Preparation of Si Surfaces: 
(Photo)(electro)chemical Passivation and Nanostructuring

Dr. Katarzyna Skorupska
<table>
<thead>
<tr>
<th><strong>Atomic Number</strong></th>
<th><strong>Element</strong></th>
<th><strong>Abbreviation</strong></th>
<th><strong>Atomic Mass</strong></th>
<th><strong>Electron Configuration</strong></th>
<th><strong>Period</strong></th>
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<tbody>
<tr>
<td>1</td>
<td>Hydrogen</td>
<td>H</td>
<td>1.005</td>
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<td>39.95</td>
<td>[Ar]</td>
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**Periodic Table of the Elements**

**Electron Configuration and Electronegativities**

1. **Electron Configuration**: Each element is represented by its electron configuration, indicating the distribution of electrons in its shells.
2. **Electronegativity**: The electronegativity values are shown for each element, indicating its ability to attract electrons in a chemical bond.

**Notes**:
- Elements are arranged in order of increasing atomic number.
- The periodic table highlights the groups and periods of elements.
- Electronegativity values range from 0 (nonmetals) to 4.0 (actinides), with 1.8 as a general threshold between metals and nonmetals.
3s  3p  3d

\[
\begin{array}{c}
\uparrow \downarrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}
\quad \begin{array}{c}
\uparrow \downarrow \\
\uparrow \uparrow \uparrow \\
\uparrow \uparrow \uparrow \\
\uparrow \uparrow \uparrow \\
\end{array}
\quad \begin{array}{c}
\uparrow \\
\times \\
\times \\
\times \\
\end{array}
\quad \text{sp}^3 \quad \text{sp}^3 \text{d} \quad \text{sp}^3 \text{d}^2
\end{array}
\]
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<th>$sp^3d$</th>
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<th>$sp^3d^2$</th>
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<td>Contributing orbitals</td>
<td>s, px, py, pz</td>
<td>s, px, py, pz, dz^2</td>
<td>s, px, py, pz, d_{x^2-y^2}</td>
<td>s, px, py, pz, dz^2, d_{x^2-y^2}</td>
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<tr>
<td>Configuration</td>
<td>tetrahedron</td>
<td>trigonal bipyramid</td>
<td>tetragonal pyramid</td>
<td>tetragonal bipyramid / octaedral</td>
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<td>Valency of Si</td>
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<td>pentavalent</td>
<td>pentavalent</td>
<td>hexavalent</td>
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<td>Bonds</td>
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<td>2 x coordination bond</td>
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<td>Example</td>
<td>crystal</td>
<td>reaction intermediates in SN2 mechanism</td>
<td>reaction intermediates in SN2 mechanism</td>
<td>(NH₄)₂SiF₆</td>
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</table>
H-terminated Si (111) surface

- dissolution of kink atoms

 Silicon is quite resistant to acids
- dissolves is HF, buffered HF (NH$_4$F)
Si dissolves well in alkaline solutions
H-terminated Silicon preparation by electrochemical treatment

1. dark current in dilute NH₄F  
2. oxidation in phthalate solution  
3. dark current in dilute NH₄F
SN₂ with F⁻ as a nucleophilic agent

Chemical reaction
(in analogy- ec process by e⁻ injection into E_{VB})

\[
SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H^+ + 2H_2O
\]

\[
SiO_2 + 3HF_2^- \rightarrow SiF_6^{2-} + H_2O + OH^-
\]

SN₂ with F⁻ as a nucleophilic agent
during chemical as well as anodic bias in the solution

\[ \text{ammonium hexafluorosilicate} \]
SRPES

beam line U49/2
SoLiAs – solid-liquid analysis system
HREELS measurements

Prof. K. Jacobi facilities
$E_{\text{ref}} - \text{Ag}^{+}/\text{AgCl}$

$E_{\text{c}} - \text{Pt}$

Drop of electrolyte

Electrolyte

Glass sphere with $\text{N}_2$ atmosphere

Electrical contact for $E_{\text{w}}$-Si

UHV
64 meV – substrate phonon
79 meV – Si-H bending mode
99 meV – Si-OH bending mode or/and Si-F stretching mode
113 meV – SiH$_2$ scissor mode
133 meV – bridge-bonded O
258 meV – Si-H stretching mode
362 meV – C-H stretching mode
456 eV – SiO-H stretching mode

E$_o$ = 6.0 eV
$\Delta E$ = 10.0 meV
low level of surface contamination

Survey spectrum of n-Si(111) for the photoelectrochemical conditioning recorded at a photon energy of 585 eV. The sample presents a coverage of C smaller than 1 Å, attesting of the very clean surface preparation.
(i) the surface chemistry

(ii) the surface morphology and topography

(iii) the electronic behavior

(iv) the influence of (photo)electrochemical conditioning.
n-type Si in alkaline solution under illumination

Initial Phase of Photoelectrochemical Conditioning of Silicon in Alkaline Media: Surface Chemistry and Topography
Marika Letilly, Katarzyna Skorupska, and Hans-Joachim Lewerenz
_J. Phys. Chem. C, Just Accepted Manuscript_ • DOI: 10.1021/jp401853p • Publication Date (Web): 16 Jul 2013
substrate: n-Si(111)
solution 0.1M NaOH, pH=13.3
illumination 50 mWcm\(^{-2}\)
Mott-Schottky plots

To determine flat band potentials $E_{fb}$

$$\frac{1}{C_{SC}^2} = \frac{2}{e \varepsilon \varepsilon_0 N} \left( E - E_{fb} - \frac{kT}{e} \right)$$

$C_{SC}$ - capacitance of the space charge region

$\varepsilon$ - dielectric constant of the semiconductor

$\varepsilon_0$ - permittivity of free space

N - donor density (electron donor concentration for an $n$-type semiconductor)

E - applied potential

$E_{fb}$ - flatband potential

Mott-Schottky plots ($1/C^2$ vs. E)

Flat band potential at $E_{flat} = -0.65$ V vs. SCE at pH=6.2

$E_{flat} = -1.07$ V vs. SCE pH=13.3

0.059 for pH

$$E = E^0 - 0.059pH$$

Mott-Schottky plots of the sample after electrochemical conditioning, in a solution of 0.1 M $K_2SO_4$ electrolyte, pH = 6.2; scan rate of 2 mV s$^{-1}$. 

![Graph showing Mott-Schottky plots with different frequencies (1 kHz, 20 kHz, 600 Hz).]
Energy band diagram

$E_{CB} - E_F$ by Fermi Dirac integral - 0.27eV

$$n = N_{CB} \exp\left(-\frac{E_{CB} - E_F}{kT}\right)$$

$N_{CB} = 3.2 \cdot 10^{19} \text{cm}^{-3}$

$n = 8 \cdot 10^{14} \text{cm}^{-3}$

$E_{fb} = -1.07 \text{ V vs. SCE at pH=13.3}$

Energy band diagram of n-Si(111) for
(a) the flat band situation (adjusted at pH=13.3, based on the Mott-Schottky plot recorded at pH=6.2) and
(b) the electronic surface condition at the anodic potential limit of the electrochemical conditioning, e.g. at -0.95 V.
H-terminated (111) surface

AFM TM

pores: 350nm average diameter, 5nm depth
diameter size distribution: > 350nm and <100nm

TEM cross-section
Chemistry at the surface:

- chemical dissolution
- electrochemical dissolution
- Si-O-Si bridge formation (electrochemical oxidation)

electrochemical processes divalent vs. tetravalent process

\[ \lambda_{esc} = 4 \text{Å for } h\nu = 150\text{eV} \]

\[ \lambda_{esc} = 15 \text{Å for } h\nu = 585\text{eV} \]
Chemical (A) dissolution processes reaction mechanisms for illuminated n-Si (111) surface in alkaline solution. The relative partial charge on particular atoms, due to electronegativity differences between neighbors, is marked as $\sigma^+$ and $\sigma^-$. The black circles (●) represent electrons. The small indicate the solvolytic attack of water molecule on a dangling bond: $b$ or on one of the two back bonds: $a$ and $c$. The dissolution process always starts from the water attack on the dangling bond at the kink atom which leads to substitution of the hydrogen by a hydroxyl group. Then the process can follow four routes which differ by the sequence of bound dissolution: 1)ac, 2)abc, 3)bac and 4)bca.

The chemical route is characterized by solvolytic attack of the Si surface atoms at kink sites which releases two $H_2$ molecules in the process of successive formation of Si-OH leading dissolution of the silicon atom and to formation of Si(OH)$_4$, soluble in alkaline solution. The reaction leaves an H-terminated surface as schematically
dissolution of Si-Si bond (2.35Å)
substitution –OH at the Si-H
electronegativity difference

probability of Si-Si bond breaking
- electronegativity difference due to Si atom tern
  - H-H, -H-OH, -OH-OH
Si-OH 0.5
Si-H 0.02
Electrochemical reaction

Kink side – surface state within band gap

Light induced excess minority hole oxidized Si

Surface radical

Dissociation of water

SN2

e⁻ injection into $E_{CB}$
Photoanodic oxide formation

at fully coordinated Si

excess minority holes interact at Si-Si

partial charge shift between layers of Si atoms

attack by hydroxyl group

radical and Si-OH formation

water splitting

hydroxyl bridge formation

\( \text{H}_2 \uparrow \)

Oxo-bridge in Si backbond formation
SRPES

escape depth $\lambda_{\text{esc}}=4\text{Å}$

\[ \Delta E = -0.4 \text{eV} \] compressive stress due to silicon oxide formation

Si : Si ox mismatch

\[ \Delta E = -0.2 \text{eV} \] H-terminated Si

\[ \Delta E = -0.5 \text{eV} \] Si kink site (two H atoms)

\[ \Delta E = -0.8 \text{eV} \] Si-OH (three backbonds), Si-H-OH (two backbonds)

\[ \Delta E = -2.3 \text{eV} \] Si(III) with one backbond to the lattice

\[ \Delta E = -3.9 \text{eV} \] SiO$_2$
\[ d_{\text{ox}} = \lambda_f \ln \left( \frac{I_{\text{ox}}}{I_{\text{Si}}} \frac{I_{\text{Si}}^\infty}{I_{\text{ox}}^\infty} + 1 \right) \]

\( \lambda_f \) – mean elastic length of photoexcited electron with kinetic energy \( E \)
\( I_{\text{Si}}^\infty, I_{\text{ox}}^\infty \) – intensities of pure elements
\( I_{\text{Si}}, I_{\text{ox}} \) – measured lines intensities
\( d \) – overlayer thickness

\[ d_{\text{ox}} = 1.5\text{Å} \]

less than a one monolayer – oxide island growth
Depletion situation at the surface
- photoexcited $h^+$ from $E_{VB}$ can reach the surface and oxidized n-Si
- $h^+$ consumed: oxygen bridge, remove H-term of Si surface atoms

Oxide
oxidation (ec) vs. dissolution (chem)

etching chem vs ec at kink site atom
Shape of pores
by
removal ratio:

double bonded Si/triple bounded Si

straight steps by three coordinated Si

removal of double bonded Si >> removal triplet bonded Si ⇒ **triangular pit** (deficit of kink site Si atoms)
removal of double bonded Si ~ removal triplet bonded Si ⇒ **circular pits** (large kink density)
Step bunched n-Si Surface (SBn-SiS) alkaline solution under cathodic bias

n-Si(111)

Chemical etching leads to the same topography

zig-zag structure (step edges in [1-12] direction)
many kink site atoms
terraces 100-250nm
H-terminated Si(111) Step bunched Si surface

(a) and (b) show the surface morphology of Si(111) with and without step bunching, respectively.

(c) and (d) depict the magnified view of the step bunching with corresponding height profiles.

The images indicate a significant difference in surface roughness and step height distribution before and after the bunching process.
smaller terraces observed (60, 80, 1000 nm)

pits on top of the terraces (15-40 nm)

pits formation by dissolution of Si atoms at the terrace surface (three back bonds, one dangling bond)

by SN2 and penta-coordinated transition state process related to defects at the Si surface
Synchrotron Radiation Photoelectron Spectroscopy (SRPES)
SN2 mechanism

-\text{OH} \text{nucleophilic agent}

\text{penta-coordinated transition state}
electrochemical process: HER
Step bunching

Condition for step bunching

\[ K_e - \text{etch rate velocity of step propagation) \neq 0} \]

\[ \frac{\partial K_e}{\partial \rho_{steps}} \neq 0 \]

\[ \rho_{steps} - \text{step density} \]

Initiated by interplay:
- solution parameters
- applied potential
- geometrical features on real surface

polymerization of silicon tetrahydroxide to polysiloxane

Electronic properties for SBn-Si surface prepared

Electrochemically vs. Chemically

SRPES

1 – electrochem.
2 – chem.

Accumulation layer only at the SBSi surface prepared electrochemically

Topography vs. electronic properties by Kelvin Probe Atomic Force Microscopy:

inhomogeneous distribution of accumulation layer

Step bunched p-Si Surface (SBp-SiS) in NaOH solution under cathodic bias

Photo-Electro-Nanostructuring in NaOH solution

I=40 mWcm$^{-2}$
Synchrotron Radiation Photoelectron Spectroscopy (SERPS) analysis

Si 2p
$\text{hv}=150 \text{ eV}$

Electronic situation
valence band onset

Counts / arb. units

Binding energy / eV

$\text{VB} \quad \text{hv}=150 \text{ eV}$

0.93 eV

Solid State Scale eV

negative charge at the surface

$\rightarrow$ Si-H
$\equiv$ Si-H
$\equiv$ Si-H
suboxides oxide

$\equiv$ Si-H

$\equiv$ Si-H OH

$\equiv$ Si-H
Si + 2H₂O + h⁺ \rightarrow SiO₂ + 4H⁺
Anodic oxide formation

![Graph showing I/mA cm⁻² vs. E/V vs. SCE for different solutions:
- 0.1M NH₄F, pH=4.0
- 0.1M NaOH
- 0.1M KHP]
The SEM images of anodic oxide obtained on n-Si (100) surface under illumination in
a) 0.1 M ammonium fluoride of pH=4.0 and
b) 0.1 M potassium hydrogen phthalate solution.

- oxidation
- dissolution

TM AFM image of anodic oxide obtained 0.1 M NaOH solution.

The SEM images of anodic oxide obtained on n-Si (100) surface under illumination in
a) 0.1 M ammonium fluoride of pH=4.0 and
b) 0.1 M potassium hydrogen phthalate solution.
Anodic oxide formation

nSi, 0.1M NH₄F, pH=4
\[ Si + 2H_2O + h^+ \rightarrow SiO_2 + 4H^+ \]
\[ SiO_2 + 6HF \rightarrow SiF_6^{2-} + 2H^+ + 2H_2O \]
\[ SiO_2 + 3HF_2^- \rightarrow SiF_6^{2-} + H_2O + OH^- \]

lattice mismatch \( V_{SiO_2} > V_{Si} \)
pores size

connection of Si substrate to electrolyte
IR absorption in range for asymmetric Si-O-Si stretching on n-Si(111) after electrochemical oscillation

normalized signals at maximum (1060 cm\(^{-1}\))

integral of IR absorption shows variations in oxide thickness +/- 5ML due to current oscillation
1ML – 0.45nm
created oxide thickness 7.7 - 12 nm

- max thickness at decreasing branch of current
- min thickness at increasing branch of current
- current min and max – thickness equal
integral of IR absorption shows variations in oxide thickness +/- 5ML due to current oscillation.

1ML – 0.45nm

created oxide thickness 7.7 -12 nm

- max thickness at decreasing branch of current
- min thickness at increasing branch of current
- current min and max – thickness equal
Synchronization mechanism and the resulting current oscillation

earlier grown oxide I
less pores
more stable against etching

later grown oxide II
more pores
less stable against etching

lateral distribution of oxide I and II in two consecutive cycles at $t_i$ and $t_{i+1}$

time-dependent oxide growth and etching of oxide I and II

resulting current oscillations