Determination of Surface Recombination Velocities for Thermal Oxide and Amorphous Silicon on Float Zone Silicon

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Introduction

Recombination at the surface of a silicon solar cell is an important factor in determining the cell efficiency. The descriptive parameter is surface recombination velocity, s. Generally, s increases as the doping of the surface increases, just as the lifetime of carriers within the crystal (τ) generally decreases as the bulk doping increases. Thus, in a comparative study of candidate surface treatments, it is important to choose a silicon surface doping level which is typical of common cell designs. Furthermore, because standard measurement techniques cannot distinguish between recombination at the crystal surface and recombination within the crystal bulk, it is desirable to choose a silicon crystal with high bulk lifetime in order to improve the sensitivity of the technique to surface recombination. In this study, 100 mm diameter float zone (FZ) silicon wafers, double side polished, with a (100) surface and 300 µm thickness were chosen: p-type (boron-doped) nominally 3 Ω-cm and n-type (phosphorus-doped) nominally 1.2 Ω-cm. The primary comparison was made between surfaces passivated with a thermally-grown oxide and those passivated with amorphous silicon deposited by the hot wire method. In addition, the degree of surface passivation associated with the thin chemical oxide created by RCA cleaning was measured, as was that associated with a temporary iodine-methanol treatment.

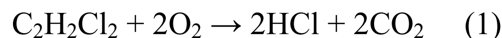
Sample Preparation

Samples for the thermal oxidation study were prepared by cutting the 100 mm diameter FZ wafers into quarters. All four quarters from each wafer were subjected to the RCA clean:

RCA1: 5:1:1 DI H_2O:NH_4OH(29%):H_2O_2 (30%) at 80°C for 10 min, then 10 min rinse;
HF Dip: 99:1 DI H_2O:HF(49%) at room temperature for 1 min, then 1 min rinse;
RCA2: 6:1:1 DI H_2O:HCl(95%):H_2O_2 (30%) at 80°C for 10 min, then 10 min rinse/dry.

Note that a thin chemical oxide resulting from the RCA2 step, estimated to be approximately 7 Å thick, is left in place (no final HF dip). Two of the wafer quadrants are put aside as reference samples so that the excess carrier lifetime in the starting wafer can be measured, while the remaining two wafer quadrants are oxidized.

Thermal oxidation was carried out in a standard quartz tube, 145 mm in diameter. Prior to wafer oxidation, the tube was cleaned using Trans 1,2-Dichloroethylene ($C_2H_2Cl_2$), known as Trans-LC, from Air Products (Schumacher). When combined with oxygen, Trans-LC produces HCl to facilitate cleaning. The reaction is:



$$C_2H_2Cl_2 + 2O_2 \rightarrow 2HCl + 2CO_2 \quad (1)$$

With the Trans-LC bubbler held at 15°C and 130 sccm of N_2 carrier gas passing through the bubbler, 90 sccm of HCl gas is produced. This is 3% of the 3000 sccm of O_2, the main gas flowing through the tube. The tube was cleaned in this way for three hours at 1050°C.

Wafers were oxidized at 1000°C for 150 min. In an effort to minimize the oxide/silicon interface state density, Trans-LC was introduced into the gas ambient as a source of HCl during the oxidation [1]. The gas flows were 3000 sccm of O_2 and 100 sccm of N_2 carrier gas flowing through the Trans-LC bubbler at 15°C. This combination is chosen to provide an optimum flow of HCl which is 2.3% of the main O_2 flow. In this way, a chlorinated oxide approximately 1200 Å thick was produced, as determined by ellipsometry measurements. The oxidation was followed by an anneal in forming gas (10% H_2 and 90% N_2) flowing at 3000 sccm at 450°C for 30 min in the same tube. Both n-type and p-type FZ wafer quadrants were processed together through oxidation and forming gas anneal.

For the amorphous silicon deposition, rectangular blanks 25 mm × 45 mm in size were cut from the FZ wafers and subjected to an aggressive cleaning sequence [2]. Amorphous silicon layers were deposited by hot wire chemical vapor deposition (HWCVD), similar to that described previously for heterojunction cell fabrication [2, 3]. On one side of the crystalline silicon blank, intrinsic amorphous silicon was deposited from an SiH_4 source to a thickness of approximately 4 nm. This is capped by a second amorphous silicon layer doped n-type with PH_3 to give an a-Si:H(i,n) structure. The opposite side of the blank had a similar intrinsic amorphous silicon layer, again capped by a second amorphous silicon layer doped p-type with B_2H_6 to give an a-Si:H(i,p) structure. After depositing these amorphous silicon layers on both sides, the sample was measured to assess the surface recombination velocity.

To obtain an accurate value of bulk lifetime, it is necessary to completely eliminate surface recombination. This condition is approached by applying a temporary chemical passivation, consisting of iodine dissolved in methanol, to the wafer surfaces. First, any surface oxide is removed by a dip in 10:1 DIH_2O:HF(49%) followed by a 30 sec rinse in DI H_2O and an N_2 blow dry. Both sides of a wafer are then coated with a solution of 280 mg of I_2 per liter of CH_3OH. The wafer is then placed in a transparent plastic zip-lock bag for lifetime testing using the photoconductivity decay (PCD) technique.

Method

The effective lifetime is determined by measuring the rate at which photogenerated excess carriers (Δn) return to their equilibrium concentration [4]. Factors contributing to effective lifetime (τ_{eff}) include Shockley-Read-Hall recombination in the crystal bulk (τ_{SRH}), Auger recombination in the crystal bulk (τ_{Auger}) and recombination at the crystal surface (s). For a symmetric structure, as employed in this study, the relationship is:

$$1/\tau_{eff} = -(1/\Delta n)(d\Delta n/dt) = 1/\tau_{SRH} + 1/\tau_{Auger} + 2s/W \quad (2)$$

where W is the thickness of the wafer. If the effective lifetime is measured and corrected for Auger recombination (since equilibrium carrier concentration is known and excess carrier concentration is measured at each instant of time), Eq. 2 can be rewritten as:

$$1/\tau = 1/\tau_{eff} - 1/\tau_{Auger} = 1/\tau_{SRH} + 2s/W \quad (3)$$

If it is further assumed that all recombination occurs at the surface and none occurs within the crystal bulk ($\tau_{SRH} \rightarrow \infty$), then an upper bound for the surface recombination velocity, s_{max}, can be expressed as:

$$s_{max} = \frac{1}{2}\,(W/\tau) \qquad (4)$$

Since high-lifetime FZ wafers were used, the true value of surface recombination velocity is expected to be only marginally lower than this upper bound. This expectation of high lifetime is checked by PCD lifetime measurements with iodine-methanol surface passivation.

Experimental Results

PCD lifetime measurements and analysis were done using the Sinton WCT-boule tester [5]. A linear fit of corrected lifetime as a function of excess carrier density was used to determine the lifetime at zero excess carrier density which is cited in this study. An example is shown in Fig. 1 in which data are accumulated over an excess carrier density ranging from 1.8×10^{15} cm^{-3} to 1.2×10^{16} cm^{-3}. The intercept of the fitted curve at $\Delta n = 0$ is at 1110 s^{-1}, corresponding to a lifetime of 903 µs. From Eq. 3 it can be seen that no variation of lifetime with excess carrier density is considered, and the shallow slope of Fig. 1 indicates this is approximately true.

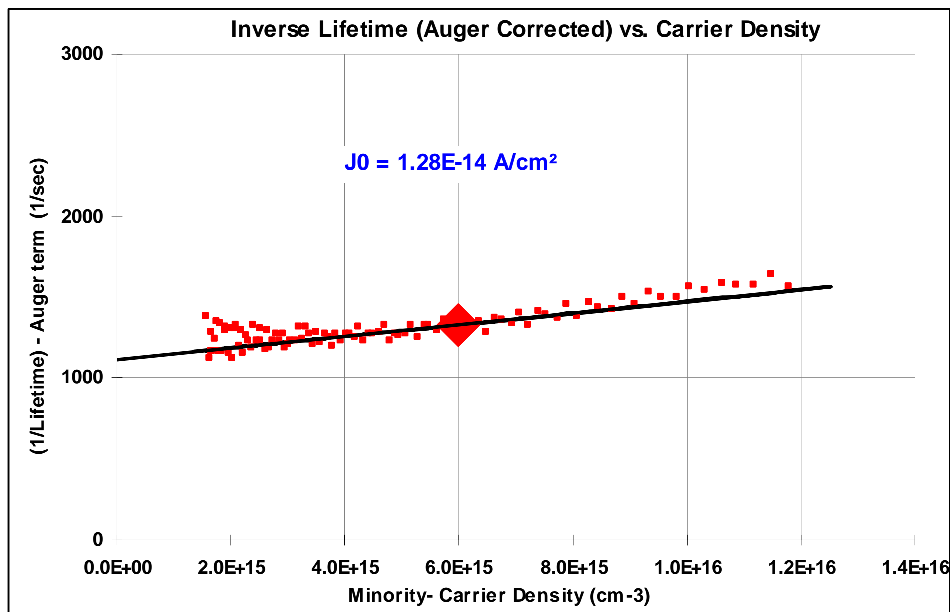


Fig. 1. Plot of corrected inverse lifetime versus excess carrier density for sample T3316-pFZ showing a τ value of 903 µs at Δn=0, corresponding to s_{max} of 17 cm/s.

Results are summarized in Table 1. In addition to τ and s_{max} which is calculated from it, the Sinton tester also determines a value of Implied V_{oc} at one sun from the measured excess carrier densities. This parameter has been found to be a reliable indicator of potential V_{oc} in the finished cell. Measurements with a Bare Si surface are those for samples having only the very thin chemical oxide remaining after the RCA2 clean. The value of s_{max} for such a surface is quite high, while the same sample with iodine-methanol surface passivation has a very low value of s_{max} and a corresponding high lifetime. It is clear that measurable surface recombination is present for the thermally oxidized samples, and that the p-FZ sample suffered degradation in bulk lifetime as well. For the samples passivated with a-Si, the s_{max} values are quite low, comparable to those obtained with iodine-methanol, and give high values for Implied V_{oc} (700 mV).

Table 1. s_{max} and implied V_{oc} inferred from transient PCD lifetime data.

Sample ID	ρ (Ω-cm)	Thickness (μm)	Surface	τ(Δn=0) (μs)	s_{max} (cm/s)	Implied V_{oc} (mV)
n1-FZ	1.2	300	Bare Si	6	2600	532
n1-FZ	1.2	300	Iodine-Methanol	1530	10	690
n3-FZ	1.2	300	Thermal oxide	241	64	650
n3-FZ	1.2	300	Iodine-Methanol	1340	12	690
p2-FZ	3.0	300	Bare Si	2	8900	501
p2-FZ	3.0	300	Iodine-Methanol	2080	7	700
p4-FZ	3.0	300	Thermal oxide	81	60*	613
p4-FZ	3.0	300	Iodine-Methanol	114	n/a	634
T3300-nFZ	1.2	300	a-Si(i,n)/a-Si(i,p)	1200	13	694
T3316-pFZ	3.0	300	a-Si(i,n)/a-Si(i,p)	903	17	700

** s calculated from thermal oxide and iodine-methanol lifetimes assuming 7 cm/s for iodine-methanol.*

Summary

PCD lifetime studies on (100) polished FZ silicon wafers indicate an upper bound for surface recombination velocity of 64 cm/s for a chlorinated thermal oxide with FGA and 13 cm/s for HWCVD a-Si:H passivation on 1.2 Ω-cm n-type. These values correspond to measured Implied V_{oc} values of 650 mV and 700 mV, respectively, consistent with what is frequently achieved for V_{oc} in finished cells having these surface passivation layers. Values of 60 cm/s and 17 cm/s, respectively, were obtained for 3.0 Ω-cm p-type FZ silicon. An upper bound for surface recombination velocity associated with iodine-methanol chemical surface passivation as low as 7 cm/s was obtained, illustrating its value in facilitating accurate bulk lifetime measurements. The initial high bulk lifetime (1530 μs) determined for n-type FZ silicon was essentially preserved through the 1000°C thermal oxidation for 150 min (1340 μs). However, a corresponding high initial lifetime (2080 μs) in p-type FZ silicon was not maintained through the same oxidation (114 μs), presumably because of the formation of recombination centers involving boron complexes.

References

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