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Frequency-Dependent Thermal Conductivity in Time Domain Thermoreflectance Analysis of Thin Films

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ABSTRACT

Over the past three decades, ultrashort laser pulses have been demonstrated to be a very powerful tool to investigate materials properties at the nanoscale. A key driving force is the high-time resolution required to study heat transfer across interfaces and in thin films. The Time-Domain Thermoreflectance (TDTR) is now widely used. This optical technique offers an interesting alternative to electrical approaches such as the 3ω method. We present a complete study of the TDTR signals. We investigate the influence of the modulation frequency on the measured signals and we show how this experimental parameter could be set to enhance or reduce the sensitivity to a specific thermal parameter. The dependence of the measured ‘‘apparent’’ thermal conductivity of the thin film as a function of the modulation frequency is discussed. Results are applied to investigate thermal properties of a series of InGaAs samples with embedded ErAs nanoparticles.

INTRODUCTION

Pump-Probe Time Domain Thermoreflectance (TDTR) has been demonstrated as a powerful technique to investigate acoustic and thermal properties at very short time and length scales. Nowadays, TDTR has proven its ability and is now fully accepted as a reference technique to measure the thermal properties^{1,2}, in the same way as the well-known 3ω method.

In 2007, Koh and Cahill observed a significant reduction of the thermal conductivity in alloy materials by varying the frequency of the heat source at the MHz scale³. Such a reduction was theoretically predicted by Volz five orders of magnitude higher⁴. The mechanics of this reduction, the competition between ballistic and diffusive effects and their impact on TDTR measurements of the thermal conductivity are still not fully understood.

In this work, we first present an analysis of the TDTR signal, we show the influence of the frequency and the waveform of the modulated heat source. Their impact on the TDTR signal and the sensitivity of certain thermal parameters are discussed. We present the experimental results on different semiconductor bulk materials and nanocomposite thin layers of InGaAs doped with ErAs nanoparticles. The frequency dependence of the thermal conductivity will be discussed.

TIME DOMAIN THERMOREFLECTANCE PRINCIPLE

Time Domain Thermoreflectance technique is based on a femtosecond pump-probe set-up where an ultrashort laser "pump" pulse generates a transient thermal response, and a weaker "probe" pulse is used to monitor the reflectivity changes of the surface. When the surface of the sample is covered by a thin metallic layer, the incident optical energy is absorbed and converted into a heat flux propagating into the sample. For most metals, the variation of reflectivity is proportional to its temperature. A schematic description of our TDTR bench is shown in Figure 1.

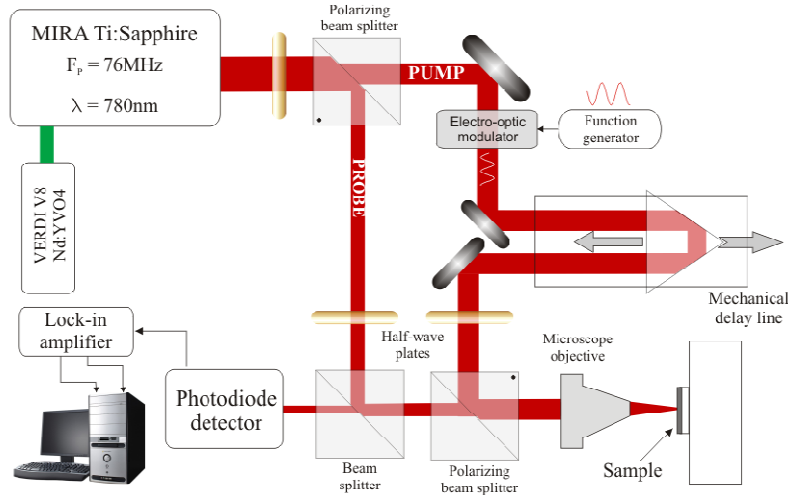


Figure 1. Time Domain Thermoreflectance experimental set-up.

Ultrashort laser pulses (~ 500 fs) coming from a Ti: Sapphire laser are separated in two beams by a polarizing beam splitter. The pump is modulated in amplitude by passing through an electro-optic modulator (EOM). This modulation was originally required to filter the signal from the noise and to allow the detection of weak reflectivity variations, but we will see in the next paragraph that it is possible to set the modulation frequency to enhance the thermal analysis. The delay between the pump and the probe pulses can be adjusted with a picosecond precision by moving a mechanical delay line ($300\mu\text{m} \leftrightarrow 1\text{ps}$). We chose to advance the pump arrival on the sample rather than delaying the probe because this configuration is less sensitive to the laser beam size variations or to any misalignment. The reflected probe beam is then detected by an ultrafast photodiode and a lock-in detection filters the signal around the first harmonic of the modulation frequency.

Homodyne optical sampling

The key driving force of the TDTR technique is its high time resolution. The picosecond resolution is achieved by a homodyne optical sampling. For clarity, principle of this technique is explained in Figure 2. This method is called homodyne optical sampling because the pump and the probe have the same repetition rate.

The signal received by the lock-in amplifier is shown on Figure 2-(d). The lock-in detection is sensitive to the amplitude and the phase of this sinusoid wave or to its real and imaginary parts, also called respectively In-Phase V_{in} and Out-of-Phase V_{out} components.

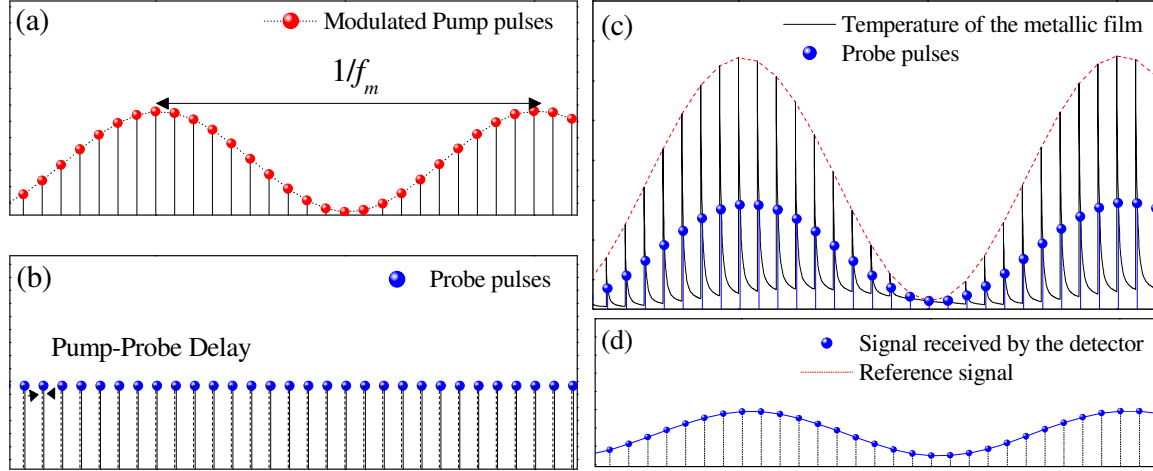


Figure 2. Principle of the homodyne optical sampling. (a) Pump pulse train modulated in amplitude by an EOM. (b) Delayed probe pulse train. (c) (black) Temperature of the surface of the metallic film and probed temperature for one delay (blue circles). (d) Signal received by the photodiode for one pump-probe delay.

Theoretical study of the TDTR signal

Theoretical interpretation of the TDTR signal is not straightforward because the time between two consecutive heat pulses is not long enough to allow the material to return to equilibrium. The thermal response of the material is given by the convolution between the response to a single laser pulse and the modulated pump pulse train. Many authors have derived the exact expressions of the TDTR signal given by the lock-in amplifier in both time^{5,6} and frequency⁷ domains. In our configuration (pump modulated then delayed), the expressions are:

$$\begin{aligned}
 V_{\text{in}}(f_m, \tau) &\propto \sum_{n=0}^{\infty} R_0(\tau + nT_p) \cdot \cos(2\pi f_m \cdot nT_p) \\
 V_{\text{out}}(f_m, \tau) &\propto i \cdot \sum_{n=0}^{\infty} R_0(\tau + nT_p) \cdot \sin(2\pi f_m \cdot nT_p)
 \end{aligned} \quad (1)$$

where f_m is the modulation frequency set by the EOM, τ is the pump-probe delay, T_p is the period of the laser (12ns) and R_0 is the surface temperature response to a single heat pulse. In 1999, Maris and co-workers presented first these expressions and used only the real part of the signal to fit the experimental data⁵. They reported the strong influence of the experimental artifacts we discussed before. In 2002, Cahill suggested to use the ratio ($-V_{\text{in}}/V_{\text{out}}$) of both components to eliminate these artifacts, as these modify V_{in} and V_{out} by the same amount⁸. In addition, fitting the ratio avoids any normalization process between the experimental and calculated signals.

In an ideal case, the lock-in detection mixes the detected signal with two pure sinusoids in quadrature to obtain the In-Phase and Out-of-Phase components and rejects the other harmonics. In some cases, the EOM and the lock-in amplifier are only able to produce square waves which in turn introduce higher harmonic components in the signal. These harmonics can be suppressed by using a resonant band-pass filter, at the modulation frequency, between the

photodiode and the lock-in amplifier. It is also possible to take these harmonics into account in the expressions of the signal. In that case, V_{in} and V_{out} are given by:

$$V_{in} \propto \sum_{n=-\infty}^{\infty} R_0(\tau + nT_p) \cdot \left\{ -\frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{(-1)^n \cos[2\pi(2m-1)f_m \cdot nT_p]}{(2m-1)^2} \right\} \quad (2)$$

$$V_{out} \propto \sum_{n=-\infty}^{\infty} R_0(\tau + nT_p) \cdot \left\{ -\frac{8}{\pi^2} \sum_{m=1}^{\infty} \frac{\sin[2\pi(2m-1)f_m \cdot nT_p]}{(2m-1)^2} \right\}$$

Odd harmonics of the modulation frequency are added to the signals. About 15% difference is observed on the experimental ratios between the two waveforms (Figure 4-(a)).

The thermal properties of the material are obtained by fitting the experimental ratio with a thermal response calculated using expressions (1) or (2). The impulse response R_0 is calculated by the so called Thermal Quadrupoles⁹ method, which solves the Fourier heat equation in the Laplace-Hankel domain considering the radial heat flow. A more detailed description of the thermal model will be presented in a future work.

Sensitivity analysis of the TDTR signal

We will now discuss about the sensitivity of the TDTR technique to the thermal properties of the sample. This sensitivity study is necessary to find out which parameters can be identified and which ones are correlated. According to Gundrum *et Al*¹⁰, we define the sensitivity function of the TDTR to a parameter p as:

$$S_p = \frac{\partial \left(-\frac{V_{in}}{V_{out}} \right)}{\partial \ln(p)} \quad (3)$$

In the case of a thermally thick layer covered by an aluminum film, the sensitivity functions for the aluminum's parameters (thickness and heat capacity), the layer's parameters (cross-plane thermal conductivity and heat capacity), and the Kapitza resistance between the aluminum film and the layer are plotted in Figure 3.

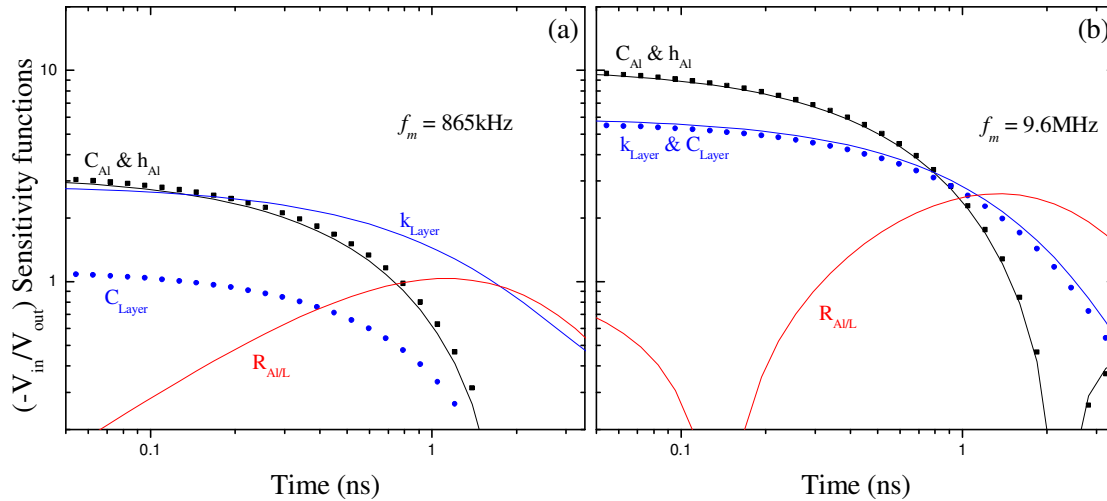


Figure 3. Sensitivity functions to the ratio $(-V_{in}/V_{out})$ for aluminum properties (thickness h_{Al} and heat capacity C_{Al}), Kapitza resistance between the aluminum film and the layer ($R_{Al/L}$), and for the thermally thick layer (thermal conductivity k_{Layer} and heat capacity C_{Layer}) at two different modulation frequencies: (a) 865kHz and (b) 9.6MHz.

The aluminum parameters (thickness and heat capacity), for different modulation frequencies, are correlated and show the highest sensitivity. At short time delay, the surface temperature of the sample is mostly determined by the term $(1/C_{Al} h_{Al})$ according to Taketoshi *et al*¹¹. These curves show the crucial impact of Al layer in the parameter identification process. As the Al heat capacity is fixed at its literature value, the main source of uncertainties comes from the thickness. Variation of $\pm 5\%$ on Al thickness produces roughly a variation of $\pm 10\%$ on the identified thermal conductivity. Usually, this thickness is determined precisely by "Picosecond Acoustic" using the time of flight of the acoustic echo. At high frequencies, the thermal conductivity and heat capacity of the layer are also correlated. In that case, TDTR technique is mostly sensitive to the thermal effusivity of the layer. At lowest frequency, the sensitivity of the heat capacity is reduced compared to the thermal conductivity. Similar remarks about these correlations have been reported by Koh *et al*³. At short time (50ps to 100ps), the TDTR signal is mostly sensitive to the thermal properties of the layer (thermal conductivity and heat capacity). At longer delay (~ 1 ns), the shape of the signal is more sensitive to the Kapitza resistance. Usually, these two last parameters are free in the fitting process. Additionally, we have found that the modulation waveform (sine or square wave) does not affect the sensitivity functions for those parameters.

EXPERIMENTAL RESULTS AND DISCUSSION

As a validation, thermal properties of many well-know materials (GaAs, InP: Fe and Sapphire) were measured for different configurations of TDTR: modulation frequency (for 865kHz and 10MHz) and modulation waveform (sine or square wave). Figure 4 shows the experimental curves and their best fits. Identified thermal conductivity for each configuration is summarized in Table I

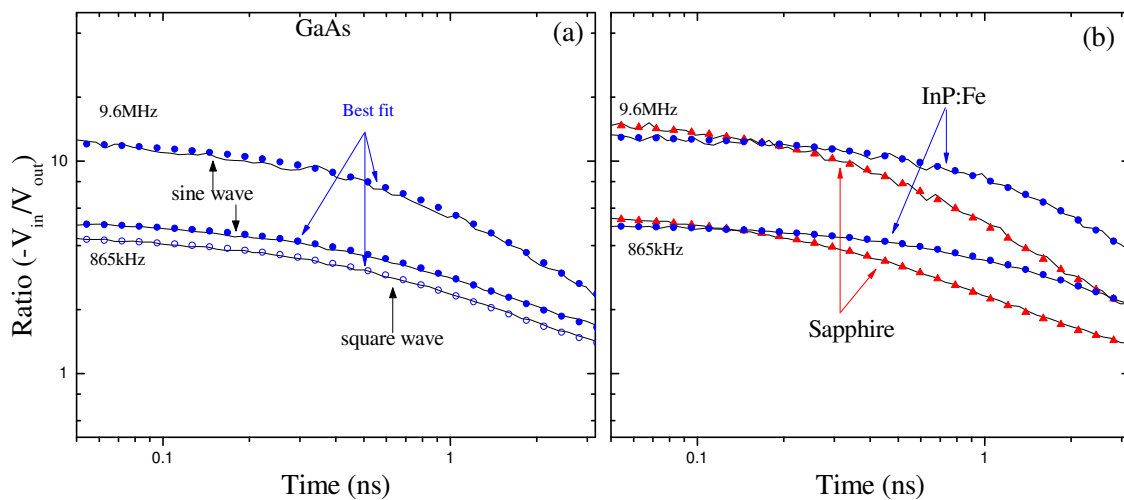


Figure 4. Experimental (solid line) and fitted (circles) ratios for 2 modulation frequencies (9.6MHz and 865kHz). (a) GaAs sample using a sine (filled circles) and a square (empty circles) wave modulation. (b) InP: Fe (blue) and Sapphire samples (red) for a sine wave modulation.

The identified thermal conductivities are in excellent agreement with the values reported in literature.

Table I. Identified thermal conductivity. Uncertainties of TDTR are about 7% at high modulation frequency and about 12% at low modulation frequency¹.

Material	Modulation frequency	Thermal conductivity (W/mK)
GaAs	865kHz (square wave)	52
	865kHz (sine wave)	50
	9.6MHz (sine)	47
Sapphire	865kHz (sine)	41
	9.6MHz (sine)	39
InP: Fe	865kHz (sine)	63
	9.6MHz (sine)	68

We investigated the thermal properties of a series of nanocomposite materials. The samples are composed by a $2\mu\text{m}$ thick layer of InGaAs doped with different concentration of ErAs nanoparticles (0, 0.3, 0.5 and 1.8%). For TDTR measurements, the top surface of the samples is covered by a 45nm aluminum layer.

Figure 5-(a) shows the experimental data and their best fit for 0.3% ErAs. The identified thermal conductivities of the layer are 3.8W/mK and 2.8W/mK for 865kHz and 9.6MHz modulation frequency respectively, the Kapitza resistance is kept constant. In Addition, we also plot on the same graph the theoretical curve assuming a layer's thermal conductivity of 3.8W/mK for 9.6MHz.

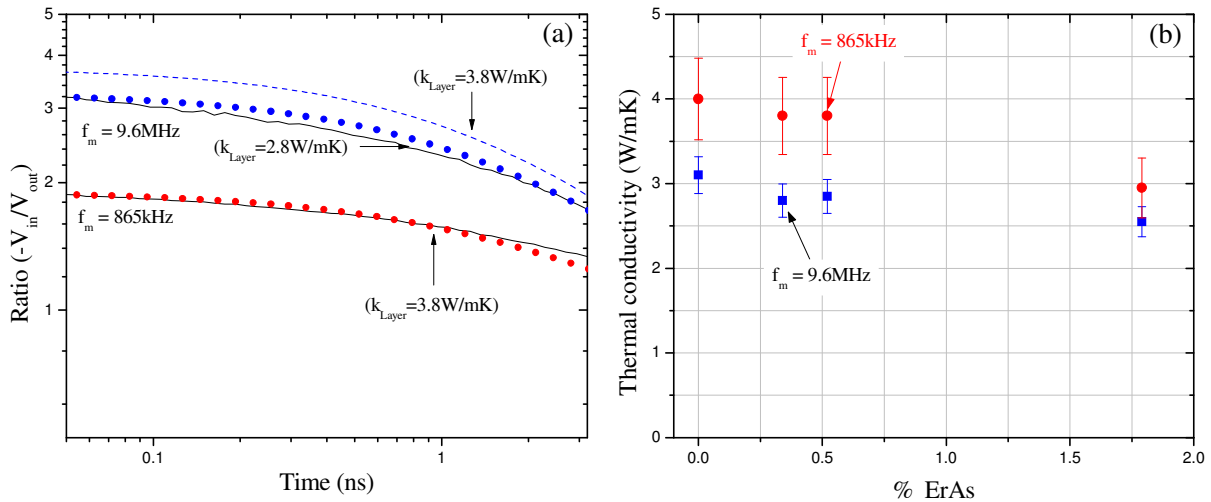


Figure 5. (a) For sample 0.3% ErAs: TDTR experimental ratio (solid lines), fitted curves (full circles), and theoretical curve calculated using at 9.6MHz using a thermal conductivity of 3.8W/mK (blue dashed line). (b) Comparison of the thermal conductivity measurements at 9.6MHz (blue squares) and 865kHz (red circles) versus ErAs concentration.

Figure 5-(b) shows the thermal conductivity of the four samples versus the concentration in ErAs at low and high modulation frequencies. We do observe a reduction in the "apparent" thermal conductivity at high frequency compare to the low frequency modulation in agreement with Koh's observations³. For the lowest ErAs concentration samples (0.5%, 0.3% and 0), the difference in thermal conductivity between the two modulation frequencies is about 30%. For the highest ErAs concentration sample, the thermal conductivity is significantly reduced and the

difference between high and low frequency modulation is also reduced to 15%. This result shows that the "apparent" frequency dependence of the thermal conductivity does not remain constant and might be tuned by changing the concentration in nanoparticles.

CONCLUSION

We present a complete analysis of the Time Domain Thermoreflectance (TDTR) signal and sensitivity functions of the thermal parameters. The modulation of pump pulses is shown as an efficient experimental parameter for heat transfer study. In the case of bulk materials, a pure diffusive model fully describes the signal. For nanocomposite and alloy materials, it fails to explain all the processes observed by TDTR; when ballistic and diffusive mechanisms play an equivalent role, both effects must be taken into account in the thermal modeling. These observations may also bring to light the potential of TDTR to probe the phonon mean free path.

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