

Effect of wet-chemical substrate smoothing on passivation of ultrathin-SiO₂/n-Si(111) interfaces prepared with atomic oxygen at thermal impact energies*

Research Article

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Abstract: Ultrathin SiO₂ layers for potential applications in nano-scale electronic and photovoltaic devices were prepared by exposure to thermalized atomic oxygen under UHV conditions. Wet-chemical substrate pre-treatment, layer deposition and annealing processes were applied to improve the electronic Si/SiO₂ interface properties. This favourable effect of optimized wet-chemical pre-treatment can be preserved during the subsequent oxidation. The corresponding atomic-scale analysis of the electronic interface states after substrate pre-treatment and the subsequent silicon oxide layer formation is performed by field-modulated surface photovoltage (SPV), atomic force microscopy (AFM) and spectroscopic ellipsometry in the ultra-violet and visible region (UV-VIS-SE).

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1. Introduction

Silicon / silicon dioxide (Si/SiO₂) is by far the most important material system for our modern information society. Without the development of silicon technology due to the unsurpassed properties of silicon and its dioxide,

the modern electronics would be unthinkable. Oxidized Si surfaces have been the object of intensive research for several decades. They are characterized in particular by: (i) high chemical stability and passivation effect, (ii) extremely high temperature stability, (iii) the diffusion-inhibiting effect against doping and impurities, (iv) precise structurability of SiO₂ on Si and (v) high electrical breakdown field strength.

Due to the advancing miniaturization of electronic components interface-specific properties, particularly of the Si/SiO₂ interface, become increasingly important. At the

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Si/SiO₂ interface it comes to a semiconductor-insulator transition, i.e., there is a junction of two materials each with different structural, chemical and electronic properties. This constellation usually favors the formation stress, defect states and dangling bonds at the interface, which all have a negative influence on the recombination and transport properties of charge carriers and thus the operation of the electronic components.

This problem of control and optimization of ultrathin tunneling oxides on silicon wafers and their interfaces is of fundamental and universal relevance to the increasing demands in the semiconductor industry and requires the development of improved preparation techniques for a diverse range of applications, particularly in microelectronics and photovoltaics. In photovoltaics, ultrathin SiO₂ layers have been successfully demonstrated to act as functional elements in various innovative solar cell concepts: e.g., as passivation layers [1, 2], as substrates for the deposition of organic molecules [3], and (iii) as barrier in Si/SiO₂ quantum well structures [4]. Main challenge for those applications is the question of whether stable, homogeneous, ultrathin SiO₂ layers produced on silicon with both structurally abrupt interfaces and low density of defect states.

Though SiO₂, which can be prepared on Si surfaces by simple oxidation methods, is characterised by high chemical and electrical stability, Buck and McKim reported as early as 1958 that the surface electronic properties can dramatically be influenced also by the way of chemical preparation [5]. It is well known from investigations of metal-oxide-semiconductor (MOS) devices that the quality of thin thermal oxide films strongly depends on interface micro-roughness and oxide density [6–8] and that interfacial defects give rise to interface electronic charges such as interface-trapped charges and fixed oxide charge [8–10]. As shown by photoconductive decay (PCD) measurements, thermally prepared oxide layers can be applied to reduce near surface charge carrier recombination losses also on textured and multi-crystalline (mc-Si) solar cells substrates [11].

Therefore, alternative wet-chemical preparation methods are required to achieve contamination-free, atomically smooth Si substrate surfaces as starting point for preparation of ultrathin oxides. As recently reported, smoothing of Si/SiO₂ interfaces on the atomic scale could be achieved by oxidation in H₂SO₄/H₂O₂ for 10 min. [12], in deionized water (DIW) at 80°C [13] or nitric acid (HNO₃ 68%) at 120°C [14–16]. The wet-chemically oxidized substrate can be directly utilized as the starting point for subsequent layer preparation or contact formation, which requires hydrophilic surfaces. Otherwise, by oxide removal in ammonia fluoride (NH₄F 40 %, pH=7.8) [12, 17, 18], or alternatively by HF (1%) [19] smooth and H-terminated,

hydrophobic surfaces can be achieved. It was shown, that the substrate surface conditioning has to be carefully optimized with respect to the substrate morphology and the subsequent layer preparation [13].

In this contribution we report on the preparation of ultrathin SiO₂ layers in the range of 9–15 Å on c-Si substrates by wet-chemical treatment with various specific oxidizing solutions and successive novel oxidation with neutral atomic oxygen from a remote plasma cracker source under ultrahigh vacuum conditions, which has proven to produce high-quality Si/SiO₂ interfaces [1, 2].

The effects of wet-chemical substrate pre-treatment, oxidation and annealing processes on the electronic properties of the Si/SiO₂ interface were investigated. Large signal surface photovoltage technique (SPV) [20–22] measurements were applied to inspect the change in electronic interface states during the initial phase of oxidation and the ongoing silicon oxide layer formation and to establish correlations between surface micro-roughness (d_r), interface charge Q_{it} and the energetic distribution of interface states $D_{it}(E)$ at polished n-Si(111) float zone (FZ) substrates.

2. Experimental

2.1. Wet-chemical substrate pre-treatment

In order to investigate the effect of wet-chemical surface conditioning of polished n-type float zone (FZ) Si(111) substrates on electronic interface properties of the subsequent prepared Si/SiO₂ interfaces, different sequences of wet-chemical cleaning, smoothing and H-termination procedures were tested as summarised in Table 1. At first all substrates were cleaned using the standard process of the Radio Corporation of America (RCA) [23]. Thereby wet-chemical oxide layers were formed in ammonia / hydrogen peroxide mixture, APM (RCA I); and hydrochloric acid / hydrogen peroxide mixture, CPM (RCA II). Immediately after rinsing in deionised water (DIW) at room temperature (RT), these wet-chemical oxide layers were removed in diluted hydrofluoric acid (HF 1 %) solution (etching time: 60 s). Alternatively the substrates were dried in a N₂ stream and stored in plastic containers at clean-room atmosphere (class 100 (ISO 5), particles <0.3µm).

In order to reduce the surface roughness in the atomic range after RCA process and oxide removal the substrates were a second time wet-chemically oxidised using boiling solution of H₂SO₄/H₂O₂ = 1:1 (treatment time: 10 min) [12]. After rinsing in DIW at RT the oxide layers were etched back in HF 1% (etching time: 60 s). Alternatively, to optimise the surface H-termination the prepared wet-chemical oxides were removed in concentrated

ammonia fluoride (NH₄F 40 %, pH=7.8) solution (etching time: 4.5 min). Subsequently the wafers were dried in a N₂ stream and immediately transferred into the vacuum chamber. In order to improve the stability of surface passivation by H-termination as well as by wet-chemical oxides, some samples have been stored in clean-room air (25°C, humidity approximately (50%).

Surface micro-roughness and oxide thickness which are unintentionally formed during wet-chemical processes, water rinsing and storage in air, were determined in the atomic scale by ex situ UV-VIS-spectroscopic ellipsometry (SE) using a J.A.Woollam Co. VASE spectrometer [24].

2.2. Preparation of ultrathin silicon oxide layers by exposure to thermalized atomic oxygen under UHV conditions

Ultrathin SiO₂ layers were prepared by oxidation of the n-type Si(111) float zone wafers under ultrahigh vacuum (UHV) conditions (base pressure of $<3 \times 10^{-9}$ mbar) using a radio frequency (RF) plasma cracker source (PCS-RF, Oxford Scientific Ltd.). This source features high cracking efficiencies and a special aperture with an ion trap that just neutral atoms are able to effuse out of the source. The released oxygen atoms are mainly thermalized. Thus, they hit the Si wafer just with thermal impact energies (i.e., $E_{\text{kin}} < 1$ eV) under true soft-landing conditions. Under these conditions homogeneous oxide layers of uniform thickness (0.9,..., 4.0 nm) without voids and with extremely low amounts of intermediate oxidation states (<5%) and low amounts of fixed oxide charges are grown. Fig. 1 shows a high resolution cross-sectional transmission electron microscopy image of such ~2 nm thick SiO₂ layer that covers a crystalline Si quantum layer. The SiO₂ layer possesses a homogeneous thickness and structurally abrupt interfaces [4].

It has been demonstrated that structural abruptness is not inherent with an increase of the density of interface states [2]. The resulting oxide layer thickness can be adjusted in the range by appropriate variation of the oxidation time (5,..., 60 min), the substrate temperature (300,..., 600°C), and the plasma power (200,..., 600 W) [25]. Due to the low oxide layer thickness, interface composition and stoichiometry can be determined in situ by analysis of the core level spectra by means of x-ray photoelectron spectroscopy (XPS). Further interface optimisation was achieved by successive hydrogenation using the same plasma cracker source to produce atomic hydrogen with thermal energies ($E_{\text{kin}} < 1$ eV). The low-energy impact of the impinging H atoms results in an effective passivation of dangling bonds at the interface without further defect generation [1, 26].

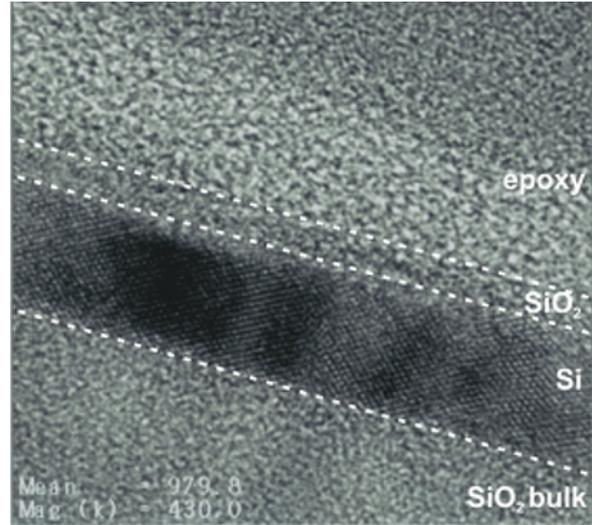


Figure 1. Cross-sectional TEM image of an ultrathin SiO₂ layer on a 7 nm Si single quantum well featuring a homogeneous layers thickness and an abrupt interface [4].

2.3. Determination of surface photovoltage and interface state densities by SPV measurements

The sensitivity of most of the defect-specific spectroscopic methods is not sufficient to detect the small number of interface defects that influence the electronic interface properties. Therefore, highly sensitive electrical methods such as capacitance-voltage (CV) or SPV measurements are necessary to determine electronic states ranging from $10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$ to $10^{14} \text{ cm}^{-2} \text{ eV}^{-1}$, which significantly define the electronic properties of the Si surfaces and interfaces [27, 28]. In this paper, large signal SPV measurements of Si substrate surfaces and subsequently prepared Si/SiO₂-interfaces are utilised, to investigate the influence of wet-chemical cleaning, smoothing and H-termination procedures on surface charge and energetic distribution of interface states. This SPV technique has the general advantage that the measurements can be carried out repeatedly during the wet-chemical treatment without any contact preparation. The measurements were carried out immediately after wet-chemical treatment, using a mica foil dielectric spacer in the same experimental set-up as recently specified in ref [22]. A transparent electrode and the sample together with the thin mica layer form a capacitor. The insulator capacity C_i is measured externally by a capacitance bridge. A pulsed laser diode (pulse length: 160 ns, wavelength $\lambda = 904$ nm and photon flux $\Phi \cong 10^{21} \text{ s}^{-1} \text{ cm}^{-2}$) was used to excite electron-hole pairs. The illumination intensity was high enough to ob-

Table 1. Optimization of wet-chemical cleaning, smoothing and H-termination processes for polished n-type Si(111) substrates.

	Fig. 3, curve	Cleaning	Storage in air	Oxide removal	Wet-chemical oxidation	Oxide removal
(0)		as prepared	12 weeks			
(1)		RCA	2 weeks	HF 1%		
(2)		RCA	-	HF 1%		
(3)		RCA	-	HF 1%	H ₂ SO ₄ /H ₂ O ₂	HF 1%
(4)		RCA	-	HF 1%	H ₂ SO ₄ /H ₂ O ₂	NH ₄ F (48%)
(5)		RCA	-	NH ₄ F (48%)	H ₂ SO ₄ /H ₂ O ₂	NH ₄ F (48%)

tain high injection conditions, to achieve flat band conditions. The surface potential Φ_s was obtained from the large-signal photovoltage pulse recorded with a transient recorder (time resolution: 5 ns) as described in [21].

The energetic distributions of the interface states $D_{it}(E)$ were determined from a series of photovoltage pulses at different field voltages U_F between a transparent electrode and the Si wafer, as firstly described by Heilig [20] in 1968. For this purpose, a varying electric field perpendicular to the surface was applied, which changes the surface potential Φ_s continuously as a function of the field voltage. 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 [29]. Due to screening effects, the influence of the field voltage U_F on the surface potential Φ_s depends on the charge Q_{it} trapped in interface states. A change in field voltage dU_F in this MIS system leads to a change in the voltage drop at the insulator dU_i and of the surface potential $d\Phi_s$, Eq. (1).

$$dU_F = dU_i + d\Phi_s. \quad (1)$$

Taking charge neutrality into account one gets

$$Q_f + Q_g + Q_{it} + Q_{sc} = 0 \quad (2)$$

and

$$dQ_g + dQ_{it} + dQ_{sc} = 0 \quad (3)$$

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

$$Q_{sc} = (2n_i \cdot \epsilon_{si} \cdot kT)^{\frac{1}{2}} F, \quad (4)$$

where ϵ_{si} is the static dielectric constant of Si. Q_{sc} is evaluated as a function of Φ_s as described in [22]. From

the definitions of the interface state density

$$D_{it}(\Phi_s) = -\frac{1}{q} \frac{dQ_{it}}{d\Phi_s} \quad (5)$$

and the insulator capacity

$$C_i = dQ_g/dU_i \quad (6)$$

and Eqs. (1, 2, 3, 4) the following dependence for the density of states as a function of the change in surface potential is derived [30]:

$$D_{it}(\Phi_s) = \frac{1}{q} C_i \left(\frac{dU_F}{d\Phi_s} - 1 \right) + \frac{dQ_{sc}(\Phi_s)}{q d\Phi_s} \quad (7)$$

Finally, Q_{sc} can be evaluated from Eq. (4) as function of the surface potential Φ_s .

3. Results and discussion

3.1. Wet-chemical substrate surface conditioning

Surface states on wet-chemically treated Si substrate surfaces originate from dangling bonds and from bonds between adsorbates and Si surface atoms. The electronic properties of the Si/SO₂ interface are dominated by stretched Si–Si bonds and silicon dangling bond defects of different backbond configurations localised in a very small interlayer of sub-oxides extended over only a few Å at the silicon/oxide interface. Therefore, the preparation of thin oxide passivation layers requires that the formation of an Si/SiO₂ interface be controlled on an atomic scale using atomically flat, H-terminated surfaces as a starting point. In this chapter, the dependence of density and energetic distribution of rechargeable states on preparation induced substrate surface roughness and surface coverage will be dealt with systematically.

3.1.1. Reduction of Si surface micro-roughness by wet-chemical oxidation and oxide removal

Our previously reported results have shown, that the surface charge and D_{it} of wet-chemically treated Si substrates are mainly determined by the preparation-induced surface micro-roughness and surface coverage [13, 31, 32]. According to these results the influence of wet-chemical oxidation and oxide removal on the surface morphology of a polished Si(111) substrate can be exemplified by AFM images ($2 \mu\text{m} \times 2 \mu\text{m}$) [33] (Fig. 2). The initially oxidised surface after RCA treatment [23] shows a high micro-roughness attributed to the rapid and irregular wet-chemical oxide growth (Fig. 2a) which can not be reduced by oxide removal in standard HF 1% solution (Fig. 2b). In contrast, after subsequent oxidation in H₂SO₄/H₂O₂ solution and oxide removal in NH₄F-solution the H-terminated Si(111) surface is characterised by a strong geometry of atomically flat areas (Fig. 2c). The triangles of atomically flat Si(111) terraces result from the etching process applying NH₄F solution containing oxygen [34].

The topography of an initially H-terminated Si(111) surface, was found to be largely unchanged after subsequent re-oxidation by H₂SO₄/H₂O₂ solution under clean-room conditions and during storage under ambient air conditions for a couple of months. As shown by an AFM-image of the same area of the sample (Fig. 2d) the initial morphology of the H-terminated surface was re-established by removal of the native oxide layer (Fig. 2e).

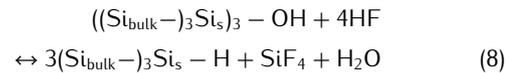
In order to verify the influence of surface micro-roughness and surface H-termination of Si substrates previous to preparation UHV of ultrathin SiO₂ layers with a thickness in the range of 9 – 20 Å, by means of atomic oxygen, various sequences of wet-chemical cleaning, smoothing and H-termination were applied (Table 1). The wet-chemical oxidation shifts the Si/SiO₂ interface into the Si bulk. Afterwards a few Ångstrom thick Si surface layer can be removed by the etch-back of wet-chemical oxide layers in HF or NH₄F solution. This principle was utilized in order to decrease the micro-roughness of the substrate surface prior to the preparation of ultrathin-oxides. For these purpose both processes – the wet-chemical oxidation as well as the oxide removal – were carefully optimized. The optimal treatment times were ascertained by in situ photoluminescence measurements as recently reported in ref. [35].

3.1.2. Preparation-induced charges on n-type Si substrate surfaces

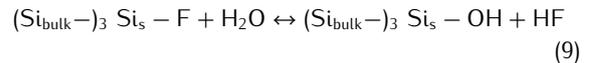
The effect of these smoothing and H-termination procedures on the surface charge and density of interface state was investigated in detail by field modulated SPV measurements carried out immediately after the final H-termination step. Fig. 3 merges the results of SPV

measurements on polished n-type Si-substrates obtained immediately after surface cleaning, smoothing and H-termination: a) surface photovoltage pulses $U_{ph}(t)$, b) surface potential vs. field-voltage and c) the calculated interface state distributions.

Fig. 3a shows the maximal values of U_{ph} and the time decays of the photovoltage transient signal, which yield information about interface recombination behaviors [63]. The maximal value and time decays were found to be strongly influenced by the wet-chemical substrate pre-treatment. After final HF treatment (Fig. 3a, curves 1 and 3) characteristic higher values of surface photovoltage were obtained compared to significant lower values after final etching in buffered NH₄F solution (Fig. 3a, curves 4 and 5). The positive charge on H-terminated surfaces is attributed to surface dipoles which result from the different electronegativities of silicon surface atom ($(\text{Si}_{\text{bulk}}-)_3\text{Si}_s-$ and hydrogen ($-H$) or other substituents ($-X$). The H-termination process in HF containing solutions can be explained by the insertion of HF into polarized $(\text{Si}_{\text{bulk}}-)_3\text{Si}_{\text{bulk}}-\text{Si}_s$ bonds leading to the removal of surface Si atoms as SiF₄ and the hydrogenation of the second silicon layer. Applying diluted HF solution, an incomplete reaction course results in remaining polarized $(\text{Si}_{\text{bulk}}-)_3\text{Si}_s-\text{F}$ and $(\text{Si}_{\text{bulk}}-)_3\text{Si}_s-\text{OH}$ bonds on the surface (Eq. 8).



Analogous reactions with the other nucleophilic species of the HF (1%) solution (H₂O and OH⁻) (Eq. 9) may also result in appearance of different values of silanol groups $(\text{Si}_{\text{bulk}}-)_3\text{Si}_s-\text{OH}$ on the surface:



The partially ionic character of the covalent $(\text{Si}_{\text{bulk}}-)_3\text{Si}_s-X$ bonds (with $-X : -H, -OH, -F$) leads to a strong polarization $\pm \Delta$ of the $\text{Si}_{\text{bulk}} - \text{Si}_s$ backbonds. The difference between the atomic electronegativities δq_{-X} of the adatoms $-X$ and the silicon surface atoms $(\text{Si}_{\text{bulk}}-)_3\text{Si}_s -$

$$\langle \delta q_{-\text{Si}} \rangle \langle \delta q_{-\text{H}} \rangle \langle \delta q_{-\text{OH}} \rangle \langle \delta q_{-\text{F}} \rangle \quad (10)$$

lead to different surface Fermi level positions after H-termination in HF (1%) compared to NH₄F- solution and thus changes in band bending, as visible in the difference of maximal U_{ph} values (Fig. 3a).

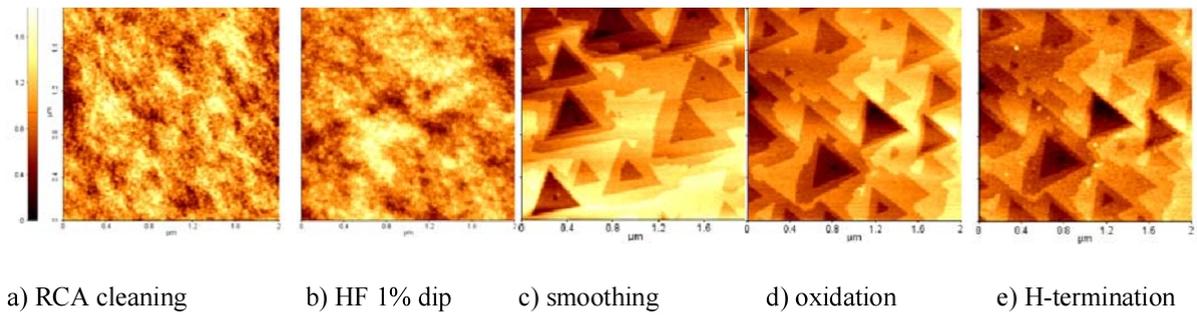


Figure 2. AFM images ($2\mu\text{m} \times 2\mu\text{m}$) of polished Si(111) surfaces (reprinted with permission from Springer [33]):

(a) after RCA treatment [23], b) after subsequent HF dip (1%, 30 s), c) after subsequent wet-chemical smoothing ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 + \text{NH}_4\text{F}$ (6.5 min), d) after subsequent wet-chemical oxidation in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ and long time storage in air, and e) after final removal of the wet-chemical oxide.

The decreasing slope of the $U_{\text{Ph}}(t)$ decay can be taken as measure for the decrease in interface recombination achieved by wet-chemical smoothing and H-termination. On RCA treated wafer after the final HF 1% step (Fig. 3a, curve 1) a faster time decay of U_{Ph} was observed as compared to samples which were additionally wet-chemically oxidized in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution after the final HF 1% step (Fig. 2a, curve 3) and after final etching in NH_4F - solution (Fig. 3a, curves 4, 5).

3.1.3. Effect of RCA cleaning, smoothing and H-termination on the Si surface state density D_{it}

Fig. 3b shows surface potential vs. field voltage, $Y_s(U_F)$ plots typically obtained on n-Si(111) samples after RCA cleaning and HF dip (curve 2), subsequent smoothing (curve 3) and H-termination (curve 6). The energetic distributions of rechargeable interface states $D_{\text{it}}(E)$, calculated by using Eq. (6, 7), are given in Fig. 3c. The minimum value $D_{\text{it,min}}$ of the energetic distribution of rechargeable interface states $D_{\text{it}}(E)$ (Fig. 3c) and its energetic position is commonly used as a technological parameter of the electronic surface quality.

The conventional RCA cleaning process [23] followed by HF 1% dip after drying and storage in air (Fig. 3c, curve 1) causes high values of surface charge and high densities of interface states in the lower half of the forbidden gap which were partially reduced by a continuous process (Fig. 3c, curve 2). A subsequent wet-chemical smoothing step by additional oxidation using $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ solution and subsequent wet-chemical oxide removal in (i) HF 1% or (ii) in NH_4F solution results in U-shaped distributions of interface states (Fig. 3c, curves 3, 4, 5) typically obtained on H-terminated surfaces. By optimized wet-chemical smoothing and H-termination processes applying NH_4F solution (ii) for the final H-termination process (Fig. 3c, curve 4) and (iii) for both RCA oxide removal and

the final H-termination process (Fig. 3c, curve 5) a significant decrease the minimum value of $D_{\text{it}}(E)$ up to $D_{\text{it,min}} \leq 3 \cdot 10^{11} \text{ cm}^{-2}\text{eV}^{-1}$, compared to $D_{\text{it,min}} \geq 2 \cdot 10^{12} \text{ cm}^{-2}\text{eV}^{-1}$ on the initial surface (Fig. 3c, curve 0) was achieved.

U-shaped distributions of D_{it} and the high D_{it} value near the band edges, which were firstly experimentally observed on Si/SiO₂ interfaces, have been attributed to specific defect centres in the oxide layer [37]. They can be understood as superposition of two groups of rechargeable states: i) the states near the band edges result from strained (Si-)₃ Si-Si(-Si)₃ bonds and decay roughly exponentially into the band gap, and ii) the groups of states symmetrically distributed around a minimum near midgap are correlated to dangling bond defects (Si_{bulk}-) Si•, which are back-bonded to Si atoms only [38, 39]. These defect groups were identified by comparison to electronic model and also by EPR measurements (P_b-centres) [38, 40], and have been identified mainly as unpaired sp^3 orbitals on trivalently bonded interface Si atoms or Si(111)-oriented Si dangling bonds pointing out of the interface into the oxide [41]. The two related defect groups on the Si(100)/SiO₂ and Si(111)/SiO₂ interfaces are the so called P_{B0} and P_{B1} centres, respectively. As shown by combined SPV, spectroscopic ellipsometry in the ultra-violet and visible region (UV-VIS-SE) and Fourier-Transform infrared ellipsometry (FTIR SE) measurements similar U-shaped distributions of $D_{\text{it}}(E)$ and low minimal values of $D_{\text{it,min}}$ (see Fig. 3c, curve 3,4,5) can be observed by H-termination of atomically flat surfaces in dry nitrogen atmosphere [31, 32].

3.1.4. Influence of preparation-induced substrate surface micro-roughness on $D_{\text{it}}(E)$

To reduce the density of chargeable interface states it is necessary to minimize interface roughness and intermediate oxidation states by optimized wet-chemical and

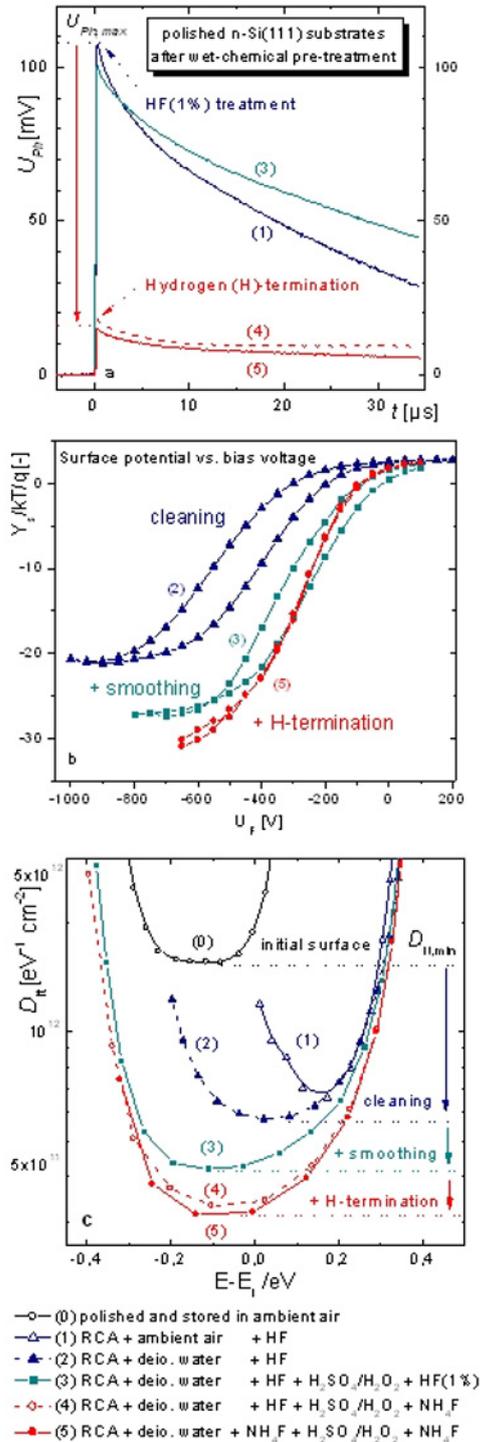
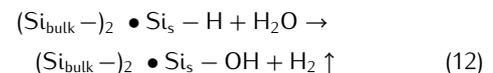
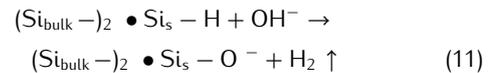


Figure 3. (a) Surface photovoltage pulses, (b) surface potential vs. field voltage $Y_s(U_f)$ plots and (c) the calculated interface state distributions $D_{it}(E)$ obtained on polished n-type FZ Si at the initial state (0), and after different cleaning (1,2), smoothing (3), and hydrogen (H)-termination processes (4,5).

UHV oxidation conditions. In order to further elucidate influence of surface micro-roughness on an atomic scale the roughness of a atomically smooth H-terminated n-type Si(111) surface was systematically increased by an additional HF(48%) treatment. These investigations have been carried out by combined UV-VIS-SE and SPV measurements after varying HF etching times t_{HF} : 5, ..., 600 s. Fig. 4 shows the comparison of SE and SPV data obtained on these set of samples with a systematic and well defined increase in surface roughness. Thereby, correlations between the $D_{it}(E)$ and the preparation-induced surface effective micro-roughness $\langle d_r \rangle$ were established. The surface state density $D_{it, min}$ at the minimum of $D_{it}(E)$ (Fig. 4, curve 1) and the density of surface states $D_{it}(-0.15 eV)$ in the lower half of the gap (Fig. 4, curve 2) at $E_F - E_i = -0.15 eV$ (E_F : surface Fermi level, E_i : intrinsic Fermi level) are plotted versus the effective surface roughness $\langle d_r \rangle$ determined by ex-situ UV-VIS-spectroscopic ellipsometry (SE) measurements [24].

$D_{it, min}$ strongly depends on the remaining surface roughness and a stepwise increase in was observed if $\langle d_r \rangle$ affects one, two, and three monolayers (Fig. 4, curve 1) [24]. Moreover, the $D_{it}(E)$ curves were found to have changed (see Fig. 3c curves 1, 2) if the surface roughness increased. While the atomically flat H-terminated surface is characterized by a U-shaped intrinsic surface state distribution (Fig. 3c, curves 3, 4, 5), a group of extrinsic states appears in addition. Therefore the density of states in the lower half of the gap $D_{it}(E_F - E_i = -0.15 eV)$ exceed the specified measuring range of the SPV method $D_{it}(-0.15 eV) > 5 \times 10^{13} cm^{-2} eV^{-1}$ as soon as the surface roughness becomes significantly greater than one monolayer (see Fig. 4, curve 2). These extrinsic states, forming a Gaussian distribution in the lower half of the forbidden gap are caused by dangling bond defects $(Si-)_2$ $(O-)Si\bullet$ which are correlated with Si atoms of a lower state of oxidation, Si^{+1} [32].

The occurrence of oxygen backbonded Si dangling bond defects indicates that the surface is not completely hydrogen terminated. We consider the competition between reactions (Eqs. 9, 10, 11) of various nucleophilic components of the HF-containing solution to be the reason for the appearance of these defects.



These results suggest that the competition reactions take place preferably at defect atoms $(Si_{bulk}-)_3 Si_s\bullet$ on the

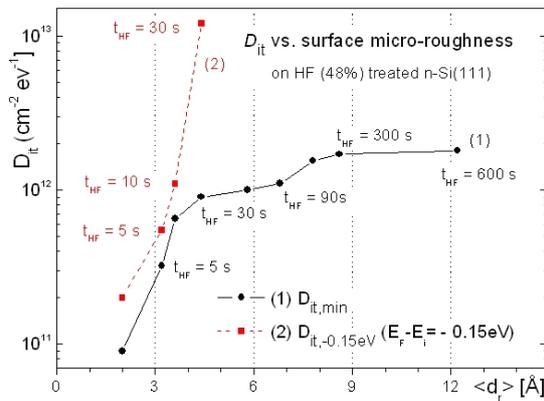


Figure 4. curve (1) Surface state density $D_{it,min}$ curve (2) and the density of extrinsic states D_{it} ($E_F - E_i = -0.15$ eV) versus effective surface roughness $\langle d_r \rangle$ determined by UV-VIS SE measurements [24] on HF(48%) -treated n-type Si(111)-surfaces.

surface and cause extrinsic states when the surface roughness increases and affects more than two monolayers.

3.2. Electronic interface properties of ultrathin SiO₂ on n-type Si(111) substrate

As demonstrated in Fig. 3, the preparation-induced D_{it} of the polished, H-terminated n-type Si substrate surfaces result from the course of two different chemical processes: the smoothing of the surface by wet-chemical oxidation as well as the final etching step in HF-containing solutions, respectively. On polished n-type Si(111) substrates the values of surface charge and D_{it} in the lower part of the gap could be significantly reduced applying a continuous process consisting of RCA cleaning, wet-chemical oxidation in H₂SO₄/H₂O₂ and oxide removal in NH₄F- solution (Fig. 3c, curve 4, 5).

Immediately after the final etching step on H-terminated substrates ultrathin oxides were prepared by utilizing thermalized atomic oxygen under ultrahigh vacuum conditions. Fig. 5 shows $D_{it}(E)$ curves determined by field depended SPV measurements on Si/SiO₂ interfaces of these ultrathin oxides prepared on the differently pre-treated n-Si(111) substrates after subsequent in situ hydrogenation using atomic hydrogen with thermal energies (Fig. 5, curves 1-6). For comparison a $D_{it}(E)$ curve obtained on the same substrate after oxidation in RCA solution and storage on air is given in (Fig. 5, curve 0).

A step-wise decrease of $D_{it,min}$ at the UHV oxidised Si/SiO₂ interfaces was achieved by optimising the substrate surface pre-treatment processes RCA cleaning, smoothing and H-termination. After the standard RCA treatment values of $D_{it,min} \geq 3.5 \cdot 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ were obtained (Fig. 5, curves 1 and 2), which could be reduced down to $D_{it,min} \approx 1 \cdot 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ by optimised wet-chemical substrate smoothing (Fig. 5, curve 3) and additional H-termination in NH₄F solution (Fig. 5, curve 4). High values of interfacial fixed charges were obtained on these RCA pre-treated samples (Fig. 5, curve 1, 2), which limit SPV investigations in the near-conduction-band region. The relationship between interface charges and roughness was previously studied using STM, AFM and high-frequency and quasi-static CV measurements. It was pointed out that the interface charge increases as a result of interface roughness and this increase is due mainly to the increase of surface area and surface orientation introduced by the roughness [10].

The novel ultrathin oxides prepared on smooth, previously HF 1% etched surfaces (Fig. 5, curve 3) exhibit a significant decrease of the interfacial fixed charges within the SiO₂. The same effect was achieved by heating the substrate to 1000°C before the oxidation, thus desorbing impurity atoms at the surface and results in the lowest minimal value of $D_{it,min}$ (Fig. 5, curve 6). Least values of interfacial fixed charges were obtained on n-type substrate surfaces after oxide removal in NH₄F solution (Fig. 3a, curves 4, 5) and on Si/SiO₂ interfaces prepared on those substrates by subsequent oxidation and in situ hydrogenation with atomic species under thermal impact conditions (Fig. 5, curve 5).

4. Conclusion

SPV investigations yielded detailed information regarding the influence of wet-chemical pre-treatment processes on interface charges and $D_{it}(E)$ of n-type Si substrates and subsequently prepared Si/SiO₂ interfaces.

In contrast to the standard RCA cleaning process [23], by an optimized wet-chemical smoothing and H-termination procedure, $D_{it}(E)$ and surface charges on the H-terminated surface substrate could be markedly reduced.

The compositional transition from an atomically flat H-terminated Si(111) surface to so prepared SiO₂ occurs abruptly through a transition layer consisting of intermediate oxidation states of Si [42]. It was shown, that the effect of optimized wet-chemical pre-treatment can be preserved during the subsequent preparation of ultrathin oxides by exposure to thermalized atomic oxygen under UHV conditions as well as subsequent hydrogenation with

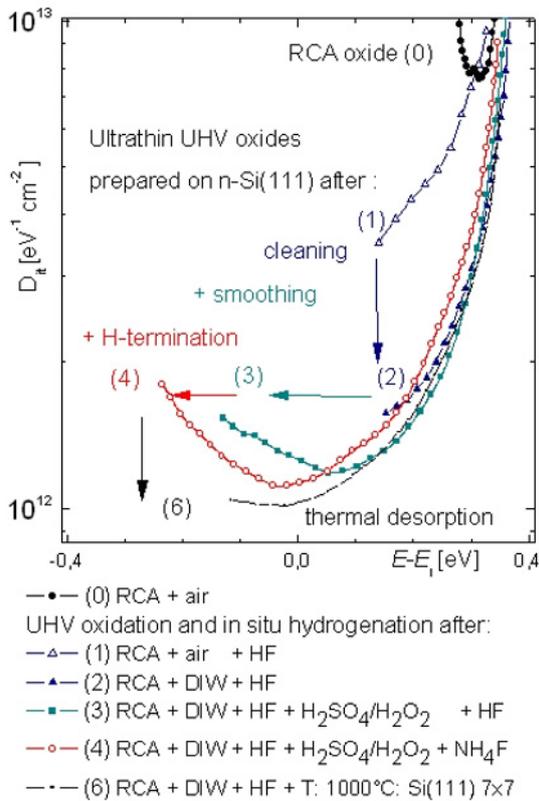


Figure 5. $D_{it}(E)$ on polished n-type Si(111) substrates after RCA treatment (curve 0) and at interfaces of ultrathin SiO₂ layers (20 Å) prepared by oxidation and in situ hydrogenation with atomic species after different cleaning (curves 1,2), smoothing (curve 3), and hydrogen (H)-termination processes (curve 4) or after thermal desorption (curve 6).

thermalized H atoms. As a result, structurally and electronically abrupt Si/SiO₂ interfaces with lower interface state density and interfacial fixed charges, as compared to conventional pre-treated substrates are formed. Moreover, interfacial fixed charges and density of states on these Si/SiO₂ interfaces could be significantly reduced by applying wet-chemically smoothed, H-terminated substrates.

With respect to functionalizing ultrathin SiO₂ layers in various innovative solar cell concepts appropriate wet-chemical treatment leads clearly to improvement of interface properties and opens new prospects for further potential applications.

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