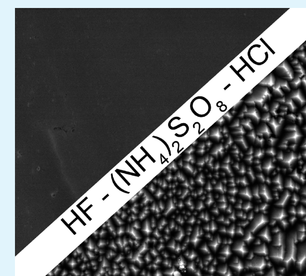
ACS APPLIED MATERIALS & INTERFACES
Research Article
www.acsami.org

$HF-(NH_4)_2S_2O_8-HCl$ Mixtures for HNO_3- and NO_x-free Etching of Diamond Wire- and SiC-Slurry-Sawn Silicon Wafers: Reactivity Studies, Surface Chemistry, and Unexpected Pyramidal Surface Morphologies

André Stapf, Christoph Gondek, Marcus Lippold, and Edwin Kroke*

Institute of Inorganic Chemistry, Technische Universität Bergakademie Freiberg, Leipziger Strasse 29, D-09599 Freiberg, Germany

ABSTRACT: The wet-chemical treatment of silicon wafers is an important production step in photovoltaic and semiconductor industries. Solutions containing hydrofluoric acid, ammonium peroxodisulfate, and hydrochloric acid were investigated as novel acidic, NO_x-free etching mixtures for texturization and polishing of monocrystalline silicon wafers. Etching rates as well as generated surface morphologies and properties are discussed in terms of the composition of the etching mixture. The solutions were analyzed with Raman and UV/vis spectroscopy as well as ion chromatography (IC). The silicon surfaces were investigated by scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM), diffuse reflection infrared spectroscopy (DRIFT), and X-ray photoelectron spectroscopy (XPS). Surprisingly, pyramidal surface structures were found after etching SiC-slurry as well as diamond wire-sawn monocrystalline Si(100) wafers with hydrochloric acid-rich $HF-(NH_4)_2S_2O_8-HCl$ mixtures. Acidic etching solutions are generally not known for anisotropic etching. Thus, the HNO_3-free mixtures might allow to replace KOH/*i*-propanol and similar alkaline solutions for texturization of monosilicon wafers at room temperature with less surface contamination. Besides, common HNO_3-based etching mixtures may be replaced by the nitrate-free system, leading to significant economic and ecological advantages.



KEYWORDS: *monocrystalline silicon, acidic etching, texturization, polishing, pyramids, photovoltaics*

INTRODUCTION

Wet-chemical treatments of silicon surfaces are frequently used for several different processing steps in photovoltaic, electronic, and other industries. They are used, for example, for saw damage removal,[1] surface cleaning,[2] and polishing or texturing of the wafer surfaces.[3−6] Polishing the wafer gives a mirrored, flat, contamination-free surface required for the fabrication of semiconductor devices. Texturization is of relevance in photovoltaics for reducing light reflection of the wafer surface in order to increase the light-trapping efficiency.

$HF-HNO_3$-based etching mixtures are the most widely used acidic etchants. Additional mixture components, such as CH_3COOH,[7,8] H_3PO_4,[9] H_2SO_4,[10] or HCl[11] influence the reactivity toward silicon, etched surface morphologies and the cleaning efficiency. Because of the isotropic etching character, acidic etchants are suitable for texturing of multicrystalline silicon wafers in the photovoltaic industry or polishing monocrystalline silicon wafers in microelectronic industry. For texturing of monocrystalline silicon wafers, alkaline mixtures, mostly consisting of KOH and *i*-propanol, are utilized at ~80 °C. On (100)-orientated wafers, the anisotropic etching behavior leads to the formation of random pyramids.[12−14] Acidic etching solutions are generally not known for an anisotropic etch attack.[9] As an exception anisotropic behavior is reported for $H_2SiF_6-HNO_3$ solutions.[15]

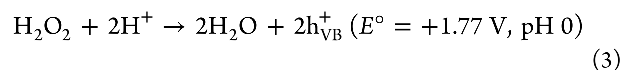
Etching of silicon in hydrofluoric acid-based mixtures is basically described as a two-step process. The oxidation of silicon is followed by dissolution of the oxidized silicon species by fluoride containing species in order to form SiF_6^{2-}.[8,16−19]

$$Si + 4h^+_{VB} \rightarrow Si^{4+} \quad (1)$$

$$Si^{4+} + 6F^- \rightarrow SiF_6^{2-} \quad (2)$$

The oxidation of silicon surface atoms in hydrofluoric acid-containing mixtures requires a standard redox potential of +0.7 V.[20] Therefore, nitric acid, hydrogen peroxide, chromium(+6) oxide, and numerous other species conduce as oxidants.[7,21,22] For industrial etching processes, nitric acid is the most common oxidant. However, etching mixtures containing nitric acid produce nitrogen oxides (NO_x) and wastewater containing massive amounts of nitrate.[23,24] This needs to be costly treated and recycled. Our current studies focus on the replacement of nitric acid by less toxic oxidants.

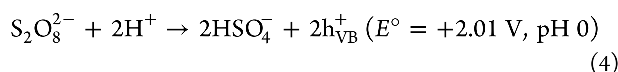
According to the standard redox potential, hydrogen peroxide and peroxodisulfate should be promising oxidants (eqs 3 and 4 are from ref 25).



$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+_{VB}\ (E° = +1.77\ V,\ pH\ 0) \quad (3)$$

Received: February 4, 2015
Accepted: March 31, 2015
Published: March 31, 2015

 © 2015 American Chemical Society
DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742



$$S_2O_8^{2-} + 2H^+ \rightarrow 2HSO_4^- + 2h_{VB}^+ \; (E^\circ = +2.01 \text{ V, pH } 0) \tag{4}$$

However, hydrofluoric acid mixtures containing either hydrogen peroxide or peroxodisulfate exhibit etching rates below 0.02 nm s^{-1} because of kinetic inhibition.[26,27] Here we report on solutions containing hydrofluoric acid, ammonium peroxodisulfate and hydrochloric acid as novel acidic etching mixtures for the treatment of silicon wafers. Etching rates and generated surface morphologies are discussed in terms of the composition of the etching mixture. Unexpectedly, anisotropic texturization of monocrystalline silicon wafers is possible at room temperature and reasonable etching rates up to 4 nm s^{-1} are observed. Results of the analysis of surface species and the characterization of dissolved intermediates are evaluated in the context of existing models for etching mechanisms.

EXPERIMENTAL SECTION

Etching Procedure and Determination of Etching Rates. ***Caution!*** *Etching experiments with hydrofluoric acid must be performed in a HF-approved fume hood with HF-resistant laboratory equipment.* For preparing the etching mixtures hydrochloric acid (37% (w/w), analytical grade, VWR), hydrofluoric acid (48% (w/w), analytical grade, Sigma-Aldrich), ammonium peroxodisulfate (analytical grade, Sigma-Aldrich) and deionized(DI) water were mixed under cooling in a PFA beaker. For the determination of the etch rates, silicon wafer pieces of approximately 100 mg ((100) orientation, boron doped, thickness of 190 μm, resistivity of 0.5−2.0 Ω cm^{-1}, Deutsche Solar GmbH, Freiberg, Germany) were placed with tweezers for 0.5 to 2 h (t_{etch}) in 30 mL of the etching mixture. Experiments were performed at room temperature with as-cut diamond-wire-sawn silicon(100) wafers as well as with as-cut SiC-slurry-sawn silicon(100) wafers and previously polished silicon(100) wafers. The etching reaction was quenched by rinsing the wafer with deionized water. Each experiment was performed using freshly prepared solutions.

The etch rate r (eqs 5, 6, and 7) is the quotient of the etched silicon layer per side and the immersion time (t_{etch}). The thickness of the removed silicon layer per side(Δd) is calculated from the mass loss obtained by differential weighing (ρ(Si) = 2.33 g cm^{-3}).

$$A = \frac{m_0}{\rho_{Si} d_0} \tag{5}$$

$$\Delta d = d_0 - d_1 = d_0 - \frac{m_1}{\rho_{Si} A} = d_0\left(1 - \frac{m_1}{m_0}\right) \tag{6}$$

$$r = \frac{\Delta d(1 \times 10^7)}{2 \cdot 3600 t_{etch}} = \left(\frac{\text{nm}}{\text{s}}\right) \tag{7}$$

where m = mass (g), ρ = density (g cm^{-3}), A = area of the wafer (cm^2), d = thickness of the wafer (cm), t_{etch} = etching time (h).

Silicon powder (approximately 0.1 g) was etched in 30 mL of the etching mixture. The etching reaction was quenched by filtering the powder and rinsing with deionized water. The powder was dried in air afterwards. Each experiment was performed in a freshly mixed solution.

Characterization of Etching Mixtures and Etched Silicon Wafers. The concentrations of fluoride, chloride and sulfate ions were monitored by ion chromatography (Dionex ICS 2000). Therefore, the etching mixture was diluted by a factor of 1:5000. The addition of 3 mL of NaOH (10% (w/w), analytical grade) converted the acids to anions. Raman spectroscopy measurements of $(NH_4)_2S_2O_8$-HCl mixtures were performed with a Bruker RFS 100/S spectrometer in 10 mm optical glass-cuvettes (VWR) without diluting the etching mixtures. For UV/vis spectrophotometry a VWR UV-1600PC spectrophotometer and Eppendorf UVette-cuvettes (10 mm) were used. The etching mixtures were diluted by a factor of 1:25. To adjust a pH value below 0.5, hydrochloric acid (37% (w/w), analytical grade, VWR) was added. Scanning electron microscopy (SEM) measurements were carried out with a Vega Tescan TS 5130 SB system. An Olympus LEXT OLS4000 confocal laser scanning microscope (CLSM) was used for determining roughness parameters, especially the root-mean-square height (Sq). This parameter represents the standard deviation of the average height (eq 8).

$$\text{Sq} = \sqrt{\frac{1}{N}\sum_{1}^{N}(h_i - h_{avg})^2} \tag{8}$$

A Nicolet 380 FT-IR-spectrometer (Thermo Electron Corporation) with Smart Collector Avatar accessory (Thermo Fisher Scientific) was used for diffuse reflectance infrared (DRIFT) spectroscopy measurements. For X-ray photoelectron microscopy (XPS) measurements, the etched silicon wafers were rinsed with DI water, dried immediately with clean room paper, and kept under an argon atmosphere to avoid oxidation by atmospheric oxygen. Thereby, short contact with air was inevitable. A Specs Phoibos 150 MCD-9 spectrometer was used with an Al−K_α source (1486.6 eV) in a vacuum of 8 × 10^{-9} mbar.

Oxidation of H-Terminated Silicon Wafers. Silicon surfaces were H-terminated by dipping in a mixture containing 10.7 mol L^{-1} hydrofluoric acid and 2.8 mol L^{-1} nitric acid for 240 s. Afterward, they were treated in aqueous solutions of ammonia peroxodisulfate (0.8 mol L^{-1}), calcium hypochlorite (0.4 mol L^{-1}), and chlorine. The latter was produced by adding 100 mL of hydrochloric acid dropwise to 5 g of manganese dioxide. The gaseous chlorine was dried by passing through sulfuric acid (98% (w/w)). The oxidized silicon surfaces were investigated by DRIFT spectroscopy.

REACTIVITY STUDIES

In HF-$(NH_4)_2S_2O_8$-HCl mixtures with a constant concentration of ammonium peroxodisulfate, the etching rates of crystalline silicon(100) wafers were determined for concentrations of hydrofluoric acid in the range from 1.0 to 5.0 mol L^{-1} and hydrochloric acid in the range from 0.0 to 7.9 mol L^{-1} (Figure 1). Etching rates up to 4.0 nm s^{-1} were observed at room temperature for high concentrations of hydrochloric acid. These reactivities are in the same range as known from KOH etching solutions at 60 °C.[12] HF-HNO_3 etching mixtures show significantly higher reactivities up to 3000 nm s^{-1}.[28]

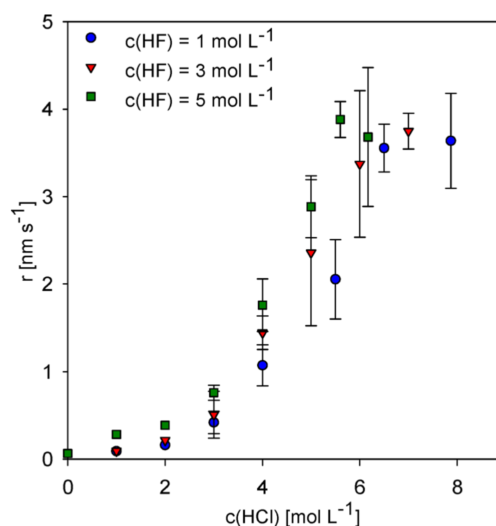


Figure 1. Etching rates of as-cut diamond wire-sawn Si(100) wafers in HF-$(NH_4)_2S_2O_8$-HCl mixtures depending on the concentrations of hydrofluoric and hydrochloric acid ($c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1}, ϑ = 20 °C). The error bars result from the standard deviation of three experiments.

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742

At constant amounts of ammonium peroxodisulfate an increase of the concentration of hydrofluoric acid causes higher etching rates. Surprisingly, the silicon etching rates depend even more on the concentrations of hydrochloric acid. From the literature, hydrochloric acid is only known as an additive for better cleaning results.[29]

The increase in the reactivity at higher amounts of hydrofluoric acid can be explained by the higher rate of dissolution of oxidized silicon surface species. Generally, the etching rates also increase by rising the concentration of the oxidizing agents. Hence, the increase in etching rates at higher concentrations of hydrochloric acid might be explained by the intermediary formation of further oxidants, e.g., chlorine species such as ClO^-, ClO_2^-, ClO_3^-, ClO_4^-, and/or Cl_2 (see below).

ANALYSIS OF THE $(NH_4)_2S_2O_8$-HCL MIXTURES

To determine possible oxidizing agents, freshly prepared mixtures of ammonium peroxodisulfate with various amounts of hydrochloric acid (without contact to silicon) were analyzed by Raman spectroscopy (Figure 2). The Raman lines at 1075 and 834 cm^{-1} can be assigned to peroxodisulfate anions.[30] The intensity of both bands decreases with higher amounts of hydrochloric acid. Additionally, the Raman line at 1050 cm^{-1} increases, which corresponds to hydrogen sulfate anions.[31] In hydrochloric acid-rich mixtures a Raman signal occurs at 504 cm^{-1}. This band may be assigned to Cl_2.[32] These results show that ammonium peroxodisulfate ions are reduced in hydrochloric acid solutions to form hydrogen sulfate ions and chlorine without contact to silicon (eq 9).

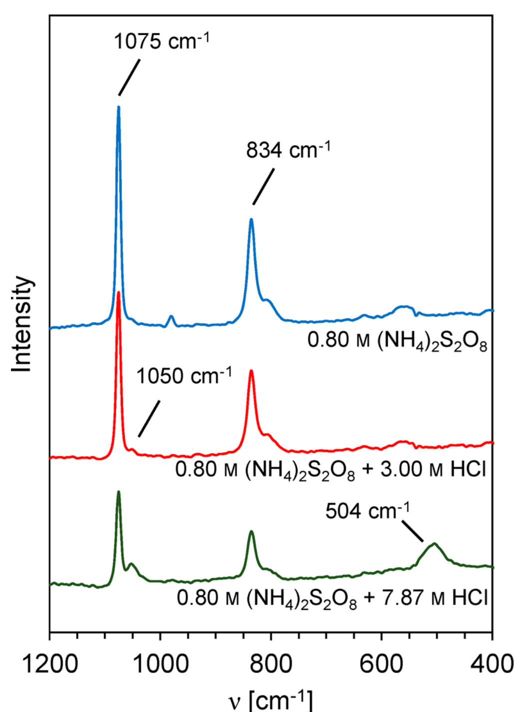


Figure 2. Raman spectra of freshly prepared mixtures of $(NH_4)_2S_2O_8$ with different amounts of HCl.

To prove the presence of chlorine, a mixture of 0.8 mol L^{-1} ammonium peroxodisulfate and 7.9 mol L^{-1} hydrochloric acid was analyzed with UV/vis spectrophotometry (Figure 3). The peak at 325 nm corresponds to chlorine in aqueous solution.[33,34] This shows that chloride ions are oxidized by peroxodisulfate to form molecular chlorine in solution according to eq 9.

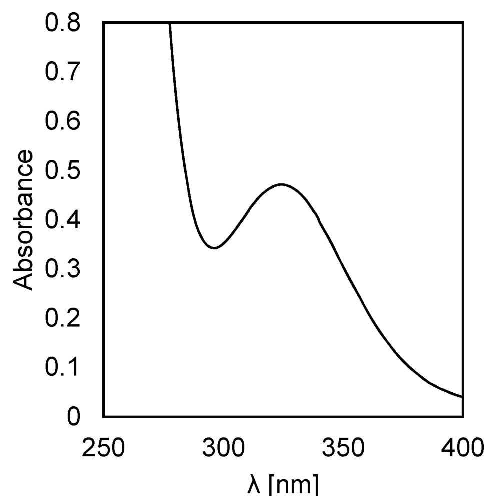


Figure 3. UV/vis spectrum of a freshly prepared mixture containing 0.8 mol $L^{-1}(NH_4)_2S_2O_8$ and 7.9 mol L^{-1} HCl, diluted 1:25.

$$S_2O_8^{2-} + 2Cl^- + 2H^+ \rightarrow 2HSO_4^- + Cl_2 \quad (9)$$

$$2H_2O(l) + Cl_2 \rightleftarrows Cl^- + HOCl + H_3O^+ \quad (10)$$

In aqueous solutions at low temperature, chlorine is known to disproportionate in order to form hypochlorous acid and hydrochloric acid (eq 10).[25] However, in solutions with high amounts of chloride ions and low pH values, aqueous chlorine is argued to be the main oxidative species because the equilibrium is shifted toward chlorine and water.[32] Therefore, hypochlorous acid is expected not to be present in relevant amounts in investigated HF-$(NH_4)_2S_2O_8$-HCl solutions. Raman spectroscopy measurements support this hypothesis. Hypochlorous acid shows Raman lines at 725 cm^{-1}. In this range, no bands were found (Figure 2).

OXIDATION REACTIONS OF H-TERMINATED SILICON SURFACES

According to the standard redox potential, both chlorine (Cl_2/Cl^-, $E° = 1.36$ V)[25] and peroxodisulfate ($S_2O_8^{2-}/HSO_4^-$, $E°$ = 2.01 V, pH = 0)[25] should be able to oxidize silicon surfaces. Therefore, H-terminated silicon wafers were treated with solutions of these oxidants in absence of hydrofluoric acid. The investigation of the obtained surfaces by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) allow conclusions concerning possible reaction pathways.

A DRIFT spectrum of the used H-terminated silicon surface is shown in Figure 4-0. The absorption bands at 2098 and 900 cm^{-1} are characteristic for several Si−H_n surface groups.[35,36] The H-terminated surface is hydrophobic.

After treating an H-terminated silicon surface with a solution containing ammonium peroxodisulfate there is still a significant H-termination on the silicon surface (Figure 4a). An oxidation of the silicon surface by peroxodisulfate is assumed to be due to the slightly wider Si−O−Si absorption band at 1100 cm^{-1} and the shoulder at 2190 cm^{-1}, which indicates oxidized O_x−Si−H_{3-x} surface groups. However, the oxidation rate is relatively low.

When adding hydrochloric acid to the ammonium peroxodisulfate solution (Figure 4b), there is an increase of

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742

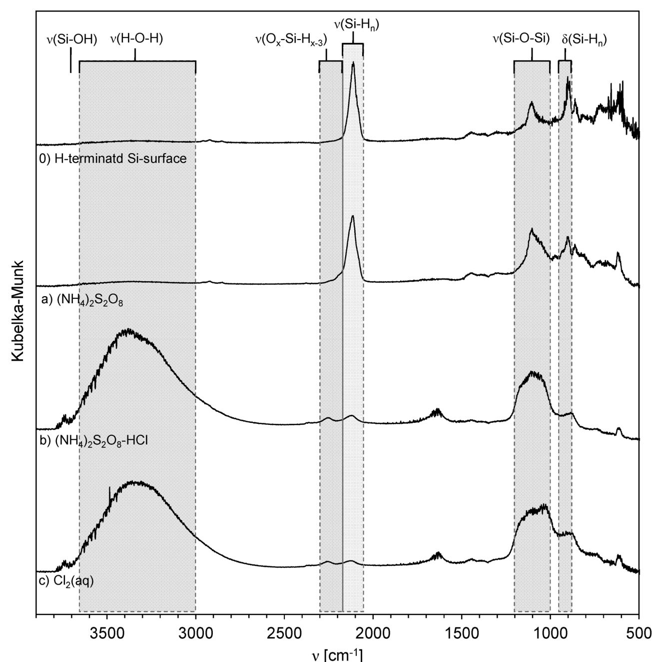


Figure 4. DRIFT spectra of (0) an H-terminated silicon surface, treated for 300 s with solutions of (a) 0.8 mol L^{-1} $(NH_4)_2S_2O_8$, (b) 0.8 mol L^{-1} $(NH_4)_2S_2O_8$ and 5.0 mol L^{-1} HCl, and (c) aqueous Cl_2.

the oxidation rate. The previously H-terminated silicon surface is oxidized as indicated by the broad Si−O−Si absorption bands at 1100 cm^{-1}. Furthermore, the remaining H-terminated surface groups indicate the oxidation of rearward silicon surface bonds(Si−Si back bonds) by insertion of oxygen atoms (O_x−Si−H_{3-x}). This is shown by a shift of the absorption band at 2098 cm^{-1}. The insertion of oxygen atoms into the polarized Si−Si back bonds is known, for example, for water, dissolved oxygen in the solution,[37] and nitric acid.[38] At 3750 cm^{-1}, there is an absorption band for Si−OH surface species. This indicates an attack on Si−H surface groups as known from alkaline solutions. Very similar results are obtained after treating an H-terminated silicon surface with an aqueous chlorine solution-(Figure 4c). Thus, chlorine should be the oxidizing agent in HF−$(NH_4)_2S_2O_8$−HCl mixtures.

To investigate the oxidation process in $(NH_4)_2S_2O_8$−HCl mixtures, the change in the absorption band at 2098 cm^{-1} of an H-terminated silicon surface was studied (Figure 5). After a short treatment time (15 s) in hydrochloric acid-rich solutions (Figure 5a) the Si−H absorption band already disappears. This indicates a direct attack of the formed chlorine on the Si−H surface bonds.

When treating H-terminated silicon surfaces in solutions containing low amounts of hydrochloric acid (Figure 5b), insertion of oxygen atoms in Si−Si back bonds can be detected after short treatment times by the shift of the absorption band to higher wavenumbers. The rate of oxidation of silicon surface by ammonium peroxodisulfate solutions without hydrochloric acid is relatively low (see Figure 4a, just a small change after 300 s). Thus, the presence of low amounts of hydrochloric acid seems to catalyze the oxidation of Si−Si back bonds by ammonium peroxodisulfate. Low amounts of hydrochloric acid might activate the peroxodisulfate ions to oxidize the Si−Si back bonds. This is also in good agreement with the above-described reactivity studies (Figure 1). HF-$(NH_4)_2S_2O_8$-HCl mixtures with low amounts of hydrochloric acid, where no chlorine or very small amounts are formed, show higher reactivity toward silicon (~0.5 nm s^{-1}) than solutions without hydrochloric acid (<0.02 nm s^{-1}). Hydrochloric acid-rich mixtures, where formation of chlorine was detected, exhibit high etching rates up to 4.0 nm s^{-1}. The different reactivities are probably caused by different species acting as oxidizing agent in the system HF-$(NH_4)_2S_2O_8$-HCl.

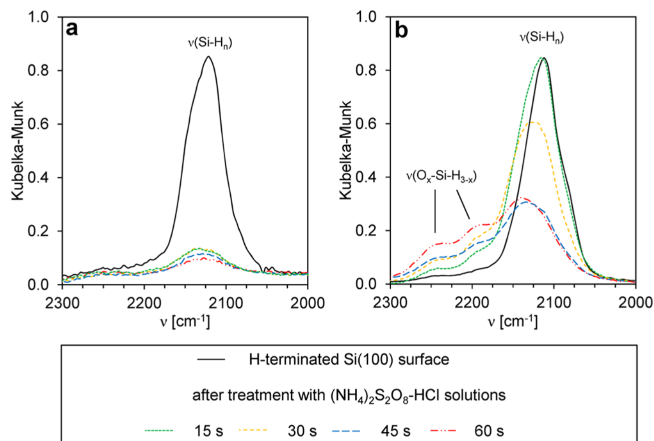


Figure 5. DRIFT spectra of silicon surfaces, after treatment with solutions of (a) 0.8 mol L^{-1} $(NH_4)_2S_2O_8$ and 7.9 mol L^{-1} HCl and (b) 0.8 mol L^{-1} $(NH_4)_2S_2O_8$ and 3.0 mol L^{-1} HCl.

■ SURFACE ANALYSIS OF SILICON WAFERS ETCHED BY HF-$(NH_4)_2S_2O_8$-HCL SOLUTIONS

The higher reactivity of HF-$(NH_4)_2S_2O_8$-HCl mixtures toward silicon enables the modification of the surface morphology. Silicon wafers treated by HF-$(NH_4)_2S_2O_8$-HCl solutions were investigated by scanning electron microscopy (SEM). Figure 6 exhibits etched surface morphologies depending on the concentration of the hydrofluoric and hydrochloric acids. After etching in mixtures with small amounts of hydrochloric acid, we observed surface polishing (Figure 6a). In these mixtures, where no formation of chlorine was detected, reactivities were lower than 1.0 nm s^{-1}. These solutions are a promising alternative for polishing monocrystalline silicon wafers without generating gaseous nitrogen oxides (NO_x).

Etching solutions with reactivities between 1.0 and 3.0 nm s^{-1} produce surface structures between texture and polish (Figure 6b−d). Surprisingly, pyramidal structures were found on silicon(100) wafer surfaces after etching in HF-$(NH_4)_2S_2O_8$-HCl mixtures with high amounts of hydrochloric acid (Figure 6e−k).

Confocal laser scanning microscopy (CLSM) was used to examine the roughness parameters of the etched surface morphologies. The diamond wire-sawn silicon wafer surface shows saw marks and cracks (Figure 7-0). The root-mean-square height (Sq), which represents the standard deviation of the average height, is 0.266 μm. The maximum height of the surface (Sz) from highest peak to lowest valley is 4.881 μm. After etching in a mixture containing less hydrochloric acid, the silicon wafer surface shows a high planarity (Figure 7b). The Sq roughness is 0.08 μm and the maximum height from lowest valley to highest peak is 0.8 μm. After etching in hydrochloric acid-rich mixtures the Sq parameter of 0.536 μm reveals roughening of the wafer surface. At the same time, the maximum height of the surface gets smaller (Sz = 4.063 μm)

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742

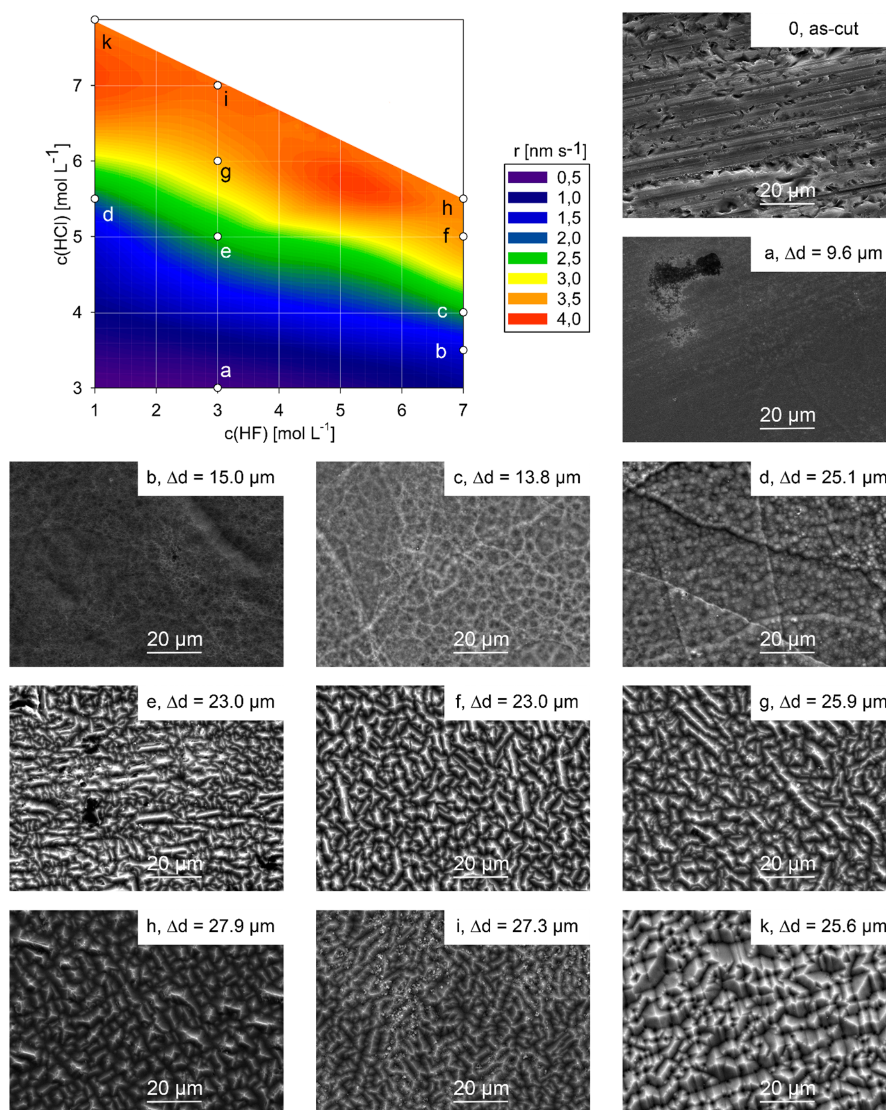


Figure 6. Reactivities and SEM images of silicon(100) wafer surfaces etched by HF-$(NH_4)_2S_2O_8$-HCl solutions: (0) as-cut, diamond wire-sawn, (a) polish etching, (b–d) transition polish/texture etching, (e–k) anisotropic texture/pyramids; ϑ = 25 °C.

because of damage removal. Figure 7a shows a regularly pyramidal structure which indicates anisotropic etching.

As mentioned above, anisotropic etching in this way is so far known only from alkaline etching solutions. For technical implementation, KOH solutions only work at high temperatures of 60–80 °C and organic additives such as iPA are necessary. With the possibility to produce similar textures on silicon(100) surfaces at room temperature without organic additives, a more energy-efficient process for texturing silicon wafers and producing solar cells should be possible. Furthermore, the problems of surface metal contaminations frequently observed for treatment in alkaline solutions are avoided by the use of the acidic HF-$(NH_4)_2S_2O_8$-HCl mixture. Figure 8 shows that hydrochloric acid-rich mixtures enable texturing of diamond wire-sawn, SiC-slurry-sawn, and pre-polished monocrystalline silicon wafers. The higher roughness observed on SiC-slurry-sawn wafer surfaces leads to large pyramids of different sizes (Figure 8a, b). The smoother the surface before etching the more equal are the edge lengths of pyramids after etching in hydrochloric acid rich mixtures-(Figure 8c–f), because the etching starts at defects and dislocations on the surface.

The unexpected change in the surface morphology leads to the presumption of different dissolution mechanisms than usually proposed for dissolution in acidic HF mixtures. Therefore, silicon surfaces obtained by etching in HF-$(NH_4)_2S_2O_8$-HCl solutions were investigated by DRIFT measurements.

Silicon surfaces etched by HF-HNO_3-H_2O solutions show an intensive surface covering with Si–H groups, indicated by X-ray photoelectron spectroscopy (XPS) studies[39] and by characteristic absorption bands at 2098 cm^{-1} in DRIFT spectra (see also Figure 4-0).[35,36] Figure 9b shows DRIFT spectra of silicon powder after etching in HF-$(NH_4)_2S_2O_8$-HCl solution with low amounts of hydrochloric acid. In this solution no chlorine was detected. The spectrum shows various Si–H vibrations indicating Si–H_n (n = 1–3) surface groups. After etching in hydrochloric acid-rich solutions, there are small bands of Si–H surface groups (Figure 9a). Because of the attack of chlorine on Si–H surface bonds, these are regenerated after the complexing step by hydrofluoric acid. The different intensities in the spectra

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733–8742

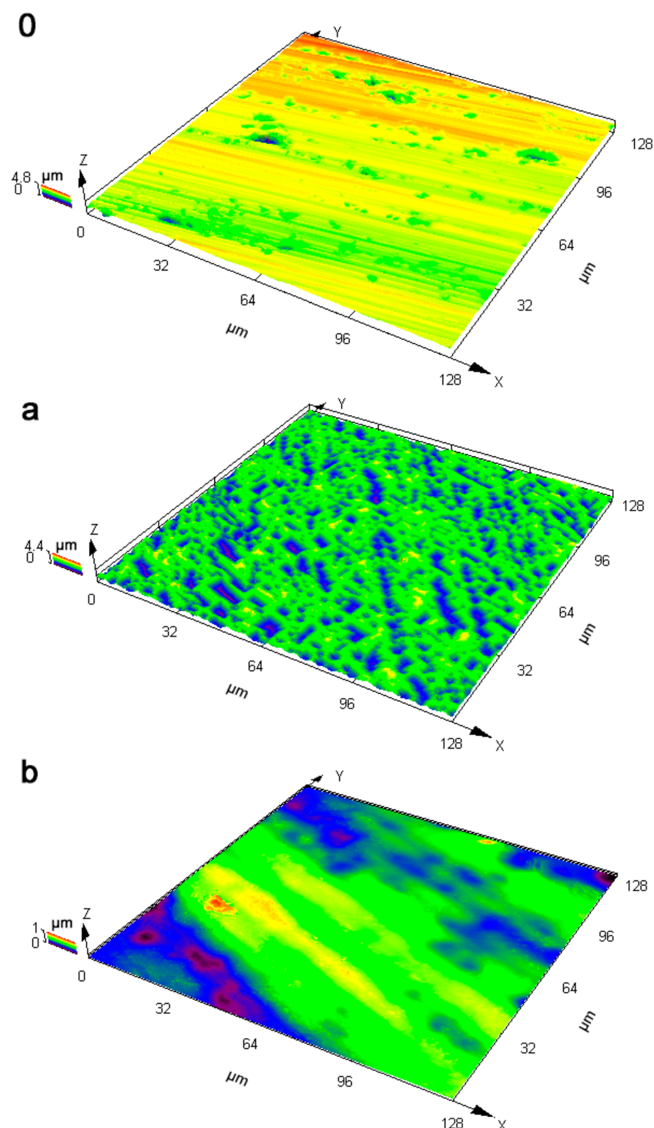


Figure 7. CLSM images of silicon(100) wafer surfaces (0) as-cut, diamond wire-sawn; etched by HF-$(NH_4)_2S_2O_8$-HCl solutions containing (a) $c(HF)$ = 1.0 mol L^{-1}, $c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1} and $c(HCl)$ = 7.9 mol L^{-1} and (b) $c(HF)$ = 1.0 mol L^{-1}, $c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1} and $c(HCl)$ = 3.0 mol L^{-1}; ϑ = 25 °C.

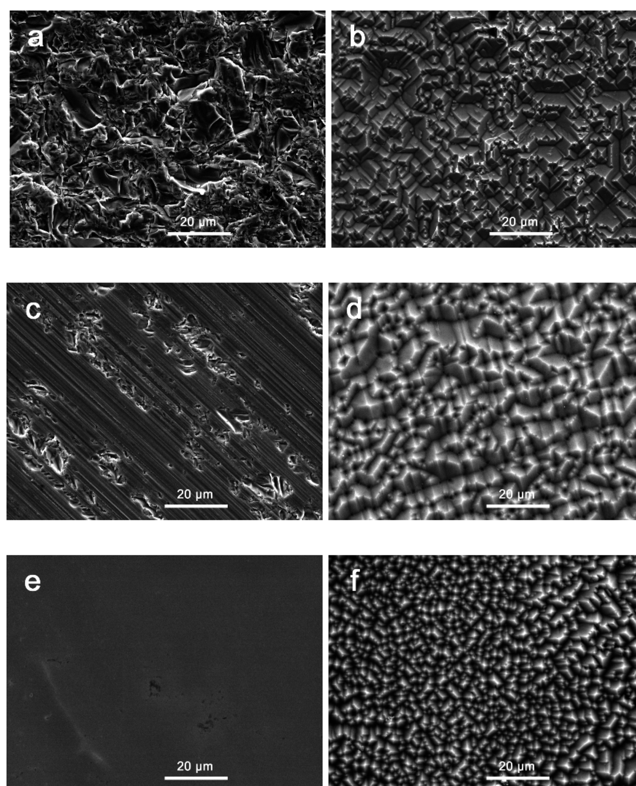


Figure 8. REM images of silicon(100) surfaces: SiC slurry-sawn, (a) before and (b) after etching, diamond wire-sawn; (c) before and (d) after etching, prepolished; (e) before and (f) after etching in mixture containing $c(HF)$ = 1.0 mol L^{-1}, $c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1} and $c(HCl)$ = 7.9 mol L^{-1}; ϑ = 25 °C, Δd = 18–26 μm.

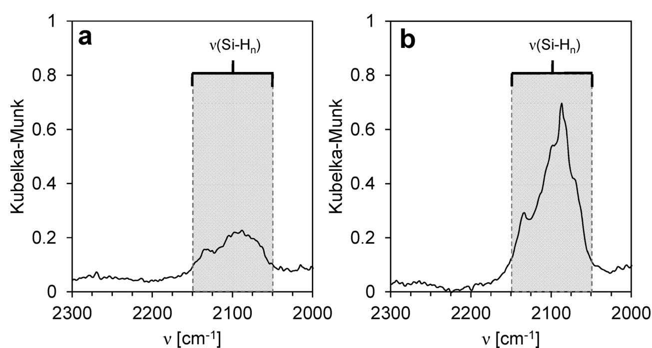


Figure 9. Detailed DRIFT spectra of silicon powder etched by HF-$(NH_4)_2S_2O_8$-HCl solutions containing (a) $c(HF)$ = 1.0 mol L^{-1}, $c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1} and $c(HCl)$ = 7.9 mol L^{-1} and (b) $c(HF)$ = 1.0 mol L^{-1}, $c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1} and $c(HCl)$ = 3.0 mol L^{-1}; ϑ = 25 °C.

in Figure 9 might originate from the varying oxidative power of the investigated mixtures (see also Figure 5).

Besides Si−H surface bonds, other silicon surface species are probably present, because of the attack of chlorine on the Si−H bond. Possible surface groups are Si−OH, Si−F, or Si−Cl. For detailed characterization of surface species, silicon wafers freshly etched by hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions were studied by XPS.

The signals in the survey scans indicate small amounts of chlorine and fluorine and high amounts of oxygen and carbon besides the signals for silicon (Figure 10a). The high amount of carbon is caused by the short contact with air, handling with PTFE tweezers, and drying with cleanroom paper. The high intensity of the peak at 532.41 eV in the O 1s region (Figure 10d) indicates oxygen-containing contaminations from air. There is also a small peak at 531.66 eV that may be assigned to Si−O bonds.[40] The signals in the F 1s region (Figure 10c) show two different surface species. The peak at 689.36 eV indicates a C−F bonding, which might be caused by contaminations by PTFE tweezers.[41] The signal at 686.88 eV cannot definitely be assigned to Si−F surface groups but could also be caused by contaminations, for example, adsorbed fluoride species. The high-resolution Cl 2p spectrum (Figure 10b) shows small amounts of chlorine atoms on the silicon wafer surface.

The high-resolution Si 2p XPS peaks were treated more intensely to identify and semiquantify the species bound to silicon. The Si 2p spectrum was processed by subtracting a Shirley-shaped background. The $2p_{1/2}$ spin−orbit component was removed assuming a spin−orbit splitting of 0.61 eV and an

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742

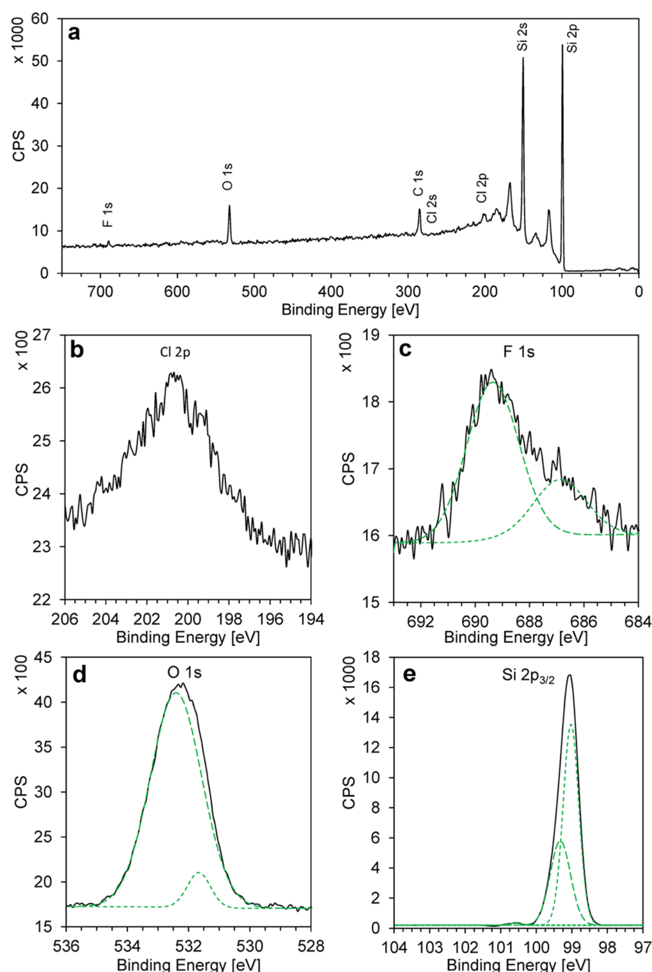


Figure 10. XPS spectra of a Si(100) surface freshly etched by HF-$(NH_4)_2S_2O_2$-HCl mixture containing $c(HF)$ = 1.0 mol L^{-1}, $c((NH_4)_2S_2O_8)$ = 0.8 mol L^{-1} and $c(HCl)$ = 7.9 mol L^{-1}, (a) survey scan and high resolution spectra of (b) Cl 2p, (c) F 1s, (d) O 1s, and (e) Si $2p_{3/2}$.

intensity ratio $(2p_{1/2}/2p_{3/2})$ of 1:2.[42] Table 1 shows experimental data compared to literature data.

The signals in the Si $2p_{3/2}$ high resolution spectra (Figure 10e) indicate bulk $Si^{(0)}$ species by a peak at 99.03 eV and SiH_n species by a peak at 99.33 eV (binding energy shift ΔE = +0.30 eV).[43] Opposed to DRIFT measurements, the silicon wafer surface seems to be highly H-terminated. Furthermore, there is a small peak at 100.60 eV (ΔE = +1.57 eV). This peak is between signals known for the oxidized silicon species $Si^{(1)}$ and $Si^{(2)}$,[42,43] and between signals known for SiCl and $SiCl_2$ surface species.[44] It may correspond to silicon surface groups with one hydrogen and one other heteroatom (Figure 11). As there are no signals with ΔE > 2.50 eV, it is supposed that there is no oxygen inserted in Si−Si back bonds.

In summary, the XPS measurements of a silicon wafer surface freshly etched by hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions indicate an H-terminated surface (Figure 11a) with hints of additional chlorine-, oxygen-, and fluorine-containing silicon surface groups, as shown in Figure 11b−f.

PRESUMED REACTION PATHWAYS

For etching silicon in HF-$(NH_4)_2S_2O_8$-HCl solutions with low concentrations of hydrochloric acid, where no formation of chlorine was observed, an electrochemical mechanism could be followed (Figure 12). The dissolution is initiated by generation of an electron hole (h_{VB}^+) by the oxidizing agent, peroxodisulfate in this case. This step seems to be catalyzed by the presence of low amounts of hydrochloric acid (Figure 5b). It allows an attack of HF to form a Si−F bond. After the second Si−H surface bond is replaced by a Si−F bond the polarized rear Si−Si bonds are attacked by HF. This leads to the formation of SiF_4 which is complexed by HF as H_2SiF_6.[39,45] $HSiF_3$ might also be formed as we have shown recently.[46]

Because of the observed anisotropy another mechanism needs to be considered for etching in HF-$(NH_4)_2S_2O_8$-HCl solutions with high concentrations of hydrochloric acid. When looking at the mechanism proposed for etching silicon in alkaline solutions, the dissolution is initiated by a nucleophilic attack of OH^- species on Si−H surface bonds.[9,47,48] The transition state of this reaction is a pentacoordinated silicon atom.[49] The formally hydridic hydrogen on top of the surface is oxidized by H−O−H to form H_2. An Si−OH bond is formed. The attraction of electrons by the OH group polarizes the Si−Si back bonds resulting in an attack of water to break these bonds. The H-termination is restored.

Similar mechanisms may be presumed for the dissolution of silicon in hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions. Ammonium peroxodisulfate oxidizes chloride ions to form chlorine (see eq 8). The oxidation step might be initiated by an attack of chlorine on Si−H surface bonds via a pentacoordinated transition state. This is supported by the

Table 1. Experimental Data of Si $2p_{3/2}$ Binding Energy Shifts(ΔE) Compared to Literature Data

	ΔE (eV)			
species	Himpsel et al.[42]	Cerofolini et al.[43]	Bogart, Donnelly[44]	experimental
$Si^{(0)}$	0.00 (BE_{abs} ≈ 99.5 eV)	0.00 (BE_{abs} = 99.30 eV)	0.00 (BE_{abs} = 99.09 eV)	0.00 (BE_{abs} = 99.03 eV)
$Si^{(SiH)}$		+ 0.13 ± 0.05		
$Si^{(SiH2)}$		+ 0.28 ± 0.01		+ 0.30
$Si^{(SiH3)}$		+ 0.47 ± 0.02		
$Si^{(1)}$	+ 0.95 ± 0.05	+ 1.01 ± 0.04		
$Si^{(2)}$	+ 1.75 ± 0.09	+ 1.84 ± 0.09		
$Si^{(3)}$	+ 2.48 ± 0.12	+ 2.86 ± 0.02		
$Si^{(4)}$	+ 3.90 ± 0.20	+ 3.63 ± 0.15		
$Si^{(SiCl)}$			+ 0.81 ± 0.04	
$Si^{(SiCl2)}$			+ 1.84 ± 0.04	
$Si^{(SiCl3)}$			+ 2.91 ± 0.06	
$Si^{(SiX)}$				+ 1.57

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742

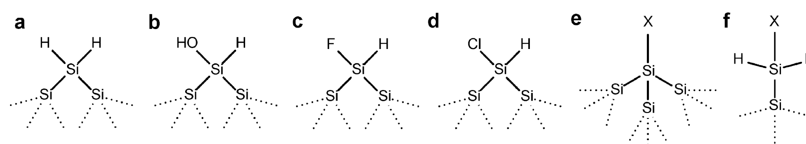


Figure 11. (a) H-terminated silicon surface and (b–d) further possible silicon surface groups after etching in hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions. (e, f) Similarly, Si-X and SiH_2X groups may be present with X = H, OH, F, Cl.

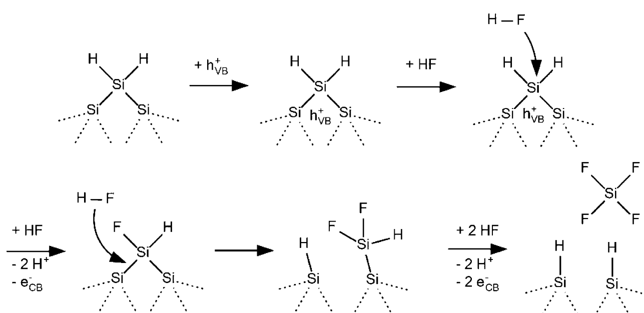


Figure 12. Reaction scheme proposed for the chemical dissolution of Si(100) surfaces in acidic fluoride containing solutions.[45]

time dependent DRIFT measurements of the oxidation of H-terminated silicon surfaces (Figure 5a) and chlorine species on the silicon surface found by XPS measurements (Figure 10b). The subsequent attack of HF on the polarized Si–Si back bonds leads to the dissolution of the oxidized surface species (Figure 13). Thereby, the H-termination is restored as shown by XPS measurements (Figure 10e). Finally, silicon is dissolved as hexafluorosilicate.

To explain different etching rates of Si(100), Si(110), and Si(111) surfaces in alkaline solutions, several approaches were found in literature, which may also be applied for etching in hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions. The low dissolution on Si(111) surfaces may be understood as an insufficient polarization of three rear Si–Si bonds by only one Si–X surface bond, where X stands for –OH or –Cl, respectively. On Si(100) surfaces, there are two Si–X bonds to polarize two Si–Si back bonds.[50,51] Furthermore, a change from tetrahedral to trigonal bipyramidal configuration is necessary in order to form the pentavalent transition state. However, only Si–H or Si–X surface groups are able to change their relative position, the angles of the back bonds are fixed by the solid lattice. So, for dissolution of Si(111) surfaces with three fixed Si–Si back bonds, a higher activation energy is needed than for etching Si(100) surfaces with only two of them.[48] This hypothesis is supported by theoretical analysis.[52]

All in all, the mechanism of silicon dissolution in chlorine containing HF-$(NH_4)_2S_2O_8$-HCl mixtures seems to be similar to alkaline silicon dissolution.

CONCLUSIONS

Hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions can be used for anisotropic texturization of monocrystalline, as-cut (SiC-slurry- and diamond wire-sawn) as well as polished silicon wafers. In contrast to HF-HNO_3-H_2O solutions, pyramidal surface morphologies similar to typical alkaline textures are generated. Relatively high etching rates up to 4.0 nm s^{-1} are observed at room temperature. Because alkaline mixtures are usually applied at temperatures of 60–80 °C, a more energy-efficient process for texturing silicon wafers and producing solar cells should be possible. Polishing of monocrystalline silicon wafers can be achieved by etching with HF-$(NH_4)_2S_2O_8$-HCl solutions containing low amounts of hydrochloric acid. These NO_x-free solutions are a promising alternative to common etching solutions without being more expensive, because $(NH_4)_2S_2O_8$ and HCl are cheap chemicals.

By the analysis of surface and solution species, it was found that peroxodisulfate is only weakly oxidizing the silicon surface. Dissolved chlorine seems to be the oxidative species in hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions. Chlorine shows different oxidation properties toward silicon compared to other oxidizing agents in acidic media.

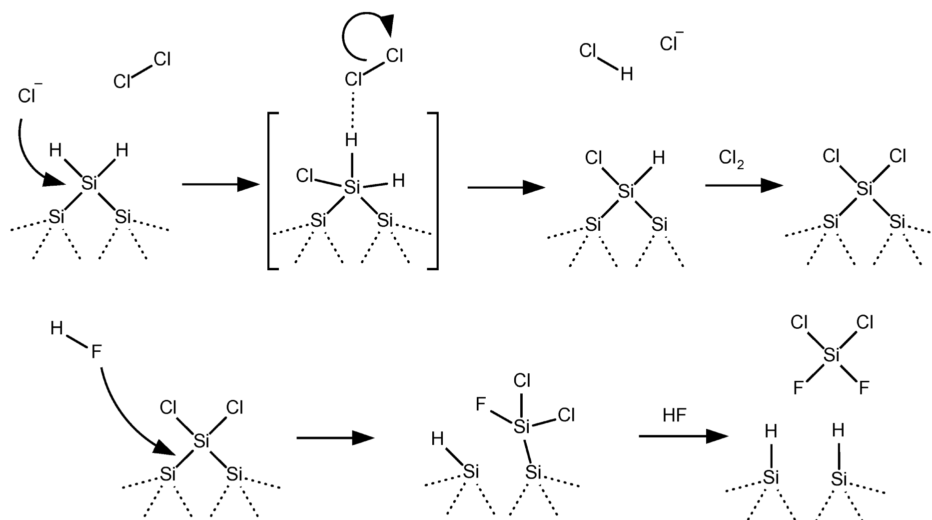


Figure 13. Reaction scheme presumed for the chemical dissolution of Si(100) surfaces in hydrochloric acid-rich HF-$(NH_4)_2S_2O_8$-HCl solutions, where chlorine was detected.

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733–8742

Currently we focus on a deeper investigation of the reaction mechanisms which are involved in the dissolution of silicon in HF-$(NH_4)_2S_2O_8$-HCl mixtures. Besides other oxidants such as hydrogen peroxide or ozone-based solutions containing hydrofluoric and hydrochloric acid are investigated. Further open questions include the potential influence of hypochlorite ions and other oxyanions of chlorine on the involved reactions, etching rates, and surface morphologies.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Edwin.kroke@chemie.tu-freiberg.de.

Funding

Financial support was in part provided within the Cluster of Excellence "Structure Design of Novel High-Performance Materials via Atomic Design and Defect Engineering(ADDE)" that is financially supported by the European Union (European regional development fund) and by the Ministry of Science and Art of Saxony.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank, in particular, B. Kutzner for ion chromatographic measurements, R. Moßig for Raman spectroscopy measurements, and M. Günthel for X-ray photoelectron spectroscopy measurements. We kindly acknowledge the Solar World Innovations GmbH for the supply of the silicon wafer material.

■ DEDICATION

This paper is dedicated to Professor Gerhard Roewer on the occasion of his 75th birthday.

■ REFERENCES

(1) Park, H.; Kwon, S.; Lee, J. S.; Lim, H. J.; Yoon, S.; Kim, D. Improvement on Surface Texturing of Single Crystalline Silicon for Solar Cells by Saw-Damage Etching Using an Acidic Solution. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 1773−1778.

(2) Reinhardt, K. A.; Kern, W. *Handbook of Silicon Wafer Cleaning Technology*, 2nd ed.; Materials Science & Process Technology Series; William Andrew: Norwich, NY, 2008.

(3) Vazsonyi, E.; De Clercq, K.; Einhaus, R.; Van Kerschaver, E.; Said, K.; Poortmans, J.; Szlufcik, J.; Nijs, J. Improved Anisotropic Etching Process for Industrial Texturing of Silicon Solar Cells. *Sol. Energy Mater. Sol. Cells* **1999**, *57*, 179−188.

(4) Park, S. W.; Kim, D. S.; Lee, S. H. New Approach to Isotropic Texturing Techniques on Multicrystalline Silicon Wafers. *J. Mater. Sci.: Mater. Electron.* **2001**, *12*, 619−622.

(5) Panek, P.; Lipiński, M.; Dutkiewicz, J. Texturization of Multicrystalline Silicon by Wet Chemical Etching for Silicon Solar Cells. *J. Mater. Sci.* **2005**, *40*, 1459−1463.

(6) Hilleringmann, U. *Mikrosystemtechnik: Prozessschritte, Technologien, Anwendungen*, 1st ed.; Teubner: Wiesbaden, Germany, 2006.

(7) Löwe, H.; Keppel, P.; Moritz, C.; Zach, D. *Halbleiterätzverfahren: Kinetik, Verfahrensgrundlagen und Anwendungsgebiete von nasschemischen Ätzverfahren für Si, GaAs, GaP und InP*; Akademie-Verlag: Berlin, 1990.

(8) Robbins, H.; Schwartz, B. Chemical Etching of Silicon: II. The System HF, HNO_3, H_2O, and $HC_2H_3O_2$. *J. Electrochem. Soc.* **1960**, *107*, 108−111.

(9) Lehmann, V. *The Electrochemistry of Silicon: Instrumentation, Science, Materials and Applications*; Wiley-VCH: Weinheim, Germany, 2002.

(10) Lippold, M.; Buchholz, F.; Gondek, C.; Honeit, F.; Wefringhaus, E.; Kroke, E. Texturing of SiC-Slurry and Diamond Wire Sawn Silicon Wafers by HF−HNO_3−H_2SO_4 Mixtures. *Sol. Energy Mater. Sol. Cells* **2014**, *127*, 104−110.

(11) Herzer, H.; Voit, H. Verfahren und Vorrichtung zur naßchemischen Behandlung von Siliciummaterial. DE 19934325543, Jul 29, 1993.

(12) Zubel, I.; Kramkowska, M. The Effect of Isopropyl Alcohol on Etching Rate and Roughness of(100) Si Surface Etched in KOH and TMAH Solutions. *Sens. Actuators, A* **2001**, *93*, 138−147.

(13) Sato, K.; Shikida, M.; Yamashiro, T.; Tsunekawa, M.; Ito, S. Roughening of Single-Crystal Silicon Surface Etched by KOH Water Solution. *Sens. Actuators, A* **1999**, *73*, 122−130.

(14) Seidel, H.; Csepregi, L.; Heuberger, A.; Baumgärtel, H. Anisotropic Etching of Crystalline Silicon in Alkaline Solutions: I. Orientation Dependence and Behavior of Passivation Layers. *J. Electrochem. Soc.* **1990**, *137*, 3612−3626.

(15) Famini, S.; Esfandyarpour, B.; Mohajerzadeh, S. Anomalous Anisotropic Etching of(111) and(100) Silicon Wafers Using Acidic Solutions. *J. Electrochem. Soc.* **2006**, *153*, G721−G725.

(16) Robbins, H.; Schwartz, B. Chemical Etching of Silicon: I. The System HF, HNO_3, and H_2O. *J. Electrochem. Soc.* **1959**, *106*, 505−508.

(17) Schwartz, B.; Robbins, H. Chemical Etching of Silicon: III. A Temperature Study in the Acid System. *J. Electrochem. Soc.* **1961**, *108*, 365−372.

(18) Turner, D. R. On the Mechanism of Chemically Etching Germanium and Silicon. *J. Electrochem. Soc.* **1960**, *107*, 810−816.

(19) Ho, C.-C.; Huang, C.-H.; Chen, B.-S.; Su, Y.-H.; Chen, K.-J.; Hsu, C.-S.; Lee, T.-H. HF/H_2O_2 Etching for Removal of Damage Layer on As-Transferred Si Layer Formed by Ion-Cut Process. *Electrochem. Solid-State Lett.* **2010**, *13*, H227−H229.

(20) Nahidi, M.; Kolasinski, K. W. Effects of Stain Etchant Composition on the Photoluminescence and Morphology of Porous Silicon. *J. Electrochem. Soc.* **2006**, *153*, C19−C26.

(21) Kolasinski, K. W. Charge Transfer and Nanostructure Formation during Electroless Etching of Silicon. *J. Phys. Chem. C* **2010**, *114*, 22098−22105.

(22) Kolasinski, K. W.; Gogola, J. Electroless Etching of Si with IO_3^- and Related Species. *Nanoscale Res. Lett.* **2012**, *7*, 323−330.

(23) Patzig-Klein, S.; Roewer, G.; Kroke, E. New Insights into Acidic Wet Chemical Silicon Etching by HF/H_2O−$NOHSO_4$−H_2SO_4 Solutions. *Mater. Sci. Semicond. Process.* **2010**, *13*, 71−79.

(24) Steinert, M.; Acker, J.; Wetzig, K. New Aspects on the Reduction of Nitric Acid during Wet Chemical Etching of Silicon in Concentrated HF/HNO_3 Mixtures. *J. Phys. Chem. C* **2008**, *112*, 14139−14144.

(25) Holleman, A. F.; Wiberg, E.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*, 102nd ed.; de Gruyter: Berlin, 2007.

(26) Lachowicz, A.; Ramspeck, K.; Roth, P.; Manole, M.; Blanke, H.; Hefner, W.; Brouwer, E.; Schum, B.; Metz, A. NO_x-Free Solution for Emitter Etch-Back. In *Proceedings of the 27th European Photovoltaic Solar Energy Conference*; Frankfurt, Germany, Sept 24−28, 2012 ; WIP: Munich, Germany, 2012; pp 1846−1850.

(27) Gondek, C.; Lippold, M.; Röver, I.; Bohmhammel, K.; Kroke, E. Etching Silicon with HF-H_2O_2-Based Mixtures: Reactivity Studies and Surface Investigations. *J. Phys. Chem. C* **2014**, *118*, 2044−2051.

(28) Röver, I.; Roewer, G.; Bohmhammel, K.; Wambach, K. Reactivity of Silicon in Aqueous Solutions. Basis for Etching and Polishing of Wafers. *Freiberg. Forschungsh., B* **2004**, *B327*, 179−193.

(29) Hattori, T. *Ultraclean Surface Processing of Silicon Wafers: Secrets of VLSI Manufacturing*; Springer: Berlin, 1998.

(30) Vorsina, I. A.; Mikhailov, Y. I. Kinetics of Thermal Decomposition of Ammonium Persulfate. *Russ. Chem. Bull.* **1996**, *45*, 539−542.

(31) Degen, I. A.; Newman, G. A. Raman Spectra of Inorganic Ions. *Spectrochim. Acta, Part A* **1993**, *49*, 859−887.

(32) Cherney, D. P.; Duirk, S. E.; Tarr, J. C.; Collette, T. W. Monitoring the Speciation of Aqueous Free Chlorine from pH 1 to 12 with Raman Spectroscopy to Determine the Identity of the Potent Low-pH Oxidant. *Appl. Spectrosc.* **2006**, *60*, 764−772.

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742

(33) Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. Equilibrium, Kinetic, and UV-Spectral Characteristics of Aqueous Bromine Chloride, Bromine, and Chlorine Species. *Inorg. Chem.* **1994**, *33*, 5872−5878.
(34) Zimmerman, G.; Strong, F. C. Equilibria and Spectra of Aqueous Chlorine Solutions. *J. Am. Chem. Soc.* **1957**, *79*, 2063−2066.
(35) Rao, G. R.; Wang, Z.-H.; Watanabe, H.; Aoyagi, M.; Urisu, T. A Comparative Infrared Study of H_2O Reactivity on Si(1 0 0)-(2 × 1),(2 × 1)-H,(1 × 1)-H and(3 × 1)-H Surfaces. *Surf. Sci.* **2004**, *570*, 178−188.
(36) Wang, Z.-H.; Urisu, T.; Watanabe, H.; Ooi, K.; Rao, G. R.; Nanbu, S.; Maki, J.; Aoyagi, M. Assignment of Surface IR Absorption Spectra Observed in the Oxidation Reactions: 2H + H_2O/Si(1 0 0) and H_2O + H/Si(1 0 0). *Surf. Sci.* **2005**, *575*, 330−342.
(37) Morita, M.; Ohmi, T.; Hasegawa, E.; Kawakami, M.; Ohwada, M. Growth of Native Oxide on a Silicon Surface. *J. Appl. Phys.* **1990**, *68*, 1272−1281.
(38) Yin, F.; Li, X. P.; Zhang, Z. Z.; Xiao, X. R. Investigation on the Surface Reactivity of Luminescent Porous Silicon. *Appl. Surf. Sci.* **1997**, *119*, 310−312.
(39) Steinert, M.; Acker, J.; Oswald, S.; Wetzig, K. Study on the Mechanism of Silicon Etching in HNO_3-Rich HF/HNO_3 Mixtures. *J. Phys. Chem. C* **2007**, *111*, 2133−2140.
(40) Thøgersen, A.; Selj, J. H.; Marstein, E. S. Oxidation Effects on Graded Porous Silicon Anti-Reflection Coatings. *J. Electrochem. Soc.* **2012**, *159*, D276−D281.
(41) Lu, X.; Wong, K. C.; Wong, P. C.; Mitchell, K. A. R.; Cotter, J.; Eadie, D. T. Surface Characterization of Polytetrafluoroethylene-(PTFE) Transfer Films during Rolling−Sliding Tribology Tests using X-ray Photoelectron Spectroscopy. *Wear* **2006**, *261*, 1155−1162.
(42) Himpsel, F. J.; McFeely, F. R.; Taleb-Ibrahimi, A.; Yarmoff, J. A.; Hollinger, G. Microscopic Structure of the SiO_2/Si Interface. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *38*, 6084−6096.
(43) Cerofolini, G. F.; Giussani, A.; Modelli, A.; Mascolo, D.; Ruggiero, D.; Narducci, D.; Romano, E. Chemical, Energetic, and Geometric Heterogeneity of Device-Quality(1 0 0) Surfaces of Single Crystalline Silicon after HF_{aq} Etching. *Appl. Surf. Sci.* **2008**, *254*, 5781−5790.
(44) Bogart, K. H. A.; Donnelly, V. M. On the Constant Composition and Thickness of the Chlorinated Silicon Surface Layer Subjected to Increasing Etching Product Concentrations during Chlorine Plasma Etching. *J. Appl. Phys.* **1999**, *86*, 1822−1833.
(45) Kolasinski, K. W. Etching of Silicon in Fluoride Solutions. *Surf. Sci.* **2009**, *603*, 1904−1911.
(46) Lippold, M.; Böhme, U.; Gondek, C.; Kronstein, M.; Patzig-Klein, S.; Weser, M.; Kroke, E. Etching Silicon with HF-HNO_3-H_2SO_4/H_2O Mixtures – Unprecedented Formation of Trifluorosilane, Hexafluorodisiloxane, and Si-F Surface Groups. *Eur. J. Inorg. Chem.* **2012**, *2012*, 5714−5721.
(47) Kelly, J. J.; Philipsen, H. G. G. Anisotropy in the Wet-Etching of Semiconductors. *Curr. Opin. Solid State Mater. Sci.* **2005**, *9*, 84−90.
(48) Baum, T.; Schiffrin, D. J. Mechanistic Aspects of Anisotropic Dissolution of Materials Etching of Single-Crystal Silicon in Alkaline Solutions. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 691−694.
(49) Campbell, S. A.; Schiffrin, D. J.; Tufton, P. J. Chemical and Electrochemical Anisotropic Dissolution of Silicon in Ethylenediamine + Pyrocatechol + Water Media. *J. Electroanal. Chem.* **1993**, *344*, 211−233.
(50) Glembocki, O. J.; Stahlbush, R. E.; Tomkiewicz, M. Bias-Dependent Etching of Silicon in Aqueous KOH. *J. Electrochem. Soc.* **1985**, *132*, 145−151.
(51) Allongue, P.; Costa Kieling, V.; Gerischer, H. Etching of Silicon in NaOH Solutions: II. Electrochemical Studies of n-Si(111) and(100) and Mechanism of the Dissolution. *J. Electrochem. Soc.* **1993**, *140*, 1018−1026.
(52) Gosálvez, M. A. Atomistic Modelling of Anisotropic Etching of Crystalline Silicon. *Ph. D. Thesis*, Helsinki University of Technology, Espoo, Finland, 2003.

DOI: 10.1021/acsami.5b01059
ACS Appl. Mater. Interfaces 2015, 7, 8733−8742