Bridging the gap between experiments and theory - studies of single crystal surfaces and interfaces -

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How to understand molecular polymer/oxide adhesion?

**Bridging experiment and theory**

**Preparation of model surfaces**
1. Single crystalline!
2. Large atomically flat plateaus!
3. Stable in electrolytes!

**Adsorption of monomolecular films**
1. Interface Microscopy/Spectroscopy!
2. Interfacial Binding?
3. Orientation?

**Probing surfaces with single molecules**
1. Desorption of single molecules by means of AFM!
2. Does it work on oxides?

**Theoretical description of the interfaces**
**Bridging Experiment and Theory in Adhesion Science**

**Model Substrates**
- Al₂O₃
- ZnO
- MgO

**Surfaces via DFT**
- Al₂O₃
- ZnO
- MgO

**DFT Studies of Adsorption on Selected Surfaces**
- Adsorption of organosilanes on ZnO
- Adsorption of organophosphonates on Al₂O₃

**Surface oxides of common engineering alloys**

**Binding Mechanisms**
- mono-dental
- bi-dental
- tri-dental

**Stability against water**
Substrate Structure

• **Ideal crystal**
  • 1 atom per unit cell
  • Cutting along a plane does not change the positions

**Ideal surface structure: „Substrate structure“**
Bulk crystal structure + rel. orientation of the cutting plane

**Miller notation:**

- Intersections: cutting plane with crystal axes in units of lattice constants
- take invers values
- multiply values with factor to achieve smallest triple of integer values
- negative number: \( \bar{n} \)
- notation \( \{hkl\} \) specifies \( (hkl) \)-planes

Coordinates (3,1,2)
Inverse (1/3, 1, 1/2)
Miller indices (263)
Preparation of ZnO(0001)-Zn surfaces

1/2 ML OH

At the surface truncation: 1/2 electron per Zn left!

E.g. an OH ad-group can accept these electrons

• Each OH can accept 1 electron to reach the full valency → 1 OH can accept one electron from 2 Zn-atoms.
• An ad-atom structure with 1/2-ML of OH can be expected to be stable.

⇒ E.g. a 2x1 OH ad-group structure.

Preparation of ZnO(0001)-Zn surfaces

**Preparation conditions:**
(1) Alkaline etching
(2) Rinsing with water
(3) Dry in stream of nitrogen
(4) Thermal treatment in humidified oxygen atmosphere


A: Dry O₂/ 1223K
B: 4% H₂O in O₂/ 1223K

Phase diagram of ZnO(0001) surface was calculated for different H and O chemical potentials and the structures favored at different pH values were determined.

Surface spectroscopy of ZnO(0001)-Zn (1/2 OH)

Surface is obviously OH covered and thereby stabilized.

M. Valtiner, S. Borodin, G. Grundmeier,
PCCP Vol. 9, 2406-2412 (2007)
Characterization of the interface: PZC

**PZC.** pH 8.7±0.2
(O/OH coverage = $\sqrt{3}/\sqrt{3}$
Structure)

*Negatively charged above PZC.*
(Adsorption of OH$^-$)

*Positively charged below PZC.*
(Adsorption of H$^+$ onto surface)

Tip.
Au-S-(CH$_2$)$_{14}$-COOH (SAM)

Electrolyte.
1mM NaClO$_4$
pH adjustment with 1mM NaOH/ HClO$_4$ -
> constant ionic strengh

**FD-approach curves**

- pH 11
- pH 9.5
- pH 8.9
- pH 8.5
- pH 8.0
- pH 7.2

At pH > 6.5
carboxylic acid
tirely de-protonated
XPS investigations on TiO$_2$ powder samples

- chemical composition of particles?
- oxidation state of Ti?
- immobilization of nanoparticles (d = 110 nm) on an Indium foil
XPS investigations on TiO$_2$ powder samples

**survey spectrum**: XPS- and Auger-Peaks

[Diagram showing XPS survey spectrum with peaks labeled for Ti, O, and C]
XPS investigations on TiO$_2$ powder samples

- **quantification** of sample composition via detail spectra

- **oxidation state of Ti** is Ti$^{4+}$ as followed by the Ti2p doublet

- significant amount of **carbon**: residues of particle synthesis and/or contaminations

- oxides and hydroxides, in total **excess in oxygen** compared to the 1:2 stoichiometry of TiO$_2$

- **no information about TiO$_2$ modification** (Anatase vs. Rutile vs. amorphous) in XPS
Preparation of TiO$_2$ single crystalline rutile surfaces

- **single crystalline** surfaces are well suited for **basic research**

- **BUT:** untreated TiO$_2$ single crystal with **poorly defined** surface structure

- **Preparation:**
  - etching for 10 to 20 min in 20 % HF
  - annealing for 24 to 36 h at 800 °C in air
Preparation of TiO$_2$ single crystalline rutile surfaces

- **well defined surfaces** for (110) and (100) orientation

- step height of 0.3 nm corresponds to the rutile unit cell (c = 0.296 nm)

Requirement of nanosized tip to measure adhesion forces
Molecular Understanding of SAMs on Al$_2$O$_3$(0001)

AFM

LEED

Molecular Understanding of SAMs on $\text{Al}_2\text{O}_3(0001)$

AFM

$\text{BE/eV}$

$\text{OH}^- \text{O}^{2-}$

$a)$

$b)$

$c)$

$d)$

$536 \ 534 \ 532 \ 530 \ 528$

$\text{slow [µm]}$

$\text{fast [µm]}$

$3.738 \text{ nm}$

$0 \text{ nm}$
Adsorbate formation on Oxide Surfaces: ODPA on Al$_2$O$_3$
Comparison of FTIR-data on different surfaces

Al/AIOOH

Al/Al₂O₃-OH (PVD)

Al₂O₃ (0001)

Al₂O₃ (1-102)

\[ \text{\textsuperscript{-2}OORP = O} \]
In-situ AFM of Monolayer Desorption on Al\textsubscript{2}O\textsubscript{3}(0001)

Top and side view on the atomic structure of the Al$_2$O$_3$(0001) and Al$_2$O$_3$(1-102) surface.

Surface terminating Al-ions vary in the distance to the next neighbor.

The stability of the resulting bonding is based on three competing influences:
- interfacial bonding types,
- adsorption free energies in competition with water and
- involved adsorption geometries.
Nanoshaving: Principle

- During conventional AFM imaging, applied forces on the surface remains less than a Nanonewton (nN). Surface remains unchanged.
- Nanoshaving: higher loads are applied in a controlled manner in order to remove material.

Continuous PET Film

- Thickness of the film can be determined.

Nanoshaved area.

200 nm
Nanoshaving: Limitations

- “Scratching” a hard surface with a “soft” material is not possible.
- The tip material (alternatively tip coating) has to be selected carefully.
- Applied load has to be correctly adjusted.

Solution: Harder materials (e.g. Silicon-nitride) or anti-wear coatings (e.g. diamond like carbon.)
Nanografting: Principle

- If nanoshaving is performed in presence of a precursor in liquid medium, adsorption takes place on the available sites. Hence, **nanografting takes place**.

  - **Al$_2$O$_3$ (0001)**-single crystal surface is covered with a shorter molecule (Hexyl-phosphonic acid, HPA, 6 carbon atoms in the chain).
  - Precursor solution contains longer molecules. (Octadecyl phosphonic acid with 17-Carbon atoms.)
  - Positive height difference is observed. No termination difference, therefore no friction contrast.
Molecular de-adhesion on terraces and step edges
Desorbing Single Macromolecules - Theory

- Rupturing of one specific bond coupled to a polymer-spacer.

- Rupturing of numerous bonds in series.

- Rupturing of numerous bonds in series in an equilibrium process. Height of desorption plateau reflects the equilibrium desorption force required to peel the polymer off the surface segment by segment.

Single Molecule Desorption Spectroscopy on ZnO(0001)

M. Valtiner, G. Grundmeier, Langmuir, 2010
Single Molecule Desorption Spectroscopy

At edges:

- COO\(^{-}\) coordinatively binds to Zn surface atoms

M. Valtiner, G. Grundmeier, Langmuir, 2010
Influence of electrostatics and polymer conformation

- **PZC**
  - pH = 10
  - pH = 9
  - pH = 8

- **pK_a**
  - pH = 6
  - pH = 5
  - pH = 4
Influence of macromolecular conformation

**Above PZC**

Polymer is *negatively charged* and due to *repulsive intra-chain forces* tertiary structure reflects a „wormlike“ structure.

Surface is *negatively charged*, therefore *REPULSION* and consequently very short desorption plateaus.

**Below PZC**

Polymer is still *negatively charged* an tertiary structure reflects a „wormlike“ structure.

Surface is *positively charged*, therefore *attraction* and consequently *desorption plateaus*.

**Below pK_{a}**

Polymer is *less and less charged* due to *attractive intra-chain forces* (H-bonding etc.) the tertiary structure reflects a connected internal structure.

Therefore, *no adsorption on to the substrate in form of long chains*. Just „bulky“ polymer bunch adsorbs.
pH-dependant forces on the polar ZnO surface

- Decreasing attractive electrostatic attraction
- Coil less stretched

Increasing double layer repulsion
PIA – SIS

Paderborn Integrated Analysis – System for Interfaces Science
techniques for sample preparation

- **load lock**
  - inward transfer of samples
  - transfer to *preparation chamber* or *UHV suitcase*

- **plasma** and **sputter** source for sample preparation
  - Ar, He, O₂, N₂, H₂O

- **sample** heating up to 1100 K for high-temperature preparation

**analytical technique:**

- **low energy electron diffraction (LEED)**
  - Surface crystallinity and adsorbate structures
Analysis Chamber

Analytical techniques:

- **X-Ray Photoelectron Spectroscopy: XPS**
  - chemical surface composition
  - oxidation state
  - type of chemical bonds

- **Scanning Auger Microscopy: SAM**
  - high resolution surface composition (150 nm resolution)

- **Scanning Electron Microscopy: SEM**
  - sample imaging (100 nm resolution)

- **UV Photoelectron Spectroscopy: UPS**
  - valence band structure of semiconductors
Scanning Probe Microscopy: SPM

- **decoupled** from preparation/analysis system due to noise and vibration reduction

- **Atomic Force Microscopy: AFM**
  - surface imaging up to atomic resolution
  - force interaction and adhesion

- **Scanning Tunneling Microscopy: STM**
  - surface imaging up to atomic resolution on conducting samples

- **variable sample temperature**
  - 120 to 500 K

- **gas dosing system**
  - e.g. in-situ water adsorption experiments
UHV system setup

Vacuum suitcase

Preparation chamber
- LEED
- plasma-/sputter sources

SPM chamber
AFM
STM

Analysis chamber
- XPS
- UPS
- SAM
- ISS
The use of single crystalline surfaces enables to measure forces on atomically defined surface structures.

The synthesis of single crystals which are stable under environmental conditions and their analysis is complex and time consuming.

At least two single crystalline surface orientation have to be investigated to predict the behaviour of amorphous surfaces.

Surfaces of single crystals can be calculated concerning their structure and surface energy.

Single crystals thus serve as basis for the combination of theoretical and experimental approaches.