THERMAL WAVE PROBING OF THE OPTICAL, ELECTRONIC AND THERMAL PROPERTIES OF SEMICONDUCTORS

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Abstract : In this paper we will demonstrate how the thermal waves have been revealed to be a good probe for the detection of free carriers dynamic and consequently for the determination of electronic parameters determination.

After the detailed description of the two setups we have used (mirage and photoreflectance), we will explain how to proceed to achieve theoretical calculations either in a 1D geometry or in a 3D one.

We will then illustrate our demonstration with examples taken in spectroscopy investigation domain (photothermal study of amorphous silicon), in thermal parameter determination, and in transport properties evaluation (photothermal study of bulk silicon or silicon wafer) with different spatial resolutions.

Finally, we will emphasize that using a dye laser for excitation instead of an Argon one and intermediate frequency modulation range, can allow more precise determination of electronic parameters.

Introduction

Thermal wave probing has been revealed to be a very interesting way to study various samples in order to solve fundamental or applied physics problems. For semiconductor studies, this technique has demonstrated its power in many cases : spectroscopic investigation of layered or complex samples, thermal diffusivity determination of bulk, layered or heterogeneous samples and transport properties measurements (minority carriers diffusivity, lifetime, surface recombination velocity...) /1/.

This paper will be divided in three parts :

In the first one we recall how to create a thermal wave, how this thermal wave can propagate in a sample and how it can be detected. This section will be illustrated with the photothermal investigation of a semiconductor sample (optical and thermal parameter determination).

In a second part, we will emphasize the ability of a mirage experiment in air to determine the surface recombination velocity of a silicon wafer by following the heat due to the photocreated carriers recombination in the bulk and at the surface of the sample. By probing the heat and the carrier distributions inside the sample, we will show that it is possible to get precise electronic parameter determination.

Finally, in a third section we will explain how a photoreflectance experiment allows the determination of the transport properties and how it is possible to choose convenient experimental parameters (frequency range and excitation wavelength) to facilitate this determination.

I Optical and thermal parameters determination with a photothermal experiment.

a- photothermal experiment setups

A photothermal experiment is the "combination" of:

- illumination of the sample with a pulsed or a modulated pump beam.
- detection of the surface or volume temperature variation related to the transformation of this light energy into heat.

This detection can be done with different experimental setups depending upon the physical parameters which are under investigation : refractive index, infrared emissivity, acoustic waves or local deformation... In this paper, we will use mainly two kinds of optical detection : the mirage for 1D experiment / 2 / and the photoreflectance for 3D configuration / 3 / setups, which both allow the detection of the surface or the bulk temperature variation with a very good sensitivity.

Fig.1 describes the mirage set up which allows the recording of the induced temperature variation of the sample. The sample is settled on a "Mirage cell" / 4 / and illuminated with the pump beam (laser beam or monochromator). The heating of the surface leads to a temperature gradient which spreads in the transparent surrounding (air or transparent liquid) and in the sample. The temperature gradient is associated to a refractive index gradient, which can be measured by the deflexion of an HeNe laser probe beam crossing it. The angular deflexion of the probe beam is detected by a silicon position sensor. It is possible to reach the photon noise with this setup, (10^{-11} rad/ $\sqrt{\text{Hz}}$ for the angular deviation which corresponds to 10^{-5} °C/ $\sqrt{\text{Hz}}$ for the sample surface temperature variation in air or 10^{-7} °C/ $\sqrt{\text{Hz}}$ if the surrounding medium is a transparent liquid as CCl_4). With this kind of detection it is possible to detect thermal waves up to 100 kHz.

Fig. 2 shows a photoreflectance setup. The sample is illuminated with a focused excitation spot ($1 \mu\text{m}^2$ to a few hundred μm^2) and the probe beam is reflected at the surface of the sample, in the heated area. In this case, the measurement is done by following the variation of the refractive index of the sample through the reflexion coefficient R. It is possible to achieve setups exhibiting a sensitivity of 10^{-6} in $\Delta R/R$ whose frequency range domain spreads up to 20 MHz / 3, 5 /.

Figure 1

Figure 2

b - thermal wave definition

In order to explain what is called a thermal wave, we have to solve the heat equation diffusion in a semi infinite medium with a plane modulated heat source located at $x = 0$. The solution is the following :

$$T(x,t) = T_0 \exp(-x/\mu) \exp(j [\omega t - x/\mu]) \quad (1)$$

where : $T(x,t)$ is the temperature at a distance x from the source and T_0 is correlated to the amplitude of the heat source.

μ is the thermal diffusion length which characterizes the heat propagation in the medium and which can be controlled by the modulation frequency $f = \omega / 2 \pi$ of the heat source. μ is related to k (thermal conductivity), to ρ (density) and C (specific heat) and f by the following expression :

$$\mu = (k / 2 \pi f \rho C)^{1/2} = (D / 2 \pi f)^{1/2}$$

where D is the thermal diffusivity. The expression (1) could describe the propagation of an optical wave, for which the real part and the imaginary part of the refractive index would be equal. So, although a thermal wave is strongly attenuated, it can reflect, diffract and propagate as a classical one.

Moreover, eq (1) indicates clearly that measuring the phaselag of the complex temperature allows the localization of heat sources in the sample.

To know the temperature distribution in the sample and in its surrounding we have to solve the heat equation diffusion in all the media (fluid, sample and backing). If the sample is a complex one (multilayered sample) we have to consider separately each layer of the sample and of the surrounding. At each interface, the

incident thermal wave, A_0 is transmitted, A_1 , and reflected, B_0 , following the thermal properties of each medium. The thermal effusivity $e = (k\sqrt{D})$ is then the analogous to the refractive index :

$$B_0/A_0 = (e_0 - e_1) / (e_0 + e_1)$$

$$A_1/A_0 = 2 e_0 / (e_0 + e_1)$$

We must underline, that a strong thermal desadaptation can be useful for the photothermal investigation of a layered sample. Reference / 6 / provides a good illustration of this characteristic.

We now want to illustrate why it is interesting to run a photothermal experiment instead of an optical one to determine the optical absorption coefficient of an amorphous silicon sample and how this method can give information on the localization of the absorbing centers, for sub-band gap energy.

c- Photothermal study of an amorphous silicon sample deposited on silica
We have used a Mirage setup, with the sample immersed in a transparent liquid (CCl₄) in order to increase the photothermal signal and the illumination achieved by using a visible and near infrared Fourier Transform spectrometer / 7 /. The modulation frequency being smaller than 100 Hz, we are in the case of a thermally thin sample (μ_s , thermal diffusion length $\gg 1$, thickness of the sample) / 8 /. The resolution of heat diffusion equation in the three media (fluid, sample and silica) leads to :

$$T_s(0,t) = \frac{I_0 \alpha l \exp(j \omega t)}{2 (k_b \sigma_b + k_f \sigma_f)}$$

for weak values of αl : the photothermal signal is linear in αl . For strong αl the surface temperature is no more proportionnal to the optical absorption coefficient α (the photothermal signal is saturated) :

$$T_s(0,t) = \frac{I_0 \exp(j \omega t)}{2 (k_b \sigma_b + k_f \sigma_f)}$$

I_0 is the incident power, k_b and k_f the thermal conductivity of the backing (the transparent silica in this case) and the fluid . σ_b and σ_f are the thermal wave vectors in the backing and in the fluid:

$$\sigma_b = j\omega / D_b \quad \text{and} \quad \sigma_f = j\omega / D_f$$

We can notice that the thermal properties of the absorbing sample do not appear in the formulas since we are in a thermally thin case; moreover, the phase is then always the same ($-\pi/4$) and does not bring any information on the optical absorption coefficient (α) determination.

On the other hand, if the modulation frequency is increased, we leave the thermally thin sample case : the thermal diffusion length becomes comparable to the thickness of the sample (thermally thick sample) and it is possible by measuring the phase, and no more the amplitude of the photothermal signal, to localize the heat sources, as we have mentioned in the last section. In the case of an amorphous silicon sample it is of importance to know the processus which is responsible of the residual absorption in the sub-band gap and to know the localization of the

absorbing centers. For a 10 μ m thick sample, the thermal diffusion length associated with a 5kHz frequency modulation, becomes comparable to the thickness of the sample. By running a high frequency modulation Mirage experiment in air we have clearly demonstrated that the absorbing centers were located on the surface of our sample / 9 /.

Figure 3

Fig 3 shows the low frequency photothermal signal amplitude versus the energy of the excitation light. We can see that the photo-thermal signal is saturated in the blue part of the spectrum (large αl). The I.R. part corresponding to small values in αl is correlated with the quality of the amorphous silicon sample / 10 /; it is then of importance to measure it with a good accuracy : it is well accomplished with this method (αl as small as 10^{-5} can be measured with our setup), as opposed to the optical transmission one because we only measure the power deposited in the sample and not the small difference between two large quantities. Finally let us notice that we can get rid by computation of the residual modulation associated with the interferences phenomena due to the high refractive index of the amorphous silicon /11 /.

Finally, let us underline that a photothermal experiment is always associated with a theoretical model. It is then very important to know with a good accuracy the thermal parameters such as the thermal diffusivity D or the thermal conductivity k of the sample and of its surrounding. We just want to recall briefly that a mirage experiment is able to determine the thermal diffusivity either in the case of a thin layer deposited on a transparent substrate in combining rear and front illumination / 12 /, or in the case of a bulk or layered sample in recording the spatial spreading of the heated spot / 13 /.

II Transport properties determination in a semiconductor with a mirage experiment

When a semiconductor is irradiated with a modulated pump beam whose energy is higher than the band gap, it is well known that free carriers are generated in addition to the heating of the sample. The photocreated carrier motion being also governed by a diffusion equation, two waves are created in the sample : a thermal

wave and a plasma wave which will act also as a distributed heat source. Neglecting the heat transfer to the surrounding fluid, we solve the two following coupled equations in order to know the temperature field $T(x,t)$ and the carrier density distribution $N(x,t)$:

$$D_C \frac{\partial^2 N}{\partial x^2} - \frac{\partial N}{\partial t} - \frac{N}{\tau} + \frac{\partial N}{\partial t} T + S_N(x,t) = 0$$

$$k_{th} \left[\frac{\partial^2 T}{\partial x^2} - \frac{1}{D_{th}} \frac{\partial T}{\partial t} \right] + \frac{E_g}{\tau} D_{th} N + S_T(x,t) = 0$$

The minority carriers are characterized by the diffusivity D_C and their lifetime τ , while the thermal parameters are D_{th} , the thermal diffusivity and k_{th} the thermal conductivity. $S_N(x,t)$ and $S_T(x,t)$ are respectively the source term for the carrier diffusion equation and for the heat diffusion one. E_g is the semiconductor gap energy / 14 /. In these equations we have neglected the acoustic waves and the thermomechanical and electromechanical coupling contributions.

Since we are in the case of a carrier density smaller than 10^{18} cm^{-3} , it is assumed that the carrier lifetime is independent of the free carrier concentration; and, therefore, Auger recombination will be neglected. Furthermore, we can neglect the $T \partial N / \partial T$ term which is related to the carrier creation due to the temperature gradient / 15 /. So, we can first solve the carrier diffusion equation and then the heat one, with the carrier density $N(x,t)$ as source term. These resolutions lead to two waves governed by :

$$\sigma_C = 1 / D_C \tau + j \omega / D_C \quad \text{for the plasma wave vector}$$

$$\text{and } \sigma_{th} = j \omega / D_{th} \quad \text{for the thermal wave vector}$$

If $\omega\tau \ll 1$ the plasma wave loses its wave like properties and the process is purely diffusive characterized by a diffusion length $\sqrt{D_C \tau}$. In the other case, $\omega\tau \gg 1$ the plasma wave comportement is analogous to the thermal wave one. In a semiconductor such as silicon and for modulation frequencies in the MHz regime, one can easily have $\omega\tau \gg 1$ and the plasma density is then a critically damped wave.

Let us consider now the photothermal study of a Silicon wafer in air, accomplished with a Mirage setup, with a 700 mW Ar^+ laser beam to produce a large excitation spot on the surface in order to eliminate the effects of the lateral diffusion and to stay in a 1D diffusion model. The thickness of the n-type wafer was about $360 \mu\text{m}$, so we have to take into account the recombination processes on both the back and front surfaces. We have used a phenomenological approach by using the surface recombination velocity, s , to modelize the recombination processes on the surface. In this case, the resolution of the two diffusion equations (carriers distribution and heat distribution) leads to very complicate analytical formulas /16 /. Let us summarize the main result which is that the surface temperature is due to the contributions of two terms:

- a surface thermal wave correlated to the very fast non radiative relaxation of the photoexcited free carriers which give the excess of energy of the photon compared to the band gap energy, within a fraction of a picosecond. This a pure

surface wave, in our case, since the excitation is done with an Argon laser (200 nm penetration length).

- a volume wave which is due to the non radiative recombination of the photocreated carriers giving up their remaining energy E_g after a time τ corresponding to their life time (on the order of μ seconds for silicon).

Depending on the geometry of the experiment (front or back illumination) and on the quality of the surface under investigation (large or small value for the surface recombination velocity), it is possible to reach with a rather good precision the electronic parameters.

We have theoretically studied the four experimental configurations of pump and probe beam to determine the most appropriate one, considering the thickness of the sample and the frequency range for which the signal over noise is sufficient / 17 /.

Figure 4 (a)

Figure 4 (b)

When exciting the damaged surface (large s), we can probe in the air in front of this surface, but the thermal wave is then dominant through out the whole frequency range, or behind the polished one. Fig.4 (a) corresponds to this second case. The electronic diffusivity being larger than the thermal diffusivity, we expect the plasma wave to reach the rear surface before the thermal one. This is clearly shown by the increased contribution of the rear surface at high frequencies. When illuminating the polished surface and probing this front surface (Fig. 4 (b)), the plasma wave are clearly present even at low frequencies. This can be explained by the random walk of the minority carriers in the bulk of the sample before their recombination at the surface.

Figure 5

To avoid the convolution effect / 18 / due to the finite size of the probe beam we have made the difference of the results obtained for two configurations (rear and front). Fig. 5 shows the experimental result and the theoretical fit. We are presently improving our experimental setup (excitation wavelength and modulation frequency) and we hope that it will be possible to determine unambiguously the back and front recombination velocities of a silicon wafer with a very simple low frequency mirage experiment.

Finally, in order to illustrate the propagation of the plasma wave and thermal wave inside the sample, we have to choose a probe which is sensitive to both the temperature and the carriers : the refractive index n is a good candidate. In the case of a silicon sample, the two terms $\partial n / \partial T$ and $\partial n / \partial N$ being opposite in sign, the photothermal signal relative to plasma wave will present a reverse sign towards the thermal wave relative one.

Figure 6

Fig 6 shows the result obtained in probing, inside the sample, the two expected waves. We have used a 1,15 μm HeNe laser as probe beam and a 15ns pulsed NdYag laser associated with a doubler as pump beam. It is clear that the plasma wave, whose wave vector is characterized with the higher value of diffusivity is visible at short times, while the thermal wave is spreading at longer times. Moreover, the quality of the surface is a dominant factor to observe the plasma wave : when the surface is highly damaged the plasma wave disappear. This experiment and its associated Fourier transform one / 20 /, have clearly demonstrated that it is possible to determine both thermal and electronic diffusivities, minority carrier lifetime and surface recombination velocity, with a good precision.

III Transport properties determination in a semiconductor with a photorefectance experiment

In this kind of experiment, the sample is illuminated with a small spot and the measurement is accomplished by following the induced photorefectance variation of the probe beam reflected on the heated area. We must underline that in the case of a semiconductor sample, the refractive index is affected not only by the temperature variation, but also by the carrier density one: the induced photorefectance ΔR can be therefore written :

$$\Delta R = (\partial R / \partial T) \Delta T + (\partial R / \partial N) \Delta N$$

As in the case of the mirage experiment inside the semiconductor, the plasma wave will be detected at short time scale (at large frequencies), while the thermal wave is dominating at long time (in the low frequency range). This method of investigation is now currently used in the microelectronic factories. Thermal wave Inc. has indeed developped an instrument using the laser induced modulated reflectance method for monitoring the dose and uniformity of ion implantation in Si and GaAs wafers, for detecting and quantifying the residual damage in silicon wafers that results from chemopolishing and scrubbing processes and for detecting and characterizing radiation damage and contamination in silicon from reactive ion and plasma etch processes / 21 /.

In order to get quantitative informations from this experiment, we have to use 3D diffusion equations, to take into account the geometry of the experiment. To obtain the three dimensionnal expressions, we have used the integral transformations (Laplace and Hankel) which are convenient for the axial geometry of the problem. By using a numerical calculation of the inverse Hankel transform / 22 /, we are able to calculate the induced photorelectance signal.

Let us consider now the figure 7 (from ref /5/) in which the amplitude and the phase of the photorelectance signal of a $\Sigma=25$ twinned boundary of a p-type silicon bicrystal have been recorded in the two cases of an impurity free boundary and a decorated one. While the impurity free boundary is well reconstructed and exhibit no electrical activity, decoration with transition metal impurities makes the boundary electrically active and generates large densities of interface traps associated with a strong recombination efficiency / 23 /. This experiment was done with a photothermal microscope build in our laboratory, whose sensitivity in $\Delta R/R$

is 10^{-6} . The photothermal results are in concordance with the electrical ones : only the decorated boundary exhibit a large variation in the photothermal investigation, which can be qualitatively explained as follows:

Figure 7

Far from the boundary the signal is mainly due to the plasma wave while near the boundary the increasing of the signal corresponds to a pure thermal wave associated with a very strong velocity recombination coefficient. The Π phase change corresponds to the reverse sign of $\partial R / \partial T$ and $\partial R / \partial N$. The excitation beam was a 30mW Argon laser, the probe beam a 0.1mW HeNe one ($1\mu\text{m}$ spots) and the modulation frequency is in the range of MHz. As expected, it is easy to detect the plasma wave at high frequency.

Figure 8

We want to underline now that it is possible to obtain useful informations on the carrier properties by using a 100 KHz modulation frequency and a larger spot than $1\mu\text{m}^2$, this configuration being more convenient in some cases. Using an excitation wavelength higher than that of the Argon laser, which corresponds to an excitation energy closer to the band gap of silicon, we can reduce the contribution

of the surface thermal wave due to the photon excitation energy in excess to the gap energy, and therefore enhance the plasma wave contribution to the photorefectance signal. Fig 8 shows a theoretical calculation, showing that it then be easy to detect the plasma wave (180° Phase shift) even at 100kHz, by using a 830 nm dye (Styryl 9) laser and a $80\ \mu\text{m}$ diameter spot / 24 /.

Finally, Fig 9 shows the experimental results / 24 / we got on a Silicon wafer sample illuminated with a 400mW 514nm Argon laser and with a 400mW 625 nm dye (Kitton Red) laser, with a $80\ \mu\text{m}$ diameter heated spot. The induced variation of the 780nm diode laser probe beam was recorded with a Silicon detector. With this setup we got a sensitivity of 10^{-6} in $\Delta R/R$. Our theoretical model has allowed to get rather good fits of our experimental data.

Figure 9

TABLE 1: Fitted Parameters

Carrier Diffusivity	De	14 cm ² s ⁻¹
Carrier lifetime	τ	50 μs
Surface recombination velocity	s	200 cm/s

Conclusion

In conclusion, this paper underlines that thermal waves can be very helpful for the electronic properties determination in the case of a Silicon sample. Photothermal investigation of semiconductors is nowadays well known in the microelectronic world. However, we have demonstrated theoretically that a judicious choice of new experimental conditions for a mirage or a photorefectance experiment (illumination wavelength, heated spot size) allows to detect the plasma

waves in an intermediate frequency range, which largely facilitates the experience. Experimental results have confirmed our calculations in the case of n, n⁺, p, p⁺ type silicon wafers. These recent investigations allow us to believe that this methodology could be extend to other semiconductor sample (GaAs, ...) and more complicated devices (SiMox...).

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