

# Surface photovoltage measurements on Si solar cell substrates after cleaning and passivation in ozone containing solutions

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## 1. Introduction

Silicon (Si) solar cell fabrication includes multiple wet-chemical cleaning steps involving large amounts of chemicals. Typical wet processes for texturing and cleaning of crystalline Si surfaces today are based either on alkaline (KOH, KOH-IPA, TMAH) or acidic (HF, HNO<sub>3</sub>) etching sequences, followed by RCA cleaning processes in alkaline (SC 1) or acidic (SC 2) H<sub>2</sub>O<sub>2</sub> containing solutions leaving the Si substrates with a hydrophilic surface [1]. In particular, for high efficiency silicon heterojunction (SHJ) solar cells surface cleaning with SC1 or proprietary mixtures and subsequent HF-dip is done, which changes the surface properties to more hydrophobic behavior. Wet-chemical oxidation with ozone dissolved in ultra-pure water (DIW-O<sub>3</sub>) is a high quality and low cost alternative to replace some of these concentrated chemical solutions. Due to an easy implementation into standard production flows, optimized DIW-O<sub>3</sub> treatments at ambient temperature can be prospectively utilized for minimizing the energy and chemical consumption in solar cell manufacturing.

As recently reported, the implementation of ozone-based cleaning, inline PECVD and screen printing in the silicon heterojunction process chain enabling efficiencies of SHJ solar cells up to 22.7% [2]. Wet-chemical oxidation processes in ozonized DIW were also developed for tunnel oxide passivated contacts (TOPCon) as an alternative to classical heterojunction solar cells enabling efficiencies up to 24.4% [3].

This contribution reports on surface photovoltage (SPV) investigations of wet-chemical substrate treatments in hydrochloric acid (HCl) and hydrofluoric acid (HF) containing DIW-O<sub>3</sub> solutions, which were developed in order to reduce the number of wet-chemical process steps, by combination of cleaning, oxidation and etching processes in the same bath. According to our earlier reported results, after sequences of DIW-O<sub>3</sub> oxidation and subsequent oxide removal in diluted HF solution on H-terminated substrates values of interface states densities  $D_{it,min} < 5 \cdot 10^{11} \text{eV}^{-1} \text{cm}^{-2}$  could be achieved, comparable to values obtained on similar substrates by the standard RCA process followed by HF dip [4].

## 2. Experimental

N-type Si solar cell substrates with random pyramids were subjected to wet-chemical treatments in DIW-O<sub>3</sub> with increasing HCl and HF content with and without pre-treatment in diluted HF solution. Then, large signal SPV measurements were carried out on these samples in order to obtain direct information about the effects of hydrochloric acid (HCl) and /or HF content on the resulting electronic interface properties, surface charge and interface state densities  $D_{it}(E)$ . The resulting maximal values of surface photovoltage and energetic distributions of rechargeable interface states were compared to those obtained on similar substrates before and after RCA treatment followed by oxide removal in diluted HF solution.

The SPV measurements were carried out directly after wet-chemical treatment without any contact preparation, using a mica foil dielectric spacer and a transparent conductive oxide front contact (TCO) in the same experimental set-up as specified in ref [4]. From the large-signal photovoltage pulses (Fig. 2a and b) recorded with a transient recorder (time resolution: 5 ns) the surface potentials  $\Phi_s$  were obtained as described in ref. [5].

The energetic distribution of interface states  $D_{it}(E)$  was determined from series of photovoltage pulses, applying varying external electric field voltages  $U_{\text{Field}}$  between a transparent electrode and the Si wafer (Fig. 1a, b) [4].

### 3. Results

Surface charge and interface state densities  $D_{it}$  on Si substrate surfaces depend on the manufacturing process, storage conditions and previous cleaning procedures.

On polished Si substrates the RCA cleaning and subsequent HF treatment procedures change the surface charge by removing surface contaminations and passivating the surface by hydrogen (H) termination (Fig. 1, curves 1).

On as cut substrates (Fig. 3a shows their surface morphology) bulk defects in the near surface region generate high values of  $D_{it}$  which cannot be reduced by surface cleaning treatments (Fig. 1, curves 2). However, the surface defects remaining after saw damage etching (Fig. 3b) decrease significantly by cleaning, surface oxidation in SC 1 and SC 2 solution followed by HF dip (Fig. 1 curves 3).

The texturization process (Fig. 3c) increases significantly the surface micro-roughness and interface state density of silicon substrates, which can be afterwards also mainly reduced by wet-chemical oxidation in  $H_2O_2$  containing solutions and subsequent oxide removal (Fig. 1, curves 4).

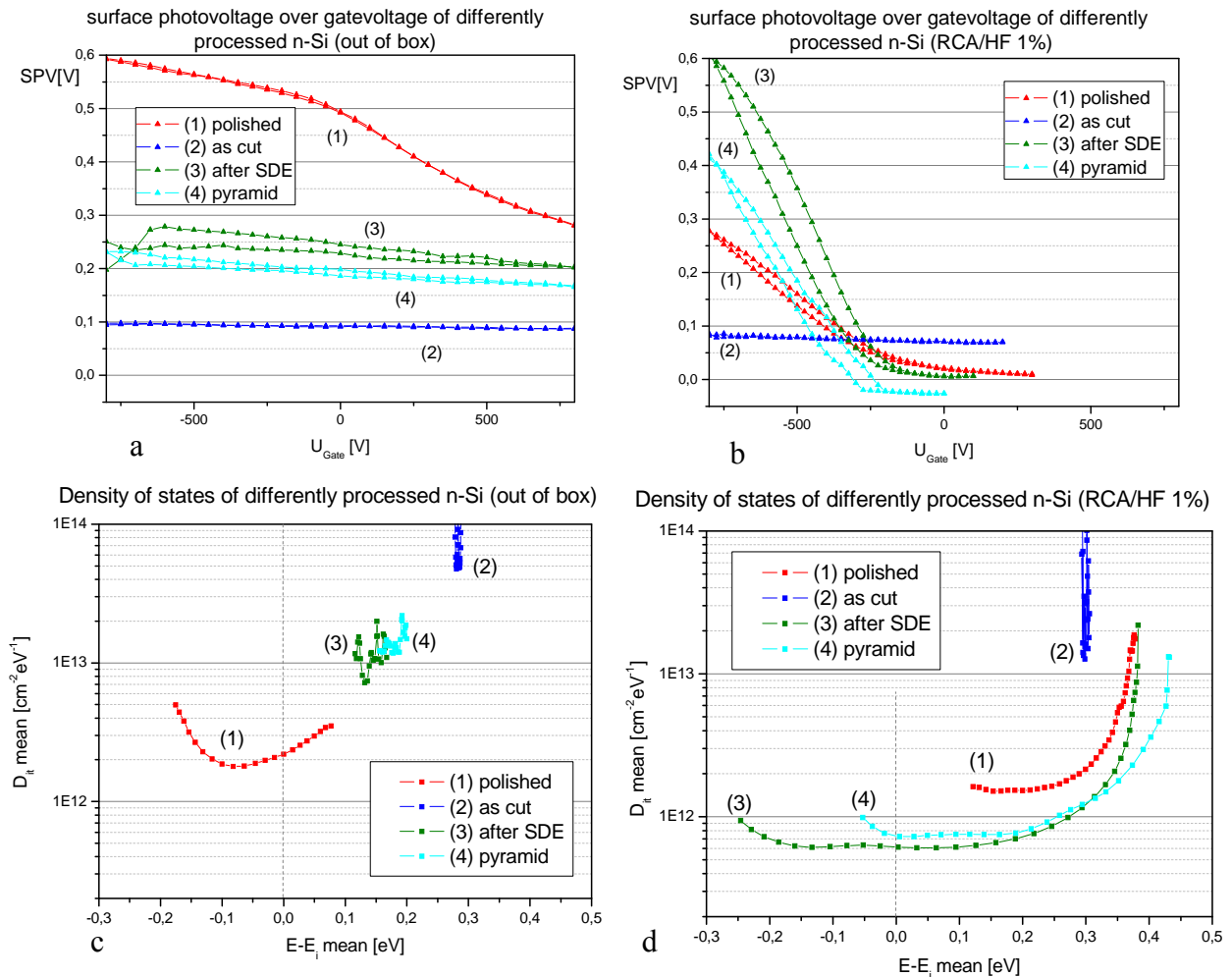


Fig. 1 Surface photovoltage vs. field voltage  $U_{Ph,max}$  ( $U_{Field}$ ) plots and resulting energetic distributions of interface states  $D_{it}$  (E) obtained on differently processed n-type Si solar cell substrates before and after RCA cleaning.

All wet-chemical etching procedures include two essential steps: the formation of a Si/SiO<sub>2</sub> interface by oxidising components of the solutions, and the removal of this oxide layer by HF. The reaction rate of these competing processes is strongly influenced by the concentration of compounds, temperature and pH-value.

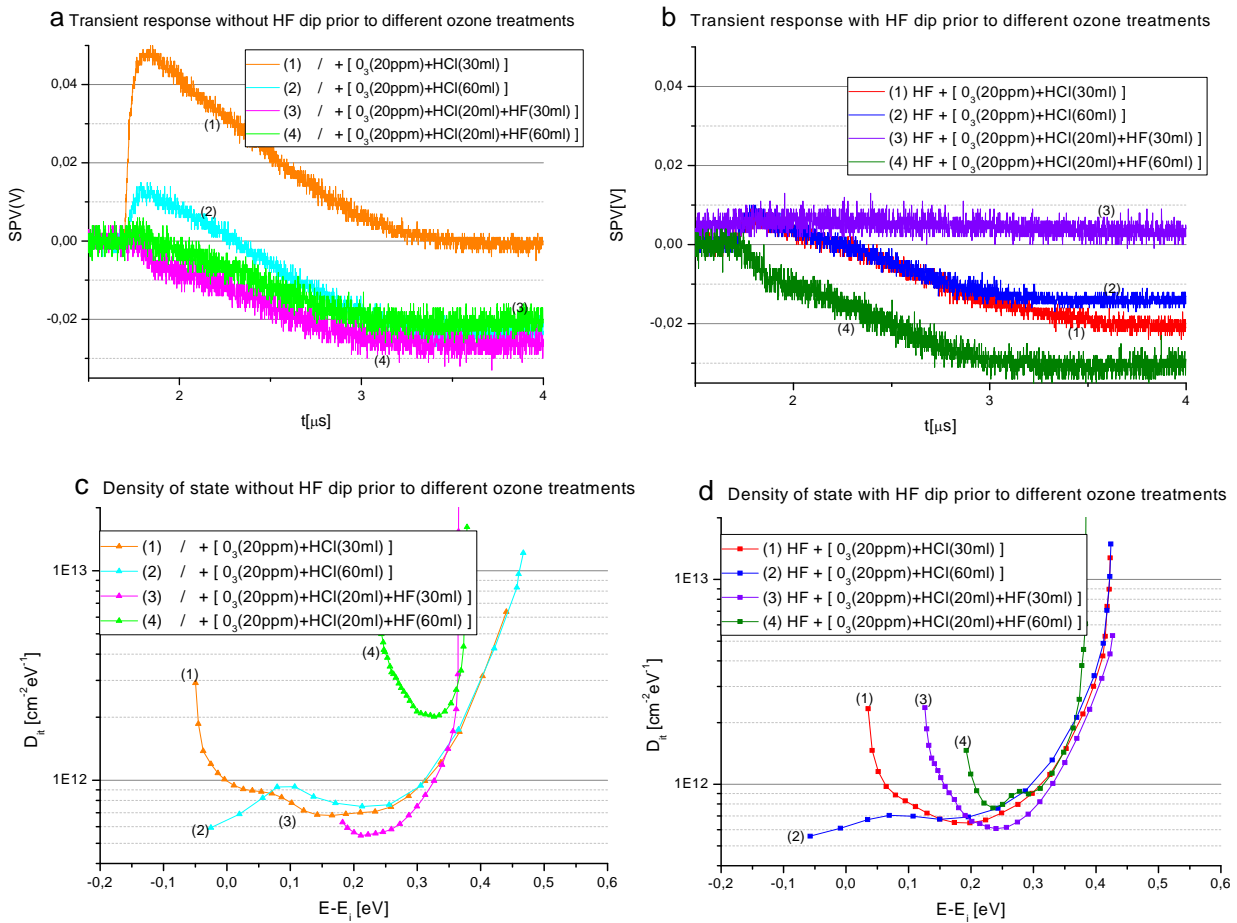


Fig. 2 Surface photo voltage transients and  $D_{it}(E)$  obtained on n-type solar cell substrates textured with pyramids after DIW- $O_3$  treatment with various HCl and HF contents, with (right) and without (left) previous HF-dip

Therefore, the development of combined one step cleaning, etching and H-termination processes requires a careful optimization of special wet-chemical solutions with respect to subsequent passivation and/or p/n junction and contact formation. The effect of HCl and HF admixtures was investigated by SPV measurements on n-type Si solar cell substrates textured by random pyramids. Similar samples, with and without HF pre-treatment, prepared in DIW containing 20 ppm  $O_3$  and rising ratio of HCl and HF were utilized to separate the influence of oxidizing and oxide etching processes on electronic interface properties. The effect of HCl admixture in hot water on the interface recombination properties of Si substrates treated prior to the deposition of all-PECVD  $AlO_x/a-SiN_x$  passivation stacks was recently successfully tested in order to replace cost intensive pre-treatments in solar cells manufacturing [6]. During wet-chemical oxidation by diluted HCl solutions the interface of wet-chemical oxides becomes smoother than the initial surface. After treatment in DIW- $O_3$  with different HCl contents wet-chemically oxidized surfaces characterized by relatively low densities of interface states were obtained without prior HF dip. Utilizing DIW- $O_3$  solutions with lower HCl concentration, the increasing surface micro-roughness due to the previous HF dip, however, results in higher densities of states in the lower part of the gap (Fig. 2, curves 1 and 2).

In order to achieve H-terminated surfaces applying only an one step process it is necessary to add HF to the DIW- $O_3$  solution. By SPV measurements during HF treatment on the wet-chemically oxidised Si substrate (not shown here) typically three phases can be distinguished, which are correlated (i) to the thinning of the oxide, (ii) to the oxide removal and the H-termination which decrease interface states, and (iii) the etching attack of the H-terminated silicon surface resulting in increasing surface micro-roughness and  $D_{it}$  [7].

Treatments in DIW-O<sub>3</sub> with different HF contents and lower HCl concentration cause a high density of interface states which appear in the lower half of the gap. (Fig. 2, curves 3 and 4).

The density of these state were found to be generally higher on HF pre-treated substrates (Fig 2), probably because the competition between oxidation, oxide removal and surface etching starts directly on the oxide free, H-terminated Si surface. The application of solutions with higher HF content additionally increases the minimal value  $D_{it,min}$  of the energetic distribution of interface states (Fig. 2 curves 4).

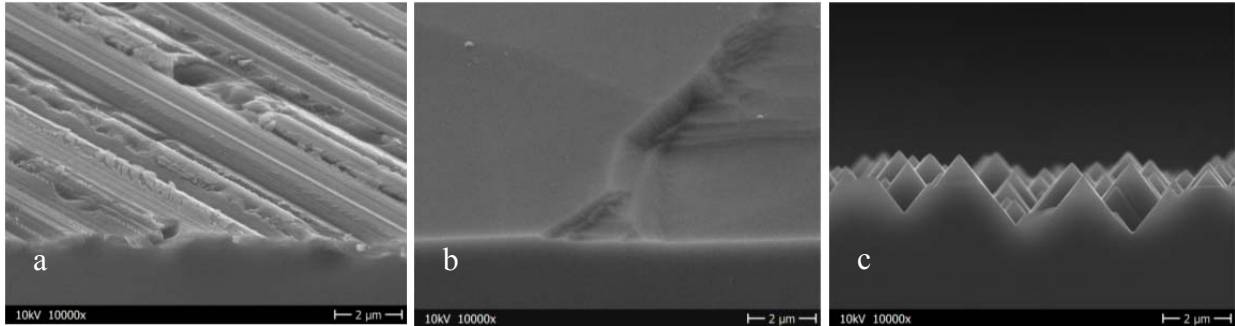


Fig. 3: SEM micrographs, (10000x) of n-type Si(100) substrates (a) as cut, (b) after saw damage etch, and (c) after anisotropic texturization in alkaline etchant KOH / IPA

Summarizing these results, it is demonstrated, that field depending SPV measurement can be used as a surface sensitive tool to investigate and optimize wet-chemical Si surface treatments. Oxidizing treatments in DIW-O<sub>3</sub> with HCl admixture can be utilized for passivation of substrate surfaces by well-defined wet-chemical oxide layers as utilized for tunnel oxide passivated contacts (TOPCon). Furthermore, depending on the O<sub>3</sub>, HCl and HF content H-terminated substrate surfaces can be prepared as starting point of subsequent PECVD deposition processes for high efficiency silicon Heterojunctions.

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