Accurate measurement of extremely low surface recombination velocities on charged, oxidized silicon surfaces using a simple metal-oxide-semiconductor structure

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The authors report a simple technique to determine the surface recombination velocity of silicon and other semiconductor surfaces which have been passivated with a dielectric layer, as a function of charge density. A metal-oxide-semiconductor structure, employing large area, partially transparent metal contacts, is used to enable the charging of the surfaces. Simultaneous measurement of the emitter saturation current density J_{oe} and the effective instantaneous lifetime τ_{inst} allows accurate extraction of the effective surface recombination velocity S_{eff} at any given injection level. Extremely low J_{oe} values of 1.8 fA cm^{-2} are measured on the silicon-silicon oxide (Si-SiO₂) interface of a thermally oxidized, charged wafer. © 2007 American Institute of Physics.

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It is well known that the presence of electrical surface charge can have a dramatic effect on the recombination rates of photogenerated carriers at the surfaces of silicon (Si) solar cells and other devices, as a result of band bending induced at the Si surface. On lightly to moderately doped silicon, the presence of a large amount of either positive or negative charge leads to low surface recombination rates corresponding to accumulation or strong inversion conditions at the surface, while the recombination rate reaches a maximum when the surface is in depletion, with approximately equal concentrations of electrons and holes.^{1,2} Even on diffused surfaces, the presence of charge can have a dramatic effect on the electrical interface properties.³ The majority of measurements of the effect of charge on surface recombination have been carried out on moderately doped silicon with a doping around $1 \text{ } \Omega \text{ cm}$, since this type of material is most commonly used for photovoltaic applications. Charging the samples is most commonly done using a corona discharge chamber, since this method has the advantage of not interfering with the optical properties of the sample being measured. Accurate determination of the charge density requires separate measurement using a Kelvin probe. Alternative methods, such as the measurement of the photovoltage using mercury probes, together with the use of a transparent conductive oxide layer for sample charging, have also been used.⁴ While these measurements have clearly shown the qualitative variation of the surface recombination rate with charge density, accurate determination of surface recombination becomes difficult as the surface recombination rate approaches very low values.

In this letter we present minority carrier lifetime measurements on lightly doped, thermally oxidized Si wafers. The use of lightly doped (10^{13} – 10^{14} cm^{-3}) material has the significant advantage that it allows the accurate determination of the emitter saturation current density J_{oe} . This parameter in turn can be used to obtain more accurate values of the

more commonly measured parameter, the effective surface recombination velocity S_{eff} .

Samples used for the experiments were float zone [(100)] *p* type wafers with a B doping concentration of $\sim 10^{14} \text{ cm}^{-3}$. Wafers were supplied lapped and etched. They were etched in hydrofluoric/nitric acid solution to remove $\sim 20 \text{ } \mu\text{m}$ from each surface, cleaved into quarters, and then given a standard RCA clean.⁵ A 50 nm thick thermal oxide was grown at $1000 \text{ } ^\circ\text{C}$ for 60 min without trichloroethylene followed by a N_2 annealing at the same temperature for 30 min, and a forming gas annealing for 30 min at $400 \text{ } ^\circ\text{C}$.

Using a shadow mask aluminium (Al) was evaporated over a circular area onto both sides of each quarter to a thickness of $\sim 5 \text{ nm}$ to create a symmetric metal-oxide-semiconductor (MOS) structure. The diameter of the metallized area was at least 5 mm larger than the sensing area of the inductive coil for lifetime measurements in order to minimize edge effects. Contact to Al layers was made using conductive silver paste, while contact to the silicon bulk was made by removing a small amount of oxide in one of the corners of the sample and applying silver paste. The final structure is shown in Fig. 1. The wafer quarter was positioned so that the metallized region was centered over the inductive coil. The metal thickness was carefully chosen to ensure minimal interference with the lifetime measurement.

While the corona discharge is an accurate alternative technique for applying surface charge, a disadvantage of the method is that it requires the sample to be moved between the measurement equipment, the corona discharge chamber, and the Kelvin probe for each data point. In contrast, the use of a MOS structure allows all measurements to be carried out without moving the sample, thus minimizing the possibility of sample damage during handling, allowing more rapid measurements, and minimizing error introduced by sample movement, or the possible decay of charges between Kelvin probe and lifetime measurements.

Measurements were carried out using the inductively coupled photoconductivity decay technique.^{6,7} The effective lifetime is determined from the rate of decay of the wafer photoconductivity following the application of a light pulse.

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FIG. 1. Schematic setup for the transient lifetime measurement using a MOS structure to allow charging of the surfaces.

In high level injection, the instantaneous decay time τ_{inst} is⁶

$$1/\tau_{\text{inst}} = 1/\tau_{\text{bulk, hli}} + (2J_{\text{oe}}n)/(qWn_i^2), \quad (1)$$

where $\tau_{\text{bulk, hli}}$ is the high level injection lifetime of the wafer bulk, n is the photogenerated excess carrier density in the wafer bulk, W is the wafer thickness, n_i is the intrinsic carrier concentration, J_{oe} is the emitter dark saturation current density, and q the electronic charge. The value of J_{oe} can be determined from the slope of $1/\tau_{\text{inst}}$ vs n after Auger recombination has been accounted for. J_{oe} is an indicator of the degree of surface passivation and a parameter of direct technological importance for photovoltaics. Measurement of J_{oe} , rather than the effective surface recombination velocity, has the advantage that it allows the unambiguous separation of surface and bulk recombinations. Both τ_{inst} and J_{oe} were measured at an injection level of $4 \times 10^{15} \text{ cm}^{-3}$. For all measurements reported here, n is uniform throughout the wafer due to the high bulk lifetime and low surface recombination rates.

Figure 2 shows the measured effective lifetime as a function of applied bias voltage V_{app} in the range -11 – $+11$ V. The corresponding applied charge density varies from $-4.7 \times 10^{12} \text{ cm}^{-3}$ to $+4.7 \times 10^{12} \text{ cm}^{-3}$. The curve displays the characteristic “U” shape, with a minimum in the effective lifetime around -1.2 V. The work function difference of the Al–SiO₂–Si system for the sample used is ~ -0.8 V.⁸ If we

FIG. 2. Instantaneous effective lifetime τ_{inst} measured at an injection level of $4 \times 10^{15} \text{ cm}^{-3}$ as a function of applied voltage.

FIG. 3. Emitter saturation current J_{oe} measured at an injection level of $4 \times 10^{15} \text{ cm}^{-3}$ as a function of applied voltage.

assume that the minimum in the effective lifetime curve corresponds to a depleted Si–SiO₂ interface, we can estimate the effective charge density due to fixed oxide charges to be $+2 \times 10^{11} \text{ cm}^{-3}$.

Figure 3 shows the measured values for the emitter saturation current density J_{oe} on the same sample. A valid measurement of J_{oe} can only be made under the conditions that (i) the surface of the sample is in low level injection and (ii) the bulk of the sample is in high level injection (as a general rule, Δn should be at least equal to $10n_0$). Both conditions must be met over the entire injection level range used to extract the value of J_{oe} . Condition (ii) is met over the entire range of V_{app} , but condition (i) clearly is not met for low values of V_{app} . Calculation of the surface doping concentration as a function of applied charge density shows that the electron or hole concentration exceeds 10^{18} cm^{-3} for applied voltages of greater than 0.3 V or less than -2.7 V, respectively. Note that while J_{oe} usually includes contributions from both the bulk and the surface regions due to the extremely sharp carrier profile in the silicon surface region resulting from the applied charge, the contribution from the silicon bulk is negligible in this case.

The parameter more usually measured in relation to surface recombination is the effective surface recombination velocity S_{eff} , defined by

$$S_{\text{eff}} = U/n, \quad (2)$$

where U is the surface recombination rate per unit area. S_{eff} is typically determined from the following equation, valid for relatively low values of S_{eff} :

$$1/\tau_{\text{inst}} = 1/\tau_{\text{bulk}} + 2S_{\text{eff}}/W. \quad (3)$$

Estimating S_{eff} therefore requires the bulk lifetime, τ_{bulk} to be known. Since τ_{bulk} cannot be separately measured, an assumed value must be used which makes it difficult to accurately determine low values of S_{eff} . However, the measurement of J_{oe} allows accurate determination of τ_{bulk} . S_{eff} can be calculated from measured J_{oe} values from the relation

$$S_{\text{eff}} = J_0(p_0 + n)/(qn_i^2), \quad (4)$$

where p_0 is the hole concentration in thermal equilibrium (10^{14} cm^{-3}).

We use Eq. (4) to determine S_{eff} at the injection level of $4 \times 10^{15} \text{ cm}^{-3}$ for the data point from Fig. 2 with the highest measured lifetime, which was obtained with $V_{\text{app}} = -11$ V.

This gives a value of τ_{bulk} of 14.4 ms. Substitution of this

FIG. 4. Effective surface recombination velocity S_{eff} as a function of application voltage, calculated from Eq. (4) (squares) and Eq. (3) (circles).

value into Eq. (3) then allows determination of S_{eff} over the entire range of applied voltages. Figure 4 shows the variation of S_{eff} as a function of V_{app} for $n=4 \times 10^{15} \text{ cm}^{-3}$. For comparison, the values of S_{eff} extracted from the application of Eq. (4) to the J_{oe} data of Fig. 3 are also shown. There is a good agreement between the two curves, except for the range of voltages where the condition that the surface be in low level injection is not met.

The lowest measured J_{oe} value from Fig. 3 is 1.8 fA/cm^2 per surface, for $V_{\text{app}}=-11 \text{ V}$. Such a value of J_{oe} on both surfaces would impose a limit on the open circuit

voltage of a solar cell of 780 mV , assuming a short circuit current of 40 mA/cm^2 . From Eq. (4), the corresponding value of S_{eff} at low injection levels (below 10^{13} cm^{-3}) is 0.012 cm s^{-1} . This value was obtained on a sample which received a standard forming gas annealing. Since it is known that the so-called alneals result in better surface passivation,⁹ particularly for positively charged surfaces, it is likely that even lower J_{oe} values can be achieved with such treatments.

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