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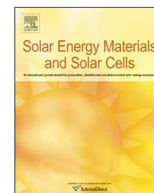

# Enhanced stability of passivation quality on diffused silicon surfaces under light-induced degradation conditions

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ABSTRACT

Significant surface related degradation (SRD) is observed in samples passivated with either $SiN_x$:H or $AlO_x$:H/$SiN_x$:H during treatment at 150 °C and 1 sun equivalent illumination intensity. Degradation of $SiN_x$:H passivation is caused by a decrease of chemical passivation quality whereas degradation of $AlO_x$:H/$SiN_x$:H is caused by a decrease of fixed charge density. SRD is, however, strongly suppressed on highly doped silicon surfaces resulting from a diffusion step. Device simulations indicate that this cannot only be explained by reduced sensitivity to changes at the silicon surface due to the diffused region, and implications for defect formation are discussed.

## 1. Introduction

Different types of light induced degradation (LID) can significantly decrease the bulk minority carrier lifetime $\tau_b$ in crystalline silicon, which directly translates to a lower efficiency of affected silicon solar cells. Examples are Light and elevated Temperature Induced Degradation (LeTID) [1–5] and boron-oxygen (BO) related LID [6–8]. Recently, it has been observed that surface passivation on crystalline silicon [9] may degrade as well after prolonged treatment under typical LID conditions [10–12]. Accordingly, degradation may occur both in the bulk and at the surface of a sample during LID experiments, making the interpretation of measurement data challenging [12].

So far, it has been shown that single layers of $SiN_x$:H as well as layer stacks consisting of $SiO_x$/$SiN_x$:H and $AlO_x$:H/$SiN_x$:H can be affected by surface related degradation (SRD). Since the latter two are used as rear-side passivation in passivated emitter and rear cell concepts (PERC) [13–15] and SRD was observed even at 60 °C and 0.1 suns in lifetime samples, it appears possible that finished PERC cells could be affected in the long term as well [12]. However, SRD has so far only been observed on lowly doped silicon. In this contribution, it will be shown that degradation of surface passivation quality is strongly suppressed on diffused silicon surfaces. Potential reasons for this observation will be discussed on the basis of device simulations.

## 2. Material and methods

### 2.1. Sample processing

Lifetime samples were made of either boron-doped float-zone silicon (FZ-Si) with doping density $N_d \approx 1.5 \cdot 10^{16}$ cm$^{-3}$ or phosphorous-doped FZ-Si with $N_d \approx 2 \cdot 10^{15}$ cm$^{-3}$. The wafers received a saw damage etch, chemical cleaning and chemical polish by the manufacturer and were shipped with a thickness of 250 µm and a thin surface oxide layer. This layer was removed by a dip in diluted HF. Further sample processing and sample labeling are illustrated in Fig. 1.

One B-doped wafer received a diffusion in $POCl_3$ ambient at 840 °C, resulting in a heavily P-doped $n^+$ emitter with sheet resistance ~55 Ω/sq. After removal of the phosphosilicate glass in diluted HF, the emitter was etched back (EEB) to ~120 Ω/sq. using an aqueous solution of HF, $HNO_3$ and $NaNO_2$ [16,17]. On other samples, heavily B-doped $p^+$ layers were formed in $BBr_3$ ambient at a drive-in temperature of 910 °C, resulting in a sheet resistance ~100 Ω/sq. The surface of diffused samples was then oxidized in a solution of $H_2O_2$ and $H_2SO_4$ at 80 °C, followed by a dip in diluted HF to remove impurities from the sample surface (Piranha clean). The resulting doping profiles were measured *via* Electrochemical Capacitance-Voltage (ECV) profiling and are shown in Fig. 2. Additional wafers received no diffusion step to serve as reference samples.

The P-diffused and a reference wafer were coated with ~75 nm $SiN_x$:H in a direct plasma-enhanced chemical vapor deposition (PECVD) at 40 kHz. B-diffused wafers and references were coated with ~10 nm

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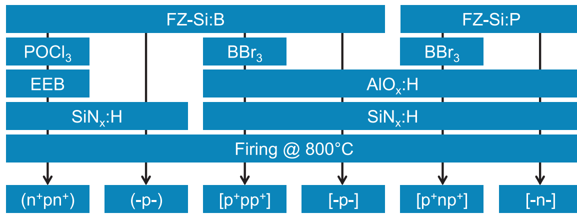


**Fig. 1.** Process flow and labeling of samples. Sample names indicate the sample structure and different brackets relate to different dielectric passivation layers.

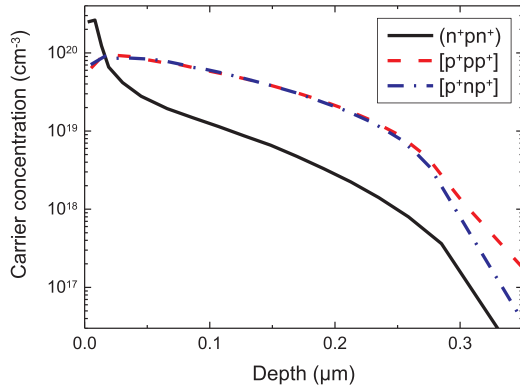


**Fig. 2.** Depth-resolved carrier concentrations measured *via* ECV profiling. In case of the $(n^+pn^+)$ sample, the emitter was already etched back to ~120 Ω/sq. before ECV profiling.

$AlO_x$:H grown by plasma assisted atomic layer deposition (PA-ALD) and capped with ~75 nm of $SiN_x$:H deposited in a remote plasma PECVD at 2.45 GHz. The refractive index of the $SiN_x$:H layers was in both cases ~2.0 at 600 nm and all layers were deposited symmetrically on both wafer sides. Finally, all samples were laser-cut to 5 cm edge length, fired in a fast firing belt furnace at measured peak sample temperature (800 ± 10) °C, and stored in darkness until sample treatment started.

### 2.2. Sample treatment and analysis

Samples were treated in ambient air on hotplates at 150 °C and (0.9 ± 0.1) sun equivalent halogen lamp illumination which was achieved by matching the short circuit current of a solar cell to that under a solar spectrum simulator [18]. Sample treatment was repeatedly interrupted to measure the effective lifetime $\tau_{eff}$ using the generalized mode [19] of a Sinton Instruments lifetime tester (WCT-120) [20] at 30 °C.

To quantitatively compare SRD, surface related saturation current densities $J_0$ are determined from measured $\tau_{eff}$ according to the method described by Kimmerle *et al.* [21]. The excess charge carrier density $\Delta n$ (also called "injection level") for the fit of $J_0$ ranges from $8{\cdot}10^{15}$ to $1.5{\cdot}10^{16}$ cm$^{-3}$ for B-doped samples and from $6{\cdot}10^{15}$ to $1.2{\cdot}10^{16}$ cm$^{-3}$ for P-doped samples. Values of $J_0$ are calculated with respect to the effective intrinsic carrier concentration $n_{ie} = \sqrt{p_0 n_0}$ at 25 °C where $p_0$ is the equilibrium hole concentration and $n_0$ the equilibrium electron concentration in the bulk. The uncertainty of $\tau_{eff}$ in a transient PCD measurement is ~8% [22,23]. To estimate an uncertainty of $J_0$ values, input values of $\tau_{eff}$ were therefore varied by ± 8% and the resulting variation in $J_0$ (~8% as well) constitutes one part of its uncertainty. It is furthermore possible that data are not strictly linear in the region of the $J_0$ fit which forms an additional source of uncertainty. For example, strong bulk recombination can have a residual influence even after correction measures as described in [21], leading to a slight curvature in data to fit. To account for this uncertainty, data were additionally fitted only in the lower or upper part of their fit ranges and the resulting difference in $J_0$, being a measure of data curvature, was weighted such that a residual influence of known bulk degradation (minimum I in Fig. 3) was covered by the total uncertainty.

In case of diffused samples, the resulting $J_0$ equals the emitter saturation current density $J_{0e}$. For non-diffused samples, $J_0$ equals the surface saturation current density $J_{0s}$ [24] under the assumption that surface related recombination happens at the silicon surface only and can therefore be described with a surface recombination velocity $S$. For strong band bending due to high fixed charge density $Q_f$ of dielectric layers, the following relationship holds [24]:

$$J_{0s} = qS\frac{2kT\epsilon_{Si}}{Q_f^2}n_{is}^2 \approx qS\frac{2kT\epsilon_{Si}}{Q_f^2}n_{ie}^2 \tag{1}$$

with the effective intrinsic carrier concentration $n_{is}$ at the sample surface and $n_{ie}$ in the bulk which differ only marginally in non-diffused samples. Here and in the following, $S$ equals the surface recombination velocity of electrons $S_{n0}$ when electrons are minority carriers at the surface and it equals the surface recombination velocity of holes $S_{p0}$ when holes are the minority species.

After treatment, selected samples were wet-chemically re-passivated using iodine ethanol (IE). To achieve this, dielectric layers were removed in diluted HF. Afterwards, ~4 µm were removed on both samples sides in a solution of acetic acid, $HNO_3$ and HF. Samples then received two Piranha cleans and were passivated using a 0.08 M iodine in ethanol solution [25–28]. To exclude outliers, $J_0$ fit ranges had to be slightly adjusted for IE passivated samples.

Selected samples were additionally analyzed at different points of treatment with corona charging (CC) series and capacitance-voltage (CV) measurements on both sample sides. CC can compensate the field effect passivation by deposition of charges of opposite sign compared to $Q_f$ of a dielectric layer. The minimal lifetime reached during a CC series

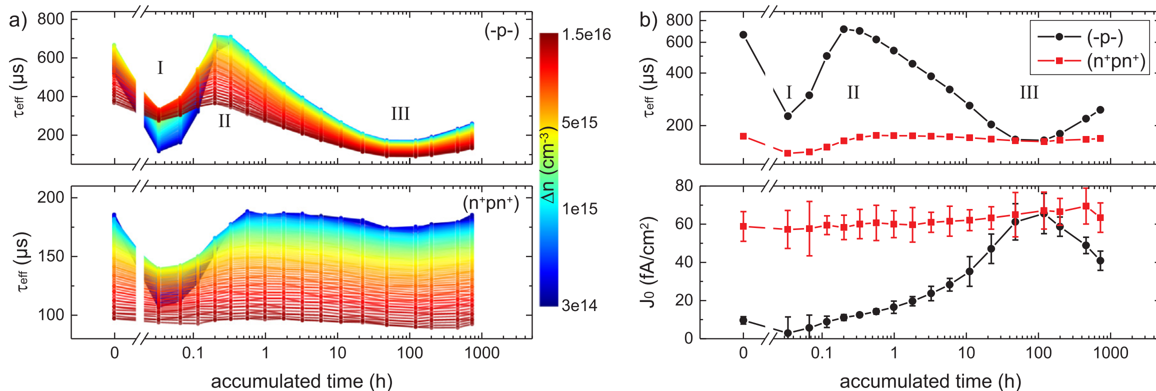


**Fig. 3.** (a) Injection resolved measurement of $\tau_{eff}$ of B-doped samples with and without P-emitter during treatment at 150 °C and ~1 sun equivalent illumination (color online). (b) Measurement of $\tau_{eff}$ ($\Delta n$ = 0.1 $N_d$) and calculated values of $J_0$ of the same samples.

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