Surface recombination velocity of silicon wafers by photoluminescence

D. Baek
*Department of Electrical Engineering and Center for Solid State Electronics Research,
Arizona State University, Tempe, Arizona 85287-5706*

S. Rouvimov and B. Kim
SUMCO USA, Salem, Oregon 97303

T.-C. Jo
Department of Mathematics, New Mexico Tech, Socorro, New Mexico 87081

D. K. Schroder[a)]
*Department of Electrical Engineering and Center for Solid State Electronics Research,
Arizona State University, Tempe, Arizona 85287-5706*

Photoluminescence (PL) and optical reflection measurements, obtained in the two-wavelength SiPHER PL instrument, are used to determine the surface recombination velocity of silicon wafers. Local measurements and contour maps are possible allowing surface recombination maps to be displayed. This instrument also allows doping and trap density measurements. Surface recombination velocities from 10 to 10^6 cm/s can be measured on low or high resistivity polished and epitaxial wafers. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1884258]

The effective lifetime in semiconductors, generally difficult to decompose into bulk recombination lifetime (τ_b) and surface recombination velocity (s_r), is important in the operation of some semiconductor devices, e.g., solar cells, pn junctions, bipolar junction transistors, thyristors.[1] The separation of bulk recombination lifetime and surface recombination velocity from the effective lifetime is quite difficult since most lifetime characterization techniques determine the effective lifetime.[1–4] To extract the bulk lifetime, the surface recombination velocity is usually minimized, requiring surface treatments such as hydrofluoric acid, iodine, silicon nitride, or oxide.[5] For extremely pure Si samples, the bulk lifetime is so high that surface recombination dominates the effective lifetime.[6] However, for lower quality, i.e., low resistivity or solar grade silicon wafers, the lifetime is lower and both τ_b and s_r must be determined. Photoconductance decay,[7] surface photovoltage,[8] and quasi-steady-state photoconductance[9] are widely used for characterizing the minority carrier lifetime and diffusion length. Separation of bulk and surface recombination is possible by varying the sample thickness[10] or by evaluating the initial decay modes of photoconductance decay.[11]

In this letter, we propose a technique for evaluating s_r of as-received and oxidized silicon wafers by photoluminescence. PL is most commonly used at low temperatures for impurity identification[12] and for determining low doping densities in Si.[13] Recently, a PL-based commercial tool, SiPHER, has been introduced, that operates at room temperature, uses the two wavelengths $\lambda = 532$ and 827 nm, measures the PL and the reflected signals, and has found application to detect defects and doping density variations in silicon wafers.[14] For example, Buczkowski *et al.* show how PL can be used to detect Si doping density variations over the 0.01–20 Ω cm resistivity range and detected misfit dislocations and oxygen precipitates.[15] We make use of the fact

that the instrument provides PL and reflectance data at two wavelengths for each measurement.

We have developed one-, two-, and three-dimensional models of the carrier distribution in semiconductors following light excitation and use these distributions to calculate PL signals to extract the various doping density and recombination components. Here we confine ourselves to the one-dimensional case. To develop the PL model, we start with the steady-state continuity equation for the excess minority carrier generation and derive the PL efficiency[16]

$$\eta_{PL}(\lambda) = \frac{\int_0^d \delta n(\lambda,z)dz}{\Phi_{in}(\lambda)\tau_{rad}} = \Phi(\lambda)[1 - R(\lambda)]F(\lambda) = I_{PL}(\lambda).$$

$\eta_{PL}(\lambda)$, depends on the photon flux density Φ, the wavelength λ, the reflectance R, the sample thickness d, the radiative recombination lifetime τ_{rad}, and the excess carrier density $\delta n(\lambda,z)$. The function $F(\lambda)$ depends on the doping N_A and trap N_T densities, surface recombination velocity, minority carrier diffusion length, radiative lifetime, sample thickness, and absorption coefficient.[16] The PL efficiency is
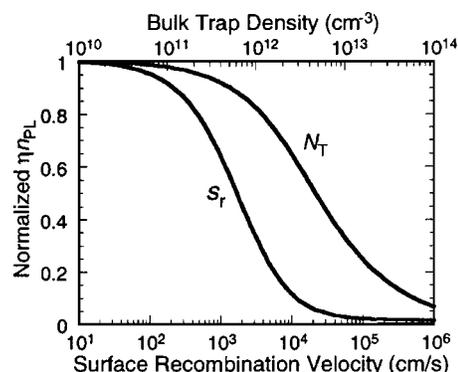

FIG. 1. Normalized PL efficiency vs bulk trap density and front surface recombination velocity.

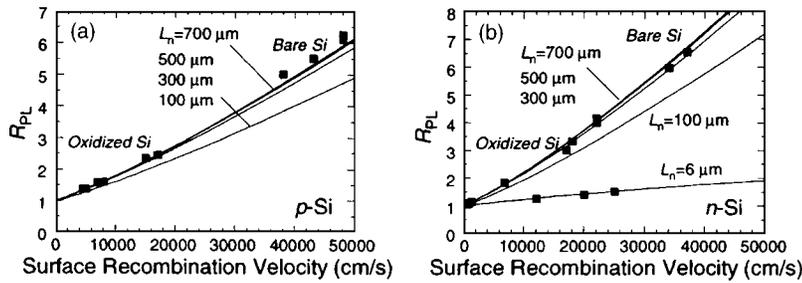a)Electronic mail: schroder@asu.edu

FIG. 2. Theoretical (lines) and experimental (points) PL intensity ratio vs front surface recombination velocity s_r as a function of diffusion length (a) p-type Si, (b) n-type Si. The high L_n data are for N_A and N_D around 10^{15} cm^{-3}. The $L_n = 6$ μm line and data are for $N_D = 10^{19}$ cm^{-3}.

almost the same for both wavelengths at s_r up to 10^3 cm/s. However, the η_{PL} for $\lambda = 827$ nm is higher than for $\lambda = 532$ nm for $s_r > 10^3$ cm/s, because most excess carriers are generated within 1 μm from the surface for $\lambda = 532$ nm and their recombination is strongly influenced by surface recombination. For $\lambda = 827$ nm most excess carriers are generated within 10 μm and the effect of surface recombination is reduced. Hence, we should be able to predict the surface recombination velocity by using the PL and reflectance signals at the two wavelengths.

We show the PL dependence on trap density and surface recombination velocity in Fig. 1 and are generally concerned with high-lifetime, low N_T wafers ($N_T \approx 10^{10}$–10^{12} cm^{-3}) with N_T variations having a relatively minor effect on the PL signal. However, surface recombination varies widely even in high-lifetime wafers, because it depends on the state of the surface, i.e., bare, passivated, contaminated, oxidized, etc. This is our motivation: N_T has little effect, s_r has a major effect, and hence one should be able to extract s_r from PL measurements.

To determine s_r, we measure the PL intensity ratio R_{PL} and the optical reflection at the two exciting wavelengths, where R_{PL} is

$$R_{PL} = \frac{I_{PL}(827)}{I_{PL}(532)} = \frac{\Phi(827)[1 - R(827)]F(827)}{\Phi(532)[1 - R(532)]F(532)}.$$

From the measured reflection data and calculated reflectivities, we determine the ratio $\Phi(827)[1 - R(827)]/\Phi(532) \times [1 - R(532)]$. This leaves only $F(\lambda)$ as the unknown. R_{PL} depends on N_A, the minority carrier diffusion length L_n, and s_r and known parameters, i.e., radiative recombination parameter B, α, and d. We calculate R_{PL} vs s_r, as shown in Fig. 2, since we know from Fig. 1 that PL depends sensitively on s_r. From the experiments we determine R_{PL} and from the R_{PL}–s_r curves, we then determine s_r. For a precise determination of s_r, L_n needs to be known and can be measured independently. However, since L_n variations have a relatively small effect on the R_{PL}-s_r curves, an educated L_n guess is sufficient for a reasonably accurate s_r determination.

We used (100) oriented CZ-grown polished and epitaxial Si wafers, front side polished, 700 μm thick. Some wafers were bare, others were oxidized at 1000 °C for 30 min for a 30 nm thick SiO$_2$ film. Five different types of as-received and oxidized wafers were used: boron and phosphorus-doped polished wafers and boron, arsenic, and antimony-doped epitaxial wafers.

Figure 2 shows R_{PL} versus surface recombination velocity as a function of L_n. A 700–300 μm L_n variation shows little R_{PL} variation, especially for low s_r. Placing the experimental R_{PL} data on these curves, yields $s_r = 500$–50 000 cm/s. The lowest s_r of 500 cm/s is for the oxidized arsenic-doped n-type wafer. To verify that our

assumed L_n data in Fig. 2 were appropriate, we determined the diffusion length of the boron-doped wafers by surface photovoltage measurements to be 400 μm before and after oxidation. We typically find s_r of n-Si to be lower than p-Si, because n-type wafers have lower surface/interface state densities or negative surface charge leads to accumulation on n-Si and depletion on p-Si. It is well known that the surface potential has a substantial effect on surface recombination. Accumulated and inverted surface have lower s_r than depleted surfaces. Such surface conditions can be attained through corona charge[17] or external electric field.[18]

To verify our method further, we rinsed boron doped Si wafers ($\rho = 15$ Ω cm) in a dilute HF/H$_2$O 1:10 solution and measured PL and L_n before and after the rinse. The L_n remained unchanged, but the PL signal increased due to passivation of dangling bonds by the HF as also observed by others.[19] Si surfaces, prepared in HF-containing solutions, are completely H-terminated and remarkably passive.[20] This is somewhat surprising since thermodynamics suggests there should be significant Si–F, bonds (Si–F and Si–H bond energies are 6.2 and 3.3 eV). However, if one considers the complete system formed by reactants, reaction products and the surface, hydrogen termination is thermodynamically favored compared to fluorine termination.

From the PL we determined R_{PL} and the surface recombination velocity, shown in Fig. 3. The surface recombination velocity is about 8700 cm/s for the as-received sample then decreased to about 800 cm/s after the HF rinse and gradually increased. It is known that a HF-terminated Si surface oxidizes when exposed to air or oxygen[21] and these measurements show that s_r increases as the HF termination effectiveness diminishes.

In summary, we developed a method to determine the surface recombination velocity of silicon wafers by photoluminescence. This method allows for fast, contactless, and nondestructive characterization of entire wafers with no sample preparation. With the aid of the reflectance data, the PL intensity ratio is extracted, calculated, and correlated to the surface recombination velocity. If the bulk diffusion
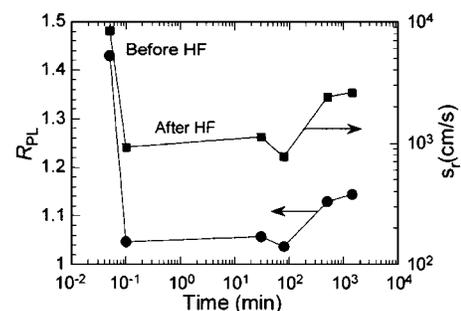

FIG. 3. R_{PL} and S_r vs time before and after HF/H$_2$O rinse.

length is above 100 μm, the surface recombination velocity can be determined and we find values of 500–50 000 cm/s depending on the wafer conditions. Bulk, epitaxial, and oxidized wafers have been characterized and we find good correlation between theory and experiment.

[1] D. K. Schroder, *Semiconductor Material and Device Characterization*, 2nd ed. (Wiley-Interscience, New York, 1998), pp. 420–508.

[2] O. Palais and A. Arcari, J. Appl. Phys. **93**, 4686 (2003).

[3] T. Lauinger, J. Schmidt, A. G. Aberle, and R. Hezel, Appl. Phys. Lett. **68**, 1232 (1996).

[4] S. J. Robinson, S. R. Wenhan, P. P. Altermatt, A. G. Aberle, G. Heiser, and M. A. Green, J. Appl. Phys. **78**, 4740 (1995).

[5] J. Schmidt and A. G. Aberle, J. Appl. Phys. **81**, 6186 (1997).

[6] H. M'saad, J. Michel, A. Reddy, and L. C. Kimerling, J. Electrochem. Soc. **142**, 2833 (1995).

[7] M. Kunst and G. Beck, J. Appl. Phys. **60**, 3558 (1986).

[8] J. Lagowski, P. Edelman, M. Dexter, and W. Henley, Semicond. Sci. Technol. **7**, A185 (1982).

[9] R. A. Sinton and A. Cuevas, Appl. Phys. Lett. **69**, 2510 (1996).

[10] E. Yablonovitch, D. L. Allara, C. C. Chang, T. Gmitter, and T. B. Bright, Phys. Rev. Lett. **57**, 249 (1986).

[11] K. L. Luke and L.-J. Cheng, J. Appl. Phys. **61**, 2282 (1987).

[12] P. J. Dean, Prog. Cryst. Growth Charact. **5**, 89 (1982)

[13] M. Tajima, T. Masui, T. Abe, and T. Iizuka, in *Semiconductor Silicon*, edited by H. R. Huff, R. J. Kriegler, and Y. Takeishi (Electrochemical Society, Pennington, NJ, 1981), pp. 72–89.

[14] SiPHER, Bio-Rad Semiconductor System Divisions (recently Accent Optical Technologies).

[15] A. Buczkowski, B. Orschel, S. Kim, S. Rouvimov, B. Sneqirev, M. Fletcher, and F. Kirscht, J. Electrochem. Soc. **150**, 436 (2003).

[16] G. Duggan and G. B. Scott, J. Appl. Phys. **52**, 407 (1981).

[17] M. Schöfthaler, R. Brendel, G. Langguth, and J. H. Werner, IEEE First World Conference, on Photovoltaic Energy Conversion (1994), p. 1509.

[18] M. Ichimura, M. Hirano, A. Tada, E. Arai, H. Takamatsu, and S. Sumie, Mater. Sci. Eng., B **73**, 230 (2000).

[19] T. Konishi, T. Yao, M. Tajima, H. Ohshima, H. Ito, and T. Hattori, Jpn. J. Appl. Phys., Part 1 **31**, 1216 (1992).

[20] Y. J. Chabal, G. S. Higashi, K. Raghavachari, and V. A. Burrows, J. Vac. Sci. Technol. A **7**, 2104 (1989).

[21] T. Miura, M. Niwano, D. Shoji, and N. Miyamoto, J. Appl. Phys. **79**, 4373 (1996).