Noncontact photothermal infrared radiometric deep-level transient spectroscopy of GaAs wafers

A. Mandelis, ^{a)} R. A. Budiman, M. Vargas, ^{b)} and D. Wolff *Photothermal and Optoelectronic Diagnostics Laboratory, Department of Mechanical Engineering,* University of Toronto, Toronto M5S 1A4 Canada

(Received 28 November 1994; accepted for publication 5 July 1995)

A novel infrared photothermal radiometric deep-level transient spectroscopy (PTR-DLTS) has been developed for semiconductor noncontact characterization and applied to GaAs wafer diagnostics. The technique is based on rate-window detection combined with wafer temperature ramping. Unlike other deep-level methodologies, PTR-DLTS should be easily implemented remotely for on-line or off-line impurity/electronic defect diagnostics and enjoys high spectral peak separation and spatial resolution limited only by the pump laser beam focus ($\geq 1 \mu m$). The impurity level in a Cr-compensated semi-insulating GaAs wafer has been detected at \sim 375 K using the 514 nm line of an Ar⁺ laser. A Te-doped GaAs sample exhibited behavior consistent with photoinjected carrier lifetime enhancement due to surface state (trap) thermal filling at elevated temperatures. © 1995 American Institute of Physics.

In this letter we report a feasibility study of the recently introduced photothermal rate-window detection technique to deep electronic level diagnostics in semiconductors. The motivation for introducing the present novel methodology was the limited availability of existing noncontact (and especially remote) deep-level transient spectroscopic techniques.²⁻⁴ These techniques tend to be quite restrictive in their applications' scope. For instance, laser-microwave deep-level transient spectroscopy (LM-DLTS) requires, for detection, the presence of free carrier concentrations within limits deter- $8.3 \times 10^{10} \le n \le 2.6 \times 10^{13} \text{ cm}^{-3}$. mined Furthermore, the spatial resolution of LM-DLTS is limited by the microwave probe-beam spotsize [on the order of 10-20 mm (Ref. 3)], which is usually too large for device structure imaging compared to the laser carrier photoinjection beam spotsize (on the order of 50–100 µm and possibly much less, $\sim 1-5 \mu m$). On the other hand, surface photovoltage deep-level transient spectroscopy (SPV-DLTS) is virtually a contacting technique, owing to the requirement for extreme closeness [0.2–0.5 mm (Ref. 5)] between the wafer surface and the transparent conducting pick-up electrode required for adequate capacitve coupling. Furthermore, the surface photovoltage technique may possibly exhibit practical difficulties in performing rapid scanning imaging of the wafer surface as it requires perfect constancy of the wafer surface-electrode distance to yield meaningful relative signals. Photothermal rate-window spectrometry of semiconductors has exhibited very good sensitivity to various impurity species in Si (Ref. 6) and in this letter we report its extension to a full deep-level spectroscopic technique in GaAs.

The infrared photothermal radiometric deep-level transient spectroscopy (PTR-DLTS) instrumentation described in this letter was described elsewhere within the context of ratewindow detection.⁶ Lock-in rate-window detection was preferred over a dual-gate boxcar integrator due to the higher signal-to-noise ratio afforded by the lock-in amplifier (LIA).⁷ The optical pump was an Ar^+ laser emitting ~ 1 W at 514 nm. The modulation square-wave form of the laser-beam intensity was controlled by an acousto-optic modulator (AOM). Temperature ramps were introduced by a heater/ temperature controller with heating rates programmed by the computer. The PTR-DLTS apparatus further allowed the acquisition of optical conductance deep-level transient spectra (O-DLTS) with the use of a metallic needle probe, a voltagepulse generator (the same as the one driving the AOM) and a Boonton Model 7200 Capacitance Meter, the output of which was connected to a second LIA. Three samples were examined: a Cr-compensated semi-insulating (SI) sample; an *n*-GaAs, Cr-compensated, and Te-doped $(8 \times 10^{17} \text{ cm}^{-3})$ wafer; and a Au-coated GaAs wafer used as a purely thermal-wave photothermal radiometric (PTR) signal wave form generator for comparison purposes. Temperature scans were performed in the range 310-400 K, which includes the O-DLTS peak at \sim 375 K due to the Cr-level in either p- or n-type GaAs.8 PTR rate-window scans of the GaAs:Cr were obtained, clearly indicating an optimal duty cycle τ_n/T_0 in the range 40%-60%, where τ_p is the pulse duration and T_0 is the pulse repetition period. The PTR-DLTS spectra of the GaAs:Cr and the GaAs:Te samples were obtained under identical experimental conditions with $\tau_p = 15 \mu s$ and repetition period 30 μ s, Fig. 1. In GaAs:Cr a peak consistent with the Cr level in GaAs appeared at \sim 370 K, Fig. 1(a), the exact position of the peak depending on the actual T_0 chosen; significant peak shifts to lower temperatures were observed when the pulse repetition period was varied between 30 and 90 μ s. The position of the rather flat GaAs: Te peak is at \sim 320 K, Fig. 1(b), the peak separation between the two samples attesting to the high spectral resolution of PTR-DLTS. Te doping in GaAs is not known to produce deep electronic levels. Furthermore, the GaAs:Te peak shifted in the opposite direction from that of the GaAs:Cr sample with varying T_0 . Therefore, the nature of this peak must be quite different from that exhibited by GaAs:Cr. The GaAs:Cr peak is broader than those obtained by Martin et al. 8 using capaci-

a)Electronic mail: mandelis@me.utoronto.ca

b)On leave from IFUG Universidad de Guanajuato, Mexico.

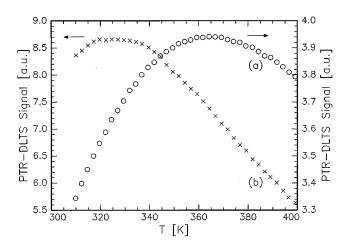


FIG. 1. PTR-DLTS spectrum of (a) Cr-compensated SI GaAs; and (b) of Cr-compensated and Te-doped n-GaAs. $\tau_p = 15~\mu s;~T_0 = 30~\mu s.$

tance O-DLTS, which is partially due to the fact that a LIA, rather than a dual-gate boxcar integrator was used for our measurements: the LIA affords high signal-to-noise ratio (SNR) and broadened DLTS peaks, whereas the boxcar integrator yields a relatively poor SNR, but sharper peaks. No DLTS peak could be found within the $T_0 < 100~\mu s$ range (which characterizes the spectra of Fig. 1) in the n-GaAs wafer coated with a $\sim 1000~\text{Å}$ thick Au layer. Further investigation showed that there is a peak for this sample in the 1 ms range, which is purely due to thermal conduction in the Au thin film, following optical absorption and the subsequent nonradiative deexcitation.

A major advantage of PTR-DLTS over DLTS methods requiring electrical contacts, such as O-DLTS, is in the strength of the signal: The latter methods exhibit a much lower signal response level from intrinsic and other high-resistivity materials, such as SI-GaAs. Neither capacitance, nor conductance O-DLTS signal could be obtained for the GaAs:Cr wafer for $T_0 < 100~\mu s$. Only for $T_0 \ge 500~\mu s$ were we able to obtain a high enough SNR in the conductance (but not in the capacitance) channel, so as to record an O-DLTS spectrum as shown in Fig. 2, in agreement with

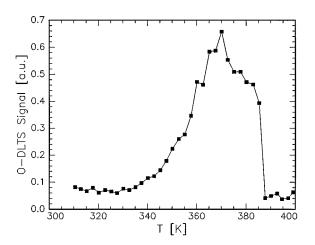


FIG. 2. Conductance O-DLTS spectrum of GaAs:Cr. τ_p =250 μ s; T_0 =500 μ s. Applied bias voltage: 0 V.

earlier reports.⁸ The signal level was more than 20 times lower than the PTR-DLTS. Nevertheless, the peak is well resolved in the 370 K range, in good positional agreement with the spectrum (a) of Fig. 1. Generally, it was observed that GaAs PTR-DLTS spectra yield optoelectronic information in the $T_0 < 100~\mu s$ range. Longer T_0 ranges, however, yield thermal-conduction transient wave forms and PTR-DLTS "spectra" characterized by peak shifts to higher temperatures with increased T_0 . This trend was similar to that observed with the GaAs:Te wafer in the PTR-DLTS spectrum (b) of Fig. 1. The $T_0 < 100~\mu s$ transient signal wave forms were quite different from thermal conduction transients, $T_0 < 100~\mu s$ are due to electronic, rather than thermal, phenomena.

The PTR-DLTS signal from semiconductors due to optically injected carriers originates from the contributions of each free excess carrier to the black-body emission measured by the mercury-cadmium-telluride (MCT) detector. For opaque semiconductors, such as the Ar-laser-excited uncoated GaAs samples in this work, if a single bulk impurity level and measurable carrier recombination at surface defect sites are involved, the PTR transient signal has been shown to have the following functional dependence:

$$\begin{split} S_1(t,\tau,\tau_s) &= \mathrm{constant} \times \left[\sqrt{\tau/\tau_s} \ \mathrm{erf}(\sqrt{t/\tau_s}) \right. \\ &+ e^{-t/\tau} W(\sqrt{t/\tau_s}) - 1 \left. \right], \quad t \leqslant \tau_p \,; \\ S_2(t,\tau,\tau_s) &= S_1(t,\tau,\tau_s) - S_1(t-\tau_p\,,\tau,\tau_s), \quad t \geqslant \tau_p \,, \end{split}$$

where $\tau(T)$ and $\tau_s(T)$ are the semiconductor bulk and surface carrier lifetimes, respectively, and W(x) is a function encountered in time-domain diffusion-type problems:

$$W(x) = e^{x^2} \operatorname{erfc}(x). \tag{2}$$

The validity of the single-level assumption was verified by fitting into Eq. (1) the PTR decay signal following the pulse cut-off versus time for both GaAs:Cr and GaAs:Te wafers. Two distinct slopes were observed and excellent fits were obtained which allowed the unambiguous estimation of τ_s from the early decay slope ($\tau_s \sim 2~\mu s$), and the estimation of τ from the late slope ($\tau \sim 20~\mu s$). The temperature dependence of the lifetimes under low injection conditions was modeled by use of the Shockley–Read–Hall (SRH) theoretical formalism. Assuming a trap density much smaller than the equilibrium intrinsic carrier density, the SRH formula reduces to 12

$$\tau(T_m) \equiv \text{constant} \times T_m^{-2} \exp(\Delta E/kT_m),$$
 (3)

where T_m is the temperature of the DLTS maximum (peak) and $\Delta E \equiv E_T - E_v$ (for p-type materials), or $\Delta E \equiv E_c - E_T$ (for n-type materials). Here the subscripts (V,C,T) stand for valence band, conduction band, and trap/impurity energy level, respectively. The PTR-DLTS maxima for several pulse repetition periods from the GaAs:Cr and GaAs:Te wafers were plotted in an Arrhenius plot in Fig. 3. Consistently with the direction of the PTR-DLTS peak shifts, the signs of the two slopes were opposite. For the GaAs:Cr sample, an activation energy of $\Delta E = 0.73$ eV was extracted from the slope

Appl. Phys. Lett., Vol. 67, No. 11, 11 September 1995

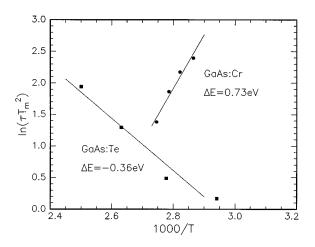


FIG. 3. Arrhenius plots of the PTR-DLTS temperature dependent lifetimes from the peak positions of several spectra of GaAs:Cr and GaAs:Te samples obtained with τ_p/T_0 =0.5 and T_0 =30, 50, 70, and 90 μ s.

of the curve. This value for the Cr-level activation energy in GaAs is in excellent agreement with the 0.6-0.88 eV value range obtained using electrical capacitance deep-level transient spectroscopy (E-DLTS)¹² and O-DLTS.⁸ Furthermore, both those conventional DLTS techniques measure carrier lifetime temperature dependences which *decrease* with increasing T, and this is also the case with PTR-DLTS. This lifetime behavior can be considered to be characteristic of thermal activation (ejection) processes from Cr traps as thermal energy from the lattice becomes available to trapped carriers, thus decreasing the trap-residence time of the carrier system with increased temperature. Unfortunately, the signal and SNR levels of our O-DLTS spectra were insufficient to perform meaningful $\tau(T)$ measurements from the peak values of curves similar to Fig. 3.

For the GaAs:Te sample, an activation energy of ΔE = -0.36 eV was extracted from the slope of the curve. The negative sign indicates that the PTR-DLTS lifetime increases with increasing T. This temperature dependence can be explained only with a different mechanism, namely that the increased density of intrinsic free carriers at higher temperatures fills up existing trapping (mostly surface) sites and thus increases the lifetime of the optically injected carriers. Sheard¹³ has used infrared PTR in the conventional frequency-domain mode and has observed similar lifetime behavior in heated Si wafers, which was further accompanied by a reduction in the surface recombination velocity. Increased lifetimes with temperature in impurity-doped Si have also been observed with LM-DLTS. 2,14 whereas SPV-DLTS of *n*-GaAs exhibited thermal-activation behavior. ⁵ Under the present configuration using an Ar⁺ laser pump with optical penetration depth on the order of 1 μ m, and in the absence of deep bulk levels to influence the photoexcited carrier recombination, the surface conditions of the GaAs:Te wafer are expected to dominate the PTR-DLTS signal, yielding an activation energy ΔE characteristic of surface-state and near-surface-state trapping processes. A similar mechanism was reported earlier with PTR rate-window detection from deep-level impurity (Cr-) doped *n*-type Si. ⁹ Changing the wafer surface treatment conditions (e.g., by a chemical etch) and/or comparing PTR-DLTS results obtained with shallow and deep penetrating photon sources, the relative bulk/surface contributions to the signal can, in principle, be deconvoluted to a large extent and the measured activation energy of the GaAs:Te sample can be better understood. Experiments with a 1.06 μ m cw Nd:YAG laser are currently under way.

Based on the foregoing evidence, there are excellent prospects for the novel technique to be developed to a remote, fully noncontacting, process quality control diagnostic for (i) real-time *in situ* characterization of semiconductorwafer native and process-induced deep-level defects; and (ii) for fast, high-spatial-resolution scanning imaging and mapping of specific defects with well-characterized PTR-DLTS peaks at particular substrate temperatures (e.g., Cr, EL2 in GaAs).

The authors would like to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada through a Collaborative Research Grant, which made this work possible, R. A. B. wishes to thank the Office of Assessment and Application of Technology, Indonesia, for financial support. M. V. would like to acknowledge the support of CONACyT, Mexico.

¹ A. Mandelis and Z. H. Chen, Rev. Sci. Instrum. **63**, 2977 (1992).

²Y. Kirino, A. Buczkowski, Z. H. Radzimski, G. A. Rozgonyi, and F. Shimura, Appl. Phys. Lett. 57, 2832 (1990).

³ Y. Fujisaki, Y. Takano, and T. Ishiba, Jpn. J. Appl. Phys. **25**, L874 (1986).

⁴J. Lagowski, P. Edelman, and A. Morawski, Semicond. Sci. Technol. 7, A211 (1992).

⁵J. Lagowski, A. Morawski, and P. Edelman, Jpn. J. Appl. Phys. 31 (Part 2), L1185 (1992).

⁶Z. H. Chen, R. Bleiss, A. Mandelis, A. Buczkowski, and F. Shimura, J. Appl. Phys. **73**, 5043 (1993).

⁷Z. Chen and A. Mandelis, Phys. Rev. B **46**, 13256 (1992).

⁸G. M. Martin, A. Mitonneau, D. Pons, A. Mircea, and D. W. Woodard, J. Phys. C 13, 3855 (1980).

⁹ A. Mandelis, R. Bleiss, and F. Shimura, J. Appl. Phys. **74**, 3431 (1993).

¹⁰W. P. Leung and A. C. Tam, J. Appl. Phys. 56, 153 (1984).

¹¹W. Shockley and W. T. Read, Jr., Phys. Rev. 87, 835 (1952); R. N. Hall, Phys. Rev. 87, 387 (1952).

¹²D. V. Lang and R. A. Logan, J. Electron. Mater. 4, 1053 (1975).

¹³S. Sheard, Ph.D. thesis, University College of London, 1987 (unpublished)

¹⁴F. Shimura, T. Okui, and T. Kusama, J. Appl. Phys. **67**, 7168 (1990).