Surface Analysis of Nanomaterials

(나노소재표면분석)

:Surface and Thin Film Analysis

(표면 및 박막분석)

장소: 공과대학 6호관 510호

시간: 화 (1-A, 1-B, 2-A, 2-B, 3-A, 3-B)

1. Analysis of Solid Surface

Analysis of Solid Surface

Wherever the properties of a solid surface are important, it is also important to have the means to measure those properties.

The surfaces of solids

play an overriding part in a remarkably large number of **processes**, **phenomena**, and **materials** of technological importance.

- Catalysis
- Corrosion, passivation, and rusting adhesion
- Tribology, friction, and wear
- Brittle fracture of metals and ceramics microelectronics
- Composites
- Surface treatments of polymers and plastics
- Protective coatings
- Superconductors
- Solid – surface reactions of all types with gases, liquids, or other solids.

Analysis of Solid Surface

The surfaces in question are not always external !!

The processes occurring at inner surfaces such as **interfaces and grain boundaries** are often just as critical to the behavior of the material

Required information

- Surface composition
  - (i.e., the types of atoms present and their concentrations)
- Surface chemistry
  - (i.e., the chemical states of the atoms)
- Arrangement of surface atoms
  - (i.e., the surface structure)

Analysis of Solid Surface

What is meant by a solid surface?

Definition of the surface

the plane at which the solid terminates

– the last atom layer before the adjacent phase (vacuum, vapor, liquid, or another solid) begins

→ Impractical!!

the effect of termination extends into the solid beyond the outermost atom layer

➡ Definition of the surface again

– Consisting of that number of atom layers over which the effect of termination of the solid decays until bulk properties are reached

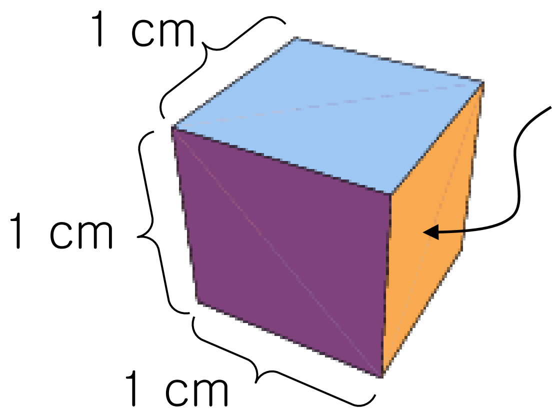
-> Decay distance is of the order of 5 – 20 nm depending on kind of materials

Analysis of Solid Surface

How many atoms in a Surface?

How many atoms are we dealing with at the surface and in the bulk of a solid?

i.e Consider a 1cm cube of metal



1 cm^2 surfaces has roughly 10^{15} atoms

Thus the total number of atoms in the cube will be $\approx 10^{23}$

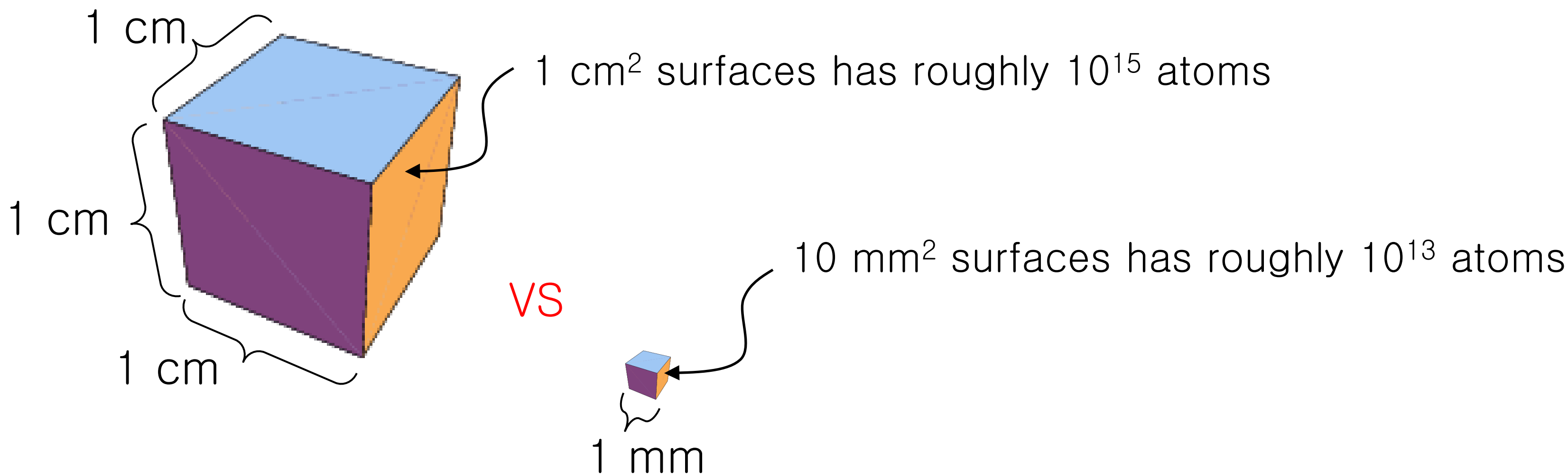
the percentage of surface to bulk atoms

$$\longrightarrow \quad s/b \approx 10^{-8} \times 100 \approx 10^{-6}\,\%$$

Analysis of Solid Surface

How sensitive?

General probing area of surface analysis technique -> $1 mm^2$



-> Top 10 layer contain 10^{14} atoms or 10^{-10} mol

Therefore, One should consider very low concentration compare to conventional chemical analysis for bulk

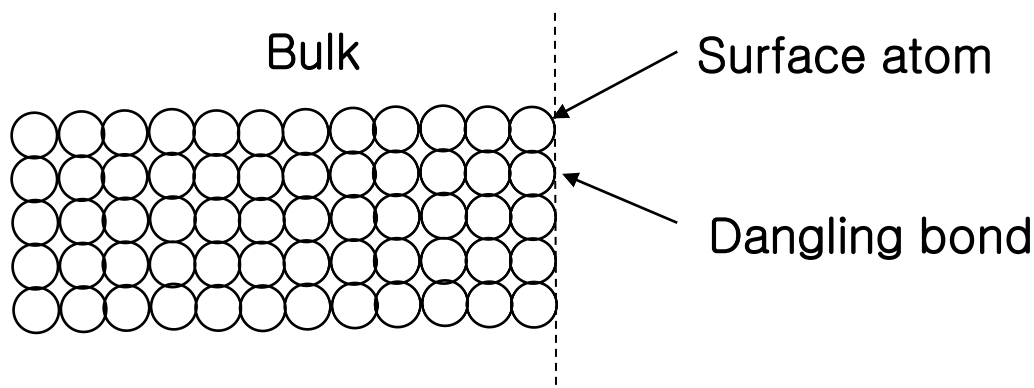
More important in nanoscale analysis

Analysis of Solid Surface

Why should surfaces be so important?

First, the properties of surface atoms are usually different from those of the same atoms in the bulk

i.e. Even at the surface of a perfect single crystal the surface atoms behave differently from those in the bulk, simply because they do not have the same number of nearest neighbors;



-> Electronic distributions are altered, and hence affect to their reactivity

Analysis of Solid Surface

Information Required for surface analysis

To understand the properties and reactivity of a surface, the following information is required:

- the physical topography,
- the chemical composition,
- The chemical structure,
- the atomic structure,
- the electronic state
- a detailed description of bonding of molecules at the surface.

-> No one technique can provide all these different pieces of information. A full investigation of a surface phenomenon will always require several techniques.

Analysis of Solid Surface

Surface analysis techniques and the information they can provide

Radiation IN / Radiation DETECTED	photon / electron	photon / photon	electron / electron	ion / ion	neutron / neutron
SURFACE INFORMATION					
Physical topography			SEM STM (9)		
Chemical composition	ESCA/XPS (3)		AES (2)	SIMS (5) ISS (6)	
Chemical structure	ESCA/XPS (3)	EXAFS (8) IR & SFG (7)	EELS (7)	SIMS (4)	INS (7)
Atomic structure		EXAFS (8)	LEED RHEED (8)	ISS (6)	
Adsorbate bonding		EXAFS (8) IR (7)	EELS (7)	SIMS (4)	INS (7)

Analysis of Solid Surface

Brief introduction of representative surface analysis technique

ESCA/XPS – Electron analysis for chemical analysis/X-ray photoelectron spectroscopy.

-> X-ray photons of precisely defined energy bombard the surface, electrons are emitted from the orbitals of the component atoms, electron kinetic energies are measured and their electron binding energies can be determined enabling the component atoms to be determined.

AES – Auger electron spectroscopy.

-> Basically very similar to the ESCA except that a keV electron beam may be used to bombard the surface.

Analysis of Solid Surface

Brief introduction of representative surface analysis technique

SIMS – Secondary ion mass spectrometry.

-> There are two forms, i.e. dynamic and molecular SIMS. In both a beam of high energy (keV) primary ions bombard the surface while secondary atomic and cluster ions are emitted and analysed with a mass spectrometer.

ISS – Ion scattering spectrometry.

-> An ion beam bombards the surface and is scattered from the atoms in the surface. The scattering angles and energies are measured and used to compute the composition and surface structure of the sample target.

Analysis of Solid Surface

Brief introduction of representative surface analysis technique

IR – Infrared (spectroscopy).

-> Various variants on the classical methods – irradiate with infrared photons which excite vibrational frequencies in the surface layers; photon energy losses are detected to generate spectra.

EELS – Electron energy loss spectroscopy.

-> Low energy (few eV) electrons bombard the surface and excite vibrations – the resultant energy loss is detected and related to the vibrations excited.

INS – Inelastic neutron scattering.

-> Bombard a surface with neutrons – energy loss occurs due to the excitation of vibrations. It is most efficient in bonds containing hydrogen.

Analysis of Solid Surface

Brief introduction of representative surface analysis technique

LEED – Low energy electron diffraction.

-> A beam of low energy (tens of eV) electrons bombard a surface; the electrons are diffracted by the surface structure enabling the structure to be deduced.

RHEED – Reflection high energy electron diffraction.

-> A high energy beam (keV) of electrons is directed at a surface at glancing incidence. The angles of electron scattering can be related to the surface atomic structure.

EXAFS – Extended X-ray absorption fine structure.

-> The fine structure of the absorption spectrum resulting from X-ray irradiation of the sample is analysed to obtain information on local chemical and electronic structure.

Analysis of Solid Surface

Brief introduction of representative surface analysis technique

STM – Scanning tunnelling microscopy.

-> A sharp tip is scanned over a conducting surface at a very small distance above the surface. The electron current flowing between the surface and the tip is monitored; physical and electron density maps of the surface can be generated with high spatial resolution.

AFM – Atomic force microscopy.

-> Similar to STM but applicable to non-conducting surfaces. The forces developed between the surface and the tip are monitored. A topographical map of the surface is generated.

Analysis of Solid Surface

Basic principal of surface analysis techniques

➡ Interrogation of the surface with a particle probe

Use various energetic particles that are come from the probe

Primary particles used in the probing beam

i.e. electrons, photons, ions, neutron or their combination

Function of the probe

Excite surface atoms

➡ emission of one or more of a variety of secondary particles such as electrons, photons, ions, and neutrals

Analysis of Solid Surface

Surface-specific analytical techniques <u>using particle or photon excitation</u>

Detection	Excitation[a)]					
	Electrons, e^-		Ions, neutrals, A^+, A^-, A^0		Photons, $h\nu$	
e^-	AES EELS EFTEM LEED	SAM RHEED	IAES INS		XPS	UPS
A^+, A^-, A^0	ESD	ESDIAD	SIMS GDMS RBS ERDA	SNMS FABMS LEIS NRA		
$h\nu$	EDXS SXAPS IPES	 BIS	GD-OES IBSCA		TXRF XRD LA RAIRS SHG ELL SNOM	 LIBS SERS SFG

a) Some of the techniques in Table 1.1 have angle-resolved variants, with the prefix AR (e.g., ARUPS), or use Fourier-transform methods, with the prefix FT (e.g., FT-RAIRS).

Analysis of Solid Surface

Surface-specific analytical techniques using non – particle excitation

Detection	Excitation			
	Heat, *kT*	High electrical field, *F*		Mechanical force
A^+	TDS	FIM	AP	
A^-	TDS			
e^-		IETS STM, STS		
(Displacement)				AFM

Analysis of Solid Surface

Surface analysis acronyms

1. **Electron Excitation**

AES, Auger electron spectroscopy

BIS, Bremsstrahlung isochromat spectroscopy (or ILS, ionization loss spectroscopy)

EDXS, Energy-dispersive X-ray spectroscopy

EELS, Electron energy loss spectroscopy

EFTEM, Energy-filtered transmission electron microscopy

ESD, Electron-stimulated desorption (or EID, electron-induced desorption)

ESDIAD, Electron-stimulated desorption ion angular distribution

IPES, Inverse photoemission spectroscopy

LEED, Low-energy electron diffraction

RHEED, Reflection high-energy electron diffraction

SXAPS, Soft X-ray appearance potential spectroscopy (or APS, appearance potential spectroscopy)

SAM, Scanning Auger microscopy

Analysis of Solid Surface

Surface analysis acronyms

2. Ion Excitation

ERDA, Elastic recoil detection analysis

GDMS, Glow discharge mass spectrometry

GD-OES, Glow discharge optical emission spectroscopy

IAES, Ion (excited) Auger electron spectroscopy

IBSCA, Ion beam spectrochemical analysis (or SCANIIR, surface composition by analysis of neutral and ion impact radiation or BLE, bombardment-induced light emission)

INS, Ion neutralization spectroscopy

LEIS, Low-energy ion scattering (or ISS, Ion-scattering spectroscopy)

NRA, Nuclear reaction analysis

RBS, Rutherford back-scattering spectroscopy (or HEIS, high-energy ion scattering)

SIMS, Secondary-ion mass spectrometry (SSIMS, static secondary-ion mass spectrometry) (DSIMS, dynamic secondary-ion mass spectrometry)

SNMS, Secondary neutral mass spectrometry

Analysis of Solid Surface

Surface analysis acronyms

3. Photon Excitation

ELL, Ellipsometry

LA, Laser ablation

LIBS, Laser-induced breakdown spectroscopy (or LIPS, Laser-induced plasma spectroscopy)

RAIRS, Reflection–absorption infrared spectroscopy (or IRRAS, infrared reflection–absorption spectroscopy, or IRAS, infrared absorption spectroscopy, or ERIRS, external reflection infrared spectroscopy)

SERS, Surface-enhanced Raman scattering

SFG, Sum frequency generation

SHG, (optical) Second harmonic generation

SNOM, Scanning near-field optical microscopy

TXRF, Total reflection X-ray fluorescence analysis

UPS, Ultraviolet photoelectron spectroscopy

XPS, X-ray photoelectron spectroscopy (or ESCA, electron spectroscopy for chemical analysis)

XRD, X-ray diffraction

Analysis of Solid Surface

Surface analysis acronyms

4. **Neutral Excitation**

   FABMS, Fast-atom bombardment mass spectrometry

5. **Thermal Excitation**

   TDS, Thermal desorption spectroscopy

6. **High-Field Excitation**

   AP, Atom probe

   FIM, Field ion microscopy

   IETS, Inelastic electron tunneling spectroscopy

   STM, Scanning tunneling microscopy

   STS, Scanning tunneling spectroscopy

7. **Mechanical Force**

   AFM, Atomic force microscopy

End of Slide