Laser-induced photothermal reflectance investigation of silicon damaged by arsenic ion implantation: A temperature study

I. Alex Vitkin, Constantinos Christofides, and Andreas Mandelis
Photoacoustic and Photothermal Sciences Laboratory, Department of Mechanical Engineering, and Ontario Laser and Lightwave Research Center, University of Toronto, Toronto, Ontario M5S 1A4, Canada

(Received 9 December 1988; accepted for publication 30 March 1989)

Laser-induced photothermal reflectance (PTR) measurements of arsenic-implanted silicon are reported. The photothermal signals as a function of temperature are presented for both annealed and as-implanted silicon films. The ability to monitor the dependence of signal on doping and on the temperature suggests a novel nondestructive means for characterization of implanted layers. The latter dependence has been qualitatively explained in terms of the temperature variation of the thermal wave effect.

In recent years, the fabrication of shallow *p-n* junctions using the ion implantation technique has received considerable attention. The implantation profile control and the uniformity of doping make ion implantation a very useful technique. However, the implantation process also introduces numerous defects into the crystal. This necessitates the annealing process, which annihilates these defects, and also electrically activates the dopants.[1]

There are many kinds of experimental techniques used to characterize the ion-implanted layers: physicochemical methods, such as Rutherford backscattering,[2,3] transmission electron microscopy,[4] etc.; electrical methods, such as deep level transient spectroscopy,[5-7] four points,[8] Van der Pauw–Hall effect dc and ac measurements,[9-11] etc.; optical methods, such as ellipsometry,[12] infrared spectroscopy,[13] etc. In addition, recent advances in high-frequency photothermal wave detection have enabled successful characterization of ion-damaged semiconductors.[14-17]

The photothermal techniques are particularly useful because of their nondestructive nature, the lack of special sample preparation, and the fast data acquisition time. In nonsemiconducting materials, the measured signal is primarily based on the temperature dependence of the sample's optical reflectivity. In a typical photothermal reflectance (PTR) experiment, a light pulse from a heating laser causes an excursion in the local temperature of the sample, and this manifests itself as a change in the intensity of the retroreflected probe beam. In such materials, change in reflectivity is directly related to the heating of the lattice by the beam; this heating affects the temperature-dependent optical constants of the material. In semiconductors, however, there is the added effect of the created electron-hole pairs (for a sufficiently energetic heating beam). This photogenerated plasma can influence the refractive index of the illuminated material in several ways. There is the dependence of the dielectric constant on the free-carrier density; there is the electroreflectance effect, whereby the photogenerated plasma may influence the wafer reflectivity by surface band bending; in addition, the thermalization of plasma with the lattice, and the subsequent interband recombination will also contribute indirectly to the PTR signal through the above-mentioned thermal effect. In general, we can write

$$\frac{\Delta R}{R_0} = \frac{1}{R_0}\left(\frac{\partial R}{\partial T}\right)\Delta T + \frac{1}{R_0}\left(\frac{\partial R}{\partial N}\right)\Delta N, \qquad (1)$$

where R_0 is the reflectivity at temperature T_0 and plasma density N_0, $1/R_0(\partial R/\partial T)$ and $1/R_0(\partial R/\partial N)$ are the temperature and the plasma coefficients of reflectivity (the latter can be negative),[17] and ΔR, ΔT, and ΔN are the local variations in the reflectance, temperature, and plasma density, respectively, brought about by the heating laser. Generally, it is difficult to determine which mechanism dominates the PTR signal in a given experiment: probably both contribute to various degrees for an arbitrarily chosen semiconductor sample. The relative importance will depend on the semiconductor—its crystallinity, its thermal and optical parameters, the relaxation time of the photogenerated plasma, etc. Ion implantation will influence the recovered signal by altering these material properties. A defect-rich (ion-implanted) sample region can modify the thermal contribution of Eq. (1) by changing the absorption coefficient and the thermal parameters,[18] and by degrading the transport coefficients. In addition, nonlinear processes such as two-photon absorption are strongly dependent on the local disorder due to the implanted impurities.[19] The induced damage will also influence the plasma contribution by decreasing the $\omega\tau$ product ($\omega =$ angular modulation frequency, $\tau =$ lifetime of photoexcited plasma), thereby decreasing the relative importance of the Drüde and the surface band bending effects.[20-22] However, the photogenerated plasma can still contribute indirectly through the thermal term via the lattice thermalization and nonradiative recombination. Thus, given the importance of the induced damage in the PTR signal generation, we expect to detect the effect of different ion doses, and to monitor the layer restoration as a function of annealing temperature.

Presently, we are interested in the dependence of the PTR signal on the experimental sample temperature. As will be shown elsewhere,[23] the thermal-wave term is expected to vary with the lattice temperature, whereas the plasma-wave contribution is essentially independent of it. Indeed, according to Kireev,[24] the radiative quantum efficiency in silicon for greater than band-gap light energy (1.4–3.5 eV) is the same (unity) for 100, 300, and 400 K. Clearly, the subsequent fate of the photogenerated carriers is dependent on lattice temperature (via recombination, trapping, transport, etc.), but the excess density is not. Thus, to first order, we expect the temperature variation of the PTR signal to arise from the thermal-wave term, even though the signal itself may contain plasma-wave contributions (this contribution

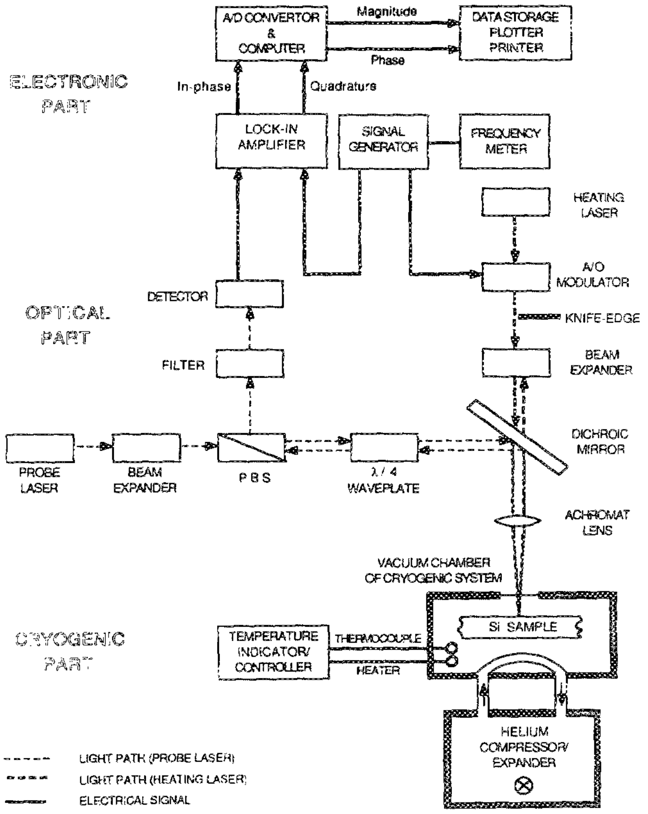

FIG. 1. Experimental setup for the laser-induced temperature-dependent PTR measurements.

is expected to be small in a heavily implanted inhomogeneous environment, where τ is much smaller than in the c-Si). This variation arises because the thermodynamic properties of the material that determine the thermal signal (thermal conductivity, specific heat) are strong functions of temperature. If the temperature dependence of these properties is taken into account,[25] the existing thermoreflectance theories,[26,27] applied to crystalline silicon, predict a signal increase with T.

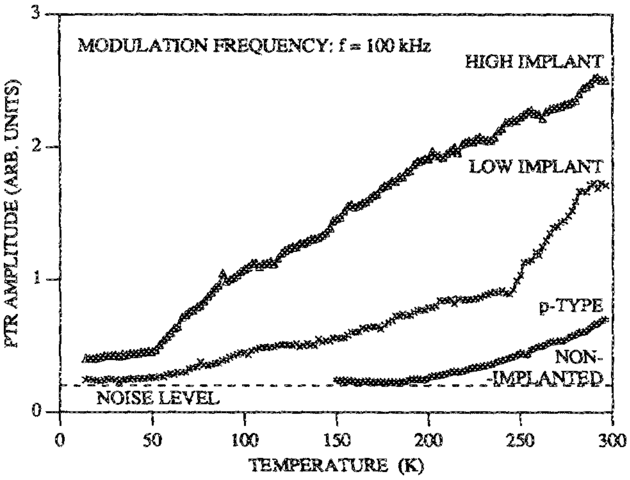

FIG. 2. PTR signal vs temperature for samples implanted at two different doses (low dose: 2×10^{14} cm^{-2} and high dose: 5×10^{14} cm^{-2}) and for a nonimplanted p-type reference sample.

In this letter, we present the extension of the conventional laser-induced PTR method to low temperatures ($\approx$20 K). The apparatus used is shown in Fig. 1; it is similar to the one employed by Opsal *et al.*,[17] with the important addition of the temperature sensing-controlling equipment. The sample is placed in the experimental chamber of a helium-cooled expander module (APD Cryogenics model PS2). Optical access is available through a vacuum-sealed quartz window. The operating pressures within the chamber were 10^{-5}–10^{-3} Torr, and the temperature range (measured with a gold:iron/constantan thermocouple) was 20–300 K. The periodic sample heating was obtained with an Ar$^+$ laser beam (488 nm), modulated by an acousto-optic modulator. The beam, of incident power approximately 20 mW, was focused normally onto the sample surface to a spot size of about 30 μm. The changes in the reflectivity of a collinear HeNe laser beam (632.8 nm) were measured by a silicon photodiode detector (UDT), operated in the sum mode. As the temperature in the experimental chamber was lowered at a rate of 3 K min^{-1}, the photodetector output was monitored in quasi-equilibrium with a fast lock-in amplifier (EG&G 5202), at a modulation frequency of 100 kHz. The in-phase and quadrature components of the measured signal were stored in a computer at regular 2 K intervals.

The examined samples were p-type (6 Ω cm) silicon wafers (100), implanted at two different doses at room temperature with arsenic (low dose: $\Phi = 2\times10^{14}$ cm^{-2}; high dose $\Phi = 5\times10^{14}$ cm^{-2}; energy = 150 keV). After implantation, some wafers had been furnace annealed at different temperatures (400, 500, 600, and 800 °C) in N_2 ambient for 1 h. The junction depth was approximately 0.4 μm.

Figure 2 shows the variation of the PTR signal with temperature for two different ion doses, as well as for one nonimplanted wafer which was used as a reference. A higher signal was observed for the high doping level sample at all measurement temperatures, which is consistent with the higher degree of lattice demage caused by the implant.[28-30] This is expected because the higher implant dose exceeds the critical amorphization dose of arsenic in silicon ($\Phi = 2.5\times10^{14}$ cm^{-2} at 300 K),[31] and thus a considerable number of point deffects have been generated, presumably in cluster aggregates.[1] The implanted layer thus formed can be better described as inhomogeneous, since its transport coefficients (mobility, conductivity, etc.) are higher than those of the amorphous material, but lower than those of a single crystal.[32,33] Therefore, the optical, thermal, and electrical parameters of our ion-implanted silicon would be expected to be somewhere between the crystalline and amorphous limits, with the low dose sample lying closer to the crystalline limit than the high dose one. As a result, its PTR signal was lower than that of the high dose sample, but higher than that of the nonimplanted one throughout the entire experimental temperature range. The increasing signal intensity is indicative of the poorer thermal properties (lower thermal conductivity, higher specific heat) of the damaged near-the-surface region that are caused by the increasing implant dose[34] and by increasing lattice measurement temperature. Again, we note that the free-carrier effect, represented by the second term of Eq. (1), may play a role at the experimental

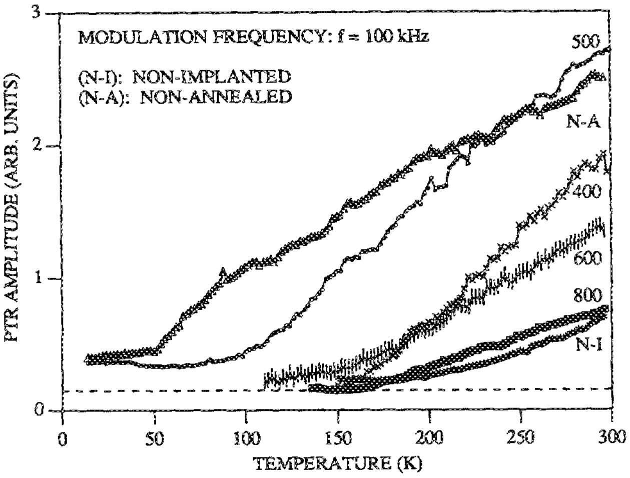

FIG. 3. PTR signal vs temperature for high dose implants ($\Phi = 5\times10^{14}$ cm^{-2}) annealed between 400 and 800 °C.

modulation frequency of 100 kHz, but the temperature dependence of the signal can be adequately explained in terms of the thermal effect alone. Phenomenologically, the PTR response of the nonimplanted sample resembles an exponential dependence of an activation process [i.e., $\Delta R \simeq \exp(-E/k_B T)$, where E is the measured activation energy ($\simeq 0.11$ eV), as calculated from Fig. 2]. This activation energy can be associated, for example, with the mechanism of local surface rearrangement involving the migration of interstitial silicon atoms.[35] The difference in the amplitudes of the output signals reveals that the sensitivity of our experimental measurement to the implant dose is somewhat lower than that of some other thermal and acoustic wave techniques.[15,18,28] The sensitivity could be improved by decreasing the spot sizes of the two laser beams and by increasing the modulation frequency, thereby confining the photothermal effect to a smaller region in the damaged layer, but the present experimental arrangement is adequate for monitoring the temperature dependence of the PTR signal.

The effect of different annealing temperatures on the PTR amplitude of several highly doped samples (5×10^{14} cm^{-2}) is depicted in Fig. 3. In general, the process of annealing is thought to decrease the degree of local disorder, and thus cause a decrease in the measured photothermal reflectance signal because of the average improvement of the sample parameters. The overall trend in the data does bear out this expectation; note, however, that the signal of the 400 °C-annealed sample is lower than that of the 500 °C sample. This apparent anomaly is known as negative annealing: its origin is associated with the formation of complex defects (arsenic multivacancies) in the 450–500 °C temperature range. Higher annealing temperatures (>550 °C) are required to dissociate these complex defects. For higher annealing temperatures, the signal approaches that of the nonimplanted silicon, indicating a high degree of crystallinity restoration, as was observed by other workers using electrical methods such as ac Hall effect and ac resistance measurements.[36]

In conclusion, we have found that the laser-induced photothermal reflectance technique is a sensitive noncontact means for characterizing the damaged silicon layers produced after arsenic ion implantation, and for studying the annihilation kinetics of the defects (the evolution of the layer as a function of annealing temperature). The dependence of the PTR signal on the lattice temperature, which has been explained in terms of the variation of the thermal wave effect, is one of the most important results of this study.

The support of the Ontario Laser and Lightwave Research Center is gratefully acknowledged.

[1] J. F. Gibbons, Proc. IEEE **60**, 1062 (1972).
[2] S. T. Picraux, in *Defects in Semiconductors*, edited by J. Narayan and T. Y. Tan (North-Holland, New York, 1981), Vol. 2, p. 135.
[3] W. M. Paulson and J. R. Wilson, in *Defects in Semiconductors*, edited by S. Mahajam and J. W. Corbett (North-Holland, New York, 1983), Vol. 14, p. 523.
[4] W. Krakow, T. Y. Tan, and H. Foell, in *Defects in Semiconductors*, edited by J. Narayan and T. Y. Tan (North-Holland, New York, 1981), Vol. 2, p. 185.
[5] N. M. Johnson, J. L. Regolini, and D. J. Bartelink, Appl. Phys. Lett. **36**, 425 (1980).
[6] G. E. Jellison, J. W. Cleland, and R. T. Yang, in *Defects in Semiconductors*, edited by J. Narayan and T. Y. Tan (North-Holland, New York, 1981), Vo. 2, p. 241.
[7] L. C. Kimerling and J. L. Benton, in *Laser and Electron Beam Processing of Materials*, edited by C. W. White and P. S. Peercy (Academic, New York, 1980), p. 385.
[8] D. C. Perloff, Solid State Electron. **20**, 681 (1977).
[9] L. J. Van der Pauw, Philips Res. Rep. **13**, 1 (1985).
[10] C. Christofides, H. Jaouen, and G. Ghibaudo, Rev. Phys. Appl. **22**, 407 (1987).
[11] H. Jaouen, G. Ghibaudo, and C. Christofides, J. Appl. Phys. **60**, 1699 (1986).
[12] H. J. Stein, J. A. Knapp, and P. S. Peercy, in *Laser and Electron Beam Interaction with Solids*, edited by B. R. Appleton and G. K. Celler (Elsevier, Amsterdam, 1982), p. 319.
[13] J. Luo, H. J. McMarr, and K. Vedam, in *Defects in Semiconductors*, edited by S. Mahajan and J. W. Corbett (North-Holland, New York, 1983), Vol. 14, p. 529.
[14] A. Rosencwaig, J. Opsal, W. L. Smith, and D. L. Willenborg, Appl. Phys. Lett. **46**, 1013 (1985).
[15] W. L. Smith, A. Rosencwaig, and D. Willenborg, Appl. Phys. Lett. **47**, 584 (1985).
[16] D. Guidotti and H. M. van Driel, Appl. Phys. Lett. **47**, 1336 (1985).
[17] J. Opsal, M. W. Taylor, W. L. Smith, and A. Rosencwaig, J. Appl. Phys. **61**, 240 (1986).
[18] G. M. Crean, S. J. Sheard, C. W. See, and M. G. Somekh, Proc. Ultrason. Symp. IEEE **1**, 597 (1987).
[19] I. W. Wylie and E. P. C. Lai, Chemtronics **1**, 69 (1986).
[20] D. Guidotti and H. M. van Driel, Appl. Phys. Lett. **49**, 301 (1986).
[21] A. Skumanich, D. Fournier, A. C. Boccara, and N. M. Amer, Appl. Phys. Lett. **47**, 402 (1985).
[22] F. A. McDonald, D. Guidotti, and T. M. DelGiudice, IBM Internal Report No. 54561, April 1986.
[23] I. A. Vitkin, C. Christofides, and A. Mandelis (unpublished).
[24] P. Kireev, *The Physics of Semiconductors* (Mir, Moscow, 1975), Chap. 6.
[25] Y. Touloukian, R. Powell, C. Ho, and M. Nicolaou, *Thermal Diffusivity* (IFI/Plenum, New York, 1973).
[26] O. Doka, A. Miklos, and A. Lorintz, J. Appl. Phys. **63**, 2156 (1988).
[27] K. Tanaka, in *Photoacoustic and Thermal Wave Phenomena in Semiconductors*, edited by A. Mandelis (North-Holland, New York, 1987), p. 441.
[28] W. L. Smith, A. Rosencwaig, D. L. Willenborg, J. Opsal, and M. W. Taylor, Solid State Technol. **29**, 85 (1986).
[29] R. A. McFarlane and L. D. Hess, Appl. Phys. Lett. **36**, 137 (1980).
[30] J. F. Zuccon and A. Mandelis, IEEE Trans. Ultrason. Ferroelect. Freq. Control **35**, 5 (1988).
[31] S. Prussin, D. Margolese, and R. Tauber, J. Appl. Phys. **57**, 180 (1985).
[32] L. Friedman, J. Non-Cryst. Solids **6**, 329 (1971).
[33] P. Nagels, *Amorphous Semiconductors* (Springer, New York, 1979).
[34] H. Wolf, *Silicon Semiconductor Data* (Pergamon, London, 1969).
[35] B. Boltaks, *Diffusion in Semiconductors* (Mir, Moscow, 1987).
[36] C. Christofides, H. Jaouen, and G. Ghibaudo, J. Appl. Phys. 15 June (1989).