APPLIED PHYSICS LETTERS VOLUME 74, NUMBER 17 26 APRIL 1999

Kinetics of surface-state laser annealing in Si by frequency-swept infrared photothermal radiometry

Mario E. Rodriguez,[a] J. A. Garcia, and A. Mandelis[b]
Photothermal and Optoelectronic Diagnostics Laboratories, Department of Mechanical and Industrial Engineering, University of Toronto and Materials and Manufacturing Ontario (MMO), Toronto, Ontario M5S 3G8, Canada

C. Jean and Y. Riopel
MITEL SSC, 18 Boul. de l'Aeroport, Bromont, Quebec J0E 1L0, Canada

(Received 4 December 1998; accepted for publication 3 March 1999)

Frequency-swept ("chirped") infrared photothermal radiometry was combined with conventional single-frequency modulation of an Ar ion laser beam to yield a quantitative study of the surface-state annealing processes induced by the low-fluence laser beam on *n*- and *p*-type Si wafers. The appearance of a signal transient was found to be strongly dependent on the electronic quality of the wafer surface and was absent in the thermally oxidized *p*-Si wafer. The low-injection minority-carrier lifetimes and diffusion coefficients were not affected by the laser-surface interaction, but the surface recombination velocity strongly decreased with time of exposure. A two-trap rate model was advanced to explain the transient behavior in terms of surface-state annealing and carrier ejection. © *1999 American Institute of Physics.* [S0003-6951(99)02017-3]

Laser infrared photothermal radiometry (PTR) has been used for the determination of the electronic transport properties of silicon wafers.[1] The remote noncontact nondestructive character of this technique makes it very useful for monitoring the lifetime, τ, surface recombination velocity, S_1, and minority-carrier diffusion coefficient, D, in semiconductors. Hiller *et al.*[2] have used PTR on as received and on thermally oxidized Si wafers. They observed a transient behavior in the case of the wafer with a native oxide under the influence of a 20 mW modulated semiconductor laser beam. No transient behavior was observed with the thermally oxidized wafer. Those authors fitted a one-dimensional theory of the frequency-domain PTR signal amplitude[3] to their data before and after the full exposure to the laser beam. They concluded that no change in the measured lifetime occurred and the surface recombination velocity decreased in the following order: laser unannealed, laser annealed and thermally oxidized wafer. Opsal *et al.*[4] using photomodulated thermoreflectance (PMTR) have hypothesized that two types of electronic traps were responsible for the observed transient behavior: intrinsic dangling-bond and lattice-disorder surface states. The transient phenomena were associated with residual damage resulting from the chemopolish and scrubbing processes used during wafer manufacture.

In this letter, we report a *quantitative* kinetic PTR study based on the real-time monitoring of the temporal evolution of the low-injection minority-carrier transport properties of two silicon wafers. We used a combination of chopped illumination and frequency-sweep ("chirped") detection. PTR frequency scans using a lock-in amplifier were also performed in the steady state following the complete saturation of the PTR transient. The two 6 in. Si wafers used in this study were provided by Mitel SCC (Bromont, Quebec, Canada). One sample was unprocessed 10–15 Ω cm *n*-type (100)-oriented wafer with oxygen content between 30 and 38 ppma. The wafers were polished and cleaned using standard procedures. The other wafer was a 20–40 Ω cm *p*-type silicon, with a thermally grown oxide.

The experimental setup for the PTR method[1,5] and the photothermal chirp frequency modulation (FM) methodology have been described in detail elsewhere.[6,7] The combined experimental setup for the simultaneous monitoring of transient evolution and FM-PTR correlation and spectral analysis is shown in Fig. 1. An Ar^+ion laser emitting at 514 nm was used as the excitation source. A square-waveform chirp from a dual-channel fast Fourier transform (FFT) analyzer was

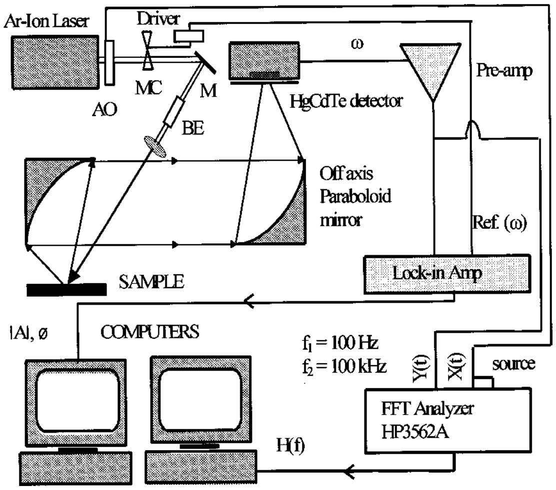

FIG. 1. Schematic representation of experimental setup used for simultaneous measurements of transient and frequency swept scans. M: mirror; AOM: acousto-optic modulator; MCT: mercury cadmium telluride detector; L: lens; LIA: lock-in amplifier; MC: mechanical chopper; FFT: fast Fourier transform. $X(t)$ is the chirp periodic waveform launched by the FFT analyzer. $Y(t)$ is the sample response to $X(t)$. $H(f)$ is the output spectral transfer function.

---

[a] On leave from CICATA, I.P.N., Unidad Queretaro, Mexico.
[b] Electronic mail: mandelis@mie.utoronto.ca

0003-6951/99/74(17)/2429/3/$15.00

© 1999 American Institute of Physics
Downloaded 20 Jul 2008 to 128.100.49.17. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

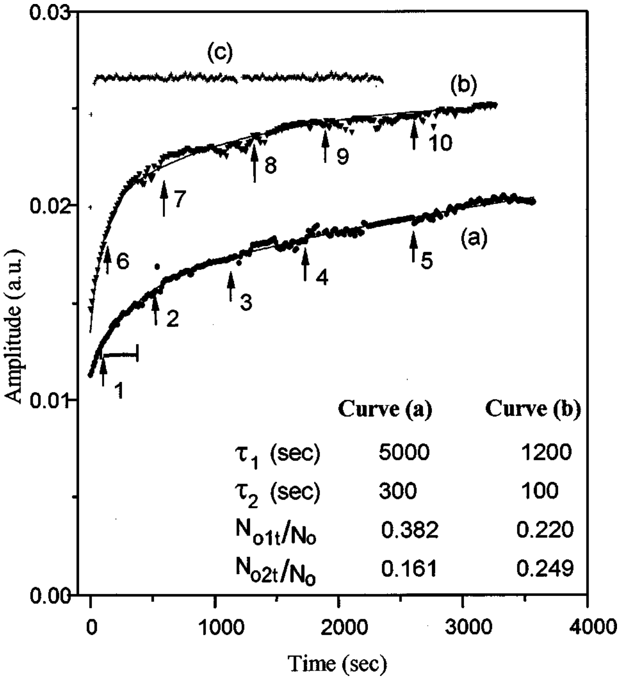

FIG. 2. Comparison of two signal transients of an (a) unirradiated and (b) irradiated spot of an *n*-type unoxidized Si wafer, and (c) an unirradiated spot of a *p*-type Si wafer with a 5000 Å oxide film. The parameters used for the fittings (solid lines) are shown in this figure. The horizontal bar on curve (a) indicates the duration of each set of frequency swept measurements (chirps). Arrows indicate the onset of each set of chirps.

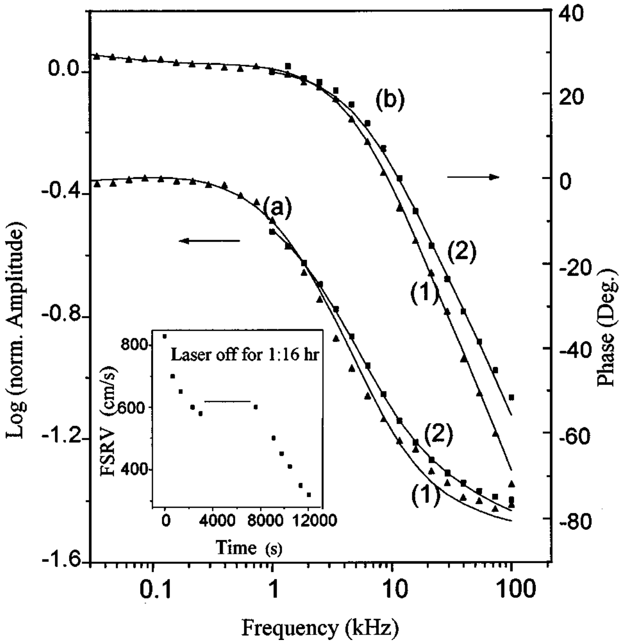

FIG. 3. (a) Experimental PTR amplitude and (b) phase responses of the *n*-Si wafer. Curve (1) corresponds to lock-in amplifier data obtained at steady state. Curve (2) is the normalized frequency-swept (100 Hz–100 kHz) transfer function, $H(f)$, corresponding to the first chirp measurement (300 s) on the same wafer. Solid lines show the simultaneous best fit using a finite-thickness model (see Ref. 8). Parameters derived from the best fits are (i) at steady state: $\tau = 110$ μs, $D_p = 10$ cm^2/s, $S_1 = 320$ cm/s; (ii) after 300 s of exposure: $\tau = 110$ μs, $D_p = 10$ cm^2/s, $S_1 = 830$ cm/s, and $L = 570$ μm. Inset: calculated surface recombination velocities of the *n*-Si wafer at different times for transients (a) and (b) of Fig. 2. The extremes of the solid line denote the radiation turn-off and turn-on times.

used to drive the acousto-optic modulator, which produced periodic frequency sweeps of the laser beam in the range 100 Hz to 100 kHz. The laser beam was simultaneously chopped at $f_0 = 83$ Hz with a mechanical chopper. The beam was then expanded, collimated, and focused on the sample surface. The incident power and the beam size were approximately 30 mW and 30 μm in diameter, respectively. The amplitude, $A(f_0,t)$, and phase, $\phi(f_0,t)$, of the PTR signal in the lock-in amplifier were recorded as functions of time. For each intermittent (quasi-steady) measurement, 1000 frequency chirps were co-added and averaged, and the spectral transfer function, $H(f)$, was generated and stored in the FFT analyzer. The kinetic time evolution of the PTR signal for both wafers was monitored. For the *n*-Si wafer, five consecutive sets of co-added chirps during a single continuous transient from start to saturation were obtained on a previously unirradiated spot, see Fig. 2. Each chirp measurement lasted 5 min. After the fifth set of chirps, the optical source was blocked for 1 h and 16 min. This allowed the signal to partially return to its preillumination value. Then the transient and five more sets of chirps (onset shown by arrows in Fig. 2) were measured again on the same spot of the wafer. When steady state was reached (>11 000 s), a final chirp measurement and a lock-in frequency scan were obtained as shown in Fig. 3. For the *p*-Si wafer, only the lock-in temporal behavior of a previously unirradiated spot was monitored. No chirps were introduced because the response was flat, Fig. 2, in agreement with the earlier PTR report.[2]

The amplitude and the phase of the PTR frequency response of the unprocessed *n*-Si at steady state, Fig. 3, were fitted simultaneously to a three-dimensional theoretical model, taking into account the laser beam spot size, the thickness of the wafer, the photoexcited minority-carrier plasma-wave generation, and the optical-to-thermal energy conversion following lattice absorption.[8] Figure 2 shows that the transient behavior of the *n*-Si sample is semireversible following the cutoff of the radiation and the 1 h 16 min recovery time. Spots on *n*-type wafers with fully reversible transients have also been observed, as well as some fully irreversible spots on oxidized *p*-type wafers. Unlike the diffusion model following step-functional excitation proposed by Opsal *et al.*,[4] a simple rate-equation model with two types of surface traps was found to agree well with our data. In this model, the rate of increase of the free carrier density (N_f) is assumed to be the result of the simultaneous annealing of both surface traps. Each annealing event, in turn, liberates one trapped carrier. The rate of signal increase is equal to the sum of the unannealed trap densities at time *t*, divided by the characteristic trap lifetimes τ_1 and τ_2

$$\frac{dN_f(t)}{dt} = \frac{N_{01} - N_{1f}(t)}{\tau_1} + \frac{N_{02} - N_{2f}(t)}{\tau_2}. \tag{1}$$

Here N_{01} and N_{02} are the total number density of traps of type 1 and type 2, respectively, before the onset of laser annealing ($t = 0$). $N_{1f}(t)$ and $N_{2f}(t)$ are the annealed trap densities at time *t* after the onset of the laser interaction. Assuming quantum yield of one, $N_{1f}(t)$ and $N_{2f}(t)$ also represent the instantaneous number density of excess free carriers liberated from the respective annealed traps. The total number density of carriers in the free and trapped states is assumed constant (N_0) at all times:

Downloaded 20 Jul 2008 to 128.100.49.17. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

$$N_0 = N_{1f}(t) + N_{2f}(t) + N_{1t}(t) + N_{2t}(t). \tag{2}$$

An expression for the fractional free carrier density at any time (t) can be obtained by solving the foregoing initial-value problem:

$$\frac{N_f(t)}{N_0} = 1 - \left[\left(\frac{N_{01t}}{N_0} \right) e^{-t/\tau_1} + \left(\frac{N_{02t}}{N_0} \right) e^{-t/\tau_2} \right]. \tag{3}$$

Here,

$$N_f(t) = N_{1f}(t) + N_{2f}(t). \tag{4}$$

Equation (3) was used to fit the experimental transient curves obtained from the unirradiated and reirradiated spot on the *n*-Si wafer. The results are shown in Fig. 2, including the values of the parameters obtained from this fit. Two very different trap lifetimes were estimated with $\tau_1 = 5000$ s and $\tau_2 = 300$ s and $\tau_1 = 1200$s and $\tau_2 = 100$ s for the unirradiated and reirradiated spots, respectively. The total fractional density of initial traps ($N_{01t} + N_{02t} = 0.543$) for the unirradiated spot is larger by about 13% than the one for the irradiated spot (0.469). The excellent fits of Fig. 2 show that two semi-reversible surface-state annealing processes can adequately explain the PTR transients from the unoxidized *n*-Si. The semireversibility indicates that the annealing process involves metastable states and is of low activation energy, such that the thermal energy available to the wafer at ambient temperature can reverse the process. This is consistent with an electron-hole surface recombination process. Unlike the diffusive interpretation given by Opsal *et al.*,[4] however, the mechanism of the present phenomenon appears to be the activation of carriers from two types of annealed trapping states, in agreement with other frequency-domain results obtained by the same authors.[4]

The phase and amplitude of the spectral transfer function $H(f)$ of the PTR signal from the frequency-sweep measurements at the onset of the laser irradiation (curve 2) and at steady state (curve 1) are shown in Fig. 3. A lock-in frequency scan was performed in the steady state and at the same spot on the *n*-Si wafer. The steady chirped amplitude and phase were normalized to those of the higher-quality lock-in signal to eliminate the instrumental transfer-function effects of the dual-gate FFT analyzer. These corrections were subsequently applied to all other quasi-steady PTR chirps. The 3D PTR model[8] was used for theoretical best fits of the data to obtain the quasi-steady and steady-state carrier transport parameters. Dramatic quantitative changes in the front-surface recombination velocity were found. On the contrary, the minority-carrier lifetime (τ) and diffusion coefficient (D_p) did not exhibit any change. These new quantitative results throughout the evolution of the transient are completely consistent with the earlier steady-state trends observed by of Hiller *et al.*[2] The temporal evolution of the front-surface recombination velocity (FSRV) for the *n*-Si sample is shown as an inset in Fig. 3. When the laser beam is turned on, S_1 starts decreasing steeply from 830 cm/s, until the laser-beam cutoff. It partially recovers after the second turn-on, and eventually decreases to reach the saturation value (steady state) at 320 cm/s.

In conclusion, we have presented a combined frequency-swept and single-frequency-modulated infrared photothermal radiometric method suitable for the simultaneous kinetic measurement of surface-state annealing temporal evolution and minority-carrier transport properties at several time windows along the transient generated by low-power laser irradiation on *n*- and *p*-type silicon wafers subjected to optical annealing.

This work was supported by Materials and Manufacturing Ontario (MMO). One of the authors (M.E.R.) wishes to acknowledge CICATA (Mexico) and COLCIENCIAS (Colombia) for their partial support.

[1] A. Mandelis, Solid-State Electron. **42**, 1 (1998).
[2] T. M. Hiller, M. G. Somekh, J. Sheard, and D. R. Newcombe, Mater. Sci. Eng., B **5**, 107 (1990).
[3] S. J. Sheard, M. G. Somekh, and T. Hiller, Mater. Sci. Eng., B **5**, 101 (1990).
[4] J. Opsal, M. W. Taylor, W. L. Smith, and A. Rosencwaig, J. Appl. Phys. **61**, 240 (1987).
[5] A. Mandelis, R. Bleiss, and F. Shimura, J. Appl. Phys. **74**, 3431 (1993).
[6] A. Mandelis, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **UFFC-33**, 590 (1986).
[7] A. Mandelis, in *Topics in Current Physics*, edited by P. Hess (Springer, Heidelberg, 1990), Vol. 47, Chap. 8.
[8] T. Ikari, A. Salnick, and A. Mandelis, J. Appl. Phys. (in press).

Downloaded 20 Jul 2008 to 128.100.49.17. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp