_{CMRD}$: percent CMRD amplitude change over the same $\Delta D$ evaluated at $\Delta = 45\%$, Figure 10. $\delta \Delta =1\%$ center-to-center pulse separation-scan increment, as shown in Figure 2.
Both sets of amplitudes exhibit the same trends (in the mean) with increasing dose, including the relatively large amplitude drop between the $4 \times 10^{11}$ cm$^{-2}$ and the $1 \times 10^{12}$ cm$^{-2}$ implanted wafers. However, the higher noise level of the time-averaged trace significantly compromises resolution and measurement precision. On the other hand, the CMRD results show much higher dose resolution and the expected monotonic amplitude decrease with increasing dose (except for the point $1 \times 10^{13}$ cm$^{-2}$, well outside the measurement uncertainty (indicated by the size of the symbols). The suppression of noise in the CMRD channel, evident from comparing Figures 8 and 10, is an inherent feature of this technique due to the differential character of the measurement mode: As the LIA signal inputs in each half-period are automatically subtracted by virtue of the LIA demodulation weighting function, $w(t)$, to suppress the baseline, a fraction of the noise power integrated over each half-period is also cancelled out in CMRD. Figures 8, 10 and Table II clearly show that the substantial noise suppression of the pairs of data sets from wafers implanted with $1 \times 10^{12}$ cm$^{-2}$ and $4 \times 10^{12}$ cm$^{-2}$, and with $4 \times 10^{11}$ cm$^{-2}$ and $1 \times 10^{13}$ cm$^{-2}$, is responsible for the fully resolved values of the PTR-CMRD signals.

The CMRD and frequency-scan amplitude dependencies on dose for $B^+$ implantation, normalized to the first datum are shown in Figure 11. In this plot the higher dynamic range of CMRD detection for this implant over the frequency-scan amplitudes is clearly seen. A numerical comparison of the relative variations is given in Table III.

Table III shows a comparison between fixed-frequency time-scanned and CMRD PTR amplitudes in dose low-resolution ranges for the $B^+$ ion-implanted Si wafers in Table I. $\Delta D$: successive dose differences between which % signal changes, $\Delta S/S$, are calculated. $\Delta S_c/S_c$: percent square-wave-modulation time-averaged trace change over the
$\Delta D$ shown in column #1 at 4 kHz. $\Delta S_{\text{CMRD}}/S_{\text{CMRD}}$: percent CMRD amplitude change over the same $\Delta D$ evaluated at $\Delta = 50\%$ with $\delta \Delta = 5\%$.

### Table III

<table>
<thead>
<tr>
<th>$AD [B^+]$ (cm$^2$)</th>
<th>$AS/Sc$ (%)</th>
<th>$\Delta S_{\text{CMRD}}/S_{\text{CMRD}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{12}$ - $4 \times 10^{11}$</td>
<td>-53.93 ± 2.08</td>
<td>-49.99 ± 0.40</td>
</tr>
<tr>
<td>$4 \times 10^{12}$ - $1 \times 10^{13}$</td>
<td>33.67 ± 4.15</td>
<td>30.58 ± 0.73</td>
</tr>
<tr>
<td>$1 \times 10^{13}$ - $4 \times 10^{12}$</td>
<td>-27.98 ± 3.14</td>
<td>-35.43 ± 0.54</td>
</tr>
<tr>
<td>$1 \times 10^{13}$ - $1 \times 10^{12}$</td>
<td>-13.74 ± 4.51</td>
<td>-15.68 ± 0.84</td>
</tr>
</tbody>
</table>

In agreement with the trends shown in Table II, the major advantage of the CMRD application is the noise suppression, which is especially effective in resolving the $1 \times 10^{12}$ cm$^{-2}$ and the $1 \times 10^{13}$ cm$^{-2}$ B$^+$-implant signals. This methodology presented in this invention is able to do high resolution monitoring of ion implanted Si wafers. Based on the results presented above, it is possible to use this methodology to detect differences between electronic transport parameters due to surface or bulk conditions (i.e. heavy metal contamination) in bare, epi-layered, oxidized and patterned silicon wafers as well as wafers with diffusion and space-charged layers.

It will be understood by those skilled in the art that while the method of the present invention has been described with respect to measuring transport, optical and other properties of materials with bandgaps such as semiconductors and optical materials, the method of the present invention may also be used to measure any property of solids that makes them responsive to a repetitive energy stimulus of waveforms as described herein, as well as for measuring the physico-chemical properties of fluids, such as liquid crystals, optically absorbing pollutant trace elements excited by an optical source of the appropriate pollutant absorption wavelength. The method may also be used for the trace analysis of gases and gas mixtures by means of similar optical/spectroscopic excitation beams, for use as vacuum and pressure gauges, pollutant sensors, spectrometers operating across any and all spectral ranges and other commercial instruments operating under the
principles of trace chemical analysis. Specifically, in liquid crystals, the method can be used to monitor changes in the optical absorption properties and infrared emissivity of the surface of the liquid crystal, through changes in the emitted radiometric or any other photothermal signal as a function of temperature and material quality. It can also be used to monitor phase transitions as a function of temperature by use of photothermal signal changes due to the changing specific heat, thermal conductivity and thermal diffusivity across the phase transition region, using any available photothermal technique. The method can also be applied as a repetitive electrical potential across the liquid crystal to diagnose minute changes in crystal quality for commercial and other applications.

The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims.
THEREFORE WHAT IS CLAIMED IS:

1. A non-destructive method for measuring physical, optical, electronic or transport properties of a material having a valence energy band separated from a conduction energy band by a bandgap energy, comprising the steps of:
   a) irradiating a material with a modulated excitation energy beam, said modulated excitation energy beam being modulated to produce a periodic waveform of period T, said periodic waveform including within each period T first and second pulses of pre-selected line-shape, said first pulse having a line-width width $\tau_1$ and said second pulse having a line-width $\tau_2$, said first and second pulses being separated by a center-to-center time delay $\Delta$ between a center of each of said first and second pulses, wherein $\tau_1$ and $\tau_2$ are not equal and $T > \Delta > (\tau_1 + \tau_2)/2$;
   b) detecting signals emitted from said material responsive to being irradiated by said modulated excitation energy beam;
   c) demodulating said signals emitted from said material; and
   d) outputting said demodulated signals and storing said demodulated signals or displaying said demodulated signals.

2. The method according to claim 1 wherein said modulated excitation energy beam has an energy equal to or greater than said bandgap energy for raising electrons from said valence energy band to said conduction energy band for producing photo-generated carriers.

3. The method according to claim 1 wherein said modulated excitation energy beam has an energy equal to or greater than an energy difference between the energy of the bottom of the conduction band and energy levels in the bandgap associated with dopants, impurity atoms or defects for raising electrons from said energy levels in the bandgap to said conduction energy band for producing photo-generated carriers.

4. The method according to claims 1, 2 or 3 including comparing said demodulated signals to stored calibration signals related to one or more of said physical, optical, electronic or transport properties of said material.
5. The method according to claims 1, 2 or 3 wherein said step of demodulating said signals includes inputting said detected signals into a signal analyzing means, wherein the signal analyzing means extracts selected direct current signal components or derivative direct current signal components from said detected signals, and wherein said selected components are inputted into a computer processing means connected to said signal analyzing means, and wherein said selected components are fitted to a theoretical model of a response of said material being repetitively irradiated by said modulated excitation energy beam to calculate any of said selected physical, optical, electronic or transport property of said material.

6. The method according to claims 1, 2, 3, 4 or 5 wherein said first and second pulses are substantially square wave pulses.

7. The method according to claims 1, 2, 3, 4, 5 or 6 wherein said excitation energy beam is a laser beam.

8. The method according to claims 1, 2, 3, 4, 5, 6 or 7 wherein said selected physical, optical electronic or transport property of said material being calculated which can be related to behavior of photo-generated carriers includes recombination lifetimes of the photogenerated carriers, minority carrier lifetimes, surface recombination velocities, carrier diffusion coefficients, alternating and direct current carrier diffusion lengths, optical absorption coefficient at a wavelength of the excitation energy beam, and thermal diffusivity of the material.

9. The method according to claims 1, 2, 3, 4, 5, 6, 7 or 8 wherein said excitation energy beam is modulated using a modulator means connected to a waveform generator which produces said periodic waveform.

10. The method according to claim 9 wherein said steps of detecting and demodulating said signals includes detecting said signals using a detection means connected to a signal
analyzing means, said signal analyzing means and said detection means being synchronized using said waveform generator.

11. The method according to claim 10 wherein said signal analyzing means is a lock-in amplifier and wherein said lock-in amplifier is referenced to a frequency of 1/T.

12. The method according to claims 10 or 11 wherein said step of irradiating a semiconductor with a modulated excitation energy beam includes scanning $\Delta$ through a selected range of $\Delta/T$ by varying $\Delta$ by an increment $\delta\Delta$ after a preselected number of periods T while keeping $\tau_1$ and $\tau_2$ fixed.

13. The method according to claims 10 or 11 wherein said step of irradiating a material with a modulated excitation energy beam includes scanning $\tau_1$ through a selected range of times by varying $\tau_1$ after a preselected number of periods T while keeping $\Delta$ and $\tau_2$ fixed.

14. The method according to claims 10 or 11 wherein said step of irradiating a material with a modulated excitation energy beam includes scanning $\tau_2$ through a selected range of times by varying $\tau_2$ after a preselected number of periods T while keeping $\Delta$ and $\tau_1$ fixed.

15. The method according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 or 14 wherein said period T of said modulated excitation energy beam is selected to be comparable to recombination rates of the photogenerated carriers in said material.

16. The method according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 or 15 including a step of real-time signal normalization for compensating for intensity fluctuations in said excitation energy beam.

17. The method according to claim 16 wherein said step of real-time signal renormalization includes directing said excitation energy beam to a beam splitter wherein a first portion of the excitation energy beam is directed to said modulating means and a second portion of said excitation energy beam is directed to a modulator to modulate said second
portion at a selected frequency, directing said modulated second portion to an input of a photodiode, and wherein an alternating current output of said photodiode is inputted into a signal processing means for demodulating a time-fluctuating amplitude of said excitation energy beam to produce a direct current signal, inputting said direct current signal into said lock-in amplifier and ratioing said extracted selected direct current signal components or derivative direct current signal components to said direct current signal.

18. The method according to claim 9 wherein said modulator means is an acousto-optic modulator.

19. The method according to claim 9 wherein said modulator means is an electro-optic modulator.

20. The method according to claims 10 or 11 including amplifying said detected signals using an amplifier connected between said detection means and said signal analyzing means.

21. The method according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wherein said material is a semiconductor material.

22. The method according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 wherein said material is an optical material.

23. The method according to claim 21 wherein said semiconductor material includes a scribeline structure on a processed wafer separating device and chip arrays, and wherein probing along the scribeline obtains measurements of signal levels which depend on minority-carrier recombination lifetimes.

24. The method according to claim 21 wherein said semiconductor material includes a layered epitaxial structure, and wherein the dopant uniformity and concentration of the epitaxial layer is monitored.
25. The method according to claim 21 wherein said semiconductor material includes ion implanted dopants, and wherein the implantation parameters (energy and dose) can be measured by either fitting the emitted signals to appropriate theoretical models or through use of calibration curves.

26. The method according to claim 21 wherein said semiconductor material is a semiconductor wafer comprising semiconductor devices including p-n junction devices, and wherein the dopant type and dose can be measured through appropriate theoretical models or through use of calibration curves.

27. The method according to claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26 or 32 including performing said non-destructive method after fabricating a semiconductor wafer or semiconductor devices from said material for quality and process control of said semiconductor wafer or semiconductor device.

28. The method according to claim 27 wherein the step of performing said non-destructive method after fabricating a semiconductor wafer or semiconductor devices is performed on a semiconductor wafer production line or on a semiconductor chip fabrication line.

29. The method according to claims 1 to 28 including adjusting the cross sectional size of the modulated excitation energy beam hitting the surface of said material, and wherein said modulated excitation energy beam is directed onto a selected surface area of the surface of said material, including repeating steps a), b), c) and d) sequentially at a plurality of pre-selected surface areas across the surface of the material, and including producing a thermoelectronic image of the material from the stored demodulated signals.

30. The method according to claims 11, 12, 13 or 14 including adjusting the cross sectional size of the modulated excitation energy beam hitting the surface of said material, and wherein said modulated excitation energy beam is directed onto a selected surface area of the surface of said material, including repeating steps a), b), c) and d) sequentially at a plurality of pre-selected surface areas across the surface of the material, and including displaying the
in-phase and/or quadrature components, or the amplitude and/or phase components of the
demodulated lock-in output versus the X-Y positions for producing a thermoelectronic image
of the material from the stored demodulated signals.

31. The method according to claims 1 to 28 including parallel image processing the emitted
signals from the material using charge coupled device, and including producing a
thermoelectronic image of the material from the stored demodulated signals.

32. The method according to claims 29 or 30 wherein said material is mounted on a
substrate holder having means for adjusting the X-Y position of said material with respect to
said modulated excitation energy beam.

33. The method according to claim 9 wherein said modulator means is a computer
controlled electro-mechanical shutter.

34. A non-destructive method for measuring physical, optical, electronic or transport
properties of fluids, comprising the steps of:
   a) irradiating a fluid with a modulated excitation energy beam, said modulated
      excitation energy beam being modulated to produce a periodic waveform of period T, said
      periodic waveform including within each period T first and second pulses of pre-selected
      line-shape, said first pulse having a line-width width τ₁ and said second pulse having a line-
      width τ₂, said first and second pulses being separated by a center-to-center time delay Δ
      between a center of each of said first and second pulses, wherein τ₁ and τ₂ are not equal and
      T > Δ > (τ₁ + τ₂)/2;
   b) detecting signals emitted from said fluid responsive to being irradiated by said
      modulated excitation energy beam;
   c) demodulating said signals emitted from said fluid; and
   d) outputting said demodulated signals and storing said demodulated signals or
      displaying said demodulated signals.
35. The method according to claim 34 including comparing said demodulated signals to stored calibration signals related to one or more of said physical, optical, electronic or transport properties of said fluid.

36. The method according to claims 34 or 35 wherein said step of demodulating said signals includes inputting said detected signals into a signal analyzing means, wherein the signal analyzing means extracts selected direct current signal components or derivative direct current signal components from said detected signals, and wherein said selected components are inputted into a computer processing means connected to said signal analyzing means, and wherein said selected components are fitted to a theoretical model of a response of said fluid being repetitively irradiated by said modulated excitation energy beam to calculate any of said selected physical, optical, electronic or transport property of said fluid.

37. The method according to claims 34, 35 or 36 wherein said first and second pulses are substantially square wave pulses.

38. The method according to claims 34, 35, 36 or 37 wherein said excitation energy beam is a laser beam.

39. The method according to claims 34, 35, 36, 37 or 38 wherein said fluid is a liquid crystal and wherein the method is used to monitor changes in the optical absorption properties and infrared emissivity of the surface of the liquid crystal, through changes in the emitted radiometric or any other photothermal signal as a function of temperature and material quality.

40. The method according to claims 34, 35, 36, 37 or 38 wherein said fluid is a liquid crystal and wherein the method is used to monitor phase transitions as a function of temperature by use of photothermal signal changes due to the changing specific heat, thermal conductivity and thermal diffusivity across the phase transition region, using any available photothermal technique.
41. The method according to claims 34, 35, 36, 37, 38, 39 or 40 wherein said excitation energy beam is modulated using a modulator means connected to a waveform generator which produces said periodic waveform.

42. The method according to claim 41 wherein said steps of detecting and demodulating said signals includes detecting said signals using a detection means connected to a signal analyzing means, said signal analyzing means and said detection means being synchronized using said waveform generator.

43. The method according to claim 42 wherein said signal analyzing means is a lock-in amplifier and wherein said lock-in amplifier is referenced to a frequency of 1/T.

44. The method according to claims 42 or 43 wherein said step of irradiating a semiconductor with a modulated excitation energy beam includes scanning $\Delta$ through a selected range of $\Delta/T$ by varying $\Delta$ by an increment $\delta\Delta$ after a preselected number of periods T while keeping $\tau_1$ and $\tau_2$ fixed.

45. The method according to claims 42 or 43 wherein said step of irradiating a material with a modulated excitation energy beam includes scanning $\tau_1$ through a selected range of times by varying $\tau_1$ after a preselected number of periods T while keeping $\Delta$ and $\tau_2$ fixed.

46. The method according to claims 42 or 43 wherein said step of irradiating a material with a modulated excitation energy beam includes scanning $\tau_2$ through a selected range of times by varying $\tau_2$ after a preselected number of periods T while keeping $\Delta$ and $\tau_1$ fixed.
Fig. 3

- $\tau / T = 10\%$
- $\tau^* / T = 5\%$
- $\tau^* / T = 2\%$
Fig. 4
Fig. 5
Fig. 6
8/11

f = 4 kHz

 PTR Amplitude (V)

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Fig. 8
9/11

Fig. 9
Fig. 10
Fig. 11

\[ \delta A = 5\% \]
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N21/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Date of the actual completion of the international search
17 June 2002

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25/06/2002

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Authorized officer
Mason, W
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