Degradation of oxide-passivated boron-diffused silicon

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Recombination in oxide-passivated boron-diffused silicon is found to increase severely at room temperature. The degradation reaction leads to a 45 fold increase in emitter recombination that saturates in ~120 days, irrespective of whether the samples received a forming-gas anneal. The degradation was also examined for diffusions stored at 50, 75, and 100 °C. The results indicate that the degradation follows a second-order reaction where the time constant of one component of the reaction is 10–40 times shorter than the other, and where the activation energy of the fast reaction is 0.19 ± 0.05 eV. Subsequent to degradation, annealing in air reduces the recombination with increasing anneal temperature saturating at ~300 °C to a value that is about four times higher than the predegradation value. A likely cause of this degradation is a reaction of atomic hydrogen at the silicon-oxide-silicon interface. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3195656]

High-efficiency silicon solar cells require low surface recombination.[1] The best-known means to attain this is with oxide-passivated lightly doped diffusions where the dopant can be either phosphorus[2,3] or boron.[2,4,5] Many solar cell designs have employed the former,[1,6,7] with phosphorus-diffused surfaces exhibiting excellent stability.[8] The same is not always true of cells with boron-diffused surfaces,[4,5,9] with the best-known example being the "passivated emitter rear-totally diffused" (PERT) cells fabricated from n-type silicon. After two years, the open-circuit voltage (V_{oc}) of these cells had decreased by an average of 38.9 mV, equating to a 2% reduction in absolute efficiency.[9]

In this work, the recombination rate associated with oxide-passivated boron diffusions is monitored over many months. A severe increase in recombination that saturates in about 120 days is observed. We examine the extent of this degradation, the activation energy E_a of the associated reaction, annealing of this degradation, and the underlying mechanism.

Symmetrical test structures were fabricated on floating zone, (100), n-type silicon wafers to allow photoconductance lifetime measurements of boron diffusions. The wafers were prepared by acid etching in hydrofluoric/nitric removing ~20 μm of saw damage, and Radio Corporation of American (RCA) cleaning[10] to remove metal and organic contamination. Subsequently a high-lifetime BBr_3 diffusion and oxide passivation was performed. This consisted of the deposition of a boron silicate glass at 850 °C for 20 min, a short N_2 drive-in at 850 °C for 20 min, a dry oxidation at 900 °C for 30 min, a removal of the oxide in HF, a dry oxidation at T_{ox} for t_{ox}, and an N_2 anneal performed at T_{ox} for 30 min, where T_{ox} and t_{ox} are supplied in Table I. All but two of the samples also received a forming-gas anneal (FGA) at 400 °C for 30 min in 95% Ar and 5% H_2. This procedure led to samples with a sheet resistance between 200 and 335 Ω/sq, an oxide thickness of 35 ± 5 nm, and an initial effective lifetime greater than 1 ms. The resulting diffusions and the quality of the passivation are similar to that used in high-efficiency silicon solar cells.[7]

To characterize the increasing recombination and the temperature dependence of the degradation, the samples were stored in air at 25, 50, 75, and 100 °C. The recombination was monitored over 160 days, where prior to each measurement the samples were cooled to room temperature. This procedure was effective in characterizing degradation of samples stored above room temperature because the time taken to cool and measure the samples was much shorter than their degradation time constants.

The WCT-100 photoconductance instrument[11] was employed to measure the effective lifetime τ_{eff} as a function of excess minority carrier concentration Δn. Extraction of the initial J_{0e} and τ_{bulk} was performed by the method devised by Kane and Swanson[2] but with modern values for the intrinsic-carrier concentration n_i (Ref. 12) and combined carrier mobility $\mu_n + \mu_p$.[13] This method could not be used after the samples degraded because the increase in emitter recombination caused Δn to vary significantly across the wafer thickness.[14] Instead, τ_{bulk} was assumed constant throughout the experiment, a reasonable assumption for n-type silicon,[15] and changes in τ_{eff} were attributed to changes in J_{0e}. This method to determine J_{0e} avoided distortions in the measurement process owing to the nonuniform Δn profile caused by large recombination at the diffused surfaces.

Figure 1 plots the J_{0e} of boron diffusions stored at room temperature as a function of time. These samples were prepared with oxidation recipe 1 (Table I). The J_{0e} of each sample increased from 30–80 to 1000–1400 fA/cm^2, saturating after $\sim 1.0 \times 10^7$ s (~120 days). The degradation was similar, irrespective of whether the samples received an FGA or whether the wafer resistivity was 5 or 1000 Ω cm.

TABLE I. Oxidation temperature T_{ox} and time t_{ox} and the subsequent sheet resistance R_s.

Recipe	T_{ox} (°C)	t_{ox} (min)	R_s (Ω/sq)
1	1100	6	200
2	1000	40	265
3	900	90	335

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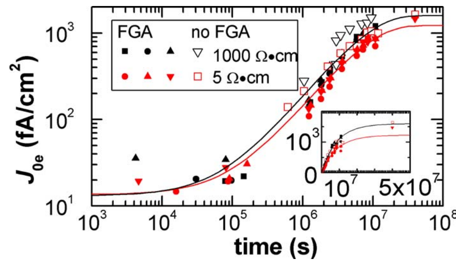

FIG. 1. (Color online) Emitter saturation current J_{0e} as a function of time for eight samples stored in air at room temperature. As denoted in the legend, the data represents samples fabricated on 5 and 1000 Ω cm n-type silicon, and samples that received and did not receive an FGA. The lines are least-squares fits of Eq. (2) to the data of FGAed samples for each wafer resistivity. The inset plots the data on linear scales.

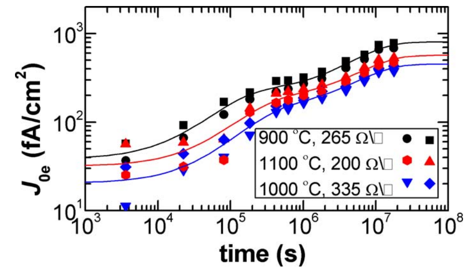

FIG. 2. (Color online) Emitter saturation current J_{0E} as a function of time for three samples stored in air at 100 °C. The samples were fabricated from 1000 Ω cm n-type silicon and received oxidation recipes 1, 2, and 3. The lines are least-squares fits of Eq. 3 to the data.

The degradation was also similar when the samples were illuminated by a halogen lamp at an intensity of 1 mW/cm^2.

The degradation of the samples stored at 25 °C followed a first-order exponential,

$$J_{0e} = J_{0e,\text{initial}} + J_{0e,\text{deg}}[1 - \exp(-t/\tau_1)], \tag{1}$$

where $J_{0e,\text{initial}}$ and $J_{0e,\text{deg}}$ are the initial and increase in J_{0e}, and τ_1 is the time constant of the reaction. The lines in Fig. 1 are a least-squares fit to the data of the FGAed samples for each resistivity. Table II lists the best-fit parameters.

Figure 2 plots the results of boron diffusions stored at 100 °C as a function of time. These samples were prepared with oxidation recipes 1, 2, and 3 on 1000 Ω cm silicon. The J_{0e} of all was found to increase from 15–80 to 500–800 fA/cm^2. This ten to 20 fold increase in J_{0e} occurred irrespective of the oxidation recipe but was less than the 30–45 fold increase observed at room temperature. Unlike the samples stored at 25 °C, the degradation does not follow a first-order exponential. Instead, it more closely follows a second-order exponential,

$$J_{0e} = J_{0e,t0} + J_{0e,\text{deg }1}[1 - \exp(-t/\tau_1)] + J_{0e,\text{deg }2}[1 - \exp(-t/\tau_2)], \tag{2}$$

where $J_{0e,t0}$, $J_{0e,\text{deg }1}$, and $J_{0e,\text{deg }2}$ are the initial and increase in J_{0e}, and τ_1 and τ_2 are the time constants of the degradation reactions. Figure 2 includes the lines of best fit for samples prepared with each oxidation recipe. Thus, storing at 100 °C allowed the observation of a fast degradation reaction, observed at room temperature, and a second slower degradation that could not be observed at room temperature.

TABLE II. Parameters from fitting of Eq. 3 to $J_{0e}(t)$ for samples fabricated on 1000 Ω cm n-type silicon. The increase in recombination ($J_{0e,\text{deg }1}$, $J_{0e,\text{deg }2}$) and the time constants (τ_1, τ_2) are presented with errors representing the 95% confidence interval.

Sample		Fast degradation		Slow degradation	
Temp (°C)	Recipe	J_{0e} , deg1 (fA/cm^2)	$\tau_1 \times 10^5$ (s)	J_{0e} , deg2 (fA/cm^2)	$\tau_2 \times 10^5$ (s)
25	1	952±40	8.9±0.4	…	…
50	1	240±50	3.2±1	1100±600	25±29
75	1	210±30	2.0±0.5	800±300	46±60
100	1	190±20	1.9±0.5	500±100	35±42
100	1	150±20	2.1±0.8	390±40	91±30
100	2	120±10	2.5±0.8	310±20	85±20
100	3	180±20	1.0±0.3	590±30	76±10

Table II lists the fast and slow degradation time constants and J_{0e} increase from the lease-squares fit of Eq. (2) to $J_{0e}(t)$ for samples stored above 25 °C, and Eq. (1) for samples stored at 25 °C, as the slow degradation process was not observable at room temperature. The error ranges represent the 95% confidence intervals and these indicate there is a low uncertainty of the fast time constant τ_1 and a larger uncertainty for the slow time constant τ_2, where it becomes reasonable for samples stored at 100 °C. The table shows that τ_1 is ten to 40 times shorter than τ_2 highlighting the different time constants of the reactions. We also find the degradation magnitude reduces with increasing storage temperature, in agreement with following annealing results.

The activation energy E_a of the fast reaction is 0.19 ± 0.5 eV as determined by performing an Arrhenius plot of the reaction rates for samples stored at 25, 50, 75, and 100 °C. The reaction rates for E_a calculation were taken to be the inverse of τ_1 the time constant of the fast reaction.

Two other reports have observed the magnitude of this degradation reaction. First, Zhao *et al.*[9] measured a decrease in V_{oc} of n-type PERT solar cells after two to three years storage in the dark at room temperature. The maximum and average decrease in V_{oc} corresponds to an increase in J_{0e} of 3300 and 270 fA/cm^2, respectively, in agreement with the results presented in Fig. 1. Here, the equivalent J_{0e} was determined using the single diode model of a solar cell, as in Ref. 16. Second, Altermatt *et al.*[4] found the J_{0e} of oxide-passivated boron diffusions of resistivity 31–213 Ω/sq to increase significantly when left in the dark for two years. When grown with *in situ* trichloroethane (TCA) the samples degraded to 400–500 fA/cm^2, whereas without TCA, the J_{0e} of the samples of this study degraded to ~2000 fA/cm^2, in agreement with the data presented in Fig. 1. These studies indicate boron diffusions degrade irrespective of resistivity and is not limited to the procedure used in this report.

The mechanism that underlies the degradation was examined further by annealing the sample at increasing temperature. One of the samples that degraded at room was first annealed in air at temperatures ranging from 25 to 275 °C using the temperature and injection-dependent lifetime spectroscopy system described by Paudyal *et al.*[17] This system permitted a monitoring of τ_{eff} during the annealing so that it could be stopped once it saturated. The system was then cooled to 25 °C to measure J_{0e} to avoid any temperature dependence in J_{0e}. To complete the experiment, the samples were annealed in N_2 at 400 °C in a quartz furnace for 30 min and the J_{0e} was remeasured.

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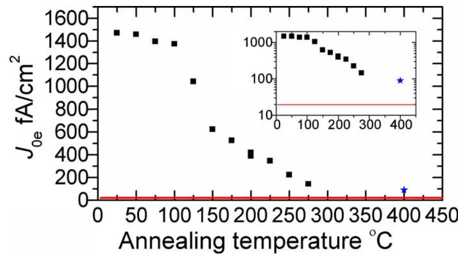

FIG. 3. (Color online) Emitter saturation current J_{0e} of a degraded sample that had been stored for over one year at room temperature. The red line shows the predegradation J_{0e}. The symbols plot J_{0e} after an anneal in air at increasing temperature. (The final anneal at 400 °C was performed in N_2). The inset plots J_{0e} on log scale.

The above procedure resulted in the J_{0e} versus annealing temperature plotted in Fig. 3. The red line indicates the as-fabricated J_{0e}. From this plot we see that there is a large reduction in J_{0e} between 100 and 175 °C, possibly indicating that one of the two mechanisms that caused the increase in recombination is strongly annealed. There is a continual smaller reduction in recombination annealing above 175 °C. Thus, the annealing significantly improved J_{0e} but even after a 400 °C, it remains four times its as-fabricated level.

We propose the degradation is caused by a reaction between the $Si-SiO_2$ interface and atomic hydrogen,[18] where P_b defects[19] are formed with an E_a of 0.2 eV.[20] A possible source of H^+ specific to these structures is boron-hydrogen (BH) complexes created in the emitter during high-temperature processing, where the dissociation of BH pairs has an E_a of 0.6 V.[21] Thus, for this mechanism to be consistent with the observed E_a of the fast reaction (0.23 ± 0.05 eV), the initial degradation cannot be limited by BH dissociation, either because (i) there is an initial excess of H^+ or (ii) the pre-exponential reaction constant of the BH dissociation is much higher than that of the P_b generation. There may be alternative sources of H^+ causing this degradation such as from the passivating oxide or the atmosphere, but these are not limited to boron-diffused structures.

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