Wet-chemical passivation of atomically flat and structured silicon substrates for solar cell application

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Abstract

Special sequences of wet-chemical oxidation and etching steps were optimised with respect to the etching behaviour of differently oriented silicon to prepare very smooth silicon interfaces with excellent electronic properties on mono- and poly-crystalline substrates. Surface photovoltage (SPV) and photoluminescence (PL) measurements, atomic force microscopy (AFM) and scanning electron microscopy (SEM) investigations were utilised to develop wet-chemical smoothing procedures for atomically flat and structured surfaces, respectively. Hydrogen-termination as well as passivation by wet-chemical oxides were used to inhibit surface contamination and native oxidation during the technological processing. Compared to conventional pre-treatments, significantly lower micro-roughness and densities of surface states were achieved on mono-crystalline Si(100), on evenly distributed atomic steps, such as on vicinal Si(111), on silicon wafers with randomly distributed upside pyramids, and on poly-crystalline EFG (Edge-defined Film-fed-Growth) silicon substrates.

The recombination loss at a-Si:H/c-Si interfaces prepared on c-Si substrates with randomly distributed upside pyramids was markedly reduced by an optimised wet-chemical smoothing procedure, as determined by PL measurements. For amorphous–crystalline hetero-junction solar cells (ZnO/a-Si:H(n)/c-Si(p)/Al) with textured c-Si substrates the smoothening procedure results in a significant increase of short circuit current \( I_{sc} \), fill factor and efficiency \( \eta \). The scatter in the cell parameters for measurements on different cells is much narrower, as compared to conventional pre-treatments, indicating more well-defined and reproducible surface conditions prior to a-Si:H emitter deposition and/or a higher stability of the c-Si surface against variations in the a-Si:H deposition conditions.

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1. Introduction

Most of the technological processes in silicon device manufacturing require the preparation of undamaged, contamination-free and chemically stable silicon surfaces for the subsequent deposition process [1]. Due to the further miniaturisation and thinning of films in device manufacturing, the wet-chemical conditioning of silicon wafer surfaces must be specially optimised with regard to the prior and subsequent process steps. Many applications additionally necessitate special crystallographic configurations of the silicon substrate surface. Evenly distributed steps on atomically flat surfaces, such as on vicinal Si(111), are advantageous as the starting point for linear or two-dimensional growth of organic molecules or biological layers. Randomly distributed upside pyramids, textured by anisotropic etching, are utilised to optimise the light trapping properties in solar cells. Poly-crystalline EFG-wafers are used to reduce the costs of substrates. The minimisation of micro-roughness and recombination losses of charge carries on silicon interfaces play a major role in device performance, product yield and reliability. The interface constitutes a major part of the device, especially in silicon thin film solar cells. Therefore, interface defects become increasingly more
critical to their energy conversion efficiency. For amorphous/crystalline silicon (a-Si:H/c-Si) hetero-junction solar cells, both the emitter and the back surface field can be produced by using a-Si:H. For these hetero-junctions, a well-passivated c-Si surface is essential prior to a-Si:H deposition, as established previously [2]. The interface recombination velocity, which can significantly reduce the efficiency of solar cells, is mainly affected by the density and the character of interface states. The solar cell performance degrades significantly if the area density of interface states, \( D_{it} \), exceeds \( 10^{11} \text{ cm}^{-2} \) [3,4].

According to our recently reported results, the minimum value of the density \( D_{it,\text{min}} \) and energetic distribution of interface state \( D_{it}(E) \) on silicon substrates were found to be strongly related to the preparation-induced interface micro-roughness and native oxide coverage as determined by spectroscopic ellipsometry (SE) measurements [5,6]. Wet-chemical preparation methods developed for microelectronics device technology have been extended to solar cell manufacturing and other applications to avoid undesired native oxidation and further contaminations of the silicon substrates. The so far optimised wet-chemical treatments cannot be applied effectively on poly-crystalline or textured substrates due to anisotropic etching.

In order to prepare smooth silicon interfaces with excellent electronic properties without these contaminations and to passivate them during the technological process, we investigated special combinations of wet-chemical etching and cleaning procedures. This paper reports the combined monitoring of electronic and morphological interface properties on atomically flat Si(111) and very smooth Si(100), on substrates with randomly distributed upside pyramids and on poly-crystalline EFG silicon. The relation between structural imperfections at silicon surfaces, interface state densities and stability of surface passivation has been intensively investigated. Surface morphology after wet-chemical preparation and storage in clean-room air were determined by AFM and SEM.

Two non-destructive and very surface sensitive techniques, the large-signal field-modulated surface photovoltage method [7] and pulsed photoluminescence spectroscopy [8], were applied to investigate both wet-chemically treated substrate surfaces and a-Si/c-Si interfaces. From these measurements, we obtained detailed information on the influence of preparation-induced surface morphology on energetic distribution of the interface state densities \( D_{it}(E) \) and the recombination loss on flat and textured silicon substrates and on the resulting a-Si:H/c-Si hetero-interfaces.

Substrate surfaces were smoothed and passivated by different wet-chemical treatments before the a-Si:H/c-Si hetero-junctions were prepared by conventional PECVD deposition. The influence of preparation-induced morphology on surface state densities at silicon substrates and the recombination loss at the resulting hetero-junctions were studied. Finally, the effect of surface passivation on the solar cell efficiency \( \eta \) and short circuit current \( I_{sc} \) of TCO/a-Si:H(n)/c-Si(p)/Al solar cells was shown.

2. Experimental

2.1. Si surface preparation

In order to obtain both various structures for different applications as well as atomically flat areas on the surface, the substrates were treated first to produce the macroscopic crystallographic configuration, followed by special sequences of wet-chemical oxidation and etching treatments to reduce the microscopic surface roughness. The preparations were generally started by the conventional standard cleaning process of the Radio Corporation of America (RCA) [9], using polished mono-crystalline Si(100) and Si(111) wafers (p and n-type, 1–10 \( \Omega \) cm) as well as poly-crystalline EFG substrates. This method has been confirmed to remove effectively particles as well as organic and metallic surface contamination. The remaining native oxides were etched back in 1% HF solution. Vicinal Si(111) substrates with various miscuts were used to achieve evenly distributed atomic steps.

Substrates with randomly distributed upside pyramids were prepared by anisotropic etching of Si(100) wafers in an alkaline (KOH) isopropanol solution and cleaned again by the RCA process. A standard acid polishing solution, containing HNO₃, CH₃COOH, H₃PO₄ and HF, was used to improve the effect of a subsequent isotropic etching step on flat and structured silicon.

The wet-chemical oxidation was carried out under clean-room conditions using different procedures: RCA I (APM: ammonia/hydrogen peroxide mixture) and RCA II (HPM: hydrochloric acid/hydrogen peroxide mixtures) at 80 °C for 10 min [9] as well as boiling solution of H₂SO₄/H₂O₂ (1:1) for 10 min [10] and deionised water at 80 °C for 120 min [11]. The H-termination was completed by removing the so prepared wet-chemical oxides using NH₄F (48%) solution for about 2 to 10 min or alternatively by etching in 1% HF for different treatment times. Samples were stored in clean-room air (25 °C, humidity approximately 50%), to investigate the stability of the surface passivation by H-termination during the technological process. To investigate the improved passivation of surface morphology by wet-chemical oxide layers, some samples were stored under ambient air condition for a few months.

2.2. Solar cell preparation

Mono-crystalline p-type Si(100) float zone wafers (0.7–2 \( \Omega \) cm) were cleaned by the standard RCA process and subsequently etched in KOH solution. This results, on both wafer surfaces, in a texture consisting of random pyramids with a height of 1–2 \( \mu \)m. Solar cells were processed, starting with the diffusion of a p⁺ back surface field (BSF). Two groups of samples were processed: (i) with deposition of the a-Si:H emitter immediately after standard RCA cleaning followed by the final etching step in 1% HF solution for 60 s (RCA + HF dip) and (ii) with emitter deposition after wet-chemical smoothing procedure. For all samples, the emitter was deposited in a conventional parallel plate 13.53 MHz RF-PECVD reactor. Identical deposition conditions were maintained, cf. refs. [2,12]: base pressure 2 \( \times 10^{-7} \) mbar, substrate
temperature 210 °C, RF power 9 mW/cm². Precursor gases were silane, SiH₄, at 10 sccm, and phosphine, PH₃ (1% in H₂), at 0.1 sccm, resulting in a doping level of 200 ppm in the gas phase. The nominal a-Si:H film thickness, measured on flat, oxidised c-Si samples co-deposited with the textured wafers, was 8 nm. It should be noted that on the textured wafers, the increased surface area results in a thinner a-Si:H film. From geometrical considerations, the mean film thickness is estimated to ~4 nm. To improve surface conductivity, a transparent ZnO:Al layer was sputtered on top of the a-Si:H emitter, followed by front and back side metallisation with Al. The Al front grid was fabricated using a photolithographic lift-off process. Finally, the emitter area (1 cm²) was defined by mesa etching. Details can be found elsewhere [2].

2.3. Characterisation methods

The silicon surface morphology was investigated by AFM and SEM immediately after wet-chemical preparation and after storage in ambient air. The AFM images were taken in contact mode (Fig. 1, F = 80 nN) or dynamic force mode (Fig. 4) with the XE-100 from PSIA using cantilevers from Budgetsensors. Either BS-Multi-75-AL (silicon) or BS-ElectriMulti75 (CrPt covered) with a force constant of 3 N/m and a resonance frequency of 75 kHz were used. The SEM investigations were carried out using a HITACHI S-4100 scanning electron microscope with a cold field emission cathode.

Pulsed photoluminescence (PL) measurements were applied to inspect the interface passivation by changes in the band–band recombination related PL of Si due to quenching of the PL by surface defects as described in refs. [8,13–15]. A dye-laser with an excitation wavelength of 743 nm (pulse width 0.5 ns, pulse energy 75 µJ) was used for PL.

For all solar cells, I–V curves were measured under AM 1.5 illumination in a solar simulator equipped with a cold stage, which was used to keep the cell temperature at 25 °C.

The SPV technique was utilised to measure the surface band-bending and the energetic distribution of the interface state density \( D_{it}(E) \) as recently specified in ref. [7]. A laser diode (902 nm, 150 ns pulse length) was used as a light source. A series of photovoltage pulses was measured with different field voltages between transparent electrode and wafer. The duration of a field voltage pulse was 100 ms, followed by an inverted but otherwise identical pulse, to minimise effects due to charge accumulation [16]. The photovoltage pulses were recorded with a transient recorder (time resolution 5 ns). The insulator capacity \( C_i \) is measured externally by a capacitance bridge. The SPV techniques have the general advantage that the measurements can be carried out repeatedly after wet-chemical treatment without any contact preparation, using a mica foil dielectric spacer.

2.4. Determination of the energetic distribution of interface states

The determination of the interface state density \( D_{it}(E) \) by a pulsed field modulated SPV method was first described in 1968 by Heilig [17]. To determine the interface state density \( D_{it}(E) \), a varying electric field perpendicular to the surface is applied, which changes the surface potential \( \Phi_s \) continuously as a function of the field voltage \( U_F \). Due to screening effects, the influence of the field voltage \( U_F \) on the surface potential \( \Phi_s \) depends on the charge \( Q_{it} \) trapped in interface states. A change in field voltage \( dU_F \) in this MIS system thus leads to a change in voltage drop at the insulator \( dU_i \) and of the surface potential \( d\Phi_s \).

\[
dU_F = dU_i + d\Phi_s \quad (1)
\]

Charge neutrality

\[
Q_i + Q_{it} + Q_{nt} + Q_{sc} = 0 \quad (2)
\]

yields

\[
dQ_{it} + dQ_{nt} + dQ_{sc} = 0 \quad (3)
\]

for the charging due to a voltage change, where \( Q_i \) is the fixed charge, \( Q_{it} \) is the influenced charge on the field electrode, \( Q_{nt} \) is the charge in rechargeable interface states and \( Q_{sc} \) is the interface charge, i.e., the projection of the complete space charge onto the interface, determined by the space charge function \( F \) except for a constant:

\[
Q_{sc} = (2n_i\varepsilon_{Si}kT)^{1/2}F \quad (4)
\]

where \( \varepsilon_{Si} \) is the static dielectric constant of silicon. \( Q_{sc} \) is evaluated as a function of \( \Phi_s \) as described in [7].

![Fig. 1. AFM images (2 µm × 2 µm) of polished Si(111) surfaces, oxidised applying H₂SO₄/H₂O₂ after RCA + HF (a), and subsequently H-terminated either by etching in NH₄F (48%) solution (6.5 min) (b) or by HF dip (30 s) (c).](image-url)
From the definitions of the interface state density
\[ D_{it}(\Phi_s) = -\frac{1}{q} \frac{dQ_{it}}{d\Phi_s} \] (5)
and of the insulator capacity
\[ C_i = \frac{dQ_{g}}{dU_i} \] (6)
and from Eqs. (1)–(6) the following dependence is derived for the density of states as a function of the change in surface potential [18]:
\[ D_{it}(\Phi_s) = \frac{1}{q} C_i \left( \frac{dU_F}{d\Phi_s} - 1 \right) + \frac{dQ_{sc}(\Phi_s)}{q d\Phi_s} \] (7)

3. Results and discussion

3.1. Surface morphology and density of states on flat, H-terminated Si(111) and Si(100)

Wet-chemical H-termination procedures generally include two essential steps: the formation of a silicon/oxide interface by oxidising solutions and the subsequent removal of this native oxide layer by HF or NH₄F containing solutions. Therefore, the preparation-induced micro-roughness of H-terminated silicon surfaces results from the course of two different chemical processes: the wet-chemical oxidation of the surface as well as the etching behaviours of silicon oxide and the silicon substrate, respectively.

The AFM images (Fig. 1) show the topography of a polished Si(111) sample, after RCA cleaning, followed by HF dip and subsequent wet-chemical oxidation applying H₂SO₄/H₂O₂ solution (Fig. 1a), and subsequent H-termination either by etching in NH₄F (48%) solution (6.5 min) (Fig. 1b), or alternatively by HF dip (30 s) (Fig. 1c). Up to twenty years ago, rather simple HF treatments were used to remove the surface oxides [19,20]. However, the Si surfaces are microscopically rough after HF dip as shown in Fig. 1c, due to the initially non-uniformly oxidised surface (Fig. 1a). Various wet-chemical treatments using NH₄F solutions have been developed, resulting in atomically smooth and H-terminated Si(111) surfaces [10,11,21–23]. Fig. 1b shows an AFM image of such an atomically flat Si(111) surface with evenly distributed steps, as prepared by NH₄F etching following a wet-chemical oxidation in clean-room conditions. These methods, however, are not so effective for Si(100) and poly-crystalline substrates. The anisotropic etching behaviour of the Si(100) surface leads to Si(111) facets [24] and prevents from achieving very low micro-roughness in all studied NH₄F containing solutions.

The relation between interface state densities and structural imperfections at Si surfaces and Si/SiO₂ interfaces has been intensively investigated, because the reduction of their densities is a main problem in the semiconductor device technology [1]. The typically U-shaped energetic distributions of interface state density \( D_{it} \) and the high density of states near the band edges, experimentally observed on Si/SiO₂ interfaces, were attributed to specific centers in the oxide by Goetzberger et al. in 1968 [25]. The U-shaped distribution of intrinsic surface states on H-terminated silicon surfaces as determined from SPV measurements (see Fig. 2) can be understood as superposition of two groups of states: (1) the states near the band edges result from strained (Si₃BBSi–Si–Si₃BBSi) bonds and decay roughly exponentially into the band gap, and (2) the groups of states symmetrically distributed around a minimum near midgap are correlated to dangling bond defects (Si₃BBSi–) on Si(111) and (Si₂BBi) on Si(100), which are back-bonded to Si atoms only [26,27]. These defect groups are identified by electronic model
consideration and also by EPR measurements as Pₓ-centers [28,29]. On the Si(111)/SiO₂ interface, this defect group has been identified mainly as an unpaired sp³ orbital on a trivalent bonded interface Si atom or Si(111)-oriented Si dangling bond pointing out of the interface into the oxide [30]. The two related defect groups on the Si(100)/SiO₂ and Si(111)/SiO₂ interface are called Pₓ₀ and Pₓ₁, respectively. The minimum value Dₓₘᵟᵣₐᵣ₉ and its energetic position is commonly used as a technological parameter of the electronic surface quality.

Fig. 2a and b compare Dₓ(E) on Si(111) and Si(100) substrates obtained immediately after wet-chemical preparation. Very high densities of states Dₓₐₘᵟᵣ₉ > 10¹² cm⁻² eV⁻¹ were found after the RCA cleaned surface on Si(111) substrates as well as on the Si(100) substrates (Fig. 2a and b, curves 1). Values of about Dₓₐₘᵟᵣ₉ > 10¹² cm⁻² eV⁻¹ were observed after removing the remaining oxide layers by the HF dip on both types of Si surfaces (Fig. 2a and b, curves 2).

To decrease the density of states, it was necessary to optimise the sequence of preparation steps considering the Si surface orientation. The first problem was to minimise the initial interface roughness between substrate and wet-chemical oxide layer by application of other oxidising solutions. On Si(111) surfaces, significantly lower interface state densities Dₓₐₘᵟᵣ₉ < 10¹¹ cm⁻² eV⁻¹ were obtained using the standard H-termination process [10], applying H₂SO₄/H₂O₂ pre-treatment and NH₄F as final etching solution (Fig. 2a, curve 3). On Si(100) the same treatment increases the surface micro-roughness due to the anisotropic etching behaviour of NH₄F solution, and in contrast to the Si(111) sample, higher densities of states Dₓₐₘᵟᵣ₉ > 2 × 10¹¹ cm⁻² eV⁻¹ were obtained (Fig. 2b, curve 3). In order to avoid an increase of the initially lower interface roughness by etching in NH₄F solution, the oxide layer, prepared by H₂SO₄/H₂O₂ on Si(100) was removed in 1% HF solution. The resulting interface state density Dₓₐₘᵟᵣ₉ > 5 × 10¹⁰ cm⁻² eV⁻¹ is given in Fig. 2b (curve 5). The effect of smoothing the interface between substrate and wet-chemical oxide layer was demonstrated by applying a non-aggressive hot-water oxidation [11]. Very low minimum values of surface state density Dₓₐₘᵟᵣ₉ < 1.5 × 10¹⁰ cm⁻² eV⁻¹ were obtained on Si(111) surfaces oxidised by a special hot-water pre-treatment at 80 °C, and etched in NH₄F solution under N₂ ambient (Fig. 2a, curve 4). The same hot-water treatment followed by NH₄F final etching solution was also found to decrease the surface state density of Si(100) surfaces to about Dₓₐₘᵟᵣ₉ > 5 × 10¹⁰ cm⁻² eV⁻¹ (Fig. 2b, curve 4).

3.2. Stability of H-termination on substrate surfaces during storage in clean-room air

The surface hydrogen-termination predominantly limits air oxidation at room temperature but does not completely inhibit native oxidation [31,32] and defect generation [33]. Native oxides, however, prevent the low-temperature growth of high-quality epitaxial and amorphous Si films and precise control of the thickness and electrical properties of thin gate oxides. The control of the growth rate of native oxide in air on initially H-terminated surfaces is, therefore, of great importance in semiconductor technology. The surface morphology and density of surface defects were found to influence strongly the growth rate of native oxide on H-terminated Si surfaces during storage in air [11,34].

Fig. 3 shows the changes of Dₓ(E) starting from initially H-terminated Si(100) (curve 1a) and poly-crystalline EFG substrates (curve 1b) during storage in clean-room air (series a and b), respectively. On EFG substrates, the standard RCA cleaning followed by an HF dip (RCA + HF dip) leads to higher values of Dₓₐₘᵟᵣ₉ > 4 × 10¹² cm⁻² eV⁻¹ (curve 1b) compared to Si(100) (curve 1a). On these substrates a faster increase of the surface state density during native oxidation was observed after 60 min (curve 2b) than on Si(100) (curve 2a). The oxidation process causes the additional appearance of dangling bond defects, correlated to silicon atoms of lower stage of oxidation, Si⁰⁺, with one back bond to an oxygen atom and with one dangling bond. This can be observed as superposition of a Gaussian distributed group of extrinsic states in the lower half of the gap, i.e. closer to the valence band edge, on the U-shaped distribution of intrinsic states [11]. Additional 2 h storage in air leads to such a high surface state density Dₓₐₘᵟᵣ₉ > 2 × 10¹² eV⁻¹ cm⁻² that the wafer cannot be used successfully for further preparations (curves 3a and b).

3.3. Smoothing and passivation of flat silicon surfaces by wet-chemical oxides

To avoid both native oxidation and particle contamination during storage in ambient atmosphere, a surface passivation...
method by thin wet-chemically prepared oxide-layers was developed. For this purpose mono-crystalline substrates as well as EFG wafers were first cleaned and H-terminated, taking the surface orientation into consideration. The wafer surfaces were subsequently re-oxidised under clean-room conditions applying different oxidising solutions. After removing the wet-chemical oxide layers in 1% HF solution, the surface state densities on the re-established H-terminated surfaces were found to be defined by the initial micro-roughness of the silicon/oxide interface [5].

The influence of growth and removal of a thin wet-chemical oxide layer on the surface morphology is exemplified by AFM images (2 μm × 2 μm) of an initially H-terminated Si(111) surface (Fig. 4). The initially H-terminated Si(111) surface was characterised by a strong geometry of atomically flat areas. The triangles of atomically flat Si(111) terraces result from the etching process applying NH4F solution containing oxygen [35]. Fig. 4a shows the topography of an initially H-terminated Si(111) surface, after subsequent re-oxidation by H2SO4/H2O2 solution under clean-room conditions and storage under ambient air conditions. The morphology of the wet-chemically oxidised interface was found to be stable during a few months. The initial morphology of the H-terminated surface was re-established by removal of the native oxide layer and the particle contamination, applying a short HF dip (1% HF, 90 s). An AFM-image of the same area of the silicon surface as displayed in Fig. 4a was taken just after the HF-dip (Fig. 4b). To prevent further oxidation the sample was put in a nitrogen atmosphere immediately after preparation and transferred to a glove box that was purged with nitrogen, where the oxygen concentration was kept below 1% when measuring the topography. The unchanged terraces of the atomically flat Si(111) are visible in both images. A similar method was successfully applied to prepare and passivate very smooth Si(100) [36]. The smoothing and passivation procedures which we developed for flat mono-crystalline Si(111) and Si(100), were also optimised for poly-crystalline and structured substrates. In the process, the wet-chemical oxidation shifts the Si/SiO2 interface into the Si bulk so that a few angstrom thick Si layer has been removed during the etch-back of the oxide by NH4F or HF containing solutions.

The effect of this treatment on the density of surface states is exemplarily demonstrated on initially rough poly-crystalline EFG substrates used in our solar cell applications. Fig. 5 shows the $D_{it}(E)$ on surfaces of EFG substrates in the initial state, covered with native oxide (curve 1) and after H-termination (curves 2–4). The standard treatments increase the surface micro-roughness due to the anisotropic etching behaviour. In contrast to the Si(111) samples, higher values of $D_{it,min} \approx 4 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$ and $D_{it,min} \approx 6 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$ were
obtained, after RCA + HF dip (curve 2) and after standard H-termination process applying NH₄F solution after H₂SO₄/H₂O₂ treatment (curve 3), respectively. The newly developed optimised smoothing procedure (wet-chemical oxidation and 1% HF dip) results in a lower surface state density, \( D_{it,\min} \approx 1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1} \) (curve 4).

3.4. Passivation of structured Si substrates for solar cell application

So far we have studied the influence of wet-chemical oxidation procedures on surface state densities of flat Si substrates. However, Si based solar cells need light trapping structures on the substrate surface for effective cell performance. These types of surface structures are typically made by alkaline etching of randomly distributed upside pyramids. In the next section, we focus on the investigation of the influence of the increased surface area and micro-roughness on the resulting density of interface states and recombination behaviour. Surface states result from strained and dangling bonds with different back-bond configurations, localised in an interlayer that extends over only a few angstroms. The anisotropic etching of pyramids leads to a strong increase of such irregularities on different crystallographic surface orientations. To reduce the density of these states, wet-chemical treatments are necessary to remove the damaged surface and to decrease the micro-roughness on the Si(111) facets of the structured substrate. Fig. 6 shows the dependence of preparation-induced \( D_{it} \) on the anisotropic etching process. The U-shaped energetic distribution of surface states obtained typically on H-terminated mono-crystalline Si(100) surfaces immediately after RCA cleaning + HF dip on the flat p-type Si(100) surfaces is given in Fig. 6 (curve 1). The etching process of pyramids by alkaline solution increases the density of surface states, and results in significantly narrowed energetic distributions of states (Fig. 6, curve 2). A subsequent isotropic etching step using a standard acidic polishing solution, however, was found to be unsuitable to decrease \( D_{it} \). The

![Fig. 6. \( D_{it}(E) \) of p-type Si(100) surfaces after RCA + HF dip (1), and subsequent isotropic etching (4), and after anisotropic etching to form randomly distributed upside pyramids (2), and after subsequent isotropic etching (3).](image-url)

![Fig. 7. SEM micrographs (tilted by 30°) of pyramids, after anisotropic etching (a), and additional NH₄F treatment (b), and after subsequent wet-chemical oxidation and HF dip (c).](image-url)
isotropic etching increases the density of interface states up to $D_{it, \text{min}} \geq 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ on pyramids as well as on the flat Si(100) surfaces (Fig. 6, curves 3–4).

Fig. 7 shows SEM micrographs obtained on the same Si(100) wafer after anisotropic etching to form randomly distributed pyramids and RCA + HF dip (a), after standard H-termination by NH$_4$F (b) and after additional subsequent oxidation in H$_2$SO$_4$/H$_2$O$_2$ and HF dip (c). The initial surface orientation of Si(100) substrate changes to Si(111) orientation on the pyramid facets during the anisotropic etching process (Fig. 7a). As known from smoothing of Si(111) surfaces, NH$_4$F containing solutions produce various ammonium salts by the reaction with Si and SiO$_2$. Depending on the level of impurities of solutions, these reaction products form (NH$_4$)$_2$SiF$_6$ deposits on the surface. These contaminations cannot be removed even by intensive water rinse, because the solubility is relatively low in water and depends on the concentration and pH of etching solutions [37]. Obviously, the formation of these deposits seems to start particularly on surface particle contaminations, or on crystallographic irregularities of the structured surfaces (Fig. 7b). The surface contamination could be completely removed after applying a subsequent wet-chemical oxidation step and HF dip (Fig. 7c).

In order to further elucidate the influence of preparation-induced surface morphology on the density and energetic distribution of surface states, various sequences of wet-chemical oxidation and etching steps using HF (1%) solution as well as NH$_4$F were applied to substrates with randomly distributed pyramids. Fig. 8 summarises the resulting $D_{it}(E)$ determined on the same sample immediately after the respective final H-termination step on the initial un-etched Si(100) surface (curve 1) and on differently treated randomly distributed pyramids (curves 2–5). As shown already in Fig. 6, the etching process of pyramids by alkaline solutions increases the density of rechargeable surface states. This behaviour results in a narrow energetic distribution of states. The density of surface states near the band edges and in the lower half of the gap, i.e., closer to the valence band edge, is a result of strained bonds and defects formed by hydroxyl groups [5].

$D_{it}(E)$ of the initially H-terminated un-etched Si(100) substrate (Fig. 8, curve 1) changes drastically by appearance of states in the lower half of the gap after anisotropic etching of pyramids and subsequent RCA + HF treatment (Fig. 8, curve 2). The surface state density is defined by the initial micro-roughness of the silicon/oxide interface, which can be reduced by subsequent wet-chemical oxidation in H$_2$SO$_4$/H$_2$O$_2$ and removing the wet-chemical oxide layer in 1% HF solution (Fig. 8, curve 3). The Si(111) surface of pyramids can also be smoothed by applying an NH$_4$F etching step resulting in a lower density of states (Fig. 8, curve 4). However, as shown in Fig. 7b, the surface is contaminated by deposits of ammonium salts, which cannot be removed by water rinsing. Therefore, best results were obtained after a smoothing procedure in NH$_4$F solution with a subsequent wet-chemical oxidation step which dissolves these contaminations. The final HF dip removes the wet-chemical oxide from the pyramids and produces a very smooth surface, as shown in Fig. 7c. The energetic distribution $D_{it}(E)$ on the smoothed pyramids (Fig. 8, curve 5) was found to be comparable to that on the initial flat Si(100) surface (Fig. 8, curve 1).

### 3.5. Influence of surface pre-treatment on recombination loss of a-Si:H/c-Si hetero-junctions

The influence of preparation-induced changes in the density of states on the recombination loss of a-Si:H/c-Si hetero-

![Fig. 8. Interface state distributions $D_{it}(E)$ of un-etched p-type Si(100) substrates (1), and after texturisation with randomly distributed upside pyramids (2–5), immediately after H-termination using various sequences of RCA, H$_2$SO$_4$/H$_2$O$_2$, 48% NH$_4$F and 1% HF solutions.](image)

![Fig. 9. PL intensities obtained on a-Si:H/c-Si hetero-junctions prepared on different Si substrates: flat Si(100) (1), Si(111) (2), and pyramids (3 and 4), after RCA + HF dip (1–3) and optimised smoothing procedure (4).](image)
The PL intensity was related to the band-to-band recombination of the light-induced charge carriers generated by a N₂ or dye laser pulse. The quenching or enhancement of the PL is due to defect formation (non-radiative recombination) or defect passivation [13,14]. A procedure to calibrate the PL intensity with defect concentration at the SiO₂/Si interface is described in ref. [15].

Fig. 9 shows PL intensities on a-Si/c-Si interfaces prepared on flat Si(100) (curve 1) and Si(111) (curve 2) substrates and anisotropically etched pyramids Si(111) (curves 3–4). A higher PL intensity was obtained for the un-etched Si(111) substrates (curve 2) compared to the un-etched Si(100) wafer (curve 1) after RCA + HF dip pre-treatment, due to a reduced micro-roughness and lower density of states at the surface. The recombination loss on randomly distributed upside pyramids was significantly reduced by applying the optimised wet-chemical smoothing procedure (curve 4), as compared to the RCA + HF pre-treatment (curve 3).

In order to verify the influence of wet-chemical pre-treatments on efficiency of amorphous–crystalline heterojunction solar cells (ZnO/a-Si:H(n)/c-Si(p)/Al) on structured substrates, the results of the standard RCA + HF dip pre-treatment were compared to the result of the smoothing method, applying a special sequence of wet-chemical oxidation and etching treatments. As shown in Fig. 10a, the resulting density of states on the anisotropically etched substrates after RCA + HF dip (curve i) was markedly reduced by applying the smoothing procedure (curve ii). Fig. 10b shows the significant increase in PL intensity on the so pre-treated a-Si:H(n)/c-Si(p) hetero-structure (curve ii) as compared to that one after simple RCA + HF dip (curve i).

For each of the two groups of samples, RCA + HF dip (i) and wet-chemical smoothing (ii), 24 solar cells of 1 cm² were processed. Then, the cell efficiencies were calculated from I–V measurements under AM 1.5 illumination. Fig. 11 shows a histogram depicting the distribution of the solar cell efficiencies for the conventional and for the smoothened c-Si surface. In addition to the histogram, the result of fitting normal (Gaussian) distributions to the data is shown. These curves should be regarded mainly as a guide to the eye, due to the limited number of samples. Fig. 11 shows a pronounced increase in efficiency for the samples with a smoothened a-Si:H/c-Si interface. The mean value increases from 16.5% to 17.8%, this is a relative increase of 8%. The best efficiency of this series (η = 18.4%) was also achieved for a cell with a smoothened a-Si:H/c-Si interface. The increase in efficiency is mainly due to a higher short circuit current, J_sc, and fill factor, while the change in the open circuit voltage, V_oc, is rather small. This is an unexpected finding: previous experimental and simulation studies [3,38] have shown, that changes in the density of interface states...
influence primarily the open circuit voltage. Additional investigations are under way to clarify this behaviour.

Another important aspect of the data in Fig. 11 is the widths of the distributions. It is obvious that for the samples with the smoothed a-Si:H/c-Si interface, all parameters fall in a much narrower distribution around the mean value. This indicates a better reproducibility of the solar cell processing when textured substrates are treated by an additional smoothing step.

4. Conclusion

We demonstrated that SPV and PL measurements can be used as a very sensitive tool to analyse preparation-induced surface electronic properties during wet-chemical processing. Summarising the results of our investigations, the preparation-induced surface micro-roughness and resulting density of rechargeable states on wet-chemically H-terminated surfaces were found to be mainly influenced by two factors: firstly, the morphology of the initial Si/SiO2 interface after wet-chemical oxidising pre-treatment and, secondly, the behaviour of the final etching by HF or NH4F containing solutions. Therefore, it is important to apply non-aggressive oxidising solutions under controlled conditions to avoid an increase of interface roughness during the oxidation process. Special combinations of wet-chemical cleaning, oxidation, etching and passivation procedures were developed taking into consideration the etching behaviours of differently oriented silicon to prepare flat surfaces on Si(111), Si(100) and on evenly distributed atomic steps, such as on vicinal Si(111), with excellent morphological and electronic properties. In addition, these flat substrate surfaces show a low contamination level and reduced native oxidation behaviour during the technological process. These surfaces could be passivated for long time storage in air by wet-chemically prepared oxide layers. The initially H-terminated surface could be re-established by a simple 1% HF dip.

For photovoltaic applications, we developed special combinations of cleaning and passivation methods to remove damaged surface layers from EFG substrate surfaces and randomly distributed upside pyramids. Compared to conventional pre-treatments, the densities of surface states near the band edges, resulting from strained bond defects, as well as in the lower half of the gap could be strongly reduced. We achieved significantly lower micro-roughness and densities of surface states \( D_{\text{so}}(E) \) by an optimised sequence of wet-chemical oxidation and etching steps. It was shown that the efficiency of solar cells is mainly influenced by the preparation-induced morphological and electronic properties of the substrate surface. An optimised smoothing procedure on textured c-Si substrates as used in (n)a-Si:H/(p)c-Si heterojunction solar cells leads to a significant increase of the solar cell parameters short circuit current \( J_{\text{SC}} \), open circuit voltage \( V_{\text{OC}} \), and fill factor, and the mean value of efficiency increases from 16.5% to 17.8%. This is a relative increase of 8%. Histograms over cells produced from smoothed substrates show a much narrower distribution of the respective parameters, which indicates a better reproducibility of the a-Si:H deposition.

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