## Dependence of the photoreflectance of semi-insulating GaAs on temperature and pump chopping frequency

H. Shen, Z. Hang,<sup>a)</sup> S. H. Pan,<sup>b)</sup> and Fred H. Pollak<sup>a)</sup> Physics Department, Brooklyn College of the City University of New York, Brooklyn, New York 11210

J. M. Woodali

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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The amplitude of the photoreflectance (PR) spectra of the direct gap of semi-insulating GaAs has been studied as a function of pump chopping frequency (2-4000 Hz) and temperature (25-198 °C). We have been able to deduce a temperature-dependent trap time and hence trap activation energy of  $0.70 \pm 0.05$  eV. Our experiment demonstrates that PR can be used as a contactless method to study deep traps in semiconductors, analogous to deep level transient spectroscopy.

Photoreflectance (PR), 1-6 a contactless form of electromodulation (EM), is rapidly becoming an important characterization method to study semiconductors<sup>1-11</sup> (bulk or thin films) and semiconductors microstructures 12-19 such as superlattices, quantum wells, and heterostructures. In PR the electric field in the material is modulated by the photoinjection of electron-hole pairs by a secondary (pump) beam chopped at frequency  $\Omega_m$ . It has been demonstrated that PR is indeed a form of electroreflectance (ER)<sup>1,2,6-8</sup> yielding in bulk or thin-film material sharp third-derivative spectra (low-field regime) or Franz-Keldysh oscillations for large modulation or large built-in dc electric fields.<sup>7,8</sup> In quantum structures PR yields first-derivative line shapes for uncoupled levels<sup>13</sup> and third-derivative spectra for tunneling states.<sup>19</sup> While considerable information has been gained from the sharp, derivative features of PR (and ER), relatively little attention has been paid to the fact that electromodulation can be used as an important optical probe of electric fields.<sup>1,2,7,8,20-22</sup> Information can be gained from studies of the other variable of PR (or ER) such as modulation frequency,<sup>9,10,14,20</sup> pump beam intensity,<sup>6</sup> wavelength,<sup>23</sup> etc. Despite its utility, the mechanism of PR is not fully understood. Several experiments have demonstrated that PR is due to the modulation of the electric field through a recombination of minority species with charge in traps.<sup>1-3,6</sup> Thus PR can be closely related to capacitance-voltage techniques such as deep level transient spectroscopy (DLTS).<sup>24</sup> However, the details of these traps have not been investigated. A knowledge of the nature of these states would elucidate the fundamental mechanism of PR. In addition, it could lead to the development of PR as a contactless (and hence in situ) method for studying these trap states.

In this letter we demonstrate that PR can be used to gain detailed information about the lifetimes and activation energies of deep trap states in semiconductors. We have studied the PR spectra ( $\Delta R/R$ ) of the direct gap ( $E_0$ ) of semi-insulating (SI) (100) GaAs as a function of  $\Omega_m$  (2-4000 Hz)

and temperature (25–198 °C). For a given temperature (T) the PR line shape is independent of  $\Omega_m$  and is a third-derivative (3d) line shape appropriate to low-field EM.<sup>1,2</sup> To verify the 3d nature of the PR spectra, we have also performed thermoreflectance (TR), a first-derivative spectroscopy.<sup>1,2</sup> There are, however, significant changes in the amplitude of the PR signal as a function of both  $\Omega_m$  and T. From the dependence of  $\Delta R / R$  on these parameters, we have been able to deduce a temperature-dependent trap time  $\tau(T)$  and hence a trap activation energy  $\Delta E = 0.70 \pm 0.05$  eV. This value in GaAs corresponds to either the surface states responsible for Fermi level pinning<sup>25</sup> or EL2.<sup>26</sup>

The PR apparatus has been described in the literature.<sup>27</sup> The pump beam was the 6328 Å line of a 1 mW He-Ne laser. The power density was about 10 mW/cm<sup>2</sup>. Modulation was accomplished by mechanically chopping the pump beam. Thermoreflectance was achieved by passing a square pulse current along a conducting strip on the front surface of the sample. The resistance of the strip was about 2  $\Omega$  and the peak-to-peak current was about 200 mA. Both PR and TR signals were observed from the same spot on the sample. The GaAs was undoped, SI material grown by the liquid-encapsulated Czrochralski method.

Shown in Fig. 1(a) are the PR spectra in the region of  $E_0$  for  $\Omega_m = 5$  Hz (dotted line) and 4000 Hz (dashed line) at T = 167 °C. The latter spectrum has been magnified by a factor of 4 for comparison purposes. The solid line is a leastsquares fit to the Aspnes third-derivative functional form for a three-dimensional critical point.<sup>2</sup> Note that the two line shapes are independent of  $\Omega_m$ . The same is true for the spectra at the other temperatures used in this study. In addition, all PR spectra were taken under conditions of low-field modulation. The TR spectrum at  $\Omega_m = 5$  Hz is displayed by the dotted line in Fig. 1(b). The dot-dashed line is the second derivative of the  $E_0$  TR spectrum. Note that this second derivative has the same line shape as the PR spectra of Fig. 1(a). Since TR is a first-derivative spectroscopy,<sup>1,2</sup> this confirms the third-derivative, and hence EM, nature of the PR spectrum even at 5 Hz. In the TR spectrum there is a large feature below  $E_0$  not seen in the PR data. At present we do not understand this peak, but it may be due to an impurity level.

<sup>&</sup>lt;sup>a)</sup> Also at Graduate School and University Center of the City University of New York, New York, NY 10036.

<sup>&</sup>lt;sup>b)</sup> Permanent address: Department of Physics, Nankei University, Tianjin, China.



FIG. 1. (a) Photoreflectance spectra of GaAs around  $E_0$  for pump chopping frequencies of 5 Hz (dotted line) and 4000 Hz (dashed line). The solid line is a fit to the Aspnes third-derivative functional form. (b) The thermoreflectance spectrum of GaAs around  $E_0$  at a modulation frequency of 5 Hz (dotted line). The dot-dashed line is the second derivative of the thermoreflectance spectrum of  $E_0$ .

In Fig. 2 we have plotted the amplitude of the PR signal,  $\Delta R(\Omega_m)/R$ , as a function of  $\Omega_m$  for several values of T. For T in the range 107–198 °C, there is a strong dependence of  $\Delta R/R$  on  $\Omega_m$  in the region between 50–1000 Hz.<sup>9,10,14</sup>

The variation of  $\Delta R / R$  with  $\Omega_m$  can be accounted for on the basis of the following considerations. The chopped pump radiation can be considered as a square wave source. When light impinges on the sample, electron-hole pairs are created. These charges are then free to fill traps and modify the electric field strength. We assume that these excess carriers abruptly change the built-in electric field. Reference 5 has dem-



FIG. 2. Amplitude of  $\Delta R(\Omega_m)/R$  as a function of chopping frequency  $\Omega_m$  for several temperatures. The solid lines are least-squares fits to Eq. (1).

onstrated that the response time is less than 100  $\mu$ s. When the light is switched off, the trap population and the electric field strength decay with a characteristic time  $\tau$ , causing a restoration of the original potential. Thus for chopping frequency  $\Omega_m$  it can be shown that the Fourier component of the PR intensity,  $\Delta R(\Omega_m)/R$ , is given by<sup>10</sup>

$$\frac{\Delta R(\Omega_m)}{R} = \sum_{i=1}^n \left(\frac{\Delta R(0)}{R}\right)_i f(\Omega_m \tau_i), \qquad (1a)$$

$$f^{2}(\Omega_{m}\tau_{i}) = \frac{4 + \Omega_{m}^{2}\tau_{i}^{2}[1 - \exp(-\pi/\Omega_{m}\tau_{i})]^{2}}{4(1 + \Omega_{m}^{2}\tau_{i}^{2})}, \quad (1b)$$

where  $\tau_i$  is the characteristic time constant of the *i*th trap state and  $[\Delta R(0)/R]_i$  is the PR signal produced by the modulation of the *i*th trap state in the limit of  $\Omega_m \to 0$ . Based on the experimental results of Fig. 2, we assume that in the frequency range of our experiment (a) n = 2 and (b)  $[\Delta R(0)/R]_2 f(\Omega_m \tau_2) \ll [\Delta R(0)/R]_1 f(\Omega_m \tau_1)$ , with  $\tau_1 > \tau_2$ .

Plotted by the solid lines in Fig. 2 are least-squares fits of Eq. (1) to the experimental data for 107 °C < T < 167 °C. From this analysis we have been able to evaluate  $\tau_1(T)$  in this temperature range.

Plotted in Fig. 3 is  $\ln(\tau_1 T^2)$  as a function of 1000/T in the temperature range  $107 \,^{\circ}\text{C} < T < 167 \,^{\circ}\text{C}$ .<sup>26</sup> Representative error bars are shown. The solid line is a least-squares fit to a linear function, yielding in activation energy<sup>26</sup>  $\Delta E = 0.70 \pm 0.05$  eV and an intercept of  $-14 \pm 2$ . Note that the points correspond quite well to a straight line.

It is possible that the results of Fig. 2, i.e., decrease in  $\Delta R / R$  with  $\Omega_m$ , might be due to a combination of TR (at low  $\Omega_m$ ) and PR. That is, the pump laser beam could be heating the sample producing a TR effect at low  $\Omega_m$ . However, Fig. 1 shows that this is not the case since the PR signal (a) does not change line shape with  $\Omega_m$  and (b) is indeed a 3d (i.e., EM) signal.

The activation energy  $\Delta E = 0.7$  eV corresponds to two different types of trap states that may occur in GaAs, i.e., surface states (responsible for Fermi level pinning)<sup>25</sup> or EL2.<sup>26</sup> The intercept of Fig. 3 corresponds to cross sections which also are appropriate for either of these trap states.



FIG. 3. Plot of  $\ln(\tau_1 T^2)$  as a function of 1000/*T*. The solid line is a least-squares fit to a linear function.

Thus at the present time we cannot determine which one is responsible for the PR. It is also possible that both mechanisms contribute in the range of our experimental measurements. Further work is needed in this area.

Figure 2 shows that PR in SI GaAs is due to trap states with different activation energies. For example, the 25 °C  $\Delta R / R$  decreases sharply at about  $\Omega_m \approx 10$  Hz, rises somewhat in the range 100 Hz <  $\Omega_m < 1000$  Hz, and then decreases. Thus in addition to the 0.7 eV trap state there are at least two other mechanisms responsible for the PR effect in this temperature range. Extension of these experiments to higher modulating frequencies and different temperature ranges would thus yield information about other trap states in this material.

In summary, we have studied the dependence of the amplitude of the PR signal from SI GaAs as a function of modulation frequency and temperature. We have been able to obtain a temperature-dependent trap time and hence trap activation energy of 0.7 eV for this material in the range of our experimental measurements. This value corresponds to either surface states responsible for Fermi level pinning or EL2. Further work is needed to clarify the role of these two processes. In addition, our experiment shows that other trap states also contribute to the PR. Thus we have obtained important new insights into the PR mechanism. Also, our results demonstrate that PR can be used as a contactless (and hence *in situ*) method for obtaining information about deep trap states analogous to DLTS.

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