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Influence of temperature and modulation frequency on the thermal activation coupling term in laser photothermal theory

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A quantitative analysis of the influence of temperature and modulation frequency on the thermal activation coupling term in laser photothermal theory is performed. Until now it was taken for granted that the coupling term is negligible only in the case of ''relatively low'' temperatures and generally when the equilibrium free-carrier density n_0 satisfies the Sablicov's, Vasil'ev, and Sandomirskii inequality. In this work an extensive computational study of this inequality in the temperature range of 300–1000 K was performed and a precise ''map'' is given concerning the violation of the inequality under various conditions including modulation frequency (0.1–10^6 Hz) and doping concentration (intrinsic to 10^{20} cm^{-3}). Some experimental photomodulated measurements have been performed in order to test the validity of the ''map.'' © *2002 American Institute of Physics.* [DOI: 10.1063/1.1484232]

I. INTRODUCTION

Since the establishment of the photomodulated thermoreflectance (PMTR) technique[1–4] a lot of progress has been made. While the technique was used extensively for room temperature measurements, attempts were also made for PMTR measurements at wide temperature ranges. In 1990 Vitkin *et al.*[5] examined the photomodulated thermoreflectance signal in connection to temperatures obtaining measurements with temperatures ranging between 40 and 300 K. Five years later, Nestoros *et al.*[6,7] made a theoretical analysis of the experimental measurements mentioned above. The analysis of these photothermal results was not complicated due to the fact that at low temperature the ''thermal activation coupling term'' (TACT) is negligible.[8,9] In fact after the analysis of Sablicov's, Vasil'ev, and Sandomirskii (SVS) it is accepted in the literature that this term is always negligible in the case of ''relatively low'' temperatures and low concentration of doping.[8,10] This has always been taken for granted in every publication with no additional questions.

In 1997 Mandelis *et al.*[11] published a primary theoretical study about the spreading of thermoelectronic waves at high temperatures. This study forms the first base for the analysis of the behavior of PMTR at high temperatures with a perspective to develop a new PMTR instrument for measurements at elevated temperatures. In fact the expansion of photothermal theory at high temperatures (300–1400) is a very important objective in the field of characterization of semiconducting films and devices. In this case, the technique offers the possibility of materializing measurements during the annealing process of optoelectronic materials and the preparation of thin films. Such a technique would be welcomed in the microelectronic industry because it would evaluate the materials nondestructively during the annealing process (crystallization process and the electronic activation of the network, in the case of implanted semiconductors). In addition, the changes of the surface of thin films could be characterized at real time. This technique could also be helpful to material scientists for real time characterization during the growth of semiconducting thin films.

The work of Mandelis *et al.*[11] was an attempt to solve a coupling equation system and evaluate the relationship of electronic plasma and thermal wave for high temperatures. In that work the authors solved the plasma and thermal differential equation systems first without the TACT and afterward by taking into account this term. With the comparison of the two solutions they obtained various conclusions concerning the influence of TACT. This interesting analysis gives excellent scientific results but it is not, however, an elegant way to understand when and under which conditions TACT must be ignored. For the development of the PMTR technique at high temperatures one has to prepare a data acquisition and analysis software package where the influence of TACT must be calculated quantitatively *a priori*.

The present work will study quantitatively and analyze the influence of temperature on the thermal activation coupling term in laser photothermal theory. This work aspires to give a clear idea of when and whether the thermal activation coupling term can be neglected or not, in relation with the temperature modulation frequency and free-carrier density. The theoretical simulation in this work can be used as an excellent ''road map'' for PMTR and photothermal radiometry (PTR) software and setups for an easier and more precise analysis and fittings of the experimental results at elevated temperatures. In this article we present the temperature and frequency ranges where the coupling term can be ignored. Section II presents a short review of the theoretical part. We avoided giving all physical coefficients versus temperature in this section in order to keep the main text short enough and attractive to the reader. This information can be found in the reference list. In Sec. III the various simulations are discussed. Comparisons with previous calculations and estimations have also been made. Section IV pre-

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sents some experimental results and critical discussion in light of the photothermal road map. Finally some concluding remarks are presented.

II. PHOTOTHERMAL THEORY

The mechanism of photomodulated thermoreflectance signal in semiconductors can be understood in terms of the induced modulation of the refractive index.[1–4] In general the PMTR signal induced from semiconductors can be divided into two main contributions: one proportional to the surface temperature (thermal-wave effect) and the other proportional to the photoinduced changes in the free carrier density (plasma-wave effect). Thus, the total PMTR induced signal depends on the excess photogenerated carrier plasma density ΔN and on the excursion of local temperature from the background value due to the photothermal effect ΔT. In order to evaluate ΔN and ΔT and obtain the induced photothermal reflectance signal, we must first solve the thermal and plasma equations for an isotropic semi-infinite medium[10]

$$\frac{\partial \Delta N}{\partial t}=D_E\nabla^2\Delta N-\frac{\Delta N}{\tau}+\frac{\partial n_0}{\partial T}\,\frac{\partial T}{\tau}+\Phi\alpha F(t) \tag{1}$$

$$\frac{\partial \Delta T}{\partial t}=D_T\nabla^2\Delta T-D_T\frac{E_g}{\kappa}\,\frac{\Delta N}{\tau}+D_T\left(\frac{h\nu-E_g}{\kappa}\right)\Phi\alpha F(t), \tag{2}$$

where D_E and D_T are the thermal and electronic (ambibolar) diffusivities, T is the recombination lifetime, n_0 is the equilibrium free carrier density, Φ is the incident photon flux, ω is the angular frequency ($\omega=2\pi f$; where f is the modulation frequency), κ is the thermal conductivity, E_g the band gap energy, $h\nu$ is the photon energy of the pump beam, t is the time, α is the optical absorption coefficient of the sample at the laser excitation wavelength, and finally $F(t)$ is the temporal modulation function of the laser beam intensity; Vasil'ev and Sandomirskii[9] first stated that, in the case of harmonic modulation function

$$F(t)=\tfrac{1}{2}(1+e^{i\omega t}), \tag{3}$$

the thermal activation coupling term [the third term on the right-hand side of Eq. (1)] is negligible in the case

$$n_0(T)\ll\frac{\kappa}{k_B D_E}\left[\frac{k_B T}{E_g}\right]^2\frac{1}{1+S^*}\,\omega\tau\sqrt{1+(\omega\tau)^2}=Q(f,T), \tag{4}$$

where S^* is the normalized surface recombination velocity ($S^*=s\mu_E/D_E$, s is the surface recombination velocity, and μ_E is the plasma diffusion length). All estimations until today concerning the above inequality converge to the same results: The quantity of the right-hand side of the inequality has the value close to $10^{16}\ \mathrm{cm}^{-3}$ for $\omega\tau=10^{-4}$ and close to $10^{20}\ \mathrm{cm}^{-3}$ for $\omega\tau=1$. From now on the right term will be referred to as $Q(T,f)$ since it is dependent on temperature T and frequency f. The left term of the inequality is also a function of temperature and is given by the relation

$$n_0(T)=n_{oi}(T)+n_{0e}(T), \tag{5}$$

where n_{oi} is the expression of the intrinsic density of free electrons and n_{oe} is the density of extrinsic dopant. The analytical expressions are given in a work published by Mandelis *et al.*[11] In order to describe the right and the left parts of the above inequality one has to write the dependence of all these factors versus temperature. All these terms have been described in the literature.[11,12–16]

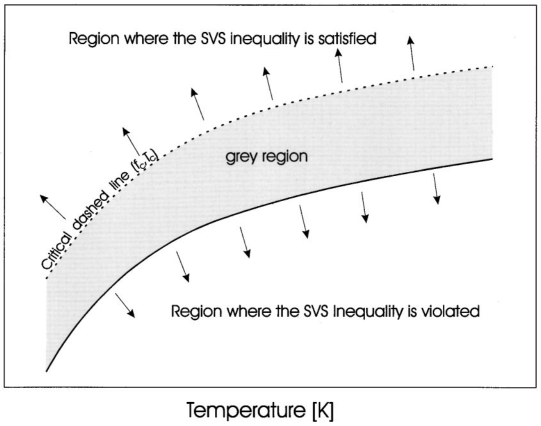

FIG. 1. A schematic of the regions where the inequality SVS is satisfied or violated. The dashed line presents the critical value where the thermal activation coupling term is negligible.

In this article, analytical and computational consideration is given in order to study the temperature and frequency domain of the validation of Eq. (4). This analysis will illuminate some effects concerning the temperature and frequency range violations of the SVS inequality. These results will show when and how the thermal activation term of the differential Eq. (1) can be neglected.

III. THEORETICAL SIMULATIONS AND DISCUSSION

Figure 1 presents characteristic curves that will be discussed below. In fact on the y axis are presented the left side, $n_0(T)$, and the right side, $Q(f,T)$ of the SVS inequality. These terms are given versus temperature. The dashed line presents the critical value where the thermal activation coupling term is negligible. Over the dashed line (the points on the dashed line are 2 orders of magnitude greater than the bold line, thus $n_0\ll Q$), the inequality of SVS is fully satisfied, while the zone between the two lines is a "gray zone." In this gray zone the inequality of SVS is not completely satisfied, but is becoming negligible as we approach the dashed line (for example by increasing the working modulation frequency).

Figure 2(a) presents the variations of $Q(f,T)$ of the inequality for various modulation frequencies and also the density of free carriers n_0 (solid line) versus temperature. The dashed line presents the critical value where the thermal activation coupling term is negligible. In this figure one can see that in the case of intrinsic silicon ($N_d=0\ \mathrm{cm}^{-3}$), at 1 MHz the right term Q varies from $\sim 1\times 10^{23}$ to $\sim 2\times 10^{19}\ \mathrm{cm}^{-3}$ in the range of 300–1000 K, respectively. These values are in good agreement with the literature.[8,10] From this curve one can come to three major conclusions: (a) The $Q(f,T)$ behavior versus temperature is not a monotonic variation. $Q(f,T)$ increases up to $\sim$550 K and then decreases with increasing temperature; (b) The inequality is almost valid in the whole

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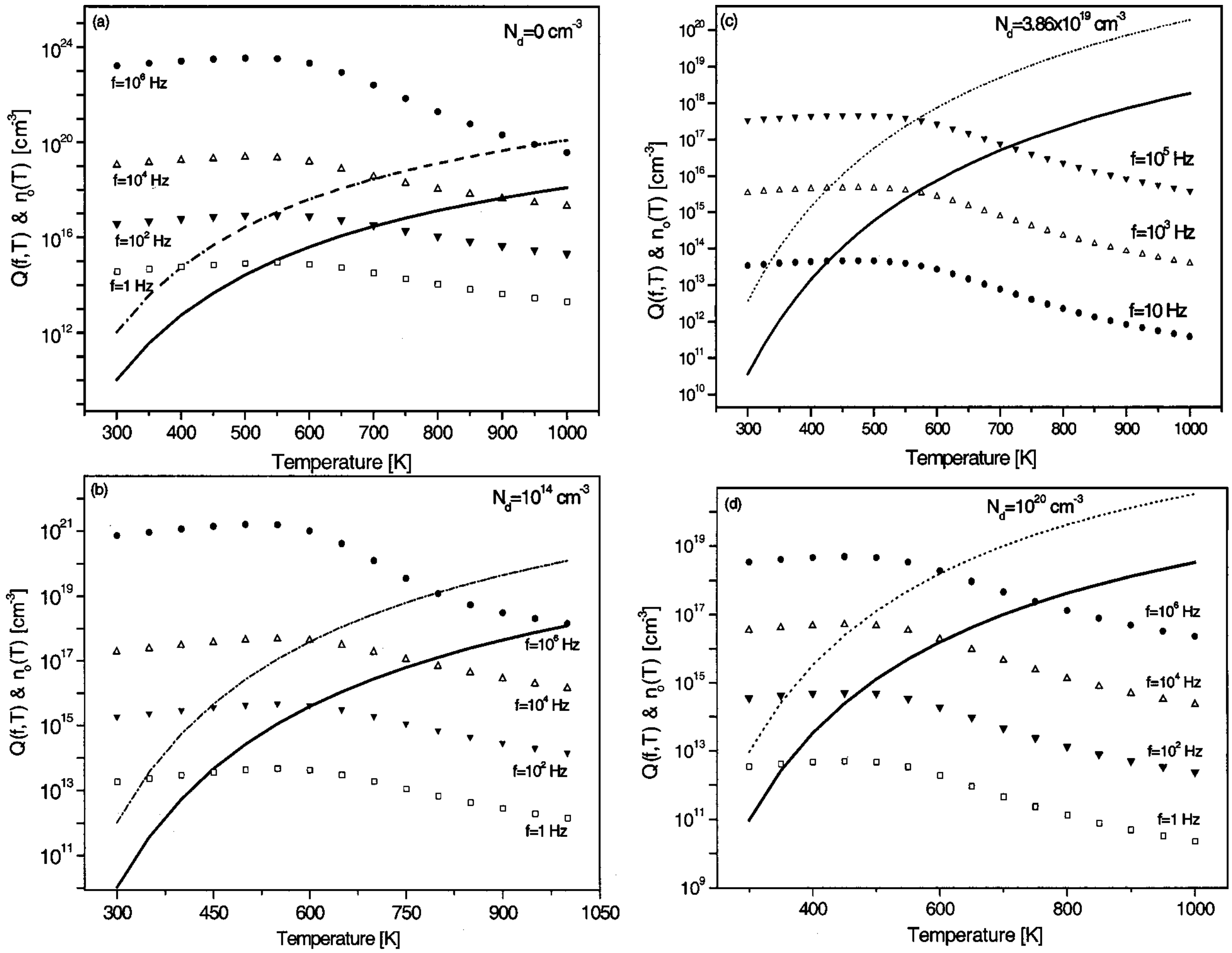

FIG. 2. The right term Q of the inequality vs temperature for various modulation frequencies and the density of free carriers n_0 (solid line). The dashed line presents the critical value where the thermal activation coupling term is negligible. Over the dashed line the inequality of SVS is fully satisfied: (a) intrinsic silicon $N_d=0$; (b) doping density $N_d=10^{14}\ \mathrm{cm}^{-3}$; (c) doping density $N_d=3.86\times 10^{18}\ \mathrm{cm}^{-3}$; and (d) doping density $N_d=10^{20}\ \mathrm{cm}^{-3}$.

temperature range except for temperatures over 950 K; and (c) The temperature range of the validation of SVS inequality is limited with increasing temperatures and decreasing modulation frequency. For example, at $f=100$ Hz over 550 K we have a violation of the SVS condition.

Figures 2(b) and 2(c) present the variations of the right term Q of the inequality for various modulation frequencies and also the density of free carriers n_0 (solid line) versus temperature for samples doped at concentrations of 1×10^{14} and $3.86\times 10^{18}\ \mathrm{cm}^{-3}$ respectively. One can see that the range of violation of the SVS inequality is now larger than in the case of intrinsic silicon. For example at 1 MHz the critical temperature appears at ~800 K for the $10^{14}\ \mathrm{cm}^{-3}$ sample and at ~900 K for the $3.86\times 10^{18}\ \mathrm{cm}^{-3}$ sample [see Fig. 2(c)].

Figure 4(d) is more representative of the influence of the thermal activation coupling term on the photothermal theory. The right term of the inequality for various modulation frequencies and the density of free carriers n_0 (solid line) versus temperature for doping concentration $N_d=10^{20}\ \mathrm{cm}^{-3}$ are presented. In this figure one can note that, for example, at room temperature one must use a modulation frequency over 1 Hz in order to satisfy the SVS condition and to be able to neglect the TACT. At high frequencies such as 1 MHz, the SVS inequality is satisfied up to 600 K. Over this temperature one has to take into account the thermal activation coupling term in order to use the photothermal theory for various experimental fittings.

In order to give the readers of this work a clearer map concerning the temperature and frequency range versus concentration doping and to see where we do not have a violation of SVS conditions we present Figs. 3(a) and 3(b). In Fig. 3(a), T_c is defined as the critical temperature over which the SVS condition is violated. Simulations are performed using frequencies $f=10^2$, 10^4, and 10^6 Hz. One can see that at 10^4 Hz and for a concentration of $10^7\ \mathrm{cm}^{-3}$ the SVS can be satisfied for temperatures lower than ~680 K, while for concentration equal to $10^{15}\ \mathrm{cm}^{-3}$ this critical temperature decreases to ~600 K. In Fig. 3(b) the critical frequency f_c versus doping concentration is presented. The simulations are performed taking as working temperatures $T=300$, 400, and 500 K. For all the data pairs (N_d, fc) lower than the solid line we have a violation of the SVS condition. One can see that at room temperature for high-doped silicon sample ($N_d>10^{18}\ \mathrm{cm}^{-3}$) by working at frequencies over 0.1 Hz one can satisfy the SVS condition and, thus, neglect the TACT. On the other hand with increasing working temperature the condition can be satisfied at higher frequencies. As clearly

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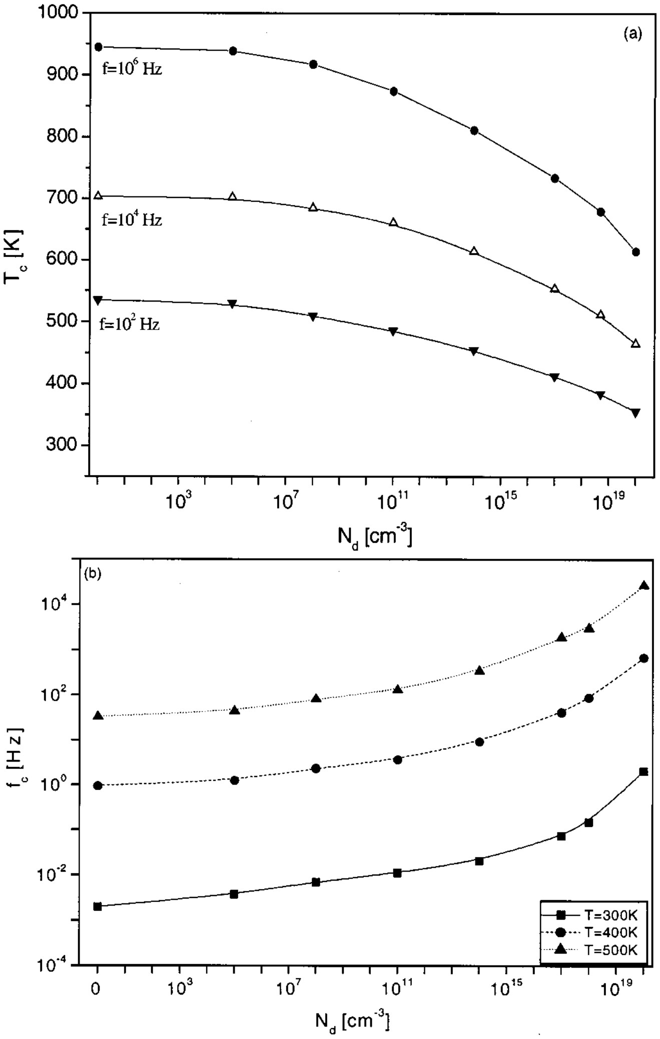

FIG. 3. (a) Critical temperature T_c vs doping concentration at $f = 10^2$, 10^4, and 10^6 Hz and (b) critical modulation frequency f_c vs doping concentration at $T = 300$, 400, and 500 K.

seen in the figure at a temperature of 400 K the SVS condition can be satisfied at frequencies larger than ~600 Hz and for 500 K at frequencies larger than 26 kHz. These results for highly doped silicon samples are in agreement with Sablicov and Sandormiskii's estimations.[10]

We must, however, point out that some of the results presented above are in agreement with some of the results presented by Mandelis *et al.*[11] These authors found that for $N_d > 10^{17}$ cm^{-3} $Q(T,f)$ is almost always lower than $n_0(T)$ and therefore, there is a violation of the SVS condition. This discrepancy is in contradiction to the work of Vasil'ev and Sandomirskii[9] since they estimated $Q(f,T)$ to be on the order of $10^{18}-10^{20}$ cm^{-3} for $\omega\tau = 1$. Nevertheless, since the best way to test a theory is the experimental verification, one can refer to some work performed in the past on high implanted (and annealed) silicon samples. For example, Nestoros *et al.*[6] used the photothermal theory to interpret their experimental results up to room temperature. By neglecting TACT they have fitted very well their experimental data both for light as well as for heavily implanted silicon. The same success was met in the past by several other researchers[6,17–20] who managed to interpret their experimental results for heavily doped silicon samples taken at room temperature by neglecting the thermal activation coupling term. All this experimental testing reinforces the finding of the present work.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Experimental setup

In this article we present some data obtained from the extension of the conventional laser-induced photomodulated thermoreflectance method to elevated temperature. The experimental configuration is similar to the one employed by Rosencwaig *et al.*,[2] with the addition of the temperature sensing–controlling equipment. The sample is placed in the experimental high temperature chamber. The sample holder is isolated by a ceramic element in order to limit the heat only around the sample. The chamber was equipped with suitable inlet and exhaust gas ports in order to allow a nitrogen gas to flow through the chamber during the photothermal measurements in order to avoid any oxidation of the semiconducting surface during the high temperature measurements. On the cell, optical access is also available through a quartz window. The periodic sample heating was obtained with an Ar+ laser beam (488 nm), modulated by an acousto-optic modulator. This beam of incident power is approximately 25 mW and was focused normally onto the sample surface to a spot size of about 20 μm. The changes in the reflectivity of the HeNe laser beam (632.8 nm) were measured by a photodiode.

B. Results at elevated temperatures

The examined samples were *p*-type (6 Ω cm) silicon wafers ⟨100⟩. One of them was implanted with a dose of 1×10^{16} cm^{-2} and then was annealed at 1100 °C in an inert N_2 atmosphere for 1 h. The second sample was nonimplanted and nonannealed.

Figure 4(a) shows the PMTR signal amplitude as a function of temperature between 300 and 620 K for a nonimplanted and nonannealed silicon sample for two different modulation frequencies: 1 and 100 kHz. First, we note that the dependence of the PMTR amplitude with modulation frequency is obvious. As was expected the signal decreases drastically with the increase of the working modulation frequency. This confirms the theoretical simulations presented in the past.[6] Another important point is the excellent agreement between experimental points and theoretical simulation both for 1 and 100 kHz. This agreement was expected. In fact by looking at Figs. 2(a) and 2(b) where the doping is zero or very low, as is the case for the nonimplanted sample, theoretical simulation where TACT is negligible can fit very well the experimental data of a low doped silicon sample between 300 and 620 K even for low frequencies such as 1 kHz.

Figure 4(b) shows the PMTR signal as a function of temperature for a very high implanted sample (dose $= 1 \times 10^{16}$ cm^{-2}) and high annealed sample at 1100 °C. The junction depth of this silicon sample implanted at this dose has been calculated to be 2.59 μm. Thus the doping dose of the wafer is approximately 3.86×10^{19} cm^{-3}. As was

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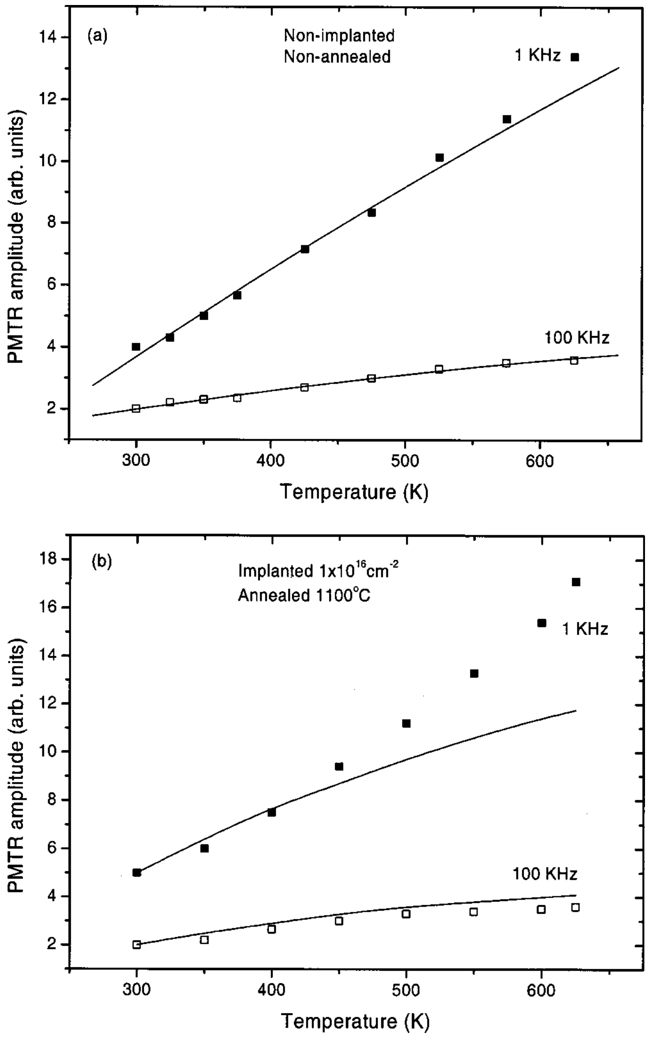

FIG. 4. (a) Experimental results and theoretical fittings (solid lines) of the PMTR amplitude as a function of temperature at two different modulation frequencies (1 and 100 kHz): (a) for the nonimplanted and nonannealed silicon sample and (b) for the sample implanted at 1×10^{16} cm^{-2} and annealed at 1100 °C.

pointed out in the last paragraph the signal decreases drastically with the increase of the working modulation frequency. On the other hand, one can note the relative good fitting for 100 kHz, as was expected. By looking carefully at the theoretical Fig. 2(c) one can note that at 100 kHz in the range of 300–620 K the experimental curves are sited in the region where the SVS inequality is almost satisfied, therefore simulation without the TACT term results in a relatively good agreement with the experimental points. On the other hand, at low modulation frequency this is not the case, as it is shown that the ‘‘best fitting’’ of the experimental results is not satisfied. There is a discrepancy, which is more important at higher temperatures, especially over 450 K. The ‘‘photothermal map’’ presented in this article foresaw this discrepancy. In fact from Fig. 2(c) one can point out that at 1 kHz, if the theoretical model does not take into account TACT it enters the gray zone and it cannot fit the experimental PMTR data obtained at 1 kHz. Over 500 K the discrepancy is very high since we are in the region of a total violation of the SVS inequality as is shown in Fig. 2(c).

V. CONCLUSIONS

In conclusion PMTR measurements form an interesting nondestructive evaluation technique for studying optoelectronic parameters in a wide temperature range. An analysis of the SVS inequality versus temperature and modulation frequency has been performed. It has clearly been shown at which temperature range one can neglect the thermal activation coupling term and, thus, analyze the experimental results using the exact solution of the diffusion equation system obtained by the Hankel transformation. Furthermore, as it was expected it has been shown that the doping density plays a major role and has to be taken into consideration in order to avoid the range of violation of the SVS inequality. The range at which there is not violation of the SVS inequality has been confirmed experimentally by performing PMTR measurements at elevated temperatures. The main results of this work can be summarized as follows:

(1) In the case of intrinsic silicon the SVS inequality is valid from low temperatures up to 900 K, by using practical working modulation frequencies.
(2) For highly doped silicon materials the SVS inequality remains valid only for special temperature and frequency conditions.
(3) For intermediate doping one has to take into account Figs. 2(a)–2(d) presented in this work.
(4) Experimental results obtained in the range of 300–620 K have shown the importance of the ‘‘photothermal map’’ both from research in academic institutions as well for the material and microelectronic industry.

Finally, it is important to note that an analysis of the SVS inequality in a wide range of temperature and modulation frequency has been performed and this is expected to help toward the temperature analysis of photothermal results. This work will also help researchers in the expansion of the PTR and photothermal deflection techniques for measurements at elevated temperatures.

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