

Surface & Interface Physics

Amare B. Belay

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Physics Department
Addis Ababa University



Surface & Interface Physics

Courses for PhD Program (Polymer Lab.)

Physics Department

Addis Ababa University

Course Number: -----

Course Title: Surface & Interface Physics

Credit hours: 3

Degree Program: PhD in Physics

Surface & Interface Physics

Teaching Methods:

- Lecture
- Presentation

Note: Minimum attendance required to be permitted to examination:
85% (AAU legislation)

Evaluation:

- Presentation 30%
- Final Examination 70%

Related and/or Prerequisite courses:

- The Semiconductors
- Semiconductor Devices
- Polymers
- Thin Films (Unavailable at AAU Physics)

Course Content:

- 1. Introduction to Surface Science**
- 2. Surface Preparation and Treatment Methods**
 - 2.1. Surface preparation methods
 - 2.2. Surface cleaning methods
 - 2.3. Surface modification methods
- 3. Thin Films**
 - 3.1. Thin film deposition methods
 - 3.2. Nucleation and graph
 - 3.3. Thin films as surface interface modifiers
- 4. Surface Energy Components and Implications**
 - 4.1. Contact angle phenomena and wetting
 - 4.2. Surface Tension
 - 4.3. Wetting and dewetting
 - 4.4. Application of surface treatments
- 5. Surface Characterization Methods**
 - 5.1. Microscopy methods
 - 5.2. Spectroscopy methods
 - 5.3. Diffraction methods
 - 5.4. Contact angle methods and other methods
- 6. Interface Engineering in Semiconductor Devices**
 - 6.1. Impact of surfaces on interfaces
 - 6.2. Interfaces in organic vs. inorganic semiconductor
 - 6.3. Metal-Semiconductor interface
 - 6.4. p-n Junction
 - 6.5. Band gap and light absorption/emission
 - 6.6. Electrons and holes injection
 - 6.7. Electrons and holes blocking
 - 6.8. Effect of electron/hole injection and blocking on device efficiency
 - 6.9. Interfaces in organic and inorganic semiconductors
- 7. Application of Nanotechnology in Surface and Interface Modification**
 - 7.1. Small molecules
 - 7.2. Nanoparticles
 - 7.3. Emerging nano-materials and nano-patterning
- 8. Interface Characterization methods**
 - 8.1. Structure and composition
 - 8.2. Electronic property

References:

1. H. Ibach, *Physics of Surfaces and Interfaces*, Heidelberg, Springer, 2006.
2. H. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Weinheim, Wiley-VCH, 2003.
3. H. Bubert, H. Jenett, *Surface and Thin Film Analysis*, Weinheim, Wiley-VCH, 2002.
4. S. Ebnesajjad, *Adhesives Technology Handbook*, Norwich, William Andrew Inc., 2008.
5. A. Korkin, P. Krstic, J. Wells, *Nanotechnology for Electronics, Photonics, and Renewable Energy*, New York, Springer, 2010.
6. P. Wurfel, *Physics of Solar Cells- From Principles to New Concept*, Weinheim, Wiley-VCH, 2005.
7. A. Makhlof and I. Tignyanu, *Nanocoatings and Ultra-Thin Films*, Philadelphia, Woodhead Publishing Limited, 2011.
8. B. Van Zeghbroeck, *Principles of Semiconductor Devices*, Ebook download, 2004.
Link: <http://www.eletrica.ufpr.br/graduacao/e-books/Principles%20Of%20Semiconductor%20Devices.pdf>
9. S. M. Sze, *Semiconductor Devices: Physics and Technology*, John Wiley & Sons Singapore Pte. Limited, 2013.
10. Prof. Helmut Föll's lecture (University of Kiel), *Semiconductors*: Link: http://www.tf.uni-kiel.de/matwis/amat/semi_en/index.html
11. Wolfgang Brüttning, Chihaya Adachi, *Physics of Organic Semiconductors*, John Wiley & Sons, Oct 5, 2012.

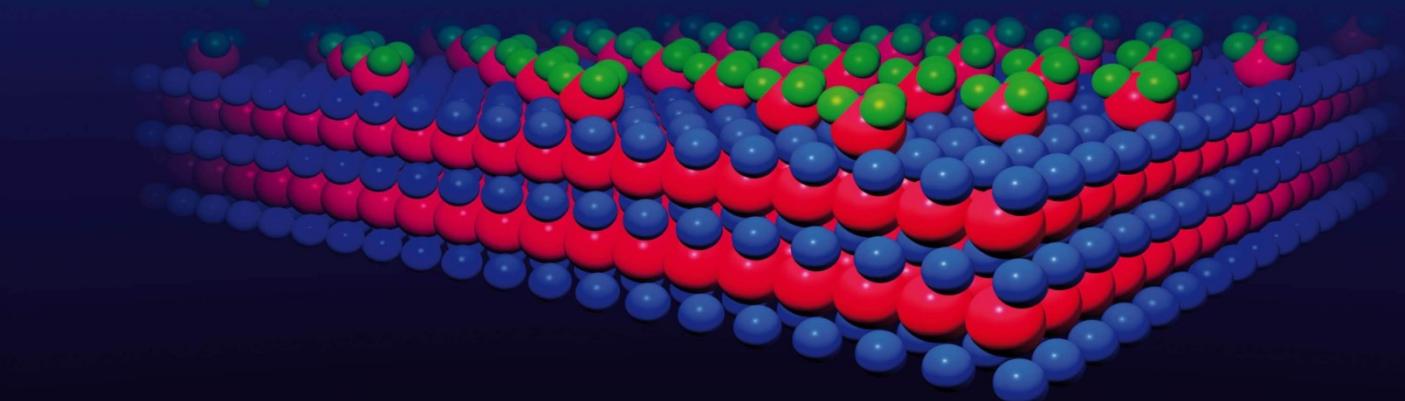


Presentation Topics

Department of
Physics

1. Water contact angle measurements and surface parameter extraction
2. Application of self assembled monolayers (SAMs) in emerging solar cells
3. The physics of surface modification, band bending and dipole barrier
4. The science of interface modifications and adhesion improvement
5. The science of a hydrophobic leaf and its extended application

Surface & Interface Physics



1. Introduction to Surface Science

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1. Introduction to Surface Science



Niels Bohr, Werner Heisenberg, and Wolfgang Pauli, ca. 1935

Nobel Prize in Physics in 1945 (Pauli Principle) - One of pioneers of quantum physics!

"God made solids, but surfaces were the work of the Devil"

Wolfgang Pauli



Many leaf surface (top/background) are hydrophobic while a cleaned glass surface is hydrophilic (bottom –left).

Why it happens in such a way?



Glass before (right) and after surface torment/cleaning (left).

Concept of Surfaces

“Surface” is the outer part of a material with different chemical and physical properties from the bulk

It corresponds to **few atomic layers** (thickness about 1-2 nm or can extend to 10 nm depending on the method)

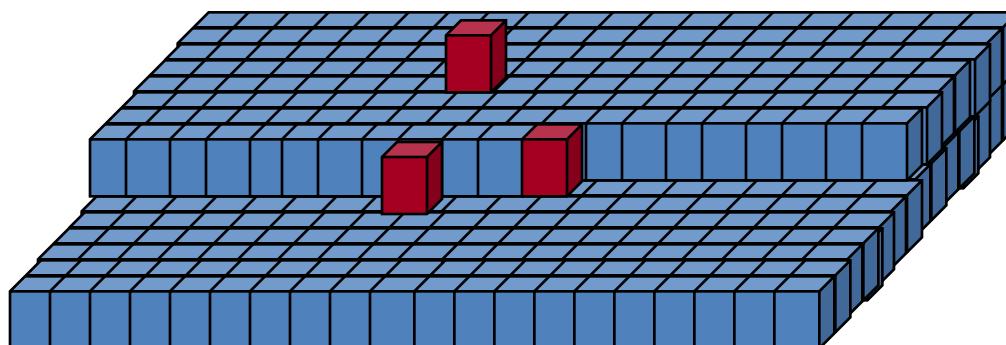
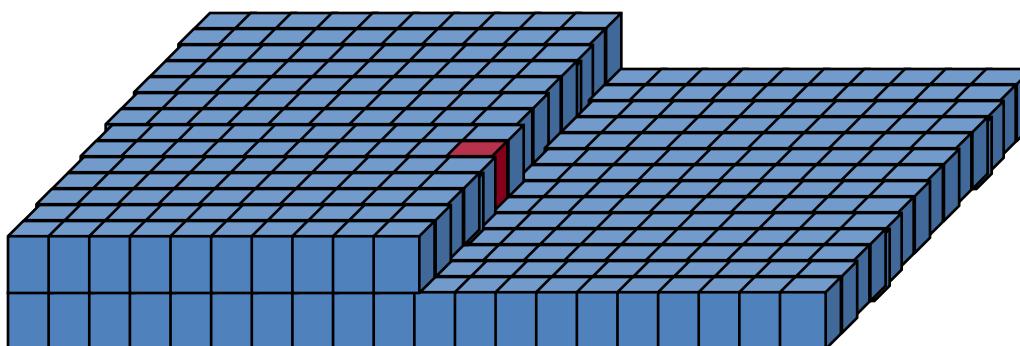
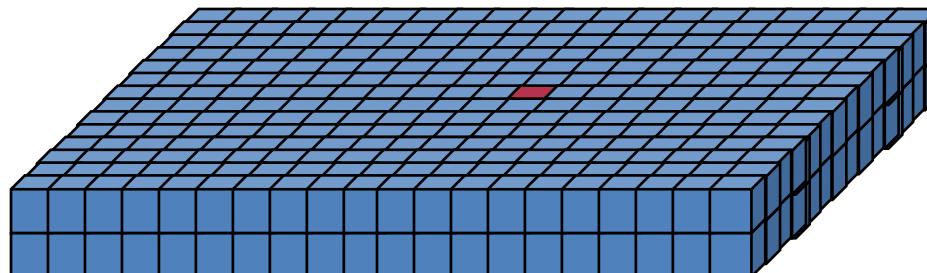
E.g., Native silicon dioxide over silicon (~1.5 nm at ambient condition)

Surfaces modify different property of materials - chemical, electrical, optical, magnetic, wetting ...

Formation:

Chemical treatment, thermal, plasma, atomic/molecular deposition, **radiation**

Surface Defects (or Imperfections)



Terrace

- Terrace atom has 5 nearest neighbors

Ledge

- Ledge atom has 4 nearest neighbors

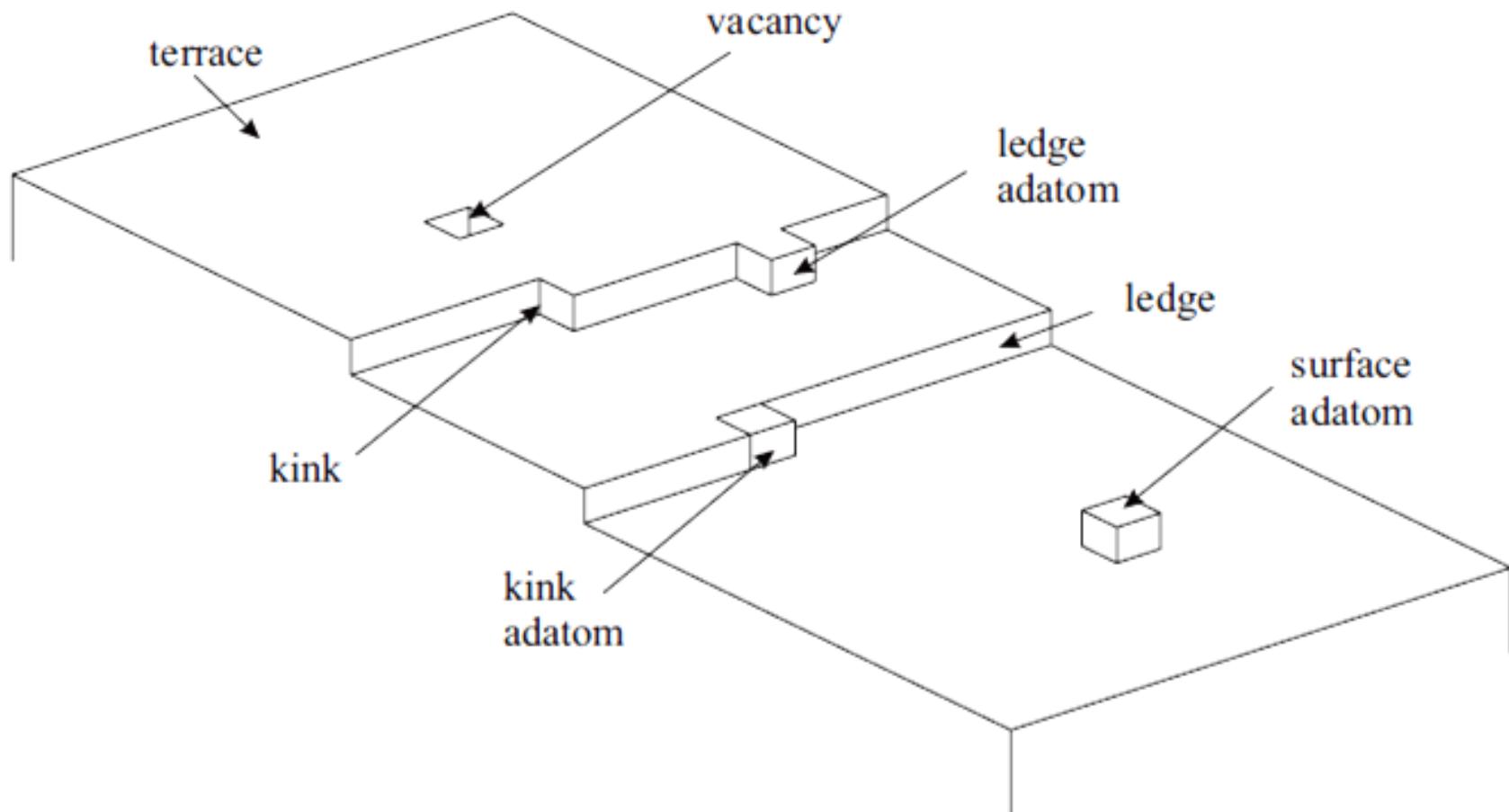
Kink

- Kink atom has 3 nearerst neighbors

Adatom

- Ledge adatom has 2 nearest neighbor
- Terrace adatom has 1 nearest neighbor

Surface Defects (or Imperfections)



Schematic view of a vicinal surface with surface defects.

Surface Science

Surface Science: the study of physical and chemical phenomena that occur at the interface of two phases, including:

- Solid–liquid interfaces,
- Solid–gas interfaces,
- Solid–vacuum interfaces, and
- Liquid–gas interfaces.

- It includes the fields of ***surface chemistry*** and ***surface physics***.
- Some related practical applications are classed as ***surface engineering***.

Surface Engineering ↔ Modification of Surface Chemistry

Surface Science

Common Interface Types

Common Interfaces of Vital Natural and Technological Importance

Interface Type	Occurrence or Application
Solid–vapor	Adsorption, catalysis, contamination, gas–liquid chromatography
Solid–liquid	Cleaning and detergency, adhesion, lubrication, colloids
Liquid–vapor	Coating, wetting, foams
Liquid–liquid	Emulsions, detergency, tertiary oil recovery

Surface Science ...

Surface chemistry:

- ❑ Somehow defined as the study of **chemical reactions at interfaces**.
- ❑ It is closely related to **surface engineering**, which aims at modifying the chemical composition of a surface by incorporation of selected **atoms/elements** or **molecules** (functional groups) .
- ➔ Produce various **desired effects or improvements** in the properties of the surface or interface.
- ➔ The adhesion of gas or liquid molecules to the surface is known as adsorption.
It can be by chemisorption or by physisorption.

Surface Science ...

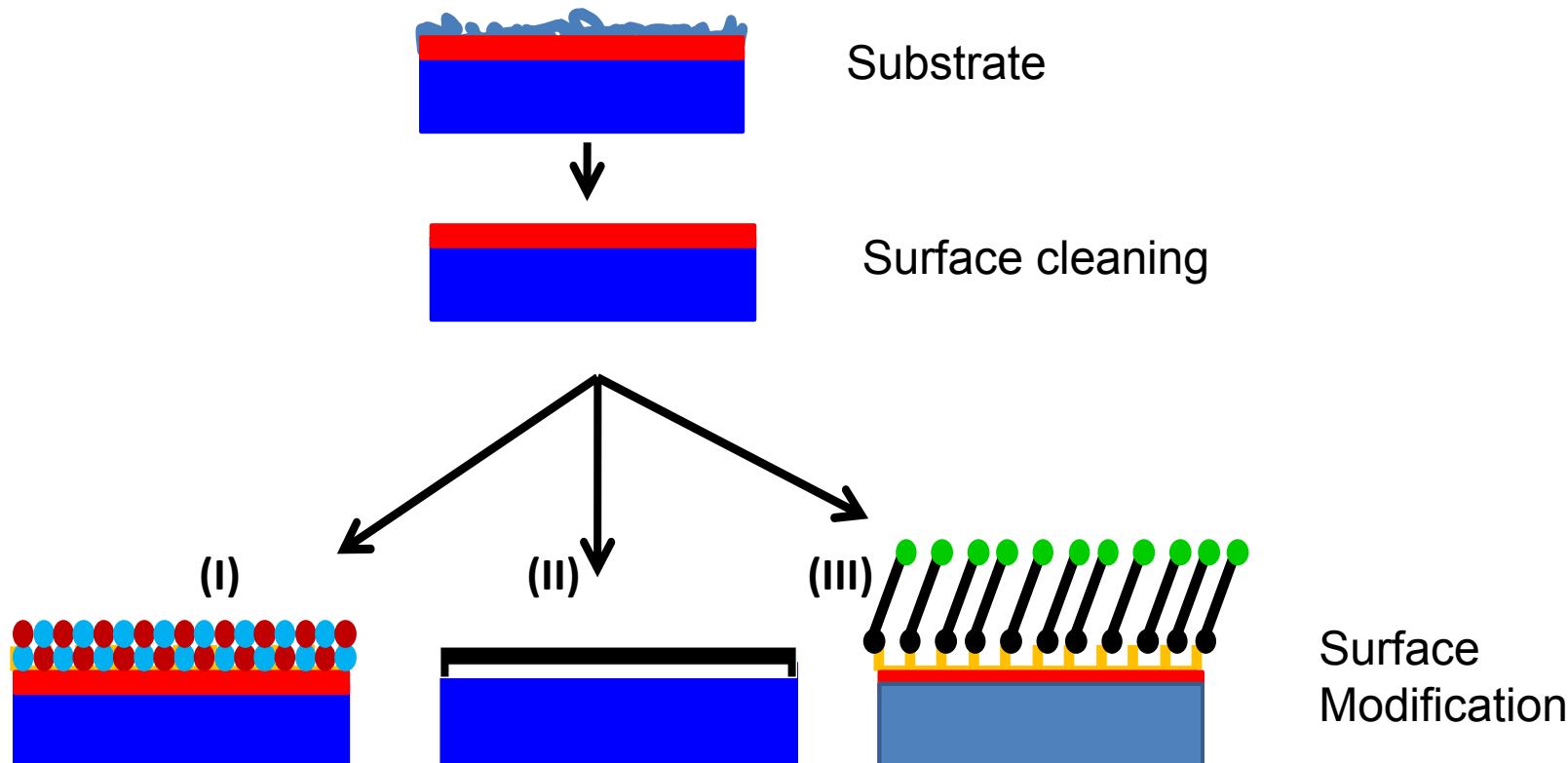
Surface Physics:

Somehow defined as the study of the physical properties surfaces:

- Surface Energy (or Surface Tension).
- Electronic property (e.g., work function)
- Structure (e.g., epitaxial growth, kinks, terrace, ledges, adatoms)
- Sticking, Friction, Surface Density of atoms ...
- Produce various **desired physical effects or improvements** in the properties of the surface or interface.

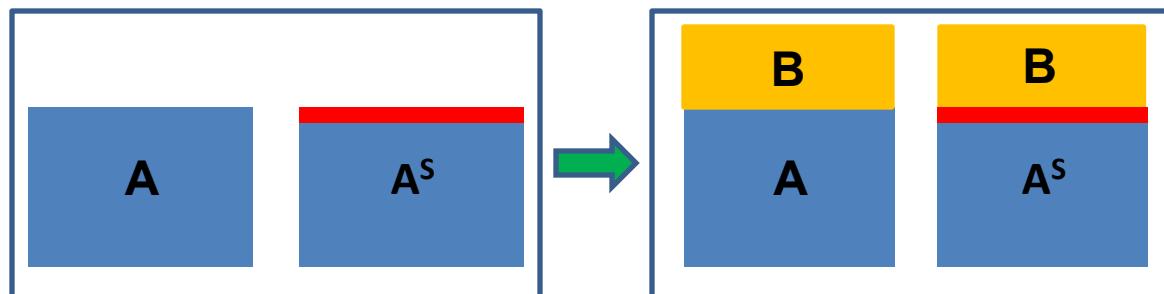
Basics of Surface Chemistry Needed in Surface Physics!

Main Surface Modification Approaches



Surface modification by three different approaches: I) deposition of atom/s (physical/chemical) by evaporation or solution processing (left), II) surface activated chemical change with reactant from atmosphere (middle), III) Self assembly or chemical bonding of molecules with designed interface matching chemistry (right).

Effect of Surface Modification on Interfaces



Possibilities of Exposure:
Schematics of a surface
before and after surface
modification (A and A^s).

New Surface → New Interface!

- **Physical** - Surface energy, cleaning, adhesion, wetting, nucleation ...

Application: Surface modification → Impact on interface

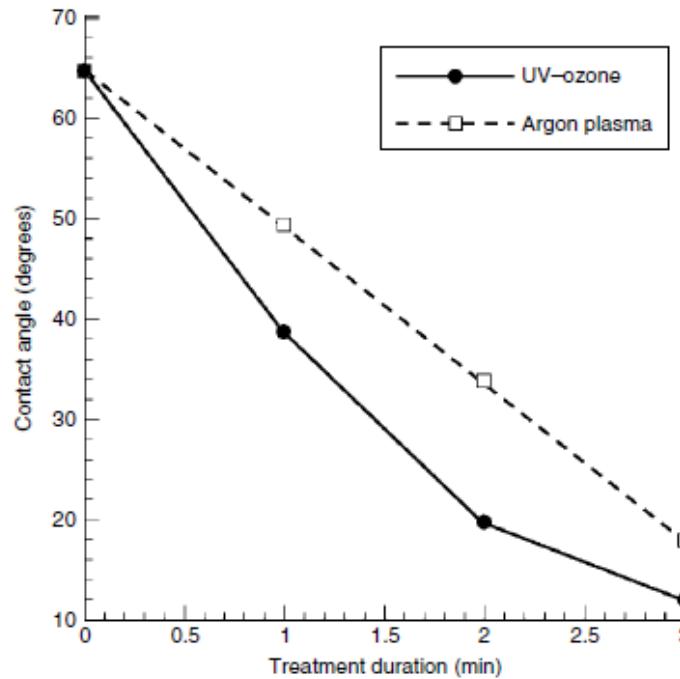
- **Electrical/Chem** - Oxidation, band bending and change transport issues

Application: Interface engineering → Device efficiency

Surface Treated vs. Untreated (New Interface, A/B vs. A^s/B)

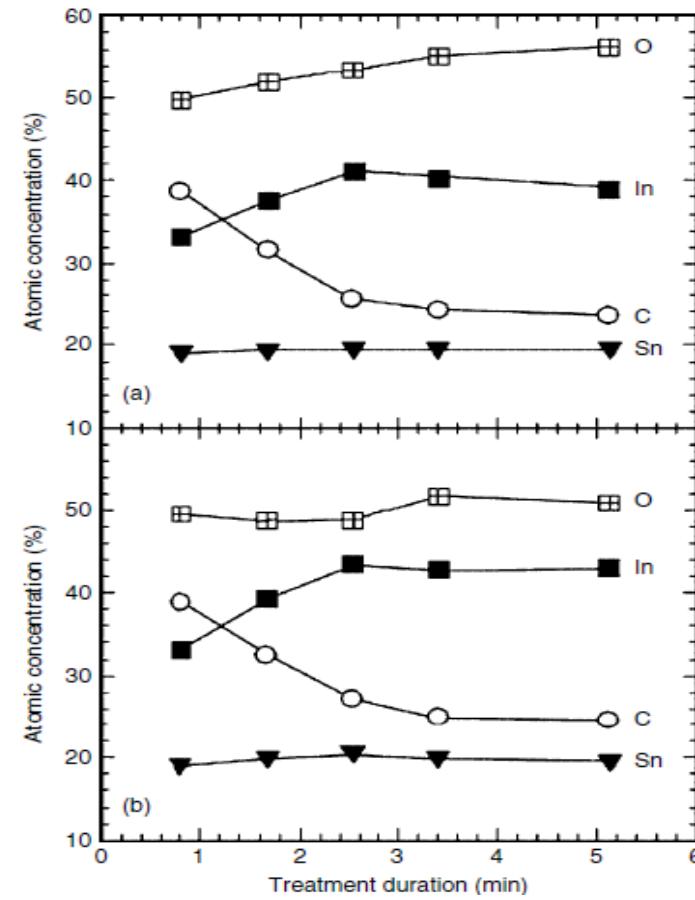
→ Diff. electronic property → Diff. interface for the same bulk materials

Example: Surface Physics (Surface Engineering of ITO)



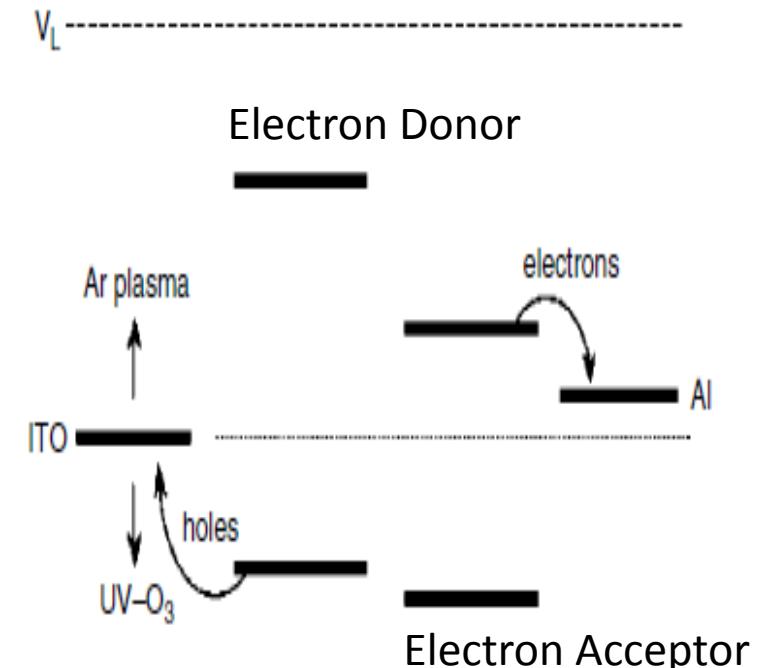
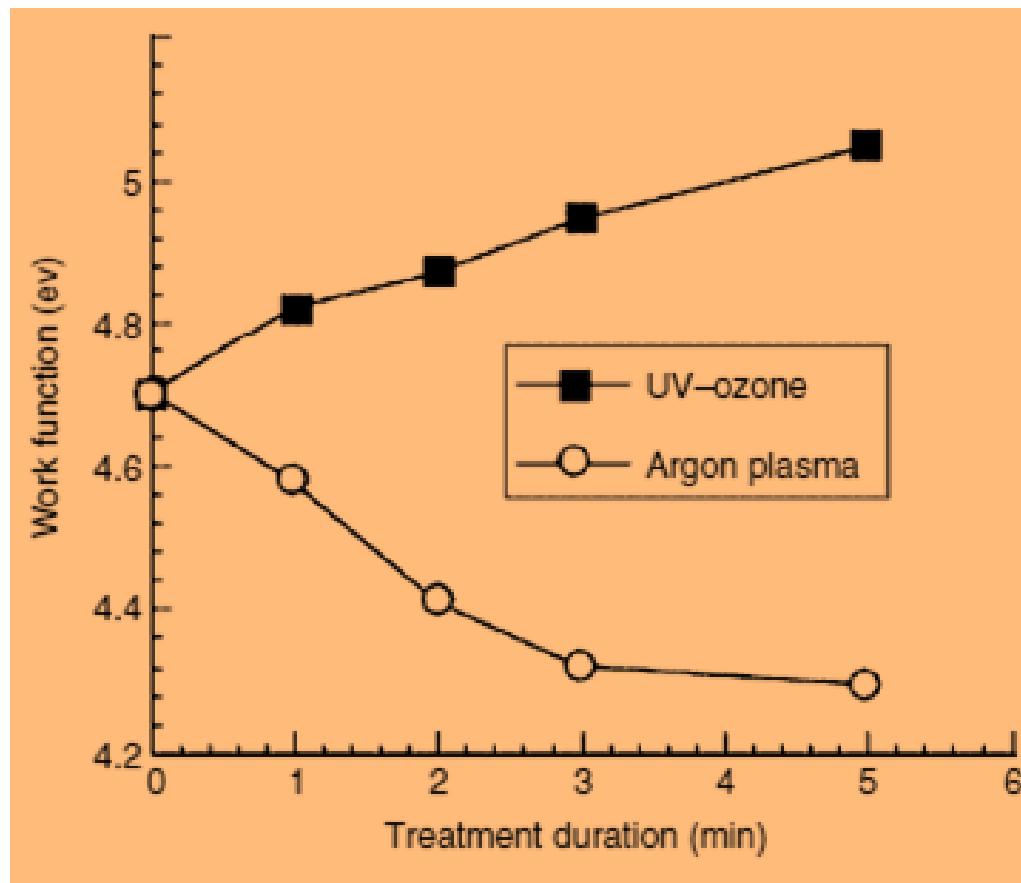
Contact angle measurement with UV–ozone and argon plasma treatments at different times.

Ref.: P. Destruel et al., Polym Int., 206, 601(2005).



Atomic concentration of an ITO surface measured at different treatment times: UV–ozone (top) and argon plasma (bottom).

Example: Surface Physics (Surface Engineering of ITO, Cont.)

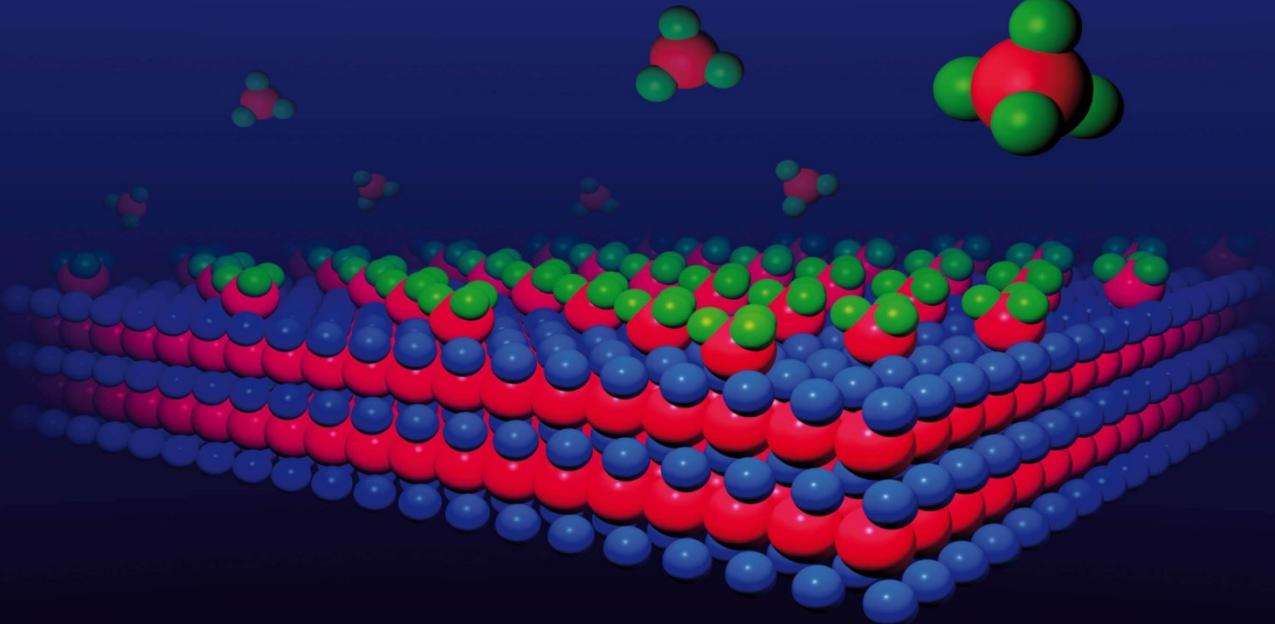


Ideal energy level diagram of ITO/Organic semiconductor interface .

ITO work function at different time for UV-ozone and argon plasma treatments.

Ref.: P. Destruel et al., Polym Int., 206, 601(2021)

Surface & Interface Physics



2. Surface Preparation & Treatment Methods

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2. Surface Preparation and Treatment Methods

- 2.1. Surface cleaning methods
- 2.2. Surface preparation methods
- 2.3. Surface modification methods

2.1. Surface Preparation and Treatment Methods

Surface Preparation: Any method of treating a surface to prepare it for coating. Surface preparation methods include washing (*surface cleaning*) with water, detergent solution, or solvent; cleaning with hand or power tools or ultrasonic bath; water washing or jetting with or without abrasive; or abrasive blast cleaning. Surface preparations are made so as to have the efficient over layer (e.g., well stick) as desired. Thus, the surface can be modified be made by physical or chemical method including washing or etching chemical or UV/Ozone

→ **Surface Preparation** may use surface cleaning and can possibly include surface modification or surface treating (change of nature of the surface) too

Surface Preparation and Treatment Methods

Surface Modification is the act of modifying (*surface treatment*) the surface of a material by bringing physical, chemical or biological characteristics *different from the ones originally found on the surface* of a material.

The modification can be done by different methods with a view to altering a wide range of characteristics of the surface, such as: roughness, hydrophilicity, surface charge, surface energy, biocompatibility and reactivity. Solid surfaces can be changed by various means such as adsorption, thin film deposition, chemical reactions, or removal of material.

Surface Preparation and Treatment Methods

Substrate Conditions & Cleaning

- Types of contamination on substrate:
 - Particles, metallic impurities, organics, native/chemical oxide
 - Sources: airborne particles, organic residue, detergent, processing
- Substrate condition affects the properties of the deposited film
 - Adhesion, grain size ...
 - Defective surface chemistry
 - Device performance, reliability ...
- Wet (chemical or physical type) or dry cleaning
- Choice of cleaning chemicals not to attack the bulk of the substrate

2.1. Surface Preparation and Treatment Methods

2.1.1. Cleaning Methods

□ Wet Chemical

- Detergent
- Organic Solvent (acetone, isopropanol ...)
- Piranha cleaning
- RCA 1 and RCA 2 ...

□ Dry Chemical

- Plasma cleaning (O_2 , N_2 , Ar_2 , ...)
- UV-Ozone or Ozone cleaning
- Vapor Cleaning (steam's ability to clean primarily based on its heat)

2.1.1. Organic Solvents

<u>Solvent</u>	formula	boiling point (°C)	melting point (°C)	density (g/mL)	solubility in H ₂ O ¹ (g/100g)	relative polarity ²	vapor pressure 20°C (hPa)
acetic acid	C ₂ H ₄ O ₂	118	16.6	1.049	M	0.648	15.3
acetone	C ₃ H ₆ O	56.2	-94.3	0.786	M	0.355	240
acetonitrile	C ₂ H ₃ N	81.6	-46	0.786	M	0.460	97
acetyl acetone	C ₅ H ₈ O ₂	140.4	-23	0.975	16	0.571	
z-aminoethanol	C ₂ H ₇ NO	170.9	10.5	1.018	M	0.651	0.53
aniline	C ₆ H ₇ N	184.4	-6.0	1.022	3.4	0.420	0.4
anisole	C ₇ H ₈ O	153.7	-37.5	0.996	0.10	0.198	
benzene	C ₆ H ₆	80.1	5.5	0.879	0.18	0.111	101
benzonitrile	C ₇ H ₅ N	205	-13	0.996	0.2	0.333	12
benzyl alcohol	C ₇ H ₈ O	205.4	-15.3	1.042	3.5	0.608	
1-butanol	C ₄ H ₁₀ O	117.6	-89.5	0.81	7.7	0.586	6.3
z-butanol	C ₄ H ₁₀ O	99.5	-114.7	0.808	18.1	0.506	
i-butanol	C ₄ H ₁₀ O	107.9	-108.2	0.803	8.5	0.552	
z-butanone	C ₄ H ₈ O	79.6	-86.3	0.805	25.6	0.327	105
t-butyl alcohol	C ₄ H ₁₀ O	82.2	25.5	0.786	M	0.389	41
carbon disulfide	CS ₂	46.3	-111.6	1.263	0.2	0.065	400
carbon tetrachloride	CCl ₄	76.7	-22.4	1.594	0.08	0.052	120
chlorobenzene	C ₆ H ₅ Cl	132	-45.6	1.106	0.05	0.188	12
chloroform	CHCl ₃	61.2	-63.5	1.498	0.8	0.259	210
cyclohexane	C ₆ H ₁₂	80.7	6.6	0.779	0.005	0.006	104
cyclohexanol	C ₆ H ₁₂ O	161.1	25.2	0.962	4.2	0.509	1.2
cyclohexanone	C ₆ H ₁₀ O	155.6	-16.4	0.948	2.3	0.281	5

Choice of the organic solvent vs. polarity of material to be removed matters!

M = miscible.

The values for relative polarity are normalized from measurements of solvent shifts of absorption spectra.

A. Wet Cleaning

♦ RCA standard cleans

SC-1 ⇒ $\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 5$, 5min, 70-85°C

- (RCA-1) → dissolving and forming a new native oxide
→ removing the particles and organics
→ fast decomposition of H_2O_2 and NH_3 at above 80°C
→ creating microroughness on the Si surface
∴ lowering the concentration of NH_4OH

Organic clean + particle clean

SC-2 ⇒ $\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 5$, 5min, 70-85°C

- (RCA-2) → removing the metallic impurities and insoluble metal hydroxides
→ no etching oxide or Si surface

Ionic clean

A. Wet Cleaning

◆ HF acid cleans

DHF \Rightarrow HF : H₂O = 1 : 10 to 100, RT, 10 sec to 1 min

- removing the SiO₂ films and silicate glasses
(ex : phosphosilicate or borophosphosilicate)
- changing the surface (hydrophilic to hydrophobic)
- Si surface : H- terminated (or passivated)

BHF(BOE, buffered oxide etch) \Rightarrow HF : NH₄F = 1 : 7

- used for removing the oxides instead of DHF
- HF₂⁻ : major etchant species
- maintaining the concentration of etchant
- stabilizing the etching rate and preventing PR liftoff in HF

A. Wet Cleaning

- ◆ **H₂SO₄ acid clean (Piranha clean)**
⇒ H₂SO₄ : H₂O₂ = 4 : 1, 10min, at 120 °C
 - referred to piranha etch, or Caros acid
 - removing the organic contaminants

- ◆ **Choline solution clean (Peroxide clean)**
⇒ C₅H₁₄NO, dilution or adding surfactant & H₂O₂
 - trimethyl-2-hydroxyethyl ammonium hydroxide
 - strong and corrosive base and Si etchant
 - excellent wetting for Si after adding H₂O₂
 - similar effect to SC-1 (removing PR or particles)



B. Dry Cleaning

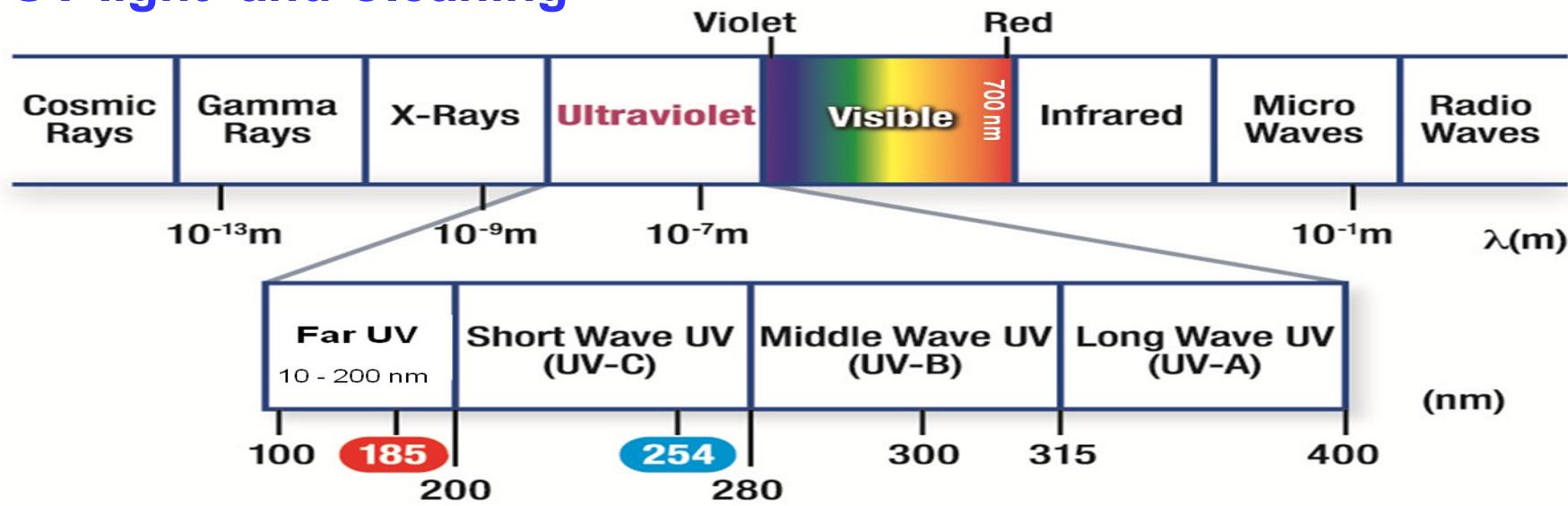
◆ Categories of dry wafer cleaning

- 1) Physical interactions
- 2) Physically-enhanced chemical reactions
- 3) Chemical thermal reaction
- 4) Mechanical technique

► Contaminants removal by dry cleaning

- 1) **Organic contaminants** : volatilization, UV/O₃ reaction, remote or downstream oxygen plasma treatment
- 2) **Native and chemical oxide, silicate glasses** : chemical etching, physical sputter etching, low-energy ECR plasma etching
- 3) **Metal and absorbed ions** : remote plasma, photo-induced reaction
- 4) **Particle** : vapor etching

UV-light and Cleaning



VUV Far-UV

- 100nm-200nm
- Medical equipment
- Nanofabrication
- Photochemistry
- Spectroscopy

Far-UVC

- 207nm-222nm
- Germicidal
- Most effective for disinfecting
- Safety for eye and skin

UV-C

- 200nm-280nm
- Germicidal
- Most effective for disinfecting

UV-B

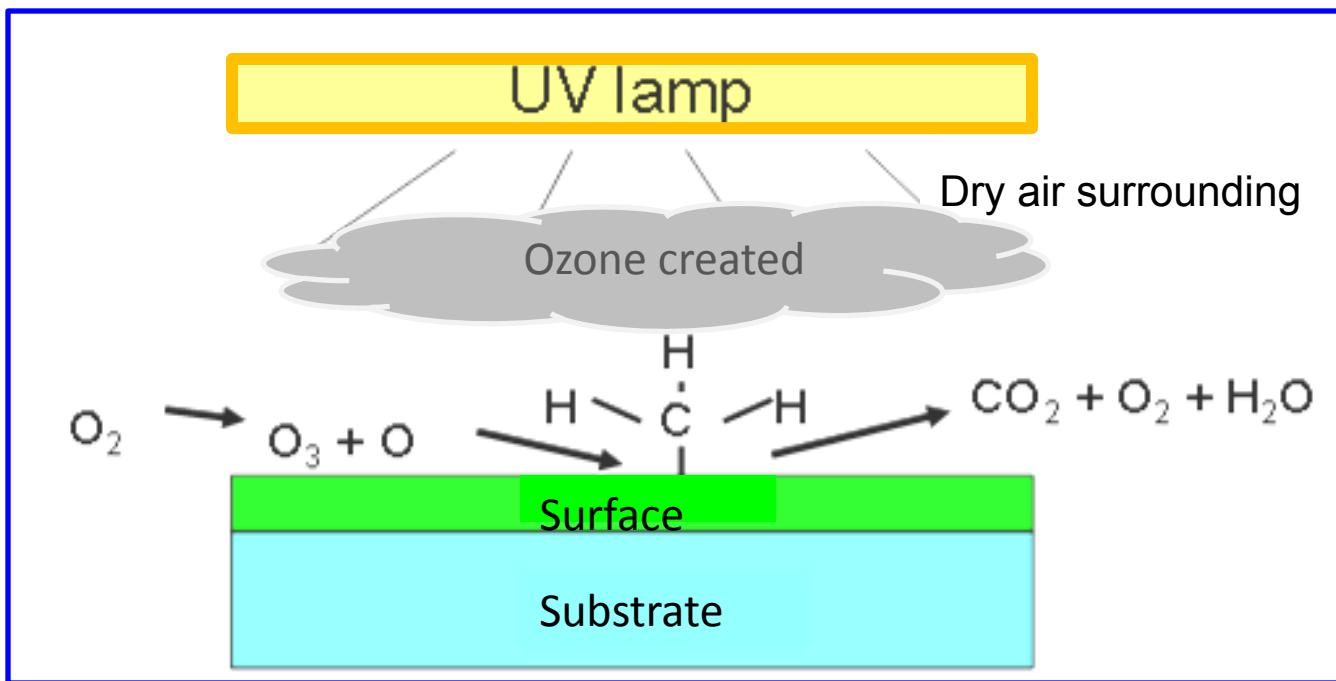
- 280nm-315nm
- Curing
- Tanning
- Medical Applications

UV-A (Near UV)

- 315nm-400nm
- Printing
- Curing
- Lithography
- Sensing
- Medical Applications

Molecules damaging/clean increases

B. Dry Cleaning



A schematic illustration of a hydrocarbon contamination removal by UV/ozone

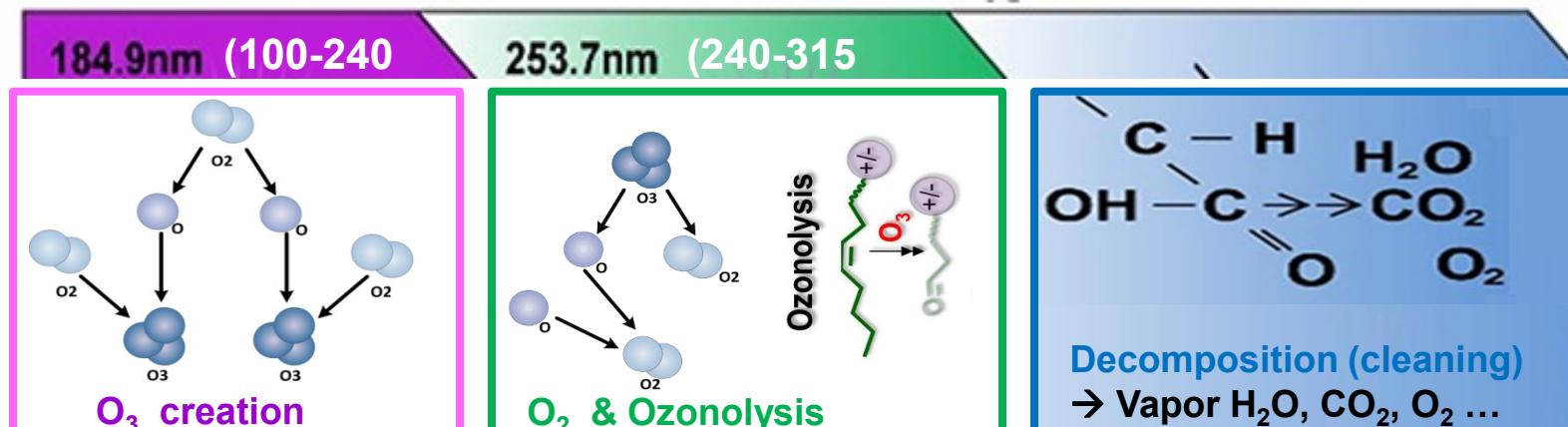
Organic contaminants + $\text{h}\nu \rightarrow$ excited organic contaminants (200~300 nm UV)



excited organic contaminants + (O, O₃) \rightarrow volatile compounds

At ~ 250 nm, UV decomposes O₃ and produces high-energy O* activated oxygen.

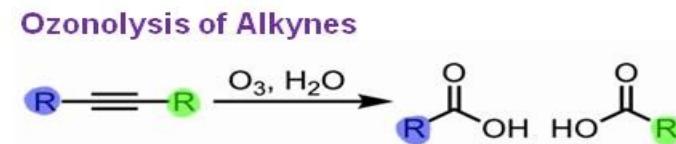
B. Dry Cleaning: UV-Ozone



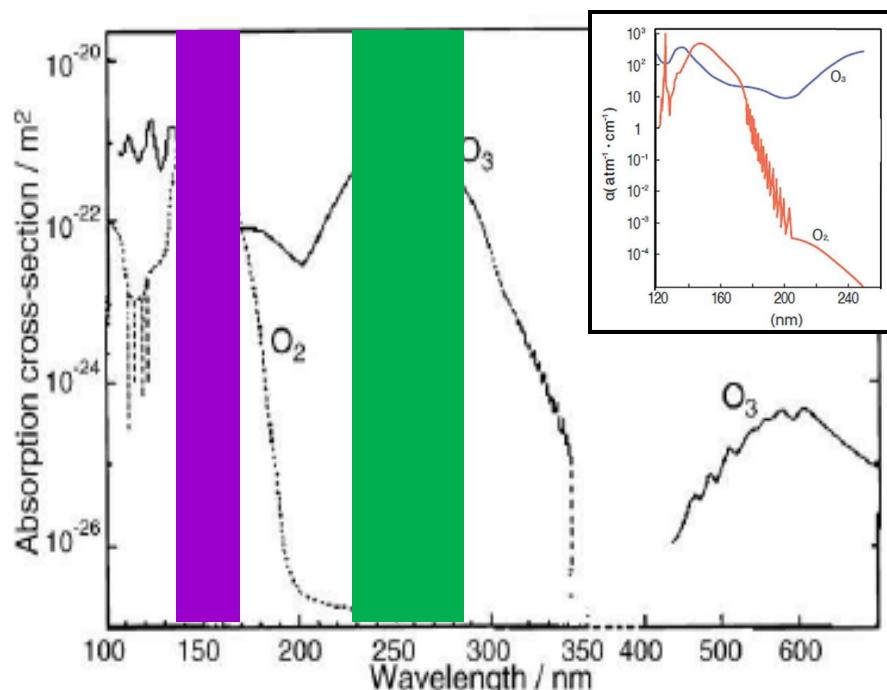
~185 nm: Changes of molecular oxygen to excited-state molecular oxygen O₂* & creates O₃.

~250 nm: UV decomposes ozone and produces high-energy O* activated oxygen & creates O₂. Here, hydroxyl radicals also are produced in the presence of water vapor. Polymer substrates are **oxidized by atomic oxygen, molecular oxygen and ozone** through the abstraction of hydrogen atoms from the polymer chains, producing radical carbon sites. Hydroxyl and carboxyl groups likely are found on the polymer surface after the ozone treatment; and this results hydrophilicity and enhancing wetting!

Ozonolysis: an organic reaction where the unsaturated bonds of alkenes (C=C), alkynes (C≡C), or azo compounds (N=N) are cleaved (split) with ozone (O₃). Examples:



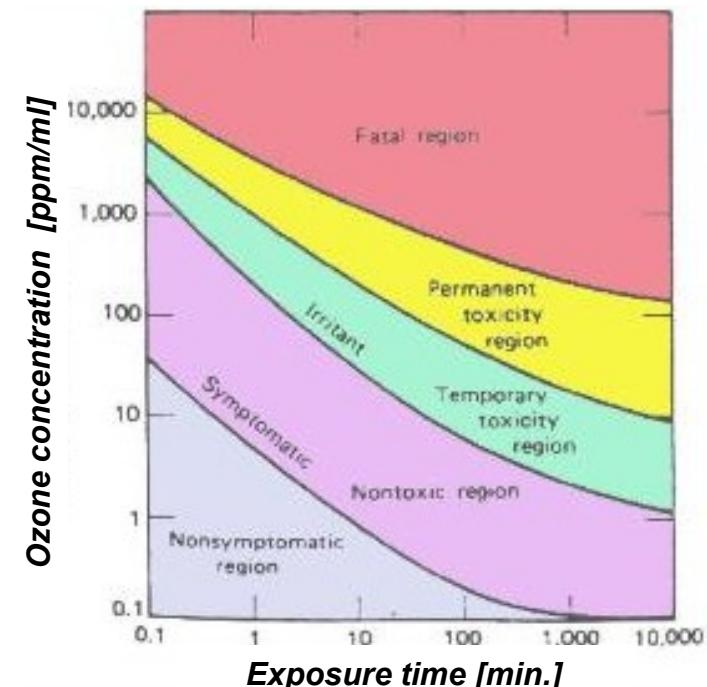
UV-Ozone/Ozone: Wavelength dependence of O_3 and O_2



Both O_2 and O_3 protect us from UV radiation!

Maximum efficacy of O_3 generation (abs. of UV radiation by O_2) is at ~ 160 nm.

Maximum efficacy of O_2 generation (abs. of UV radiation by O_3) is at ~ 255 nm.



Ozone safety spectrum

Special Issue Invited Review

Ozone Generation by Ultraviolet Lamps[†]

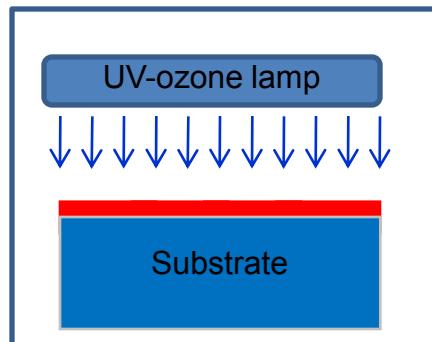
Holger Claus*

Ushio America, Inc., Cypress, CA

Received 3 December 2020, revised 15 January 2021, accepted 28 January 2021, DOI: 10.1111/php.13981

M. Salvermoser, *Ozone Sci. Eng.* 30, 228 (2008).

B. Dry Cleaning : UV-Ozone Exposure

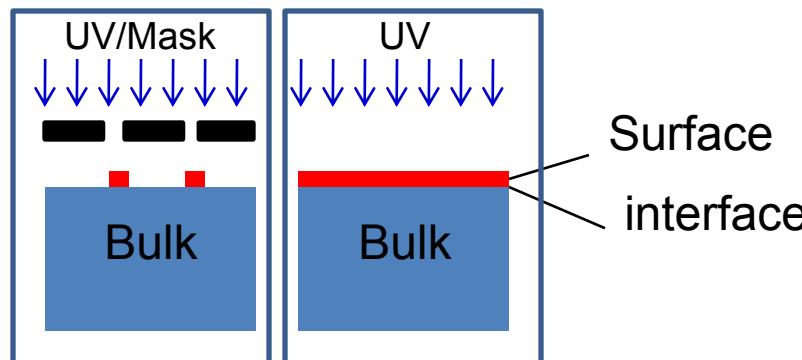


Schematics (left) and image (right) of a UV-Ozone cleaner.

UV Ozone Cleaner:

- Highly effective for non-acidic and dry cleaning (no need of solution)
- Uses intense 185 nm and 254 nm ultraviolet light.
- In the presence of oxygen, the 185 nm (absorbed O₂) produces ozone and while the 254 nm (absorbs C-H, ozone) excites organic molecules on the surface.
- Non-destructive removal/cleaning of organic contaminants
- Surface energy change → **Surface modification**
- Surface oxidation → **Electronic property change**

B. Dry Cleaning : Main Effects of UV-Ozone Exposure



Possibilities of Exposure:

Schematics of a UV-Ozone exposure over a patterned mask (left) and hole surface application of UV. Mask can be lithographic or metal mask.

- **Physical** - Surface energy, cleaning, adhesion, wetting, nucleation ...

Application: **Surface Modification → Patterning (site selective deposition)**

- **Electrical** - Oxidation, band bending and charge transport issues

Application: **Interface engineering → Device efficiency**

Exposed vs. Unexposed of material A (interfaced with material B, A/B)

→ Diff. electronic property → Diff. interface for the same material

B. Dry Cleaning : UV-Ozone Exposure for Surface Modification

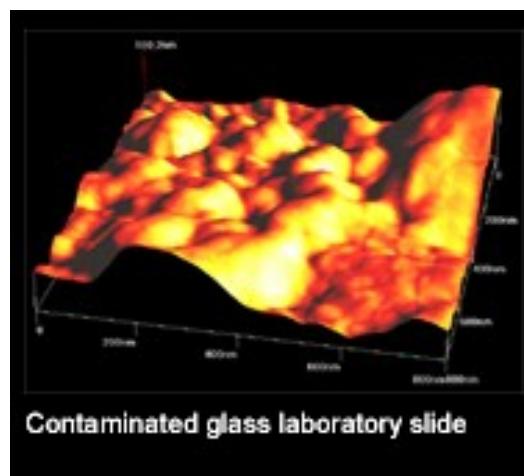


New Coverslip: wetability
before UV Ozone treatment

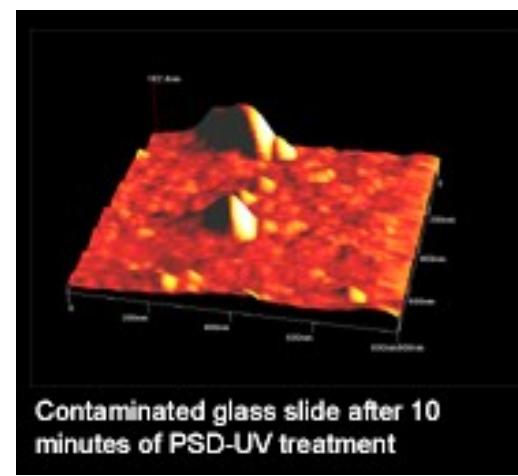


New Coverslip: wetability
after UV Ozone treatment

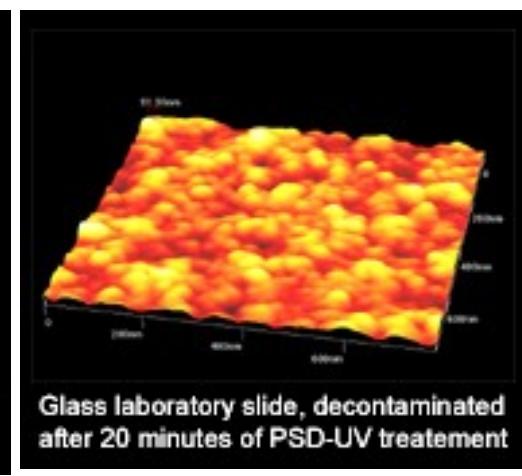
Cleaning "new" glass surfaces with a UV-Ozone cleaner (using room air)
→ **Enhances wetting (contact angle decreases drastically, ~ 0° to 30°)**



Contaminated glass laboratory slide



Contaminated glass slide after 10
minutes of PSD-UV treatment



Glass laboratory slide, decontaminated
after 20 minutes of PSD-UV treatment

AFM study of contaminated glass slide surfaces before and after UV-Ozone Cleaner treatment
→ **Surface cleaning, smooth organic surface**

B. Dry Cleaning

► UV/Cl₂ Cleaning

- UV exposure in a Chlorine ambient
 - remove metallic contaminants by volatilization
 - lift metallic contaminants off the surface
- Not enough to remove alkali metals (Ca, Na...)
 - need additional treatment
- Not need additional elevated temperature nor reduced pressure
- Problem : non-uniform, excessive etching of silicon resulting in rough surfaces

B. Dry Cleaning

◆ Plasma Enhanced Cleaning

● Direct plasma cleaning

- Ion-induced damage of the substrate
 - Radiation-induced oxide defect
- Metallic contaminants and/or alkali ions penetrate the substrate
 - recontaminate the substrate

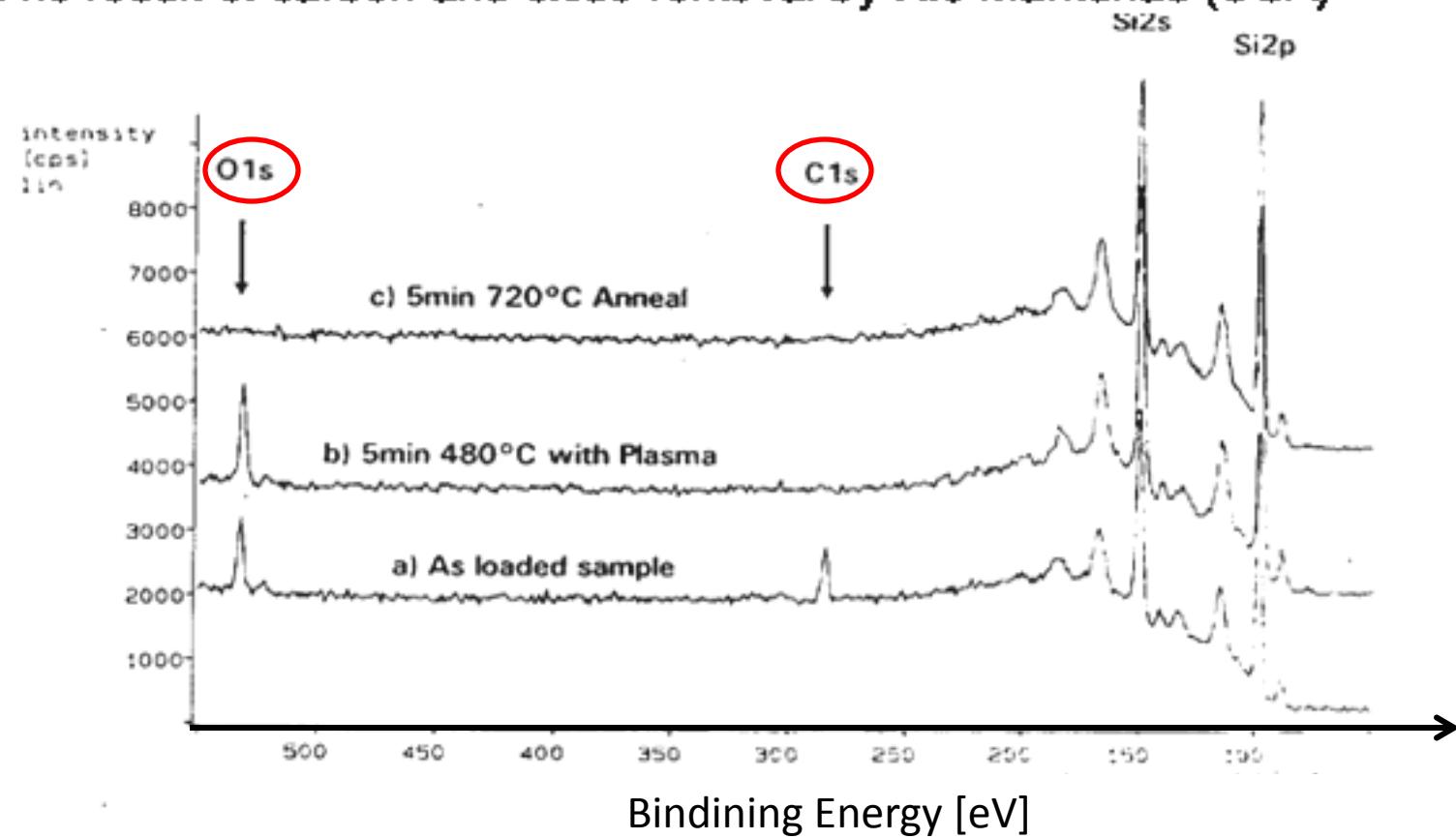
● Remote plasma cleaning

- By generating an active plasma in a spatial region remote from the substrate
 - Avoid ion acceleration into the substrate
- * O₂ plasma → Remove organic contaminants
- * HCl : Ar plasma → Remove metallic contaminants
Problem of corrosion
- * NF₃ : H₂ : Ar plasma → Etch native/chemical oxide

B. Dry Cleaning

● Remote H₂ plasma :

The result of carbon and oxide removal by R.J Markunas (USA)



B. Dry Cleaning

◆ Photochemically-Enhanced Cleaning

- Low pressure vapor UV lamps as the radiation sources
→ energies required for efficient photolysis
- Uniform high intensities for wavelengths (150 ~ 600 nm)

Types of Photochemical Reactions:

- I. Photo-dissociation: $AB + h\nu \rightarrow A^* + B^*$
- II. Photo induced rearrangements, isomerization: $A + h\nu \rightarrow B$

► UV/O₃ cleaning

- Oxidize and volatilize organics from surface
- Pre-oxidation surface treatment
- Organic removal prior to metallization
- Surface carbon and hydrocarbon removal
- Strip photoresist
- Remove polymer films after RIE process (reactive ion etching)

2.3. Surface-Treatment Technologies

Technique	Process(es)	Types	Technology Status	Comments
Abrasion	Mechanical	Dry or wet blasting, hand or machine sanding	Obsolete	Labor-intensive, dirty, applicable only for low production volumes, must deal with residuals.
Solvent cleaning	Physical and Chemical	Wiping, immersion, spraying or vapor degreasing	Obsolete	Safety, disposal and environmental concerns (i.e., emissions)
Water-based cleaning	Physical	Multistep power wash	Contemporary	Low environmental systems impact, high volume capacity, and relatively low cost.
Chemical etching with acids or bases	Chemical	Immersion, brushing, rinsing, spraying	Obsolete	Safety issues due to the use of corrosive, toxic materials and hazardous-waste disposal problems.
Chemical primers	Chemical	Solution application of poly ethyleneamine, polyurethanes, acrylates, chlorinated polymers, nitrocellulose, or shellac	Mature	Requires specific equipment, and different primers are necessary for specific end-use requirements.
Flame treatment	Thermal and chemical	Available for flat films or three-dimensional configurations	Mature	Fire hazard, limited to some extent to thermally insensitive materials.

2.3. Surface-Treatment Technologies ...

Technique	Process(es)	Types	Technology Status	Comments
Corona discharge	Electrical and chemical	Available for both conductive and dielectric substrates	Contemporary	Applicable primarily to films and webs
Gas plasma	Electrical and Chemical	Available for film or three dimensional applications can use ac, dc, or microwave frequency	Contemporary	Convenient and cost effective; non toxic materials or disposal issues; can be effective in numerous different configurations
UV and uv/ozone	Electrical and Chemical	For distinct parts in batch systems.	Developmental, Contemporary	Generally only in batch format and requires longer residence times
Evaporated acrylate coatings	Physical and Chemical	Currently for webs and films only	Developmental, Contemporary	Still being developed for commercial-scale applications
Fluorination	Chemical	Short exposure to elemental fluorine can be batch or continuous	Developmental, Contemporary	Specialized equipment required for delivery and monitoring fluorine.
Electrostatic discharge control	Electrical	Can be in the form of charge dissipation or charge neutralization	Contemporary	Equipment can be simple through complex and expensive, depending on the application

2.3. Surface-Treatment Technologies ...

Abrasion is the process of scuffing, scraping /scratching, wearing down, marring, or rubbing away

Corona treatment (sometimes referred to as air plasma) is a surface modification technique that uses a low temperature corona discharge plasma to impart changes in the properties of a surface. The corona plasma is generated by the application of high voltage to an electrode that has a sharp tip.

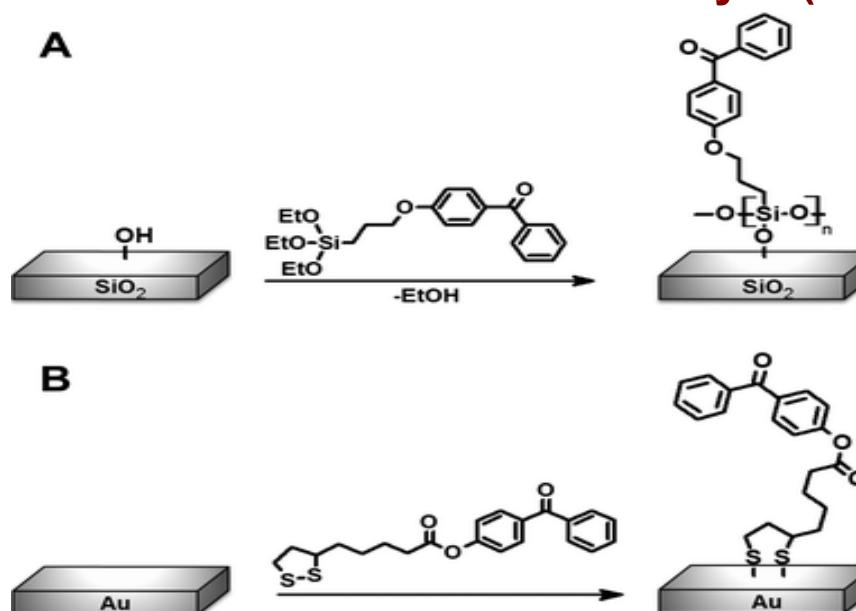


Flame treatment is the application of a gas flame to the surface of a material to improve adhesion

2.4. Surface Modifications: Surface Functionalization and SAMs

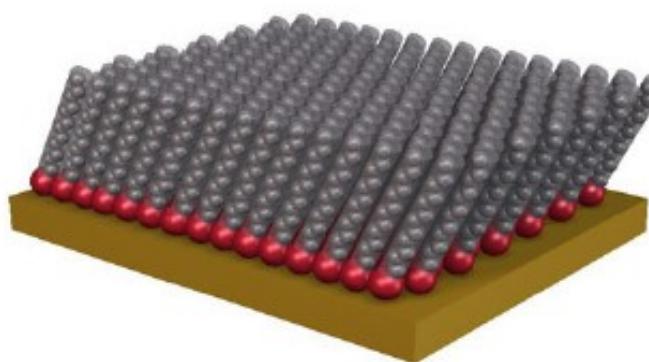
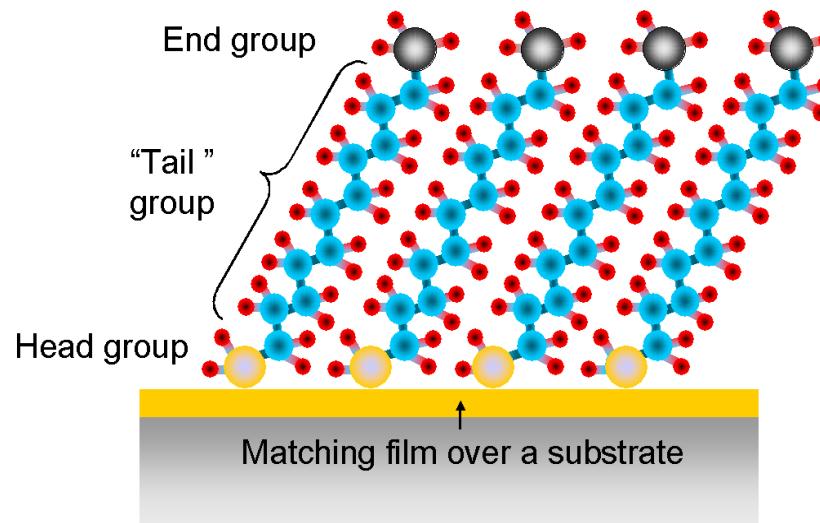
Surface Functionalization introduces chemical functional groups to a surface. This way, materials with functional groups on their surfaces can be designed from substrates with standard bulk material properties. Prominent examples can be found in semiconductor industry and biomaterial research.

→ Use of self assembled monolayer (SAMs)



Surface functionalization of a silicon wafer (A) and a gold surface (B)

Surface Modifications: Surface Functionalization and SAMs

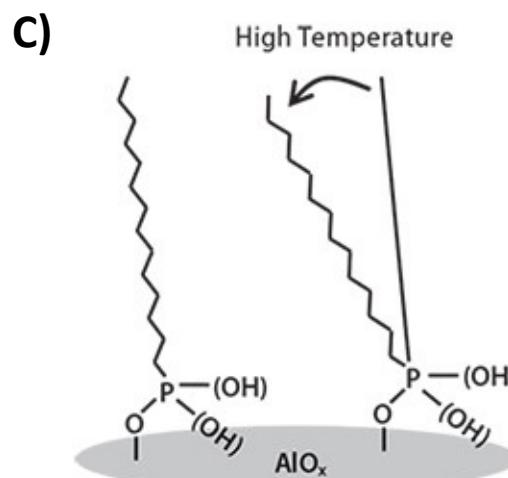
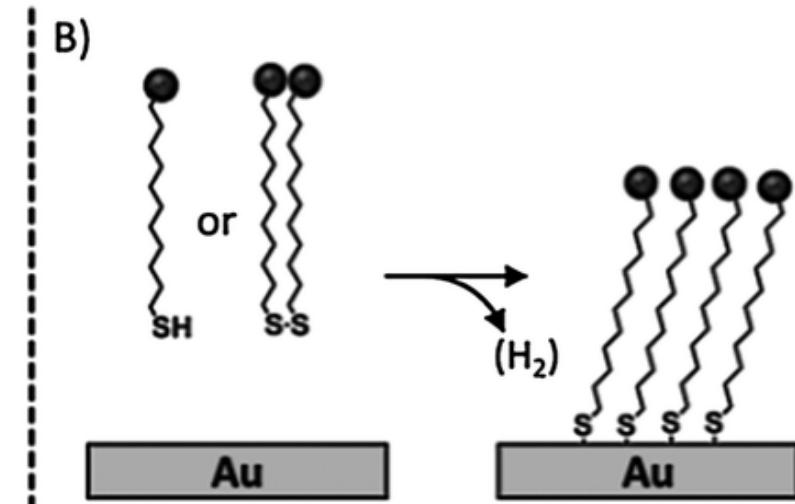
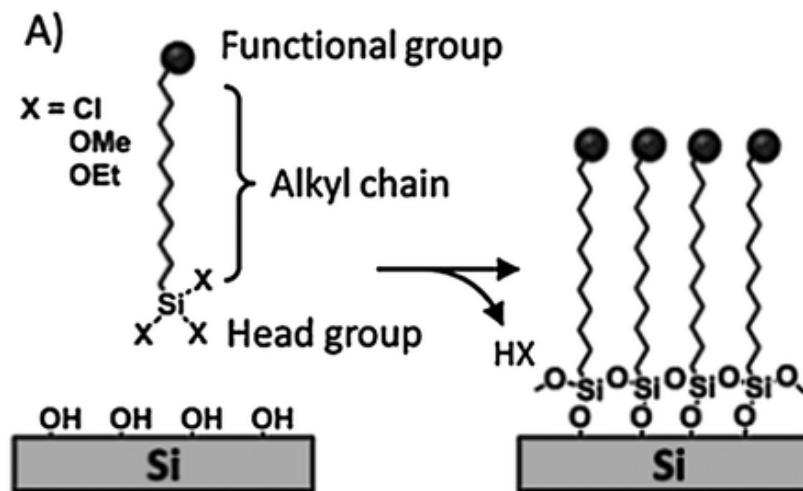


SAMs head, tail and functional or head groups (top) and 3D pattern over a surface (B)

SAMs:

- Head-substrate matching
→ Bond formation
- Functional group can add other SAM
- SAMs are specific

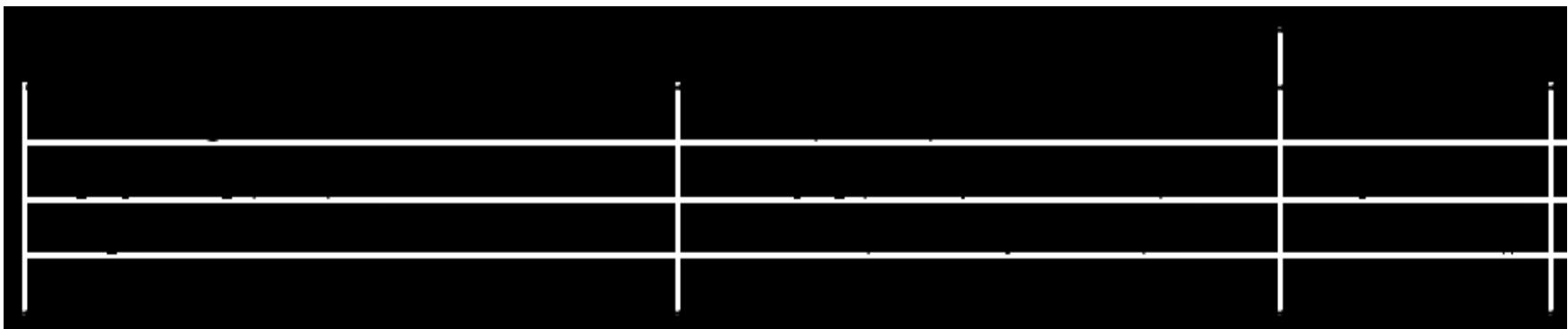
Surface Modifications: Surface Functionalization and SAMs



Different SAMs for Different Substrate

- Si-O-Si (**Silane**)
- Au-S-H (**Thiol**)
- Al-O-P (**Phosphonic**)

Surface Modifications: Surface Functionalization and SAMs



Different SAMs:

- a) Thiol for different metals like gold, silver, copper ...
- b) Phosphonic for Tin or Indium oxides
- c) Carboxylic for Tin or Zinc oxides
- d) Other SAMs according to possible substrate-SAMs bonding

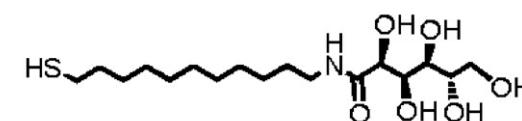
Surface Modifications: Different SAMs vs. Same Head Group

A

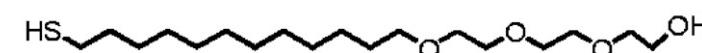
Pentadecanethiol, PDT



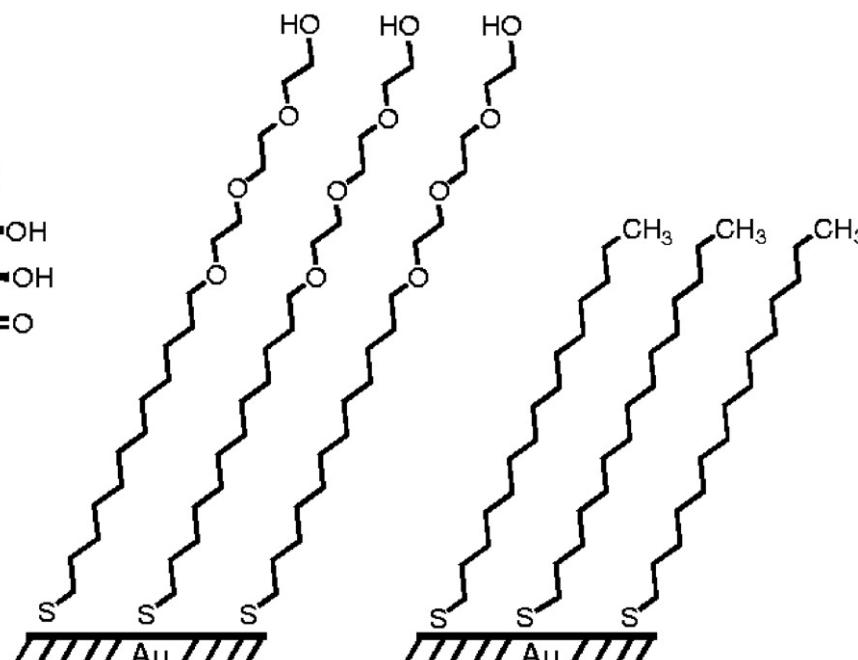
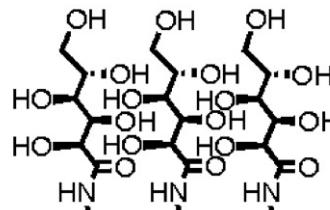
L-gulonamide-terminated undecanethio-



(1-mercaptopoundec-11-yl)tri(ethylene glycol)



B



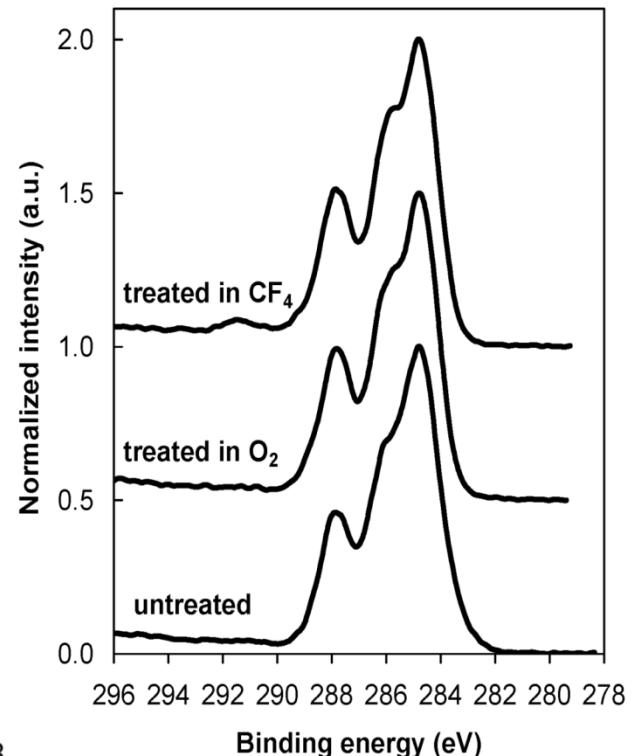
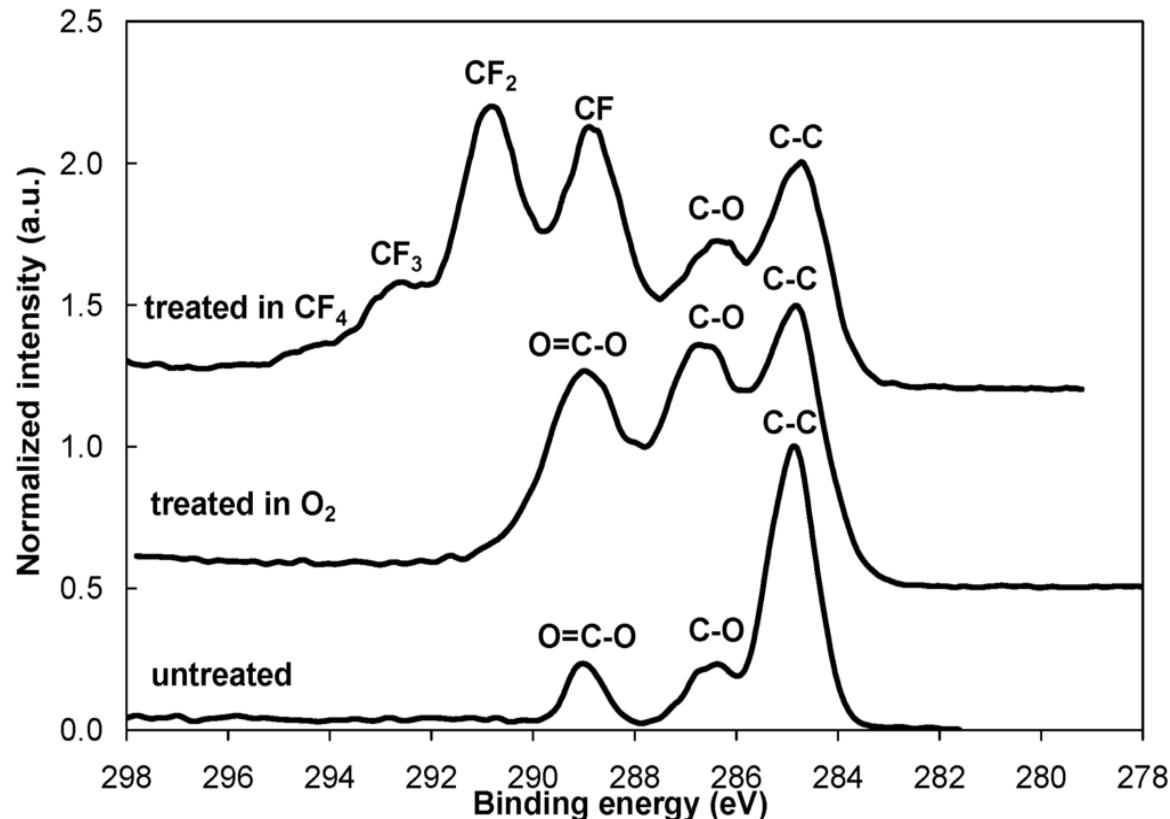
Because of different tail and head group (while the same head group), the chemical, electrical and physical property varies

B1

B2

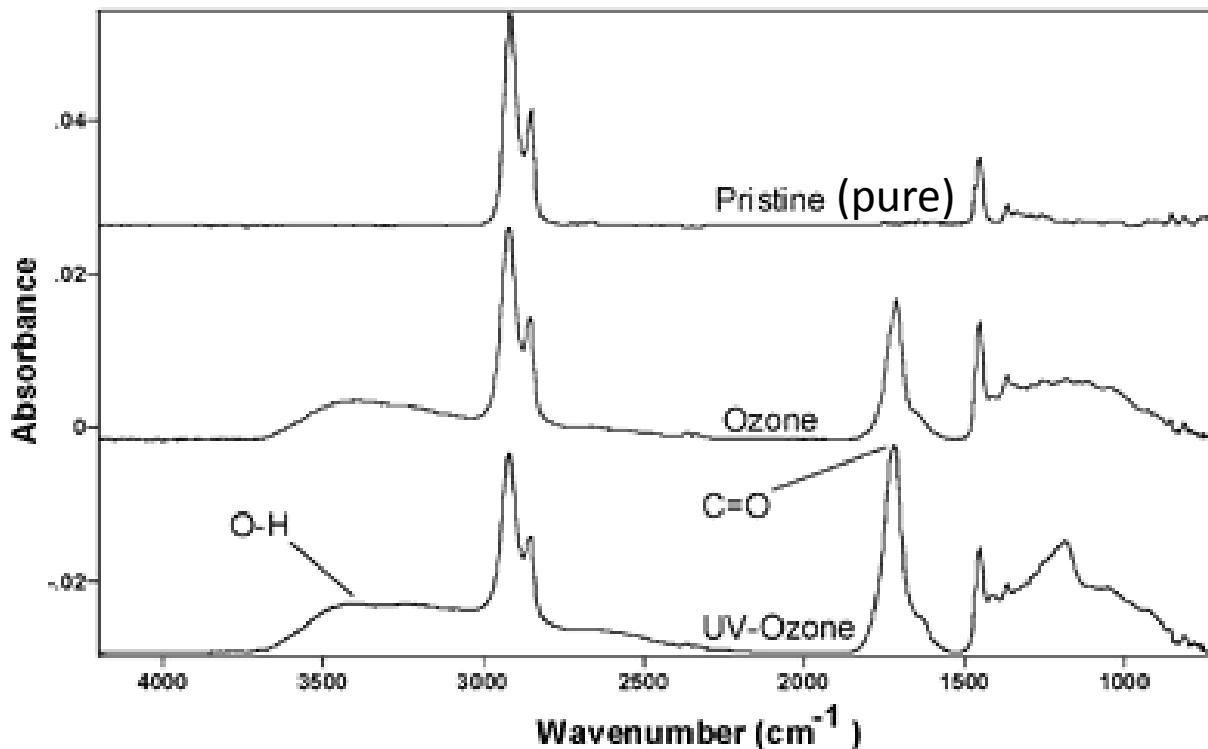
B3

Surface Modifications: Chemical treatment



XPS high-resolution spectra of carbon C1s for the control polyethylene terephthalate (PET) sample and for the PET samples treated in O₂ and CF₄ plasma.

Surface Modifications: UV light or UV/Ozone



Infrared spectra from Zeonex E48R (Cyclic Olefin Copolymer (COC) is an amorphous polymer) before and after oxidation with ozone and UV-ozone.

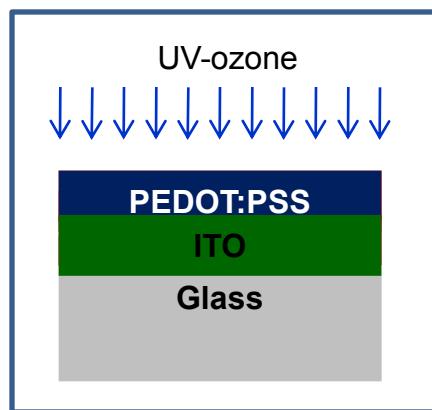
Tricks and Parameters of Exposure:

Partial surface exposure (shadow mask), UV-Ozone vs. Ozone or UV alone, temperature, exposure time, lamp-sample distance

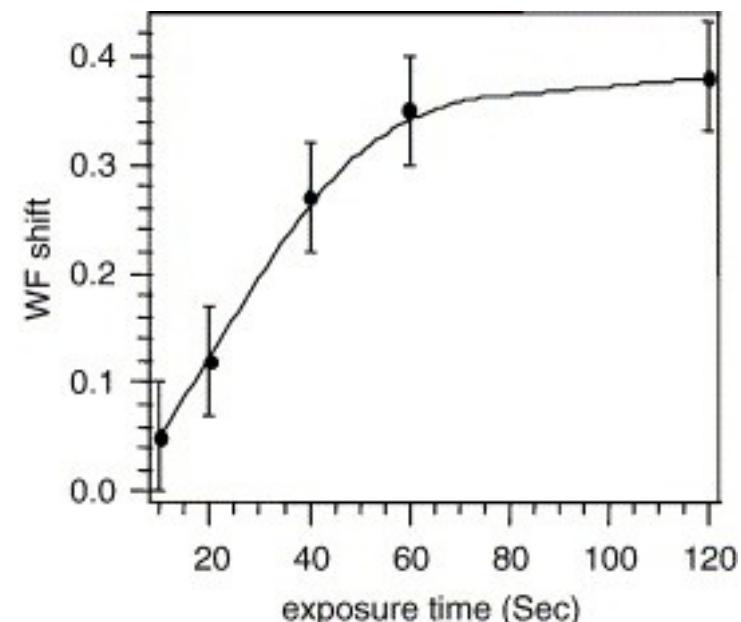
Surface Modifications: UV light or UV/Ozone ...

UV-Ozone Exp. of PEDOT:PSS: Surface/Electronic Modification

Experimental



UV-ozone exposure of PEDOT-PSS



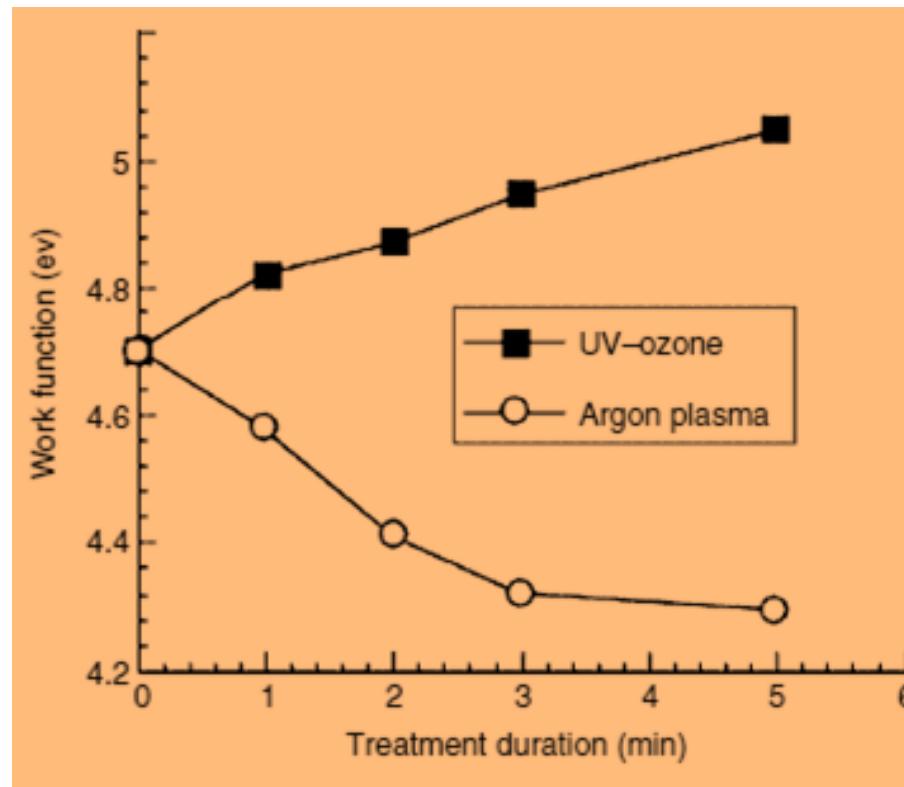
Effect of the UV-ozone exposure on PEDOT-PSS:

- Increase in work function and conductivity
- Improved roughness
- Both surface and bulk effect !

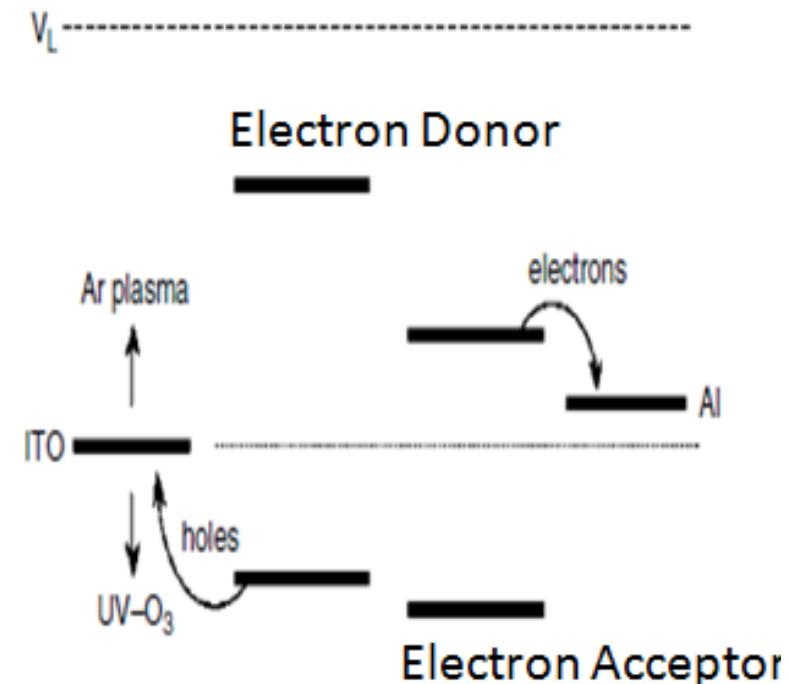
Work function shift as a function of the time of ozone treatment for PEDOT:PSS

2.5. Surface Modifications:

Plasma in Electronic Property Modification



ITO work function at different time for UV-ozone and argon plasma treatments.

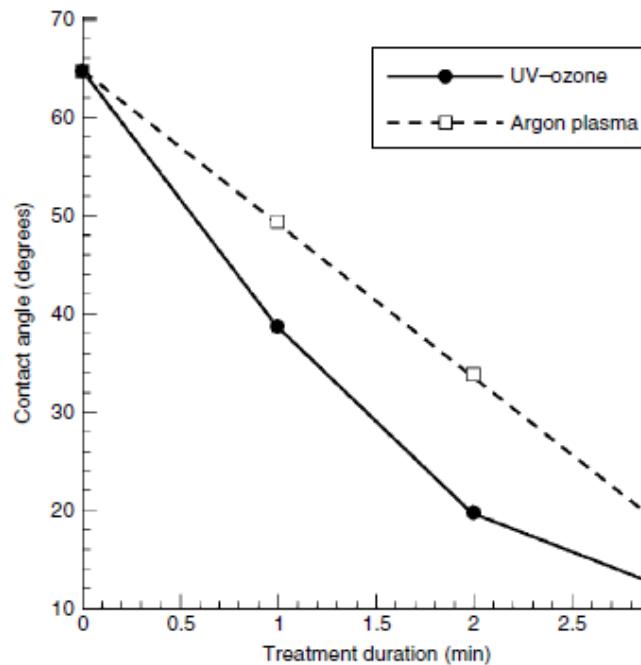


Ideal energy level diagram of ITO/Organic semiconductor interface .

Ref.: P. Destruel et al., Polym Int., 206, 601(2005)

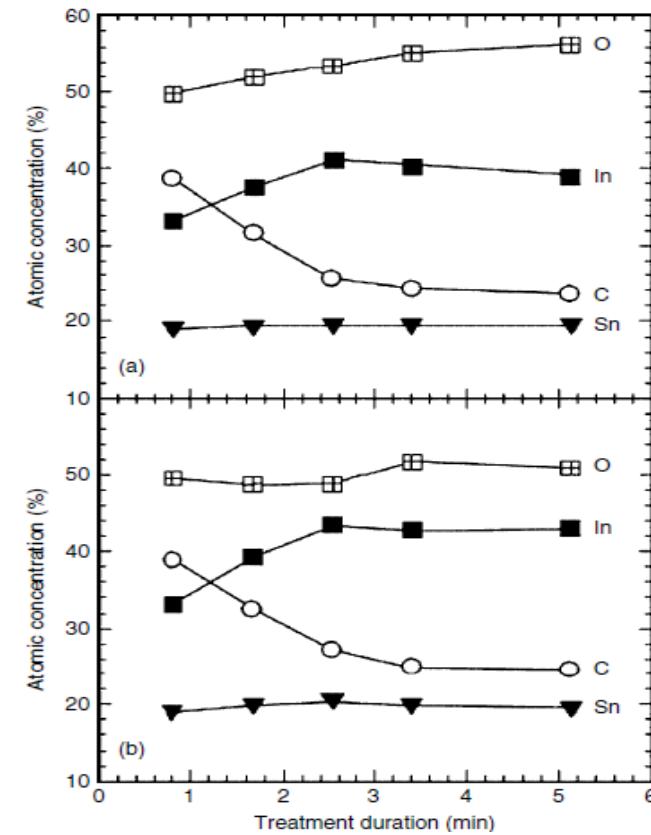
2.5. Surface Modifications:

Plasma in Electronic Property Modification



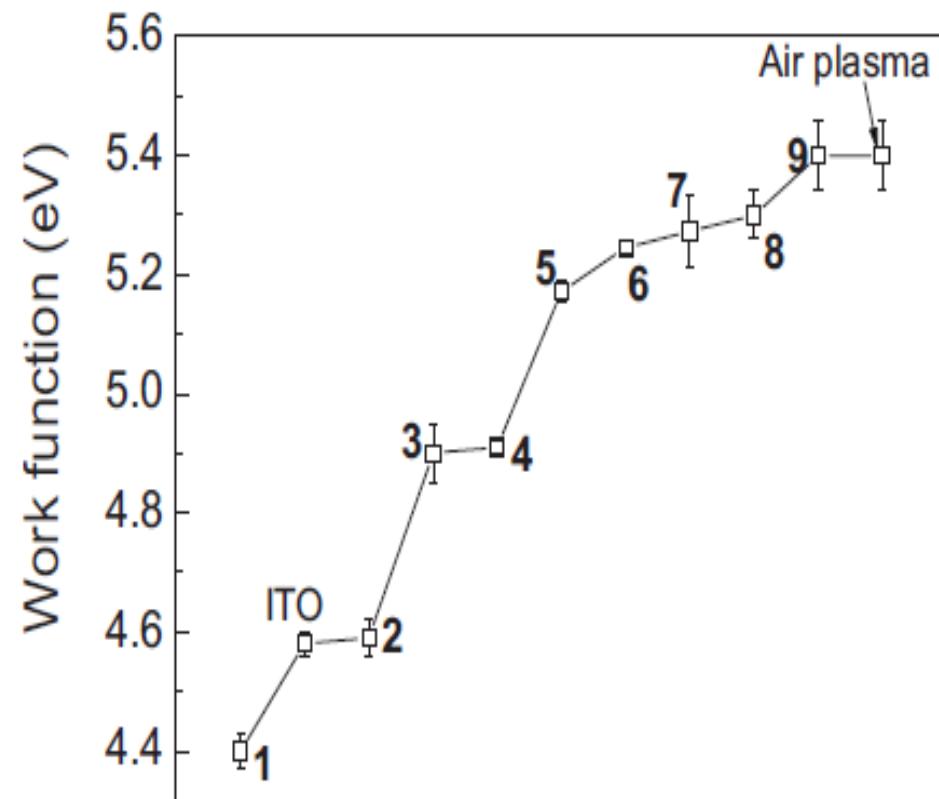
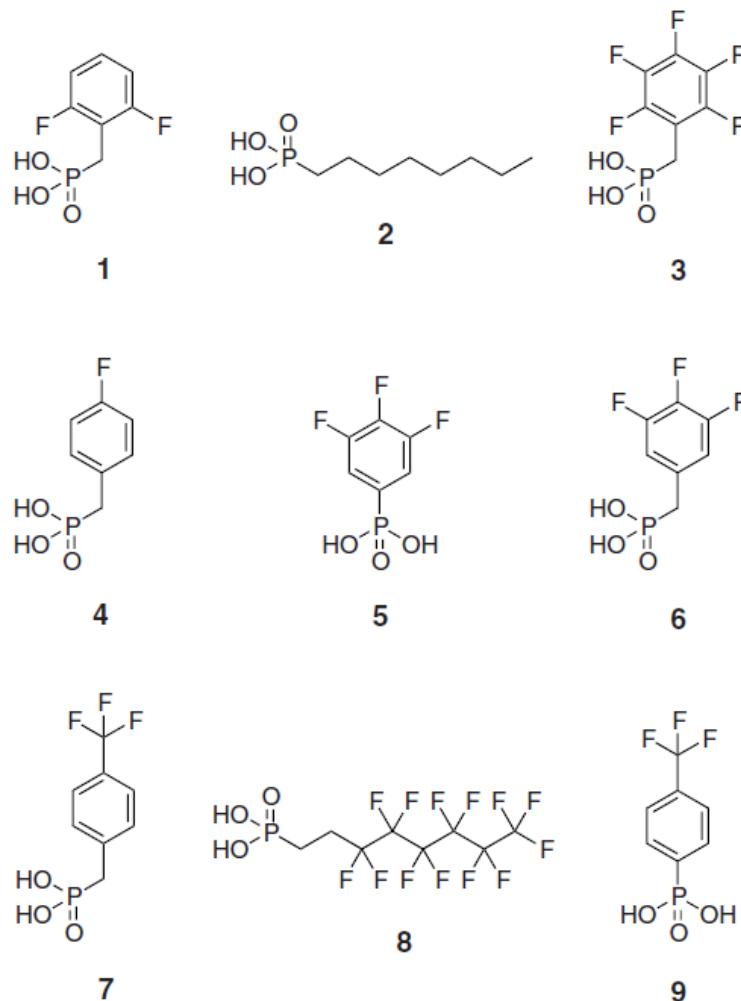
Contact angle measurement with UV–ozone and argon plasma treatments at different times.

Ref.: P. Destruel et al., Polym Int., 206, 601(2005).



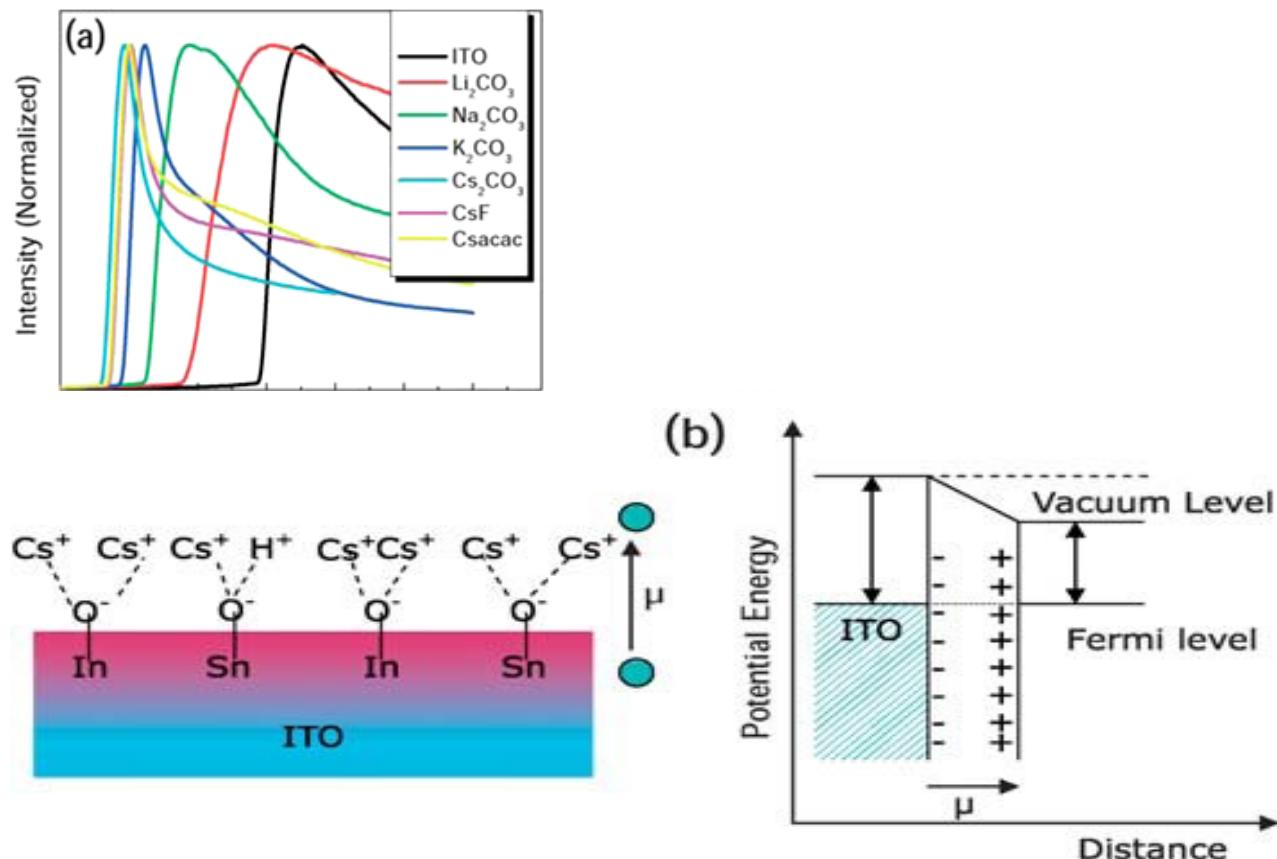
Atomic concentration of an ITO surface measured at different treatment times: UV–ozone (top) and argon plasma (bottom).

Surface Modifications: SAMs in Electronic Property Modification



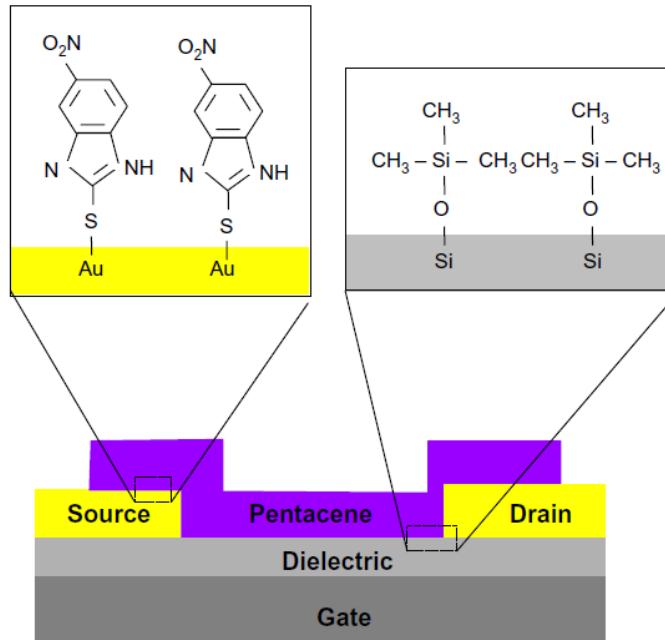
Different SAMs (1-9) and their impact on the work function of ITO after surface treatment.

2.5. Surface Modifications: SAMs in Electronic Property Modification

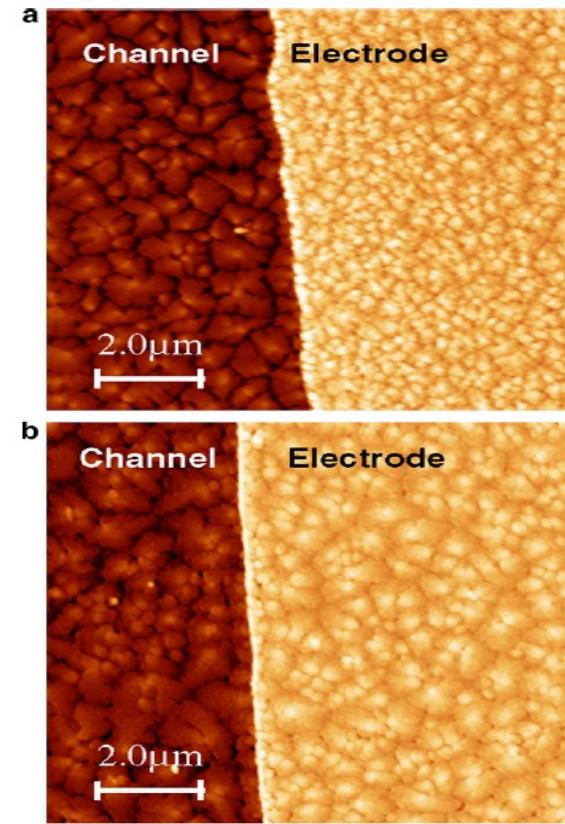


Variation of secondary electron edge with different buffer layers on ITO, (b) scheme for the formation of dipole layer on ITO and its effect on reducing the ITO work function.

Surface Modifications: SAMs on film growth & physical property

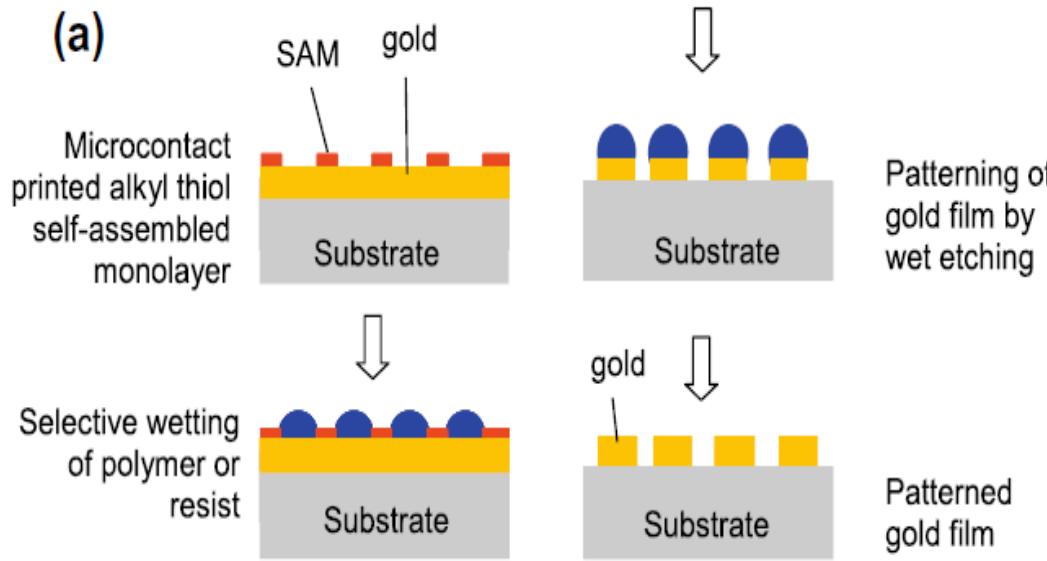


The bottom drain and source contacts (gold) were treated by 2-Mercapto-5-nitrobenzimidazole (MNB) and the gate dielectric (silicon oxide) by hexamethyldisilazane self-assembled monolayer (SAM) prior to the deposition of the pentacene film.



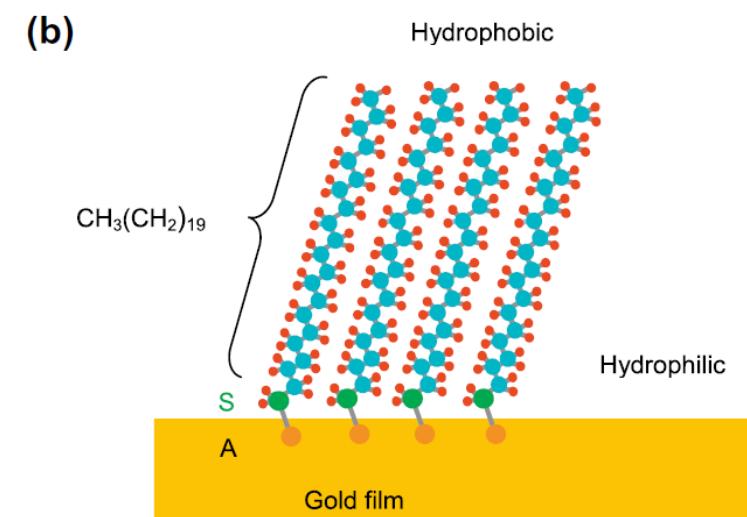
drain/source region the pentacene film was prepared on pure gold (a), and (b) 2-Mercapto-5-nitrobenzimidazole (MNB) pretreated gold .

Surface Modifications: SAMs on film growth & physical property



Patterning of gold film by wet etching

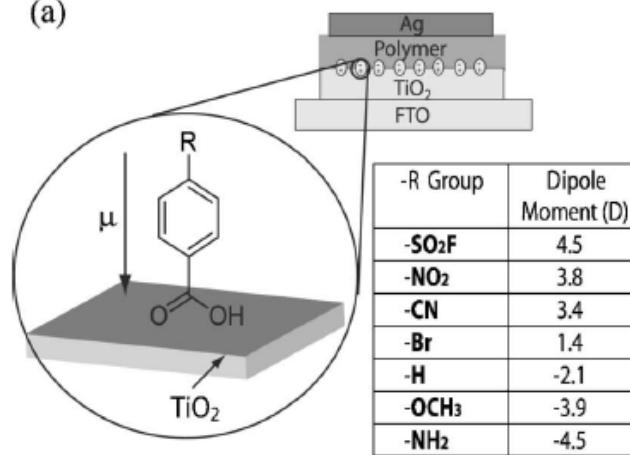
Patterned gold film



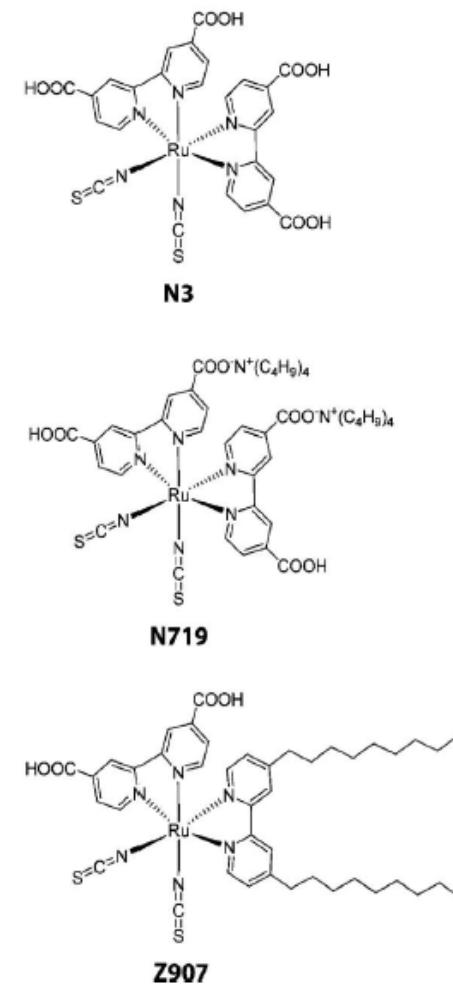
Patterning of gold by microcontact printing of thiol based SAMs. The thiol based SAMs acts as selective surface wetting agent for a polymer or resist. The gold or silver films were patterned by a potassium iodide/iodine (KI/I_2) etching solution.

3.3. Interface Modification

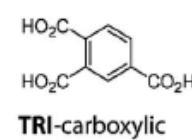
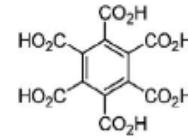
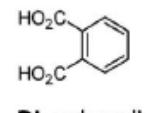
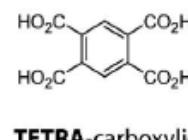
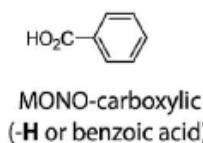
(a)



(c)

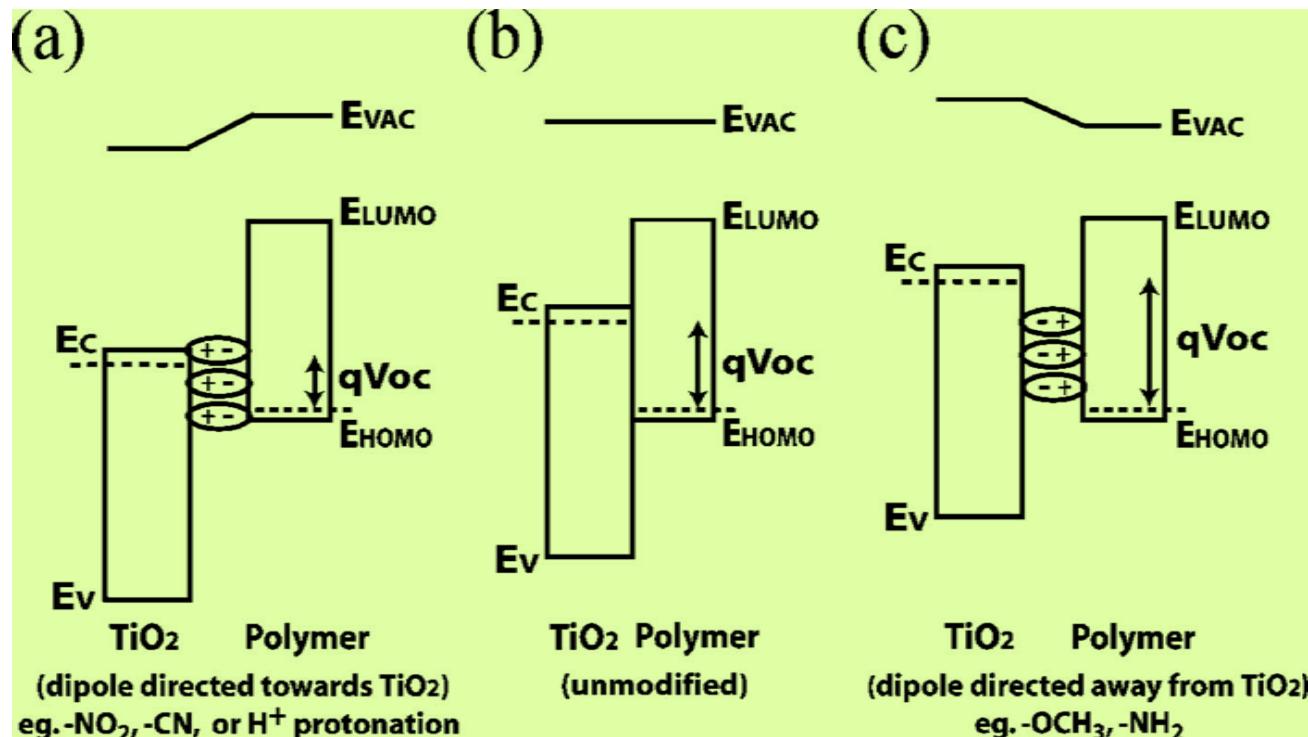


(b)



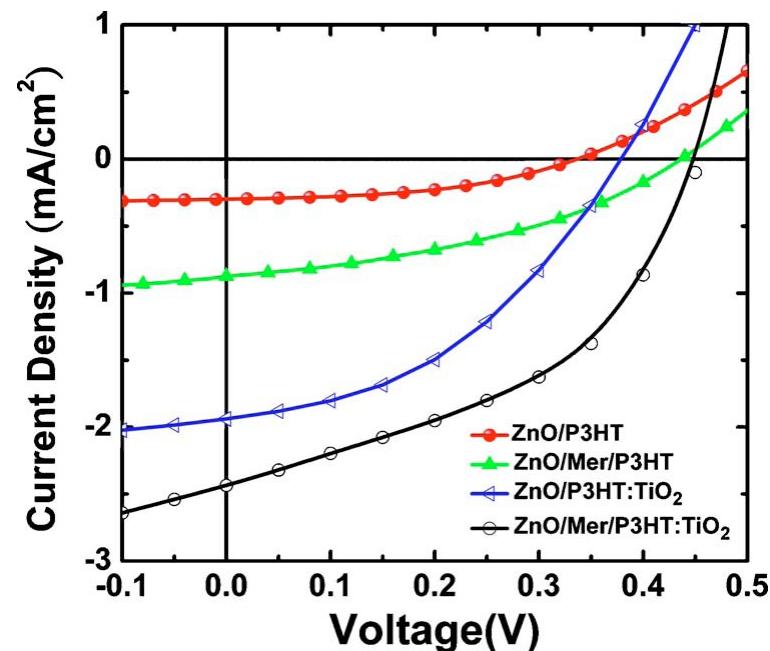
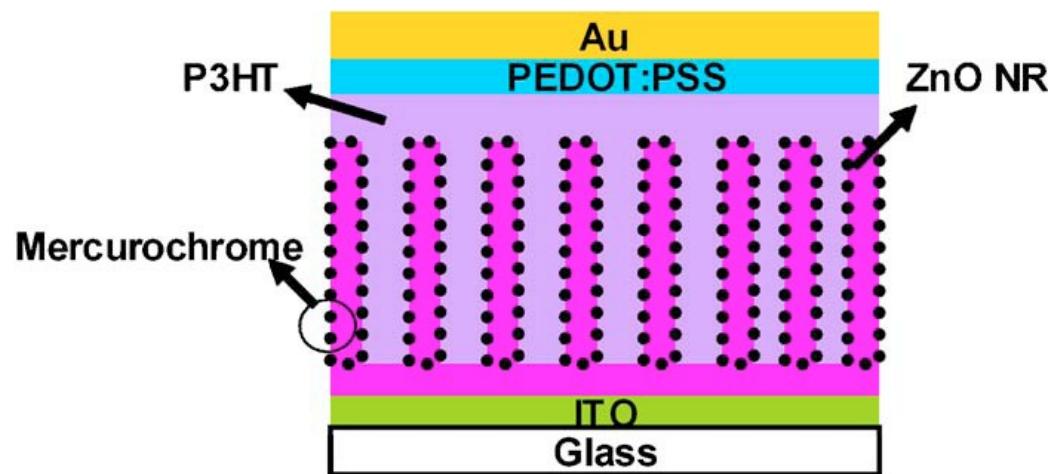
- a) Schematic of bilayer TiO_2 /polymer devices with dipolar modification of titania surface. The table lists the substituent $-R$ group on the para position of the benzoic acid accompanied with calculated dipole moment.
- b) Molecular structures of the benzene carboxylic molecules with varying amount of carboxylic acid groups.
- c) Molecular structures of the three Ru(II) dyes as IM.

3.3. Interface Modification



- Schematic of bilayer TiO_2 / polymer devices with dipolar modification of titania surface. The table lists the substituent $-R$ group on the para position of the benzoic acid accompanied with calculated dipole moment.
- Molecular structures of the benzene carboxylic molecules with varying amount of carboxylic acid groups.
- Molecular structures of the three Ru(II) dyes as 1M.

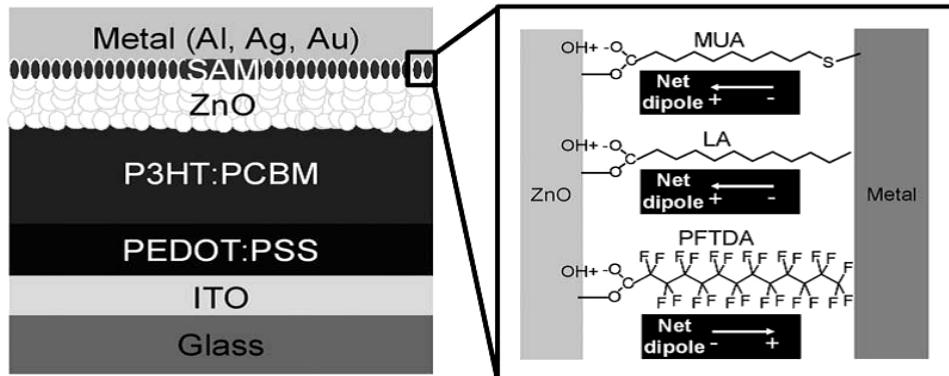
3.3. Interface Modification



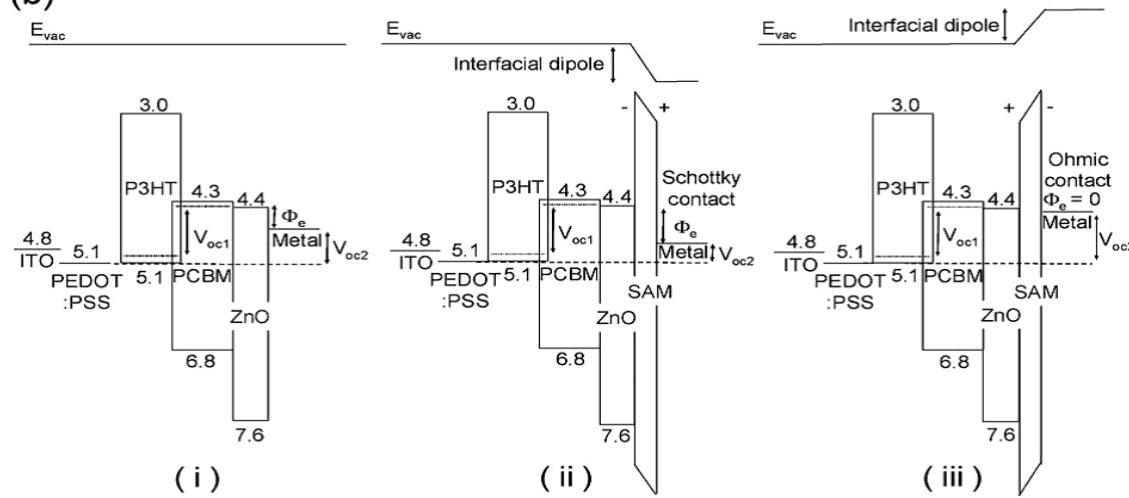
A schematic structure of the nanostructured ZnO/P3HT hybrid photovoltaic device with mercurochrome ($C_{20}H_8Br_2HgNa_2O$) as interface material

3.3. Interface Modification

(a)



(b)



(a) Device architecture of the polymer solar cell with self-assembled-monolayer-modified ZnO/metal bilayer cathodes, and the chemical structures of the self-assembling molecules used in this study. b) Schematic illustration of the energy level diagram of the devices with (i) a metal-only cathode; (ii) a ZnO/metal bilayer cathode; (iii) a ZnO/SAM/metal cathode with an interfacial dipole directed towards the metal surface; and (iv) a ZnO/SAM/metal cathode with an interfacial dipole directed away from the metal surface.

Main Surface Modification Related Characterizations

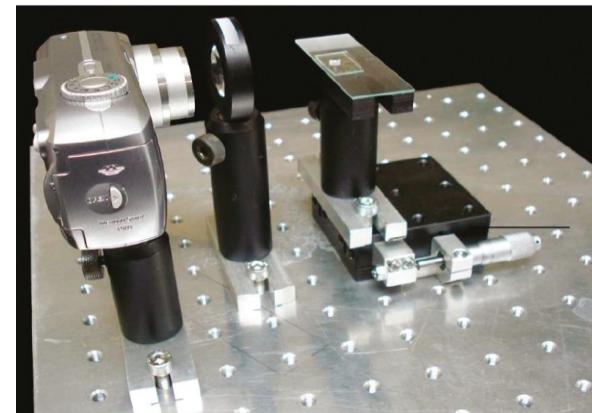
□ Physical

SEM (Scanning Electron Microscopy)

AFM (Atomic Force Microscopy)

Contact angle measurement surface energy

→ Hydrophilic, hydrophobic, wetting/dewetting



□ Chemical & Electrical

NMR, FTIR, elemental analysis methods

XPS/UPS (X-ray/UV photoelectron spectroscopy)

→ Oxidation (XPS), band structure or bending (UPS)

A contact angle measurement setup

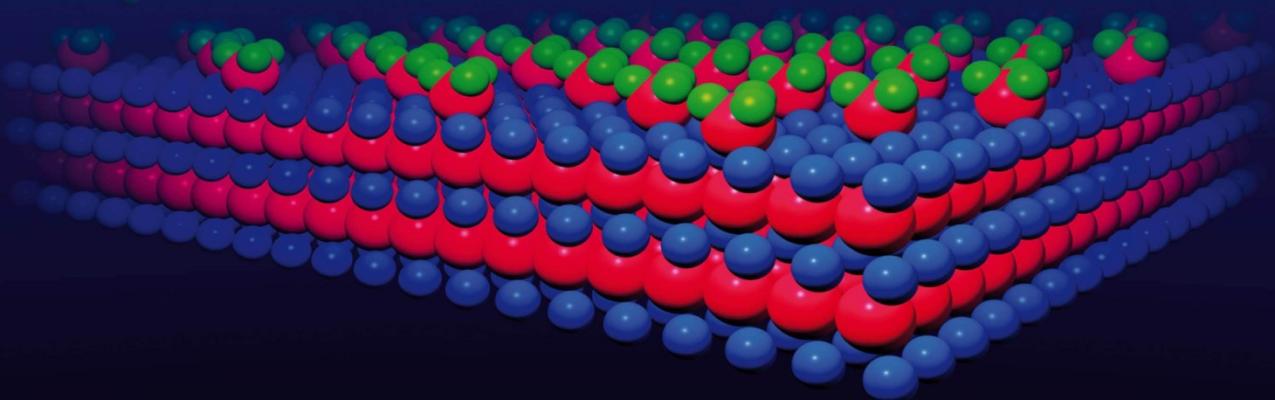
Tribology

The study of science and engineering of interacting surfaces in relative motion. It includes the study and application of the principles of friction, lubrication and wear. Tribology is a branch of mechanical engineering and materials science.



Tribology is essential in evaluating high wear components such as air compressors, gear boxes, gas and diesel engines, hydraulic systems, and spindle bearings. Tribology will detect the earliest stages of wear before the wear starts to generate any vibration signals. E.g., excessive wear of the teeth of the metal gears due to sudden changes in wind and other issues

Surface & Interface Physics



3. Thin Films

Amare B. Belay

3. Thin Films

- 3.1. Thin film deposition methods
- 3.2. Nucleation and graph
- 3.3. Thin films as surface and interface modifiers

3.1. Introduction (I)

Why thin films?

Thin films are deposited onto bulk materials (substrates) to achieve properties unattainable or not easily attainable in the substrates alone.

thin-film property category	typical applications
optical	<ul style="list-style-type: none">reflective/antireflective coatingsinterference filtersdecoration (color, luster)compact disks (CDs)
electrical	<ul style="list-style-type: none">insulationconductionsemiconductor devices
magnetic	<ul style="list-style-type: none">memory disks
chemical	<ul style="list-style-type: none">barriers to diffusion or alloyingprotection against oxidation or corrosiongas/liquid sensors
mechanical	<ul style="list-style-type: none">tribological (wear-resistant) coatingshardnessadhesionmicromechanics

Introduction (II)

Cr on plastic parts:

hardness, metallic luster, protection against UV light
(same functionality as bulk Cr, much cheaper and lighter)

TiN on tools:

hardness, low friction, chemical barrier against alloying of tool and work piece
(a tool made solely from TiN would be too brittle and fail too easily
and would be much too expensive)

multilayers: different materials are deposited successively
optical interference filters (alternating high and low indexes of refraction)

alternating layers of GaAs and (GaAl)As nm-thick films
(novel electrical properties, governed by the periodicity of the "superlattice")

-

Thin vs. Thick Films

"thin" films:

prepared by deposition of single atoms or molecules
(from the gaseous or liquid phase)

"thick" films:

prepared by deposition of particles consisting of many atoms/molecules
(e.g. wall paint)

"thin" films may be thicker than "thick" films

3.1. Thin Film Deposition Methods

Thin Film Deposition – Chemical and Physical

Chemical: A chemical reaction is made for the thin film to be deposited



Physical: Physical method used for deposition

→ no need of chemical reaction

method can be evaporation or spin-coating and the like

E.g., Aluminium metal evaporated over another metal by evaporation

- Variety of Chemical Vapor Depositions (**CVD**) are used to layer on subsequent structural and sacrificial layers
- Physical Vapor Deposition (**PVD**) is used for deposition of metals and some organic molecules

3.1. Thin Film Deposition Methods (cont.)

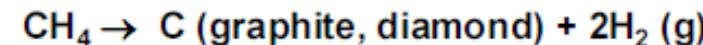
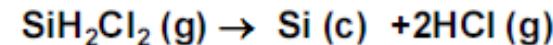
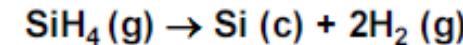
3.1. Chemical deposition methods:

- Chemical Vapor Deposition (CVD)
 - Electrodeposition
 - Thermal oxidation
- A volatile compound of the material to be deposited **chemically reacts with other gases and produces a nonvolatile solid** that deposits atomically on the substrate)
- These processes exploit the creation of solid materials directly from chemical reactions in gas and/or liquid compositions or with the substrate material.
- The solid material is usually not the only product formed by the reaction.
➔ Byproducts can include gases, liquids and even other solids.

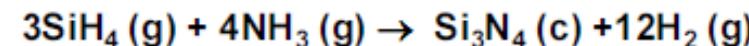
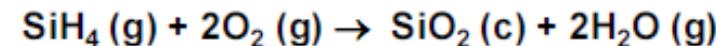
3.1. Thin Film Deposition Methods (cont.)

Typical CVD reactions:

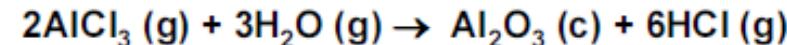
pyrolysis (thermally activated decomposition)



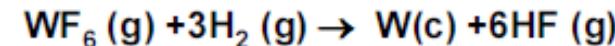
oxidation



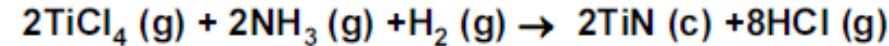
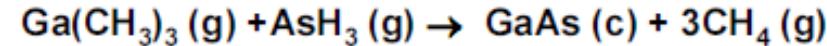
hydrolysis



reduction



exchange



3.1. Thin Film Deposition Methods (cont.)

Typical CVD reactions:

gas supply and security

- damage to persons and equipment must be avoided if reaction educts and products are dangerous
- controllable and stable gas flow control
- minimization of contamination

gas flow characteristics

- homogeneity of the reaction (convection, diffusion)
- forced convection (pressure gradient)
- free convection (temperature gradient, buoyancy)

3.1. Thin Film Deposition Methods (cont.)

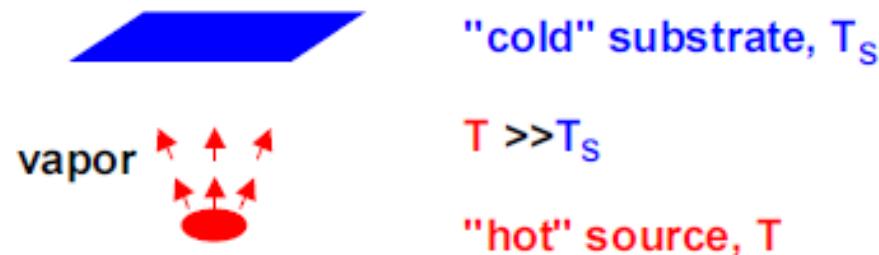
3.1.1 Physical deposition methods:

- ❑ Physical Vapor Deposition (PVD)
 - Evaporation in vacuum condition (mainly $>10^{-6}$ Pa)
- ❑ Sputtering
 - Bombardment by fast, heavy and non-reactive ions, ejection of atoms sputtering by noble gas ions
- ❑ Laser ablation
 - Laser (ballistic) action
- ❑ Spin coating (and spraying)

- Controlled transport of atoms or molecules from a solid source to the substrate thermal or non-thermal, ballistic
 - Material deposited is physically moved on to the substrate
 - No chemical reaction is needed during deposition

3.1.2. 1. Physical Vapor Deposition (PVD)

- all materials have an equilibrium vapor pressure, $p_e(T)$
(T: source temperature)
- at sufficiently high temperature, the gas impingement rate $\Phi = \Phi(p_e)$ can be high enough to cause deposition of material (thin-film growth) on a cold substrate ($T_s \ll T$, T_s : substrate temperature)



- Co-deposition of materials at controlled rate for doping and metal alloys
- Evaporation can be made using electron beam (instead of heat supply)

Method dominant to deposit metals and small molecules!

3.1.2.2. Evaporation of Compounds and Alloys

only very few **compounds** evaporate as molecules

⇒ vapor composition and film stoichiometry do not differ from that of the source

e.g. SiO , B_2O_3 , GeO , SnO , AlN , CaF_2 , MgF_2)

most compounds decompose,

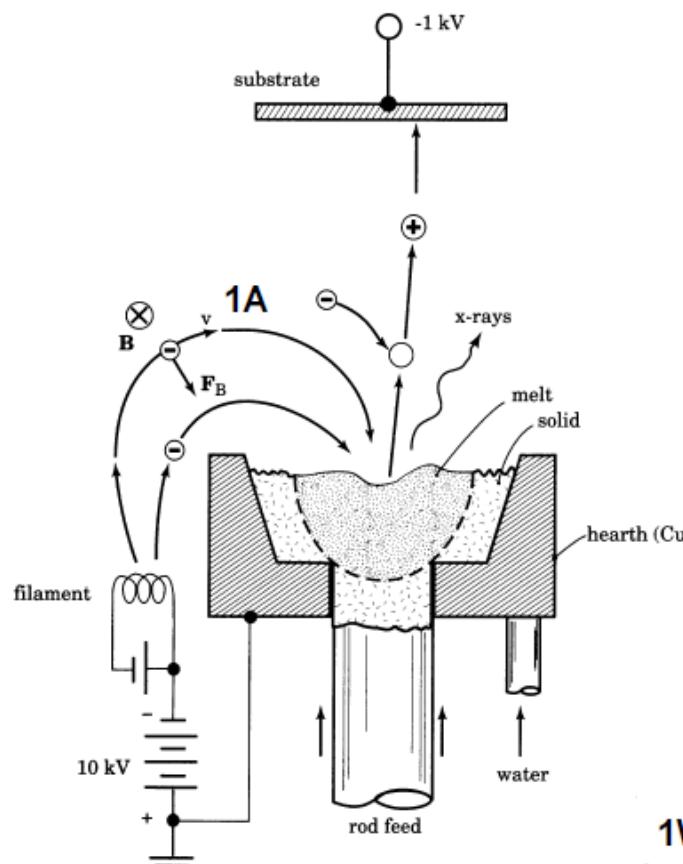
e.g. (1) $\text{Ag}_2\text{Se}(\text{s}) \rightarrow 2\text{Ag}(\text{g}) + \frac{1}{2}\text{Se}_2(\text{g})$
 (2) $\text{SiO}_2(\text{s}) \rightarrow \text{SiO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

⇒ separate sources (1) or O_2 partial pressure (2- reactive evaporation) required

evaporated **metal alloy films** are widely used:

- Al-Cu metallization in integrated circuits, (electromigration, Ch. 11)
 - Fe-Ni magnetic data storage
 - etc.

3.1.2.3. Electron-Beam Evaporation



Smith 8.5

1W/cm^2 for evaporation
 0.1W/cm^2 for kinetic energy of vapor atoms
 10W/cm^2 for radiation heat loss
 kW/cm^2 for heat conduction into the crucible

} power consumption

suitable for almost all evaporants

heated filament: thermionic electron emission

no direct lines of sight filament-evaporant and filament-substrate: no contamination of the film/coating of the filament

electron acceleration (1...10 kV)

electron deflection by magnetic field (Lorentz force)

high power (kW): can evaporate high melting point materials

water cooled crucible: material only melts at the surface, no alloying with crucible etc.

3.1.2.4. Sputtering

to achieve evaporation, binding energy must be supplied

a-thermal/ballistic energy transfer:

bombardment by fast, heavy and non-reactive ions, ejection of atoms

sputtering by noble gas ions

"atomic billard"

ions are extracted from a plasma

typical ion energies: 500eV...10keV

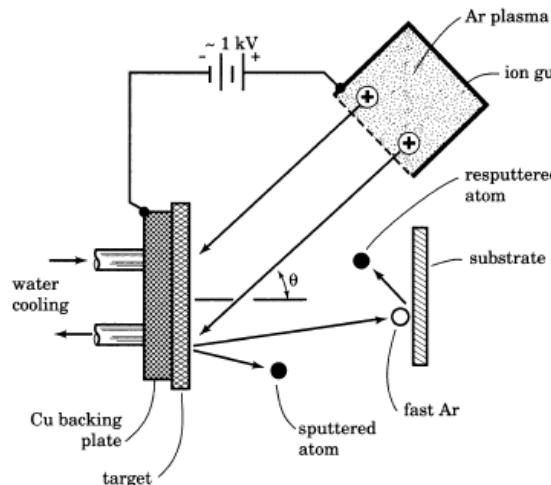
(binding energies: 1-5eV)

plasma control is essential

plasma: gas with significant fractions of ionized molecules and free electrons

target can be far away from plasma or part of a glow discharge

3.1.2.5. Sputtering

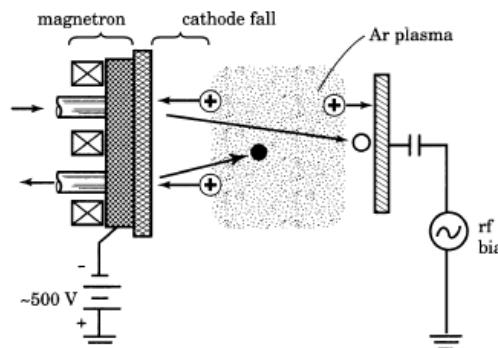


ion beam sputtering

target = evaporant

glow discharge

Smith 8.25



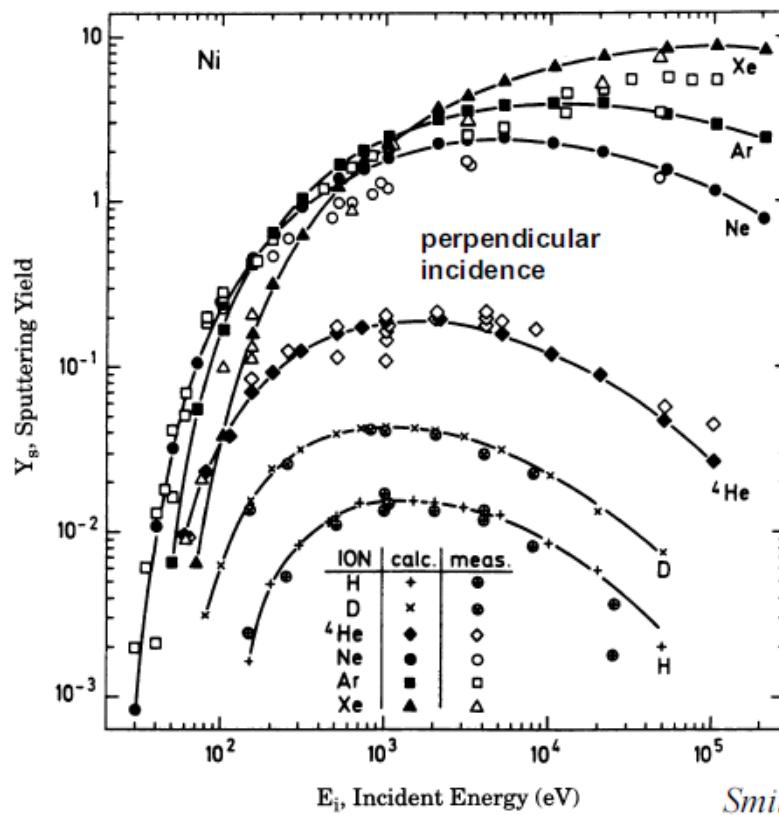
□ To achieve evaporation the binding energy should overcome

- Thermal/ballistic energy transfer
- Bombardment by heavy, fast, non heavy ions → eject atoms deposited
- Thin not as smooth as evaporation
- Can be RF, magnetron sputtering
- **Reactive sputtering possible**

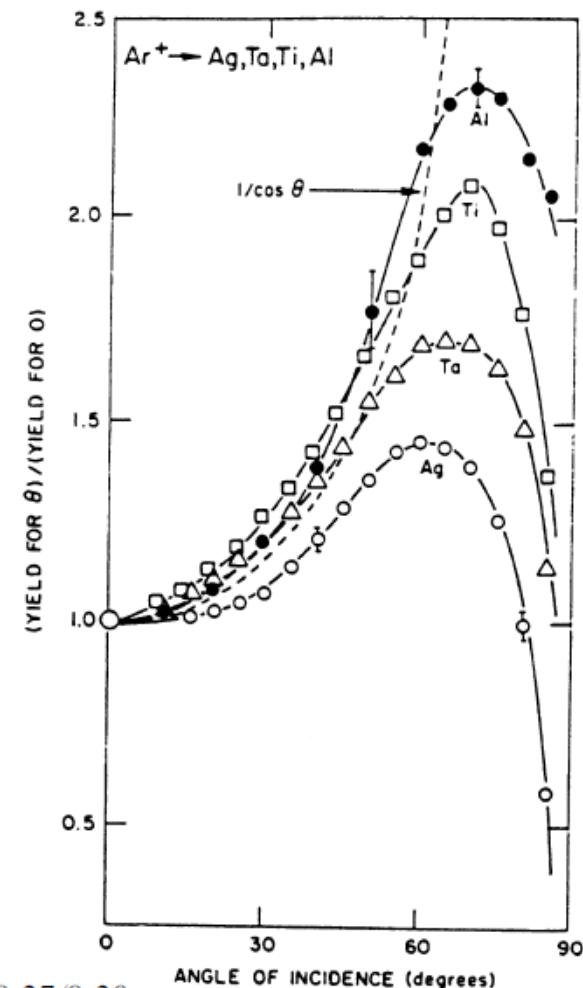
3.1.2.6. Sputtering

sputtering yield:

of atoms ejected per incident ion

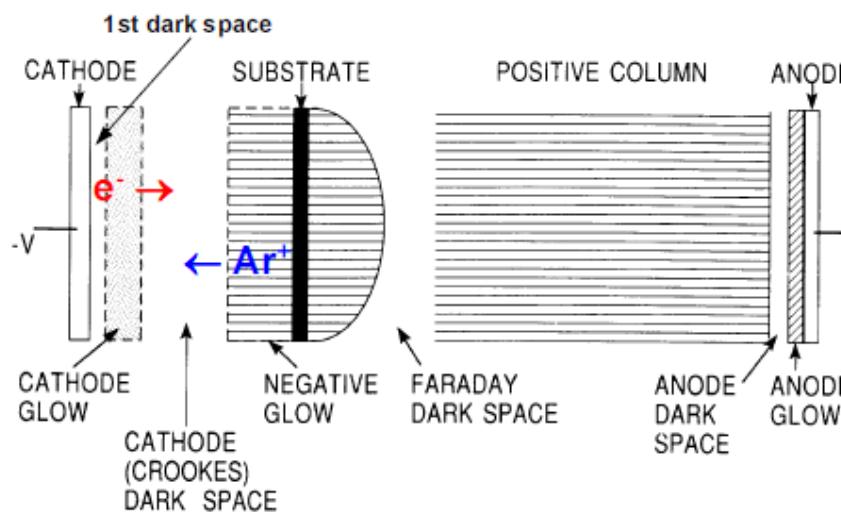


Smith 8.27/8.29



3.1.2. DC Glow Discharge

glow: atoms are excited by inelastic collisions and relax into their ground state by photon emission



discharge in steady state
(ignition process is complicated)

cathode: emission of e^- (thermal, photoeffect, field emission), positive ions from the plasma sputter cathode atoms

1st dark space...negative glow: e^- accelerate towards the anode and ionize gas atoms

negative glow: maximum ionization rate

Crooke's dark space...cathode glow: ions accelerate towards the cathode

substrate is placed inside the negative glow and acts as anode

Ohring 3.14//4.3

other parts of glow discharge do not appear

3.1.3. Sputtering Alloys

main reason for widespread use of sputter techniques:

sputtering allows for the deposition of films
having the same composition as the target source
(after a conditioning phase)

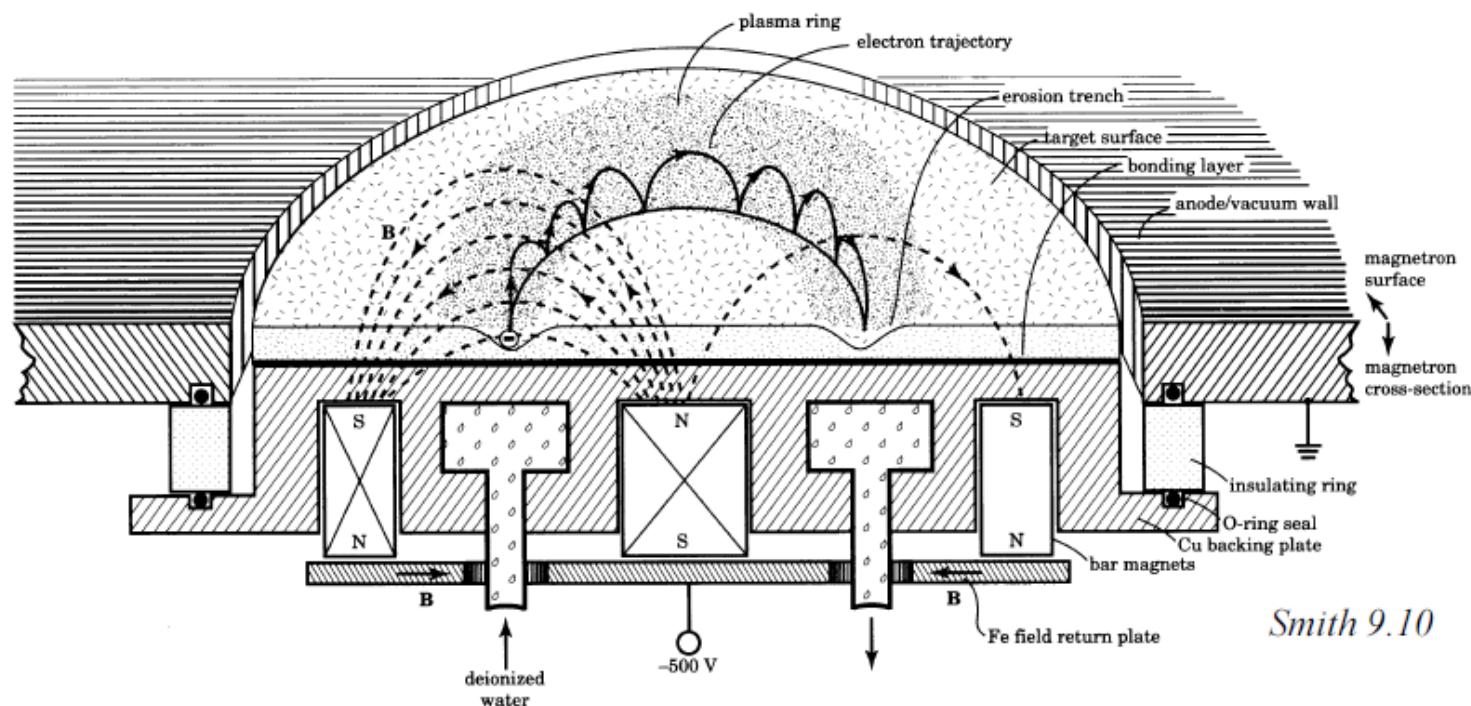
different target atoms have different sputter yields (preferential sputtering)

⇒ surface composition ≠ bulk composition
(negligible solid-state diffusion at room temperature provided)
in contrast, melts homogenize readily

3.1.4. Magnetron Sputtering

additional magnetic field traps electrons longer in the plasma region (Lorentz force)

⇒ higher sputter rate at lower pressure, higher film purity, less diffuse scattering of sputtered atoms, localization of plasma, erosion trench



Smith 9.10

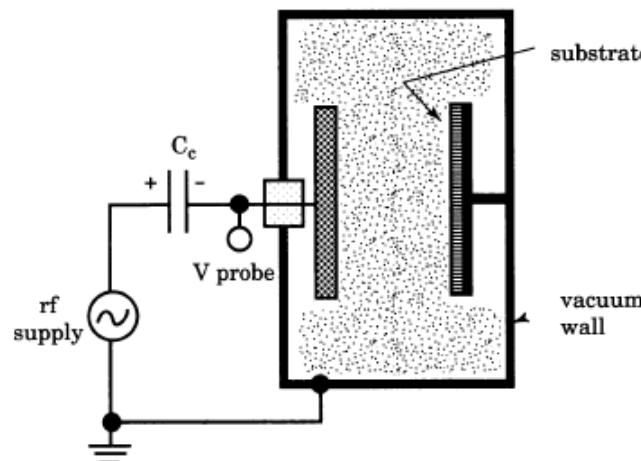
3.1.5. Reactive Sputtering

inert sputter gas is mixed with a reactive gas (N_2 , H_2 , O_2 , S_2 , CH_2 , CH_4 , ...)

these molecules dissociate in the plasma and react with sputtered atoms
to nitrides, hydrides, oxides, sulfides, carbides, etc.

partial pressure ratio Ar/N_2 etc. determines stoichiometry

3.1.6. Radiofrequency (RF) Sputtering



Smith 9.19

comprehensive explanation is difficult (see Smith)

some facts without further explanation:

- during a rf period electrons and ions accelerate towards the electrodes
- ion current \propto electrode area
- electron current is independent of electrode area
- small electrode (target) collects net negative charge
- target develops a negative bias voltage
- capacitance C prevents de-charging and target remains negative
- positive ions hit target only, no sputtering of container walls

3.1.7. Pulsed Laser Deposition (PLD)

e.g.

pulsed excimer laser

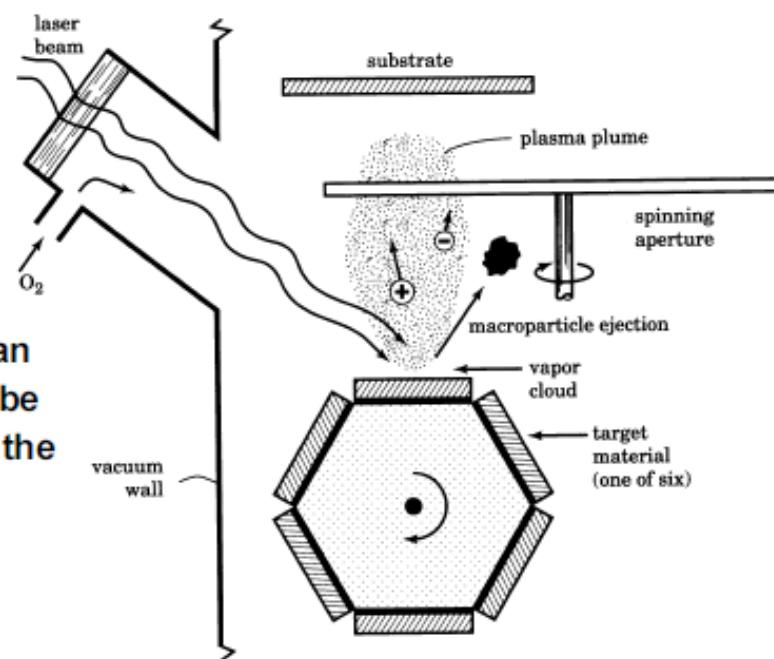
2 J/cm² in 20 ns

$\lambda = 248 \text{ nm}$

power density

10^8 W/cm^2

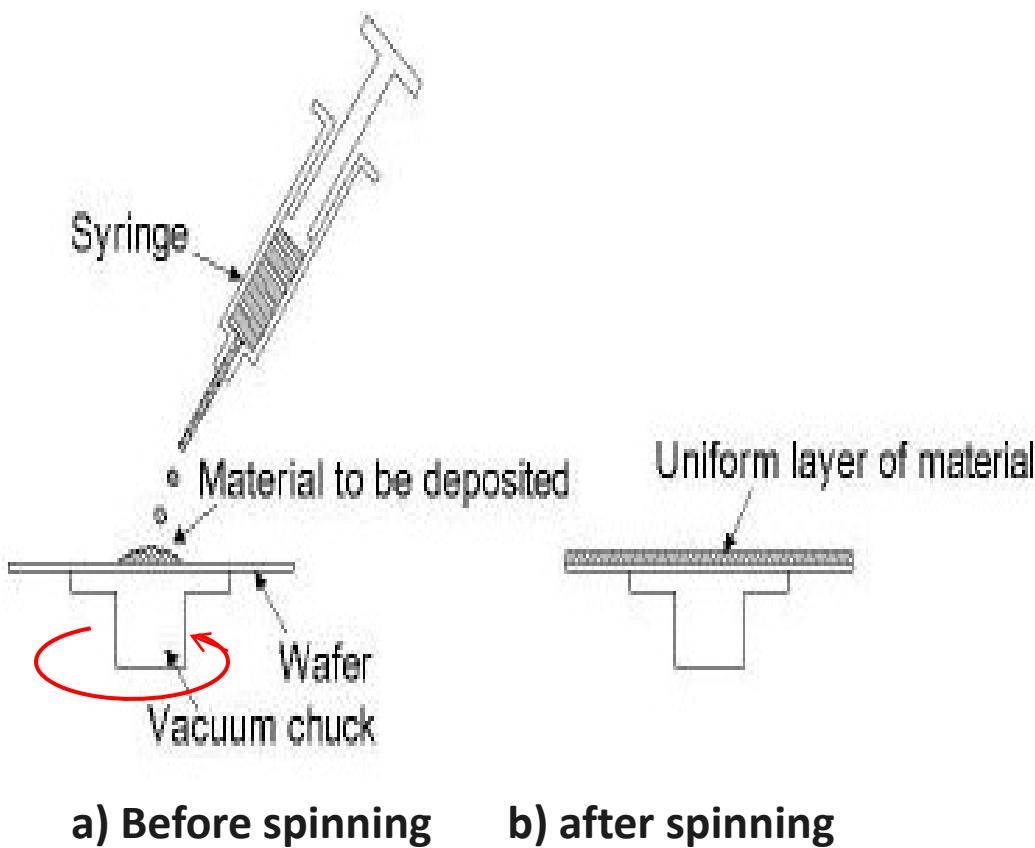
reactive gas can
be added, will be
dissociated in the
plasma



Smith 8.9

- Bond break at a given wavelength of a laser/photon
- Explosive evaporation of the source
- Reactive case possible

3.1.5. Casting (spin-coating)



Process steps (i –iv)

- i. Film to be deposited in solution form
- ii. Solution dropped on substrate
- iii. Spin-coating (typically 4,000 - 8,000 rpm/min) at a defined time (e.g., 1 min)
- iv. Solvent evaporates (heating applied)

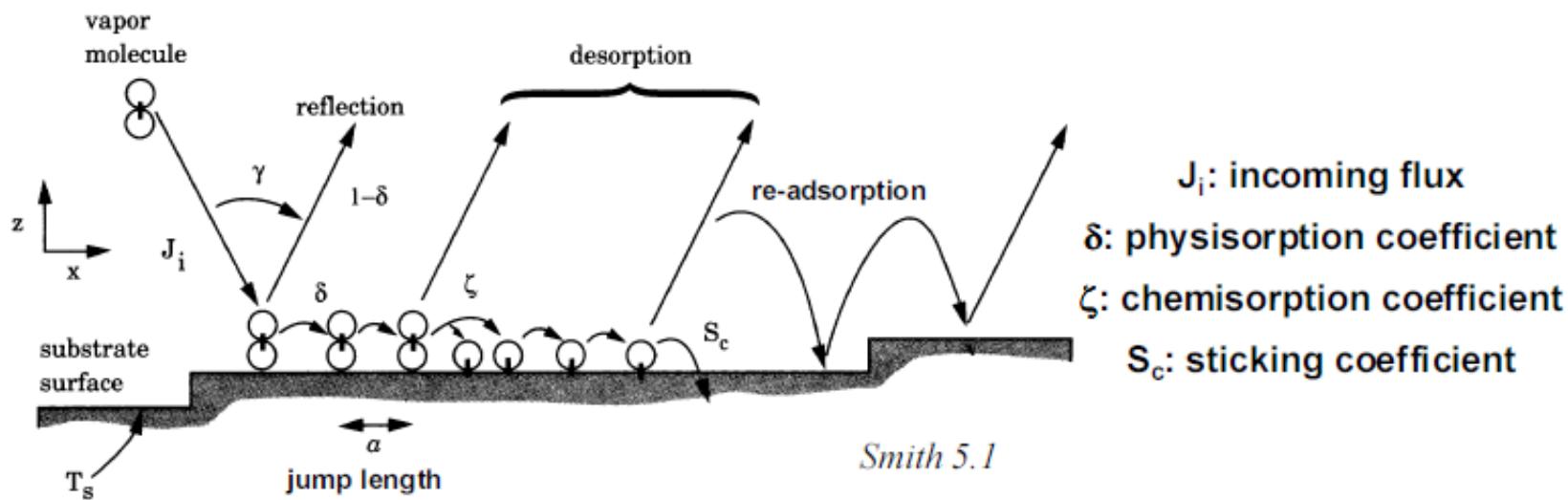
- Film thickness determined by rpm and viscosity
- Film quality determined by solvent and substrate

Dominant method to deposit polymers !

3.2. Thin Film Growth

Basic steps of thin film growth:

1. adsorption (**physisorption**) of atoms/molecules
2. surface diffusion
3. formation of molecule-molecule and substrate-molecule bondings (**chemisorption**)
4. nucleation: aggregation of single atoms/molecules
5. structure and microstructure formation (amorphous- polycrystalline - single-crystalline, defects, roughness, etc.)
6. changes within the bulk of the film, e.g. diffusion, grain growth etc.



3.2. Thin Film Growth

ζ : fraction of molecules that dissociate and form chemical bondings

S_c : fraction of molecules that stay adsorbed on the experimental time-scale

in case of solid-vapor equilibrium: $S_c \rightarrow 0$ and $\zeta > 0$

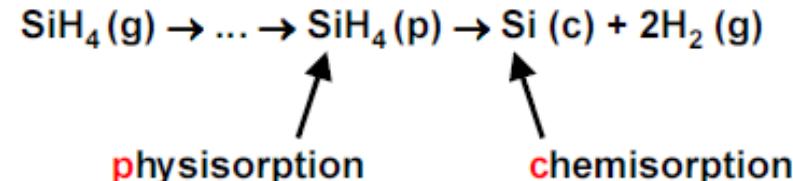
3.2.1. Adsorption

Molecule arrives from the vapor phase:

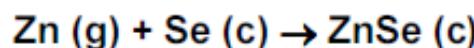
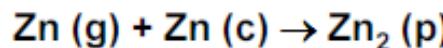
- attractive force at distance of a few atomic diameters from the substrate
- non-polar molecules: van-der-Waals forces
- polar molecules: stronger forces
- transfer of kinetic energy to the substrate, adsorption

3.2.1. Adsorption

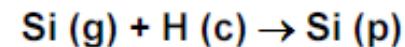
precursor adsorption: weak bonding as a precursor to strong bonding



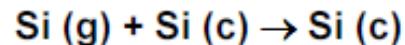
alloy films: 2 components in the vapor phase



H-passivated surface:



chemisorption only on non-passivated sites



stronger bonding at surface steps

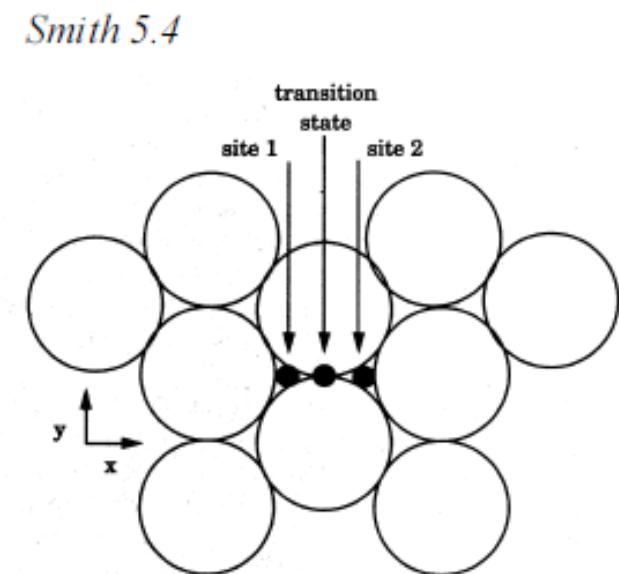
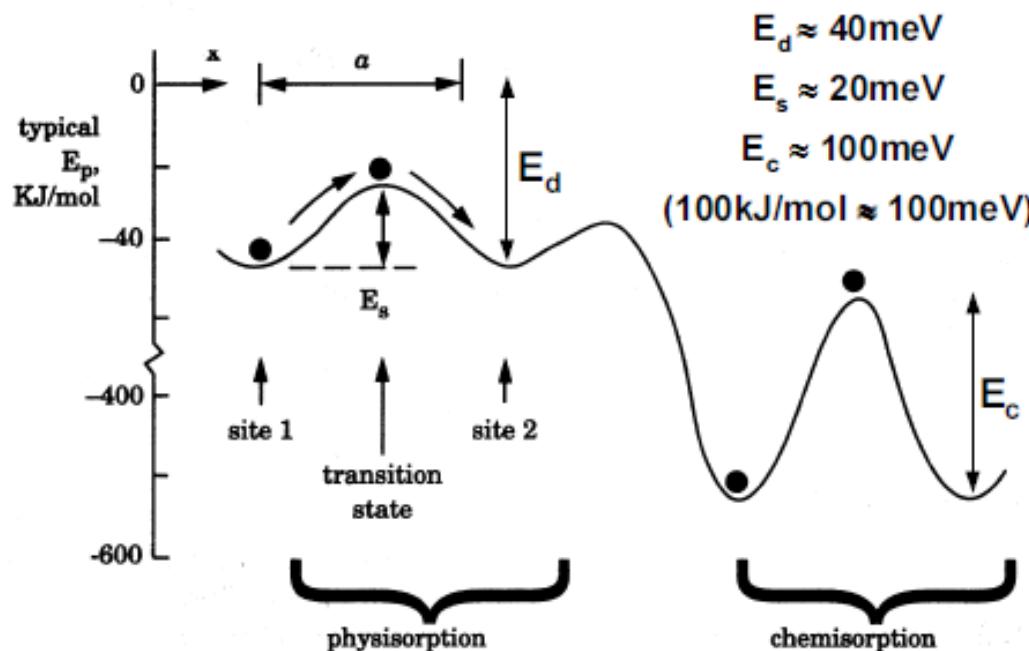
metal atoms on non-metallic substrates:

metal-metal bondings stronger than metal-substrate bondings

3.2.2. Surface Diffusion

extremely important for thin film formation

- allows adsorbed species to form clusters (homogeneous nucleation)
- allows adsorbed species to find heterogeneous nucleation sites (steps etc.)
- adsorbed atoms move in potential energy "landscape" generated by substrate or thin film surface atoms: **diffusion, hopping**



3.2..2. Surface Diffusion

$E_s < E_d, E_c$: only partial breaking of bonds

molecular hopping rate: $k_s = v_{0s} \cdot \exp\left(\frac{-E_s}{R \cdot T_s}\right)$ (influence of substrate temperature, T_s)
 $(v_{0s} \approx 10^{13} \dots 10^{16} \text{ Hz: attempt frequency})$

diffusion: random walk, not directed,

equal hopping probabilities for forward and backward motion

diffusion length, Λ : $\Lambda = r \cdot \sqrt{N_0} \approx a \cdot \sqrt{N_0} = a \cdot \sqrt{k_s \cdot t}$

(r: rms change in distance per hopping event, N_0 : number of hops

a: lattice constant, t: diffusion time)

$$\left. \begin{array}{l} v_{0s} = 10^{13} \text{ s}^{-1} \\ E_s = 20 \text{ meV} \\ E_s = 200 \text{ meV} \\ T = 1000 \text{ K} \\ t = 1 \text{ s} \\ a = 0.3 \text{ nm} \end{array} \right\} \begin{array}{l} \Lambda = 300 \mu\text{m} \quad (\text{physisorbed}) \\ \Lambda = 5 \text{ nm} \quad (\text{chemisorbed}) \end{array}$$

$E_p = 0$: enthalpy in the vapor phase, no kinetic energy
 $\Delta_f H$: enthalpy of formation of Y_2
 E_d : desorption barrier (physisorbed)
 E_r : reaction barrier ($p \rightarrow c$)
 E_a : reaction barrier vapor $\rightarrow (c)$
 E_c : enthalpy in chemisorbed state

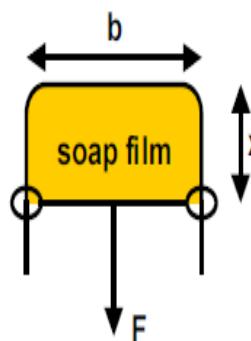
strong influence of bonding conditions!

3.2.3. Nucleation

Surface energy per unit area, γ : energy per unit area needed to create or increase a surface

(non-constant number of surface atoms) unit: Jm^{-2}

Surface stress: force per unit length needed to increase a surface or work performed in enlarging a surface, (constant number of surface atoms, solids only) unit: Nm^{-1} , includes strain contribution



$$\Delta W = 2 \cdot \gamma \cdot \Delta A = 2 \cdot \gamma \cdot \Delta x \cdot b$$

$$\frac{F}{b} = \frac{\Delta W}{\Delta x \cdot b} = 2 \cdot \gamma$$

force acts tangentially
tends to decrease surface area

surface energy exists because bonds are broken to create/increase the surface
(surface stress: bonds are elastically strained)

strong driving force: minimization of surface energy (spherical soap bubble)

fundamental to thin film growth:

surface energy can be minimized by surface diffusion

chemical composition
crystallographic orientation
atomic reconstruction

$$\gamma \cdot A \rightarrow \min$$

surface topography

3.2.3. Nucleation

thin film nucleation: interplay of 3 surface energies per unit area

γ_s : substrate free surface

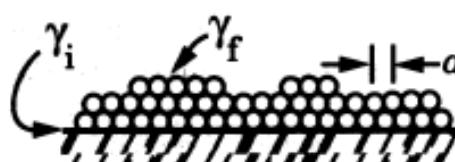
γ_f : film free surface

$$\sum \gamma_j A_j \rightarrow \min$$

γ_i : substrate/film interface

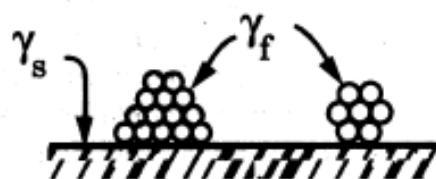
relative magnitudes of these quantities strongly influence nucleation

(provided that nucleation is **not kinetically limited** and can approach equilibrium)



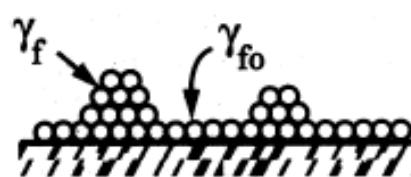
Smith 5.8 or Ohring 5.2//7.2

$\gamma_i + \gamma_f < \gamma_s$ layer-by-layer growth (Frank-van der Merwe)



island growth (Volmer-Weber)

minimization of total surface energy:
low- γ facets of islands



few ML layer-by-layer, then crossover to island growth
(not only a γ - effect, see Ch. 7 - Epitaxy) (Stranski-Krastanov)

3.2.3. Nucleation

3D- nucleation (islands) is usually undesirable

mitigation strategy: change one or more of the γ_j such that $\gamma_i + \gamma_f < \gamma_s$

- γ_i is lower for materials with same type of bonding (metallic/covalent/ionic)
- γ_i is lower in case of chemical reactivity

Au on glass 3D- nucleation

Cr on glass 2D- nucleation O-Si \rightarrow Si-Cr/O-Cr bondings

Au on Cr 2D- nucleation, strong metallic bonding

Au / Cr / glass layer-by-layer, wetting
Cr is an intermediate 'glue' layer; 3-10nm sufficient
(continuous layer)

Ti: similar good bonding material

3.2.3. Nucleation

alternative methods to prevent island growth:

ion beam irradiation of the substrate surface

(breaks bonds, enhances reactivity, destroys islands

i.e. disturbs equilibrium - ion beam irradiation is often very effective)

apply a surfactant

reduces γ_f more than γ_s

(water on glass: drops - soapy water on glass: layers)

$$\gamma_i + \gamma_f > \gamma_s$$



$$\gamma_i + \gamma'_f < \gamma'_s$$

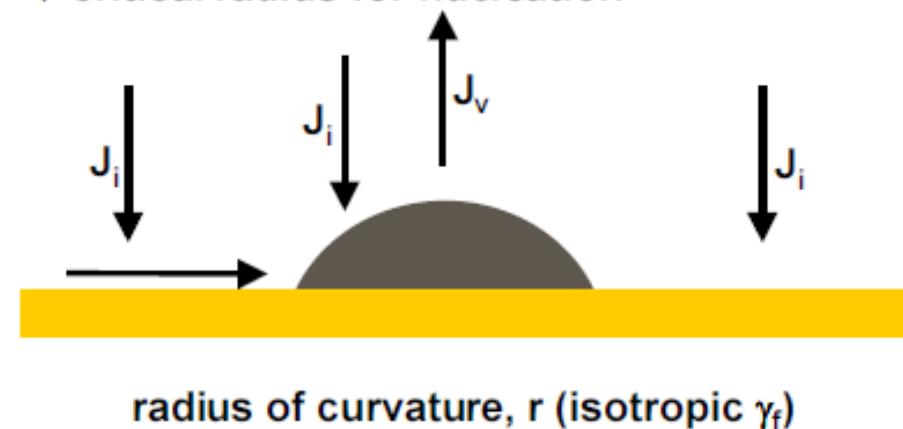
3.2.3. Nucleation

heterogeneous nucleation

- takes place at "active" surface sites (steps, defects, contamination); low local γ_i
- atoms reach these sites by diffusion or directly from the vapor phase

homogeneous nucleation

- at random positions
- if sufficient high number of atoms meet through diffusion to form a stable nucleus
- surface energy \rightarrow critical radius for nucleation



Similar to Smith 5.3

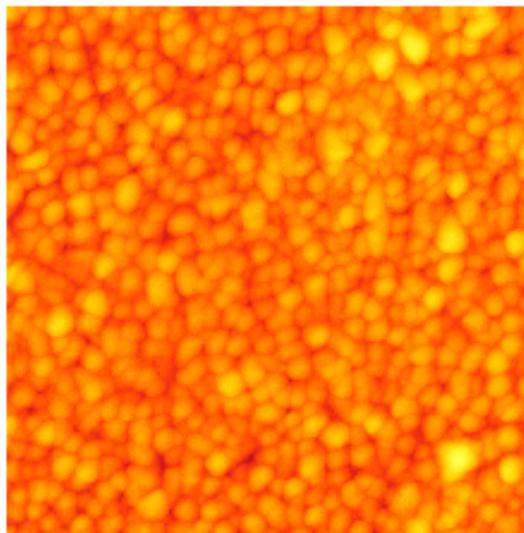
3.2.3. Nucleation

high deposition rate & low substrate temperature:

⇒ fine- grained polycrystalline or amorphous film, coalescence at small average thickness, relatively smooth

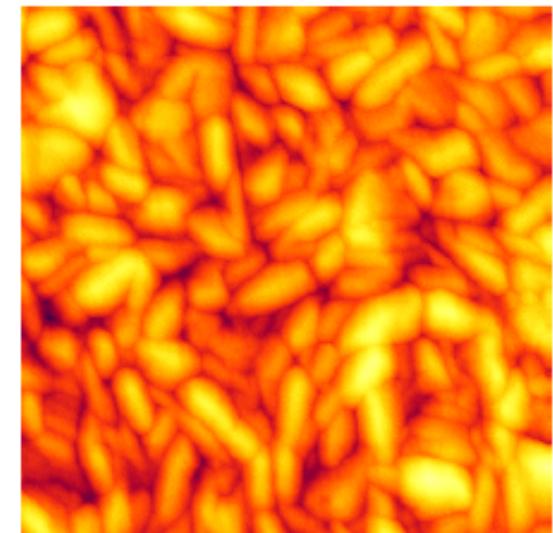
low deposition rate & high substrate temperature:

⇒ coarse- grained polycrystalline (or single- crystalline film), coalescence at high average thickness, relatively rough

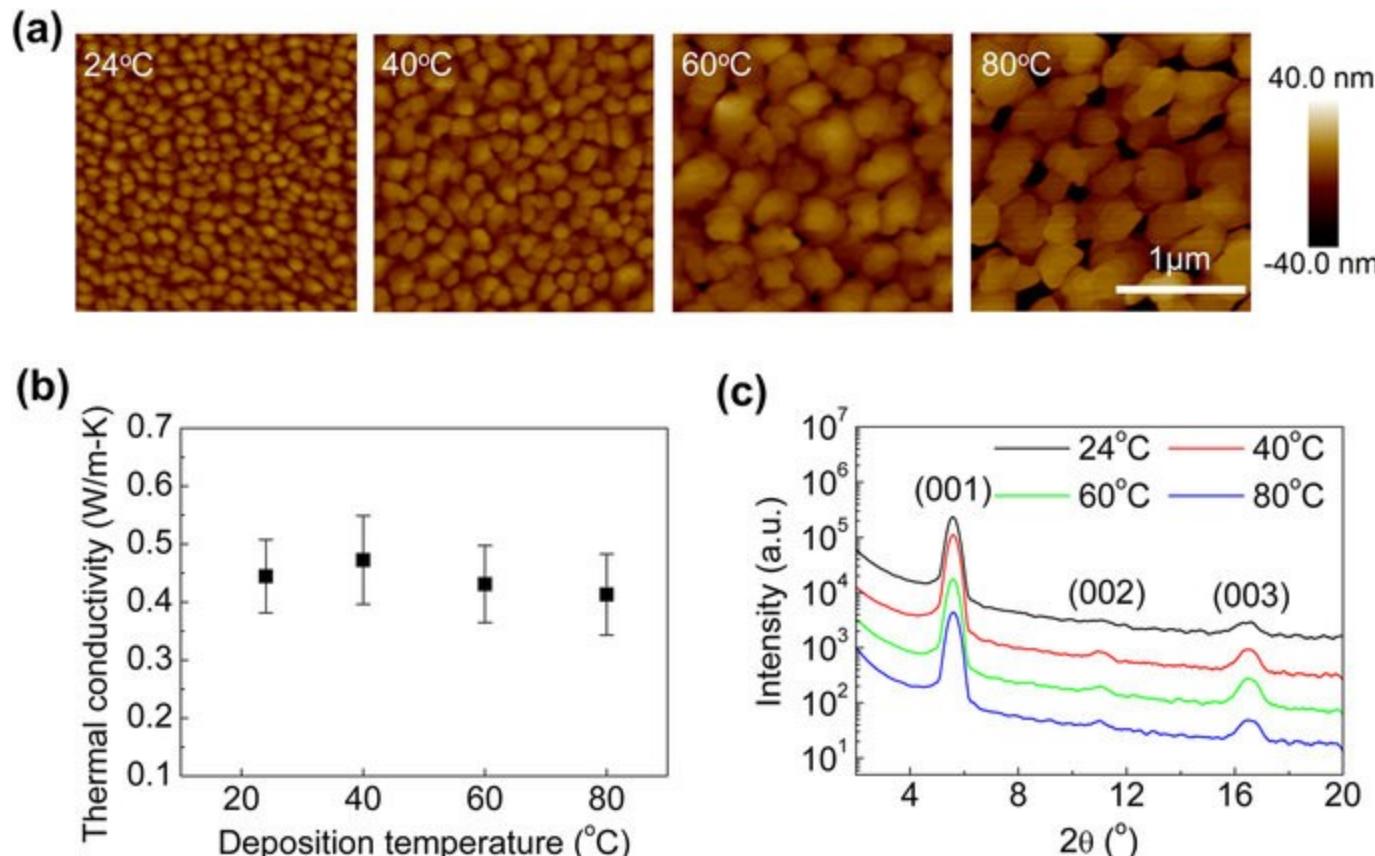


Cr_2N films (U. Geyer),
 $t_f = 500\text{nm}$
STM - scansize: 500nm

← $T=300\text{K}, \Delta z=10\text{nm}$
 $T=550\text{K}, \Delta z=30\text{nm} \rightarrow$

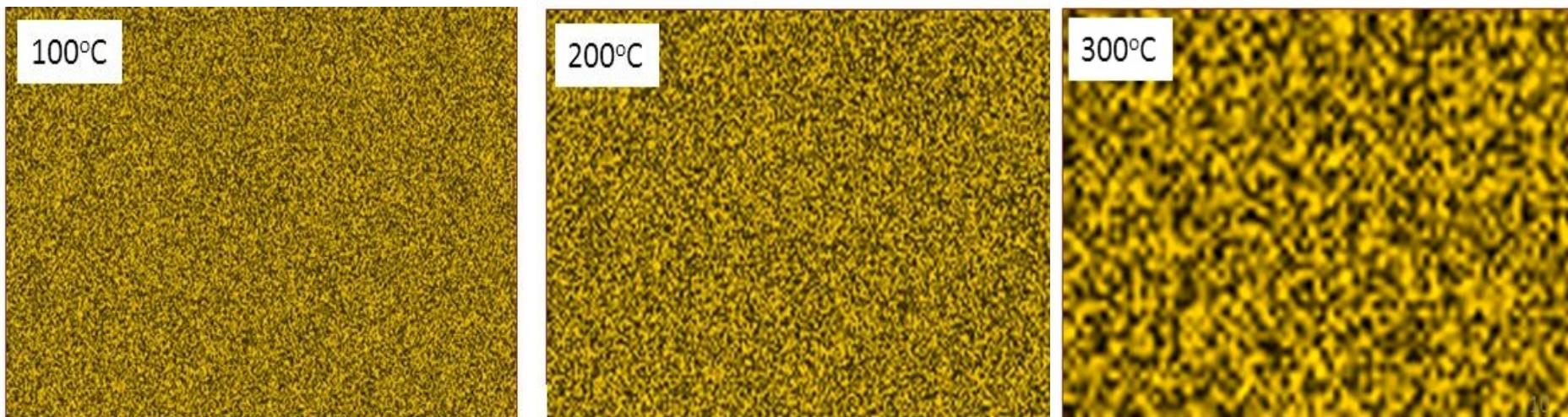


3.2.4. Film Morphology Factors: Deposition Temperature



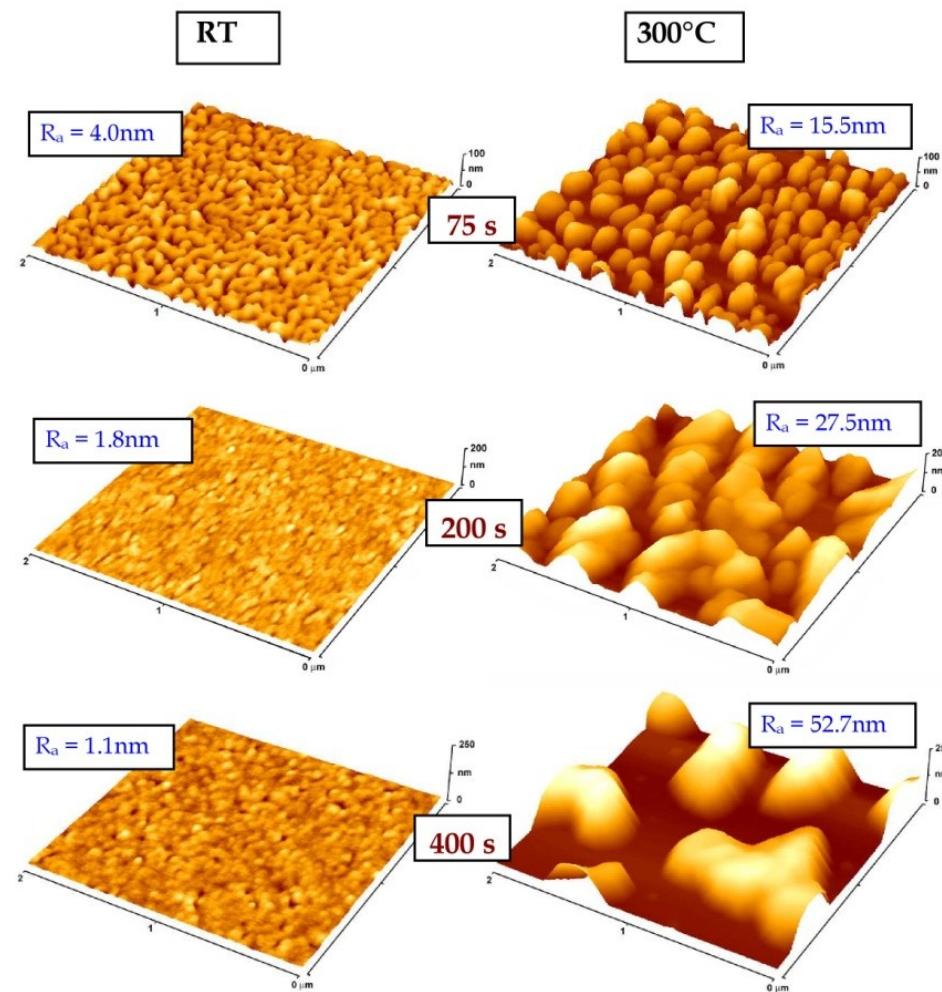
(a) AFM images of surface morphology of DNTT thin films at different deposition (evaporation) temperatures, 24 °C, 40 °C, 60 °C and 80 °C. (b) Thermal conductivity of samples at different deposition temperature, and C) XRD characterization of the smaples.

3.2.4. Film Morphology Factors: Substrate Temperature



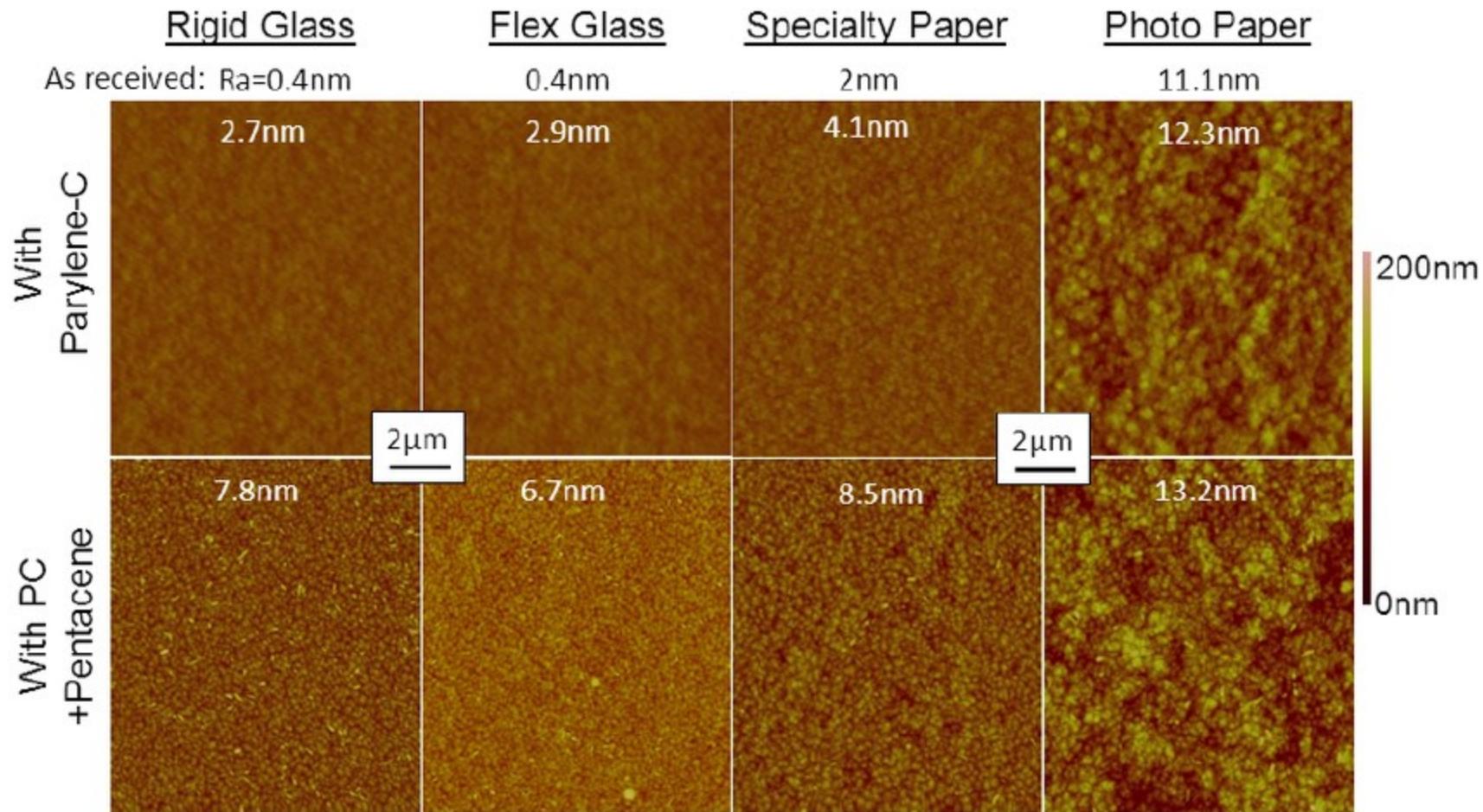
100 Å thick gold films deposited at 100, 200 and 300 °C by vacuum evaporation

3.2.4. Film Morphology Factors: Deposition Time

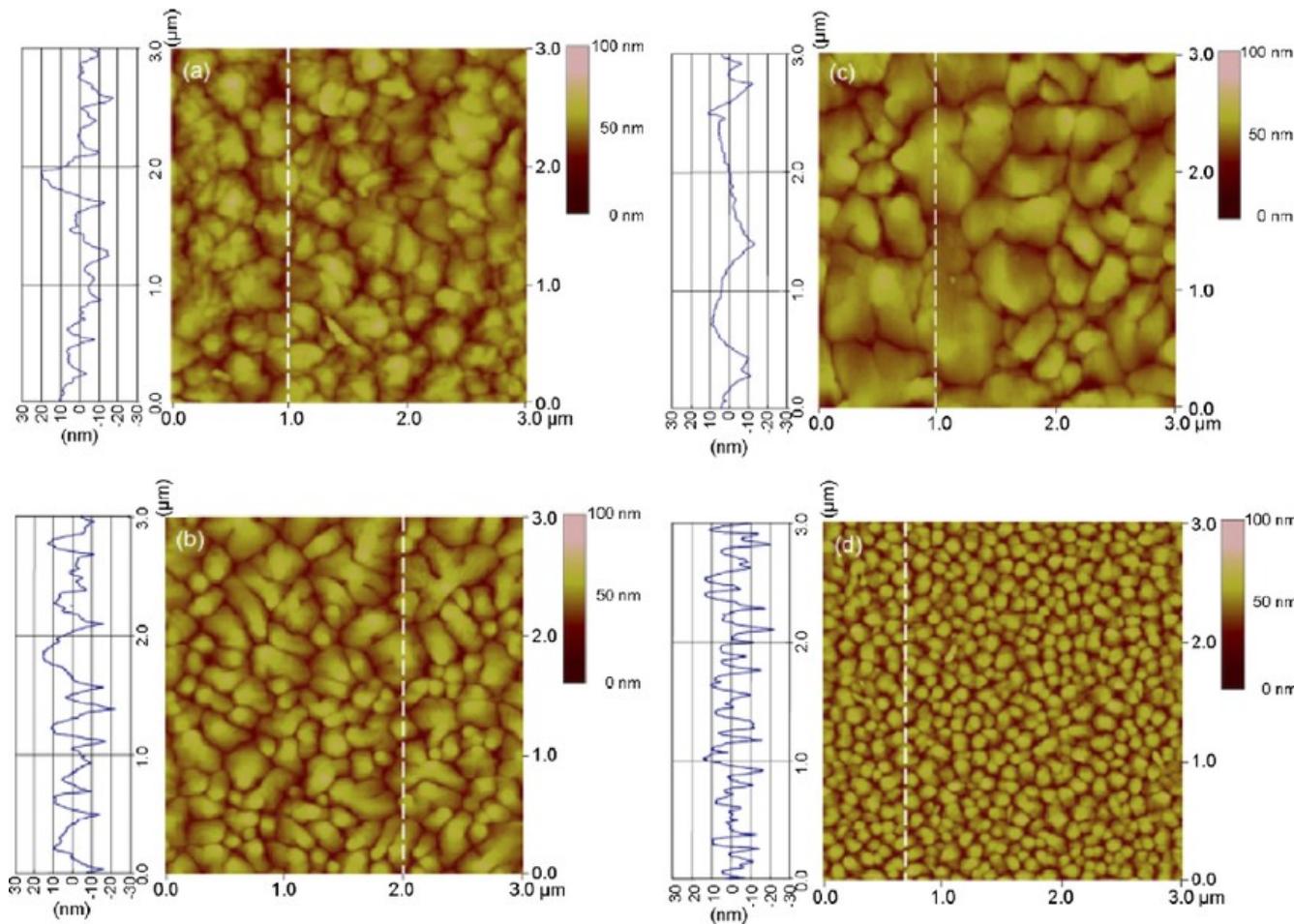


AFM scans of gold structures sputtered for 75, 200 and 400 s on glass

3.2.4. Film Morphology Factors: Substrate Type



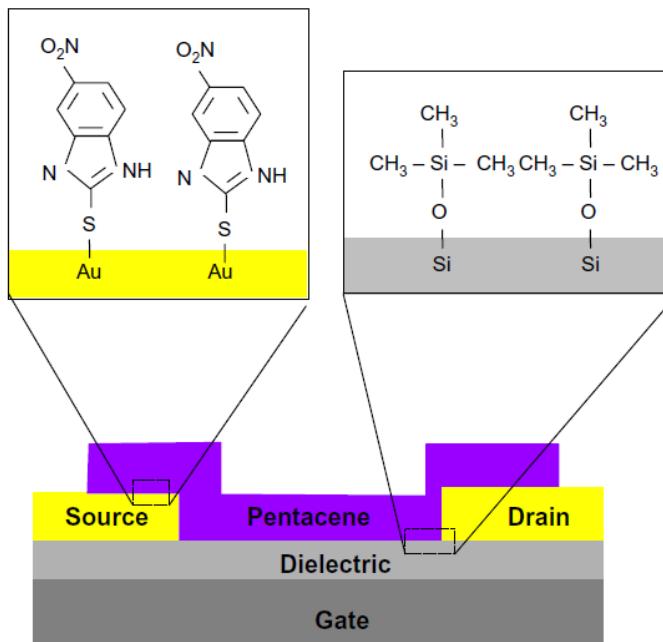
3.2.4. Film Morphology Factors: Rate of deposition/evaporation rate



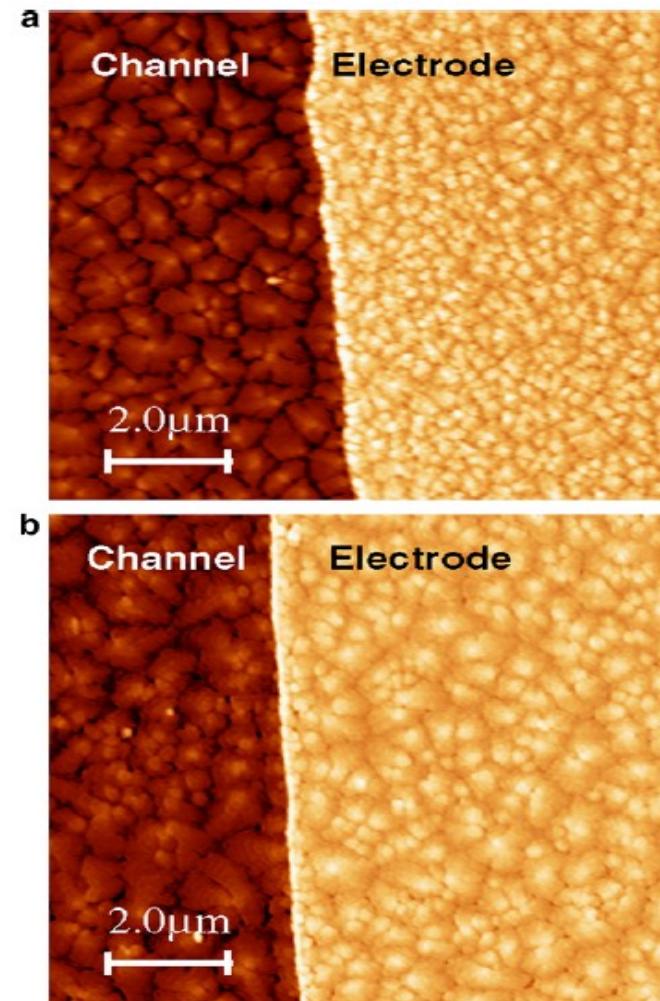
T. Itoh et al., *Applied Surface Science*, 253, Issue 14, 6196–6202 (2007).

AFM images of pentacene surface of different evaporation rate, (a) 0.13 nm/s (b) 0.08 nm/s and (c) 0.02 nm/s on glass substrate. AFM image of Pentacene on Au is presented

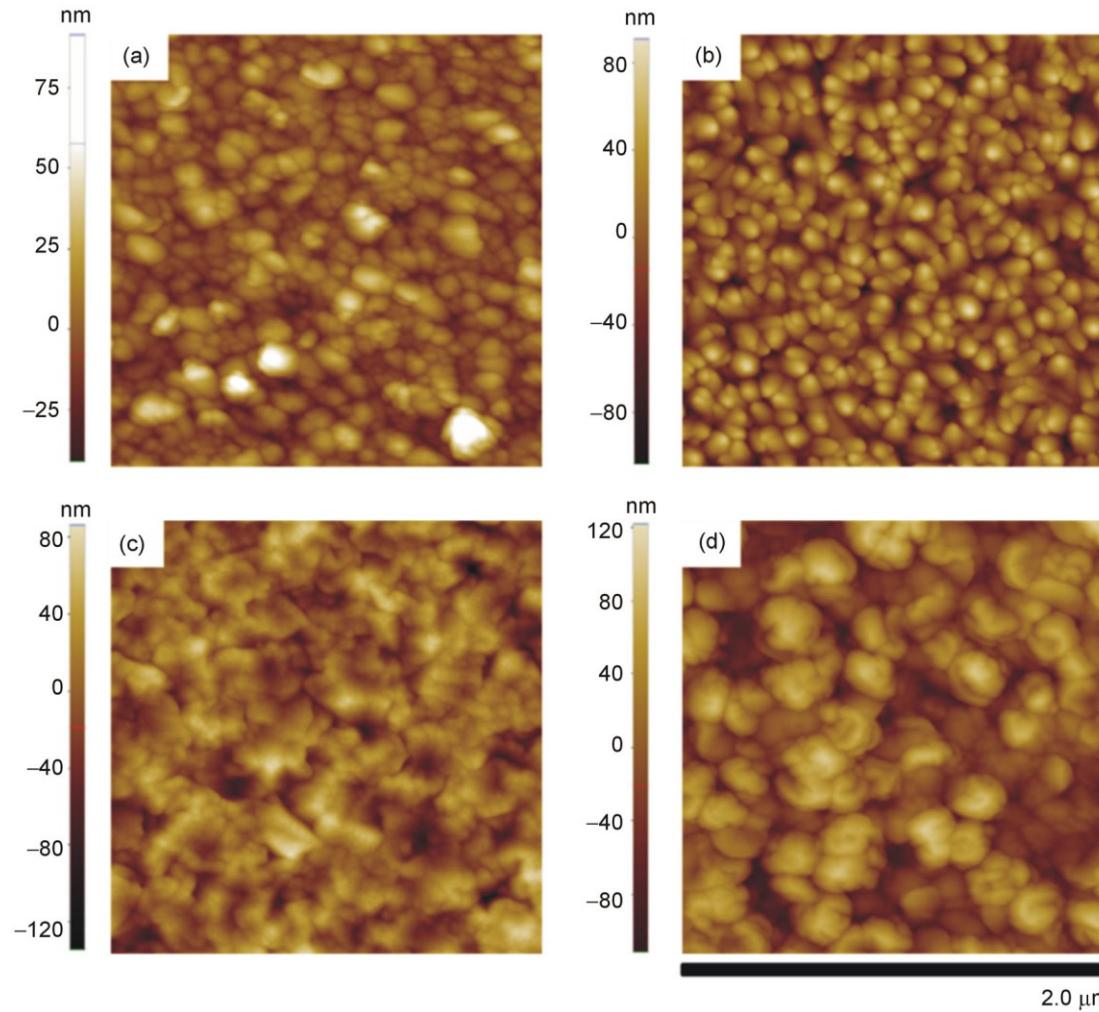
3.2.4. Film Morphology Factors: Substrate Treatment



The bottom drain and source contacts (gold) were treated by 2-Mercapto-5-nitrobenzimidazole (MNB) and the gate dielectric (silicon oxide) by hexamethyldisilazane self-assembled monolayer (SAM) prior to the deposition of the pentacene film.



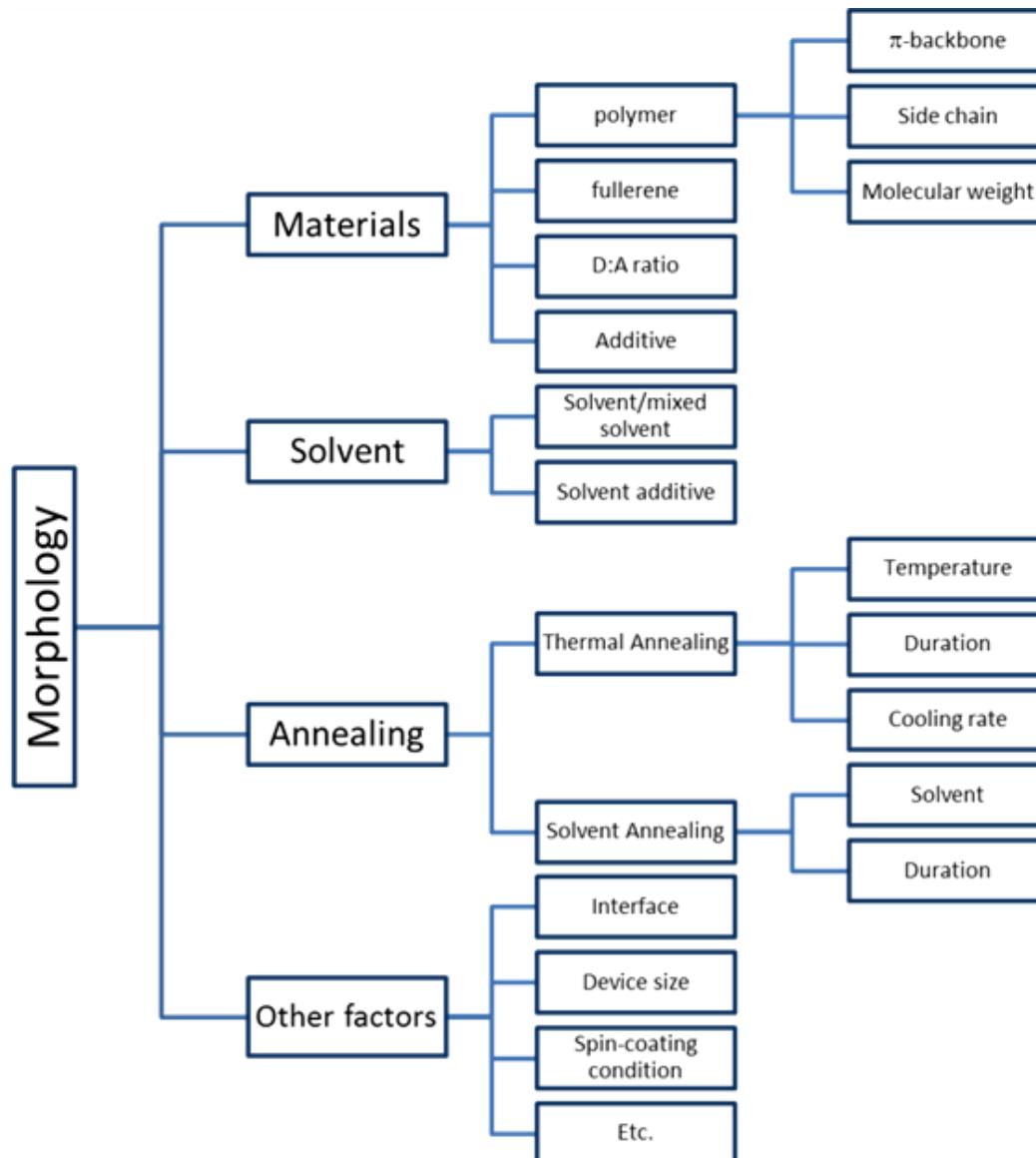
3.2.4. Film Morphology Factors: Doping and Impurities



Erica Pereira da Silva,
et al., *Materials
Sciences and
Applications*, 4, 7
(2013).

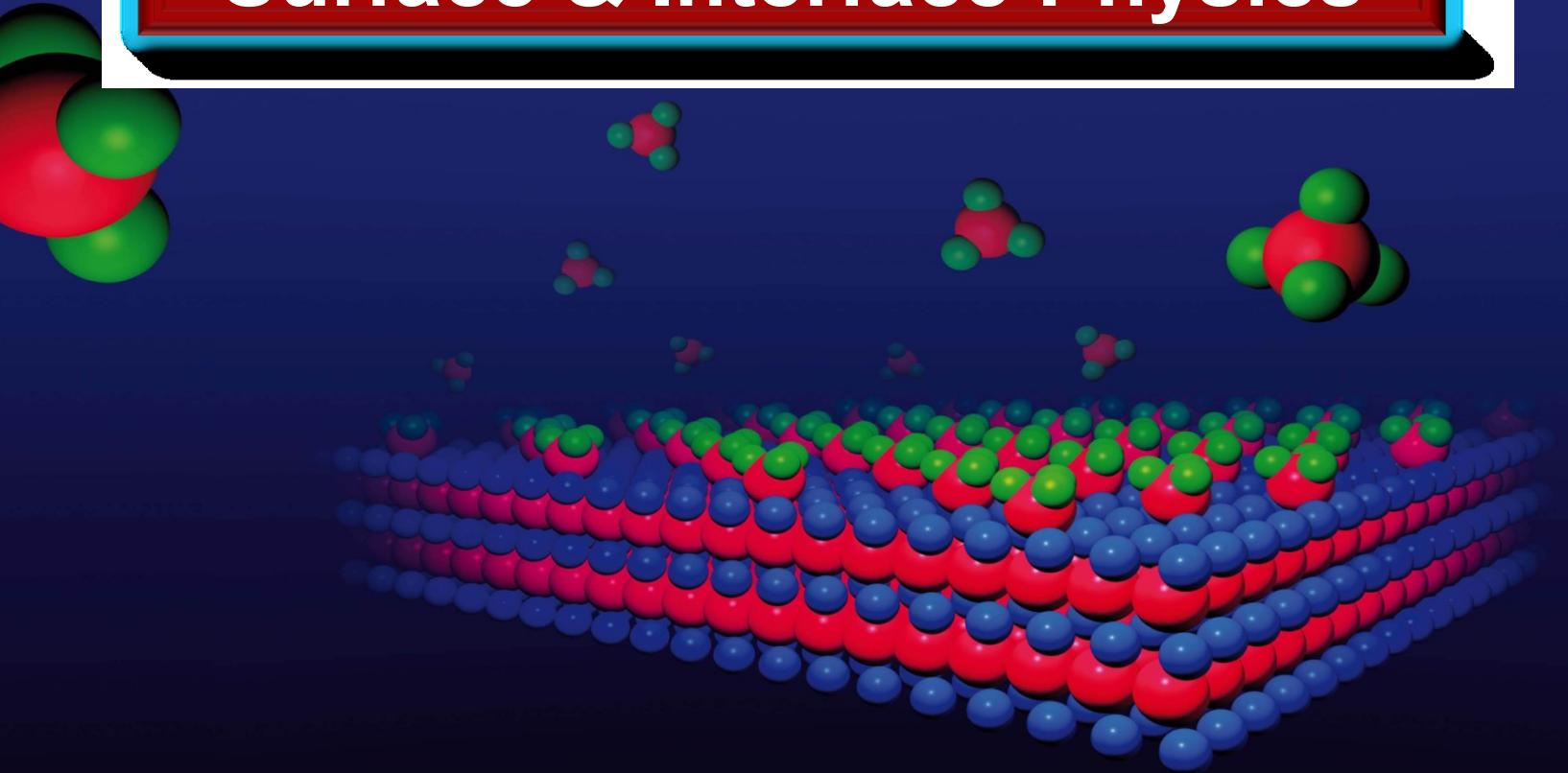
AFM images ($2 \mu\text{m} \times 2 \mu\text{m}$) of ZnO and ZnO:Al films deposited onto glass and silicon substrates.
(a) ZnO (glass), (b) ZnO:Al (glass), (c) ZnO (Si) and (d) ZnO:Al (Si).

3.2.4. Film Morphology Factors: Materials, Solvent, Annealing



Summary of parameters that influence the morphology of the bulk heterojunction solar cells (BHJ) active thin film.

Surface & Interface Physics



4. Surface Energy Components & Implications

Amare B. Belay

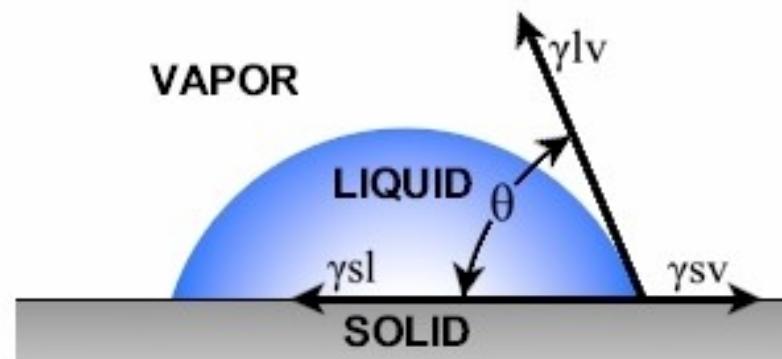
4. Surface Energy Components & Implications

- 4.1. Contact angle and wetting
- 4.2. Surface tension
- 4.3. Wetting and dewetting
- 4.4. Work of adhesion
- 4.5. Surface treatments and surface energy

Contact Angle

Young's Equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv} \cos\theta$$

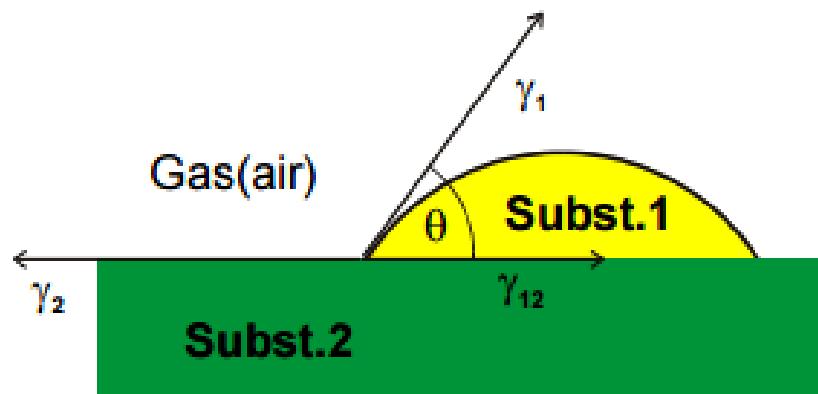


γ^{sl} is the solid/liquid interfacial free energy

γ^{sv} is the solid surface free energy

γ^{lv} is the liquid surface free energy

Young's equation



When the liquid does not spread, a drop has a contact angle on the surface. The balance between the forces on the surface gives:

$$\text{Youngs Equation: } \gamma_2 = \gamma_{12} + \gamma_1 \cos \theta$$

NB: Only valid in “dry wetting”

In cases with “wet wetting”, the surface pressure of the liquid vapor on the solid is substantial. In these cases, γ_2 becomes lowered by the surface vapor pressure π .

$$\text{So that: } \gamma_2 = \pi + \gamma_{12} + \gamma_1 \cos \theta$$

Expressed by the work of adhesion we can write:

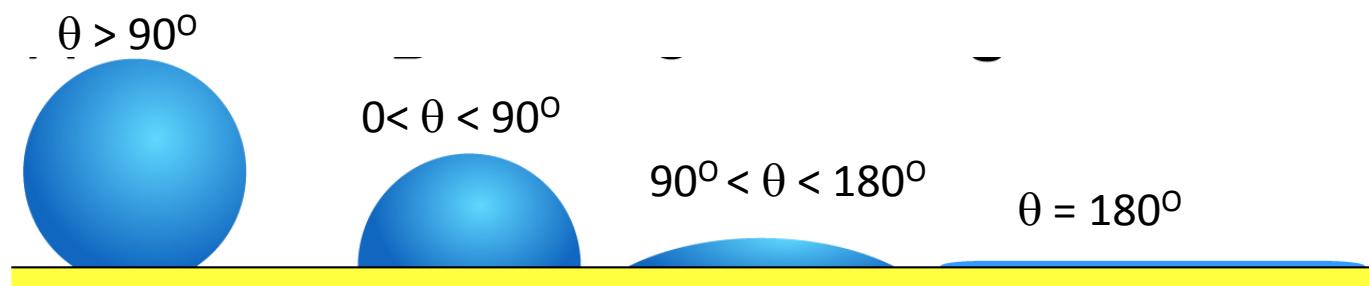
$$W^a = \gamma_1 + \gamma_2 - \gamma_{12} = \gamma_1 + \gamma_1 \cos \theta = \gamma_1(1+\cos \theta) \quad \text{This is the Young - Dupree equation}$$

Factors Affecting Contact Angle

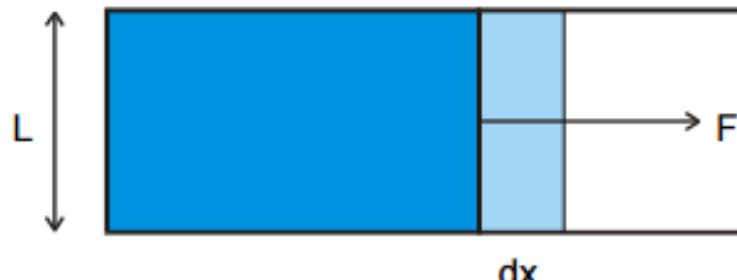
- Surface tension
- Surface energy of solid surface
- Interaction forces between liquid and molecules
- Surface roughness
- Temperature of liquid

Contact Angle Vs. Interactions

Contact angle	Degree of wetting	Strength of:	
		Solid/liquid interactions	Liquid/liquid interactions
$\theta = 0$	Perfect wetting	strong	weak
$0 < \theta < 90^\circ$	high wettability	strong	strong
		weak	weak
$90^\circ \leq \theta < 180^\circ$	low wettability	weak	strong
$\theta = 180^\circ$	perfectly non-wetting	weak	strong



Surface tension and surface energy



Surface tension form force:

The force, F , involved in stretching a film is: $F = \gamma L$ γ = surface tension (constant)

This means: $\gamma = F/L$ i.e. force/unit length Units: N/m or mN/m (= dyn/cm in c.g.s units)

Surface energy from work:

The work, dW , involved in increasing the surface by a length dx is: $dW = dG = \gamma L dx = \gamma dA$

This means: $\gamma = dG/dA$ i.e. free energy/unit area Units: $J/m^2 = N/m$

Surface tension and surface energy are interchangeable definitions with the same units

Surface energy, or interface energy, quantifies the disruption of intermolecular bonds that occur when a surface is created

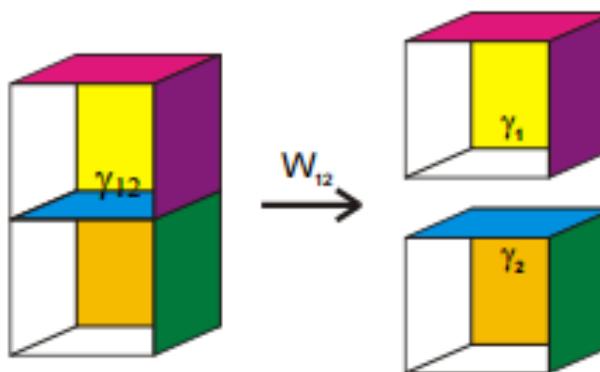
Typical Surface Energies

Material	Surface Energy J.m ⁻²
KCl	0.11
Zn	0.11
LiF	0.34
Mica (in Air)	0.38
Mica (in vacuum)	5.0
CaF ₂	0.45
NaCl	0.50
Pb	0.76
MgO	1.15
Si	1.24
Glass	4.4
Al ₂ O ₃ (Sapphire)	6->32
Al ₂ O ₃ (Polycrystalline)	20->40
Limestone	24.
SiC	32.
C (Diamond)	5.24
C (Graphite)	68.
Granite	200.
Fe (Cast Iron)	1520.

Since brittle fracture creates new surfaces, the surface energy varies inversely with the tendency to brittle failure.

Work of adhesion and work of cohesion

Work of adhesion

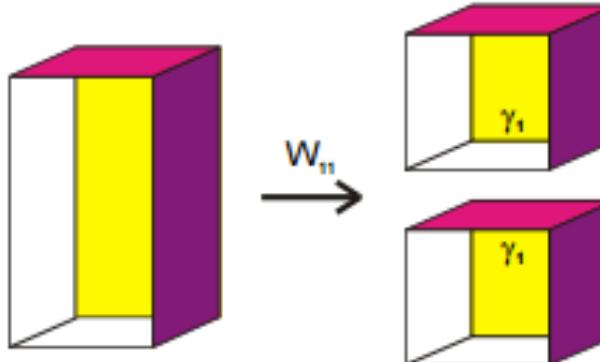


The **work of adhesion** between 2 (incompatible) substances is:

$$W^a = W_{12} = \gamma_1 + \gamma_2 - \gamma_{12}$$

or: $\gamma_{12} = \gamma_1 + \gamma_2 - W^a$

Work of cohesion



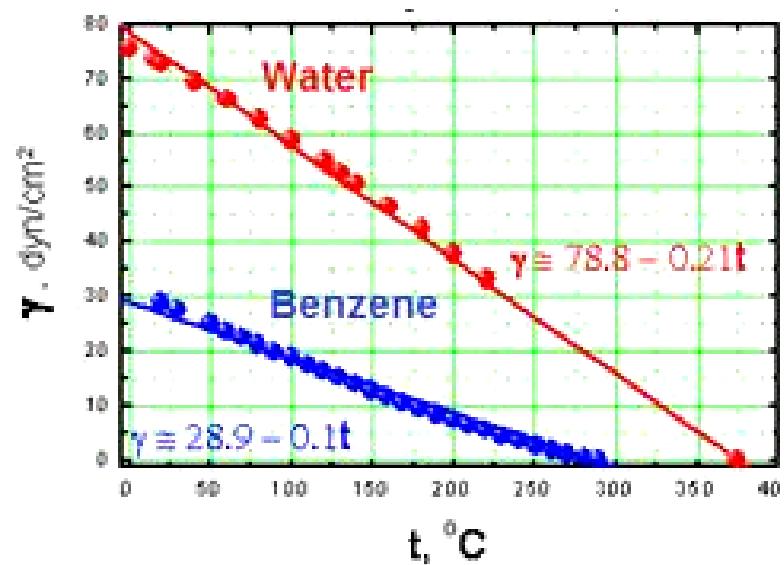
The **work of cohesion** of a single substance is:

$$W^c = W_{11} = \gamma_1 + \gamma_1 - 0 = 2\gamma_1$$

I.e. $\underline{\gamma_{12} = 0.5 (W^c_1 + W^c_2) - W^a}$

Factors affecting surface tension

- Type of liquid**
 - Water has greater surface tension than oil
- What is mixed in the liquid**
 - Soapy water has lower surface tension than water without soap
- Temperature**
 - Molecules in a hot liquid have high energy and are not bound tightly as in cooler liquid



Surface Tension of water and benzene at different temperature

Fowkes' theory

Fowkes' theory is based on 2 fundamental assumptions: Additivity and the geometric mean

1. Surface forces (energies) are additive: $\gamma = \gamma^d + \gamma^p + \gamma^h + \gamma^i + \gamma^{ab} + \dots$

where d = dispersion force

p = polar force

h = hydrogen bonding force

i = induction force (Debye)

ab = acid/base force

... etc.

2. Geometric mean is used for the work of adhesion for each type of force (energy):

$$W_{12}^d = 2(\gamma_1^d \gamma_2^d)^{1/2}, W_{12}^p = 2(\gamma_1^p \gamma_2^p)^{1/2}, W_{12}^h = 2(\gamma_1^h \gamma_2^h)^{1/2}, \text{etc.}$$

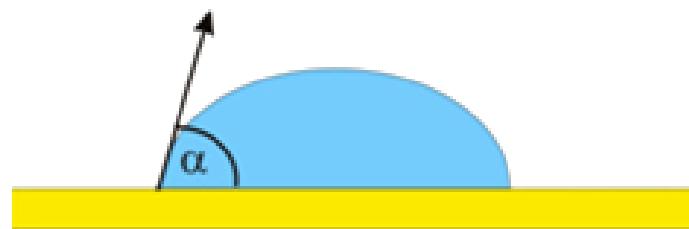
The general expression for W_{12} is: $W_{12} = \gamma_1(1 + \cos \theta) = W_{12}^d + W_{12}^p + \dots$

And for γ_{12} thus: $\underline{\gamma_{12} = \gamma_1 + \gamma_2 - 2(\gamma_1^d \gamma_2^d)^{1/2} - 2(\gamma_1^p \gamma_2^p)^{1/2} - \dots}$

By using a liquid that only interacts with the surface by dispersion forces, we can write:

$$W_{12} = \gamma_1(1 + \cos \theta) = 2(\gamma_1 \gamma_2^d)^{1/2} \quad (\gamma_1 = \gamma_1^d) \quad \text{and} \quad \gamma_2^d = \frac{\gamma_1(1 + \cos \theta)^2}{4}$$

Wetting and dewetting

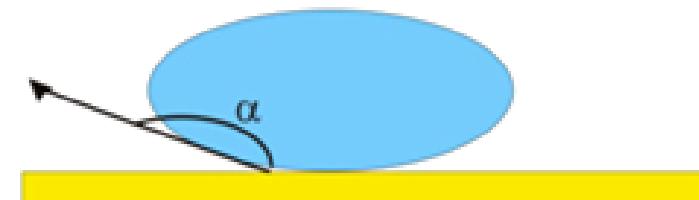


Wetting

Adhesion Forces > Cohesive Forces

Spreading of the liquid on the surface of the solid.

Contact Angle $0 < \theta < \pi/2$



Dewetting

Adhesion Forces < Cohesive Forces

The liquid pulls itself together into the shape of a droplet.

Contact Angle $\pi/2 < \theta < \pi$

Spreading Coefficient and Wetting vs. Dewetting

Spreading coefficient,

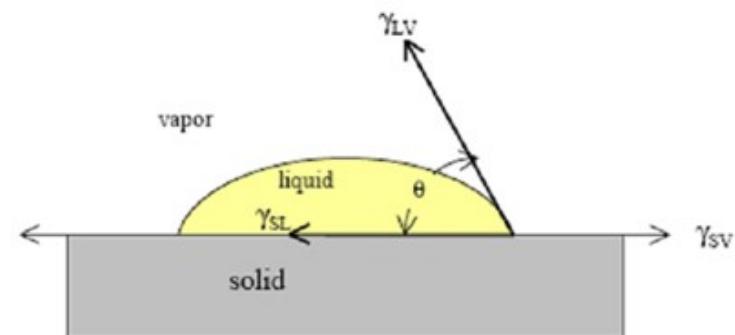
$$S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$$

Young-Dupre equation

$$S = \gamma_{LG} (\cos\theta_c - 1)$$

$S \geq 0 \rightarrow$ Wetting

$S < 0 \rightarrow$ Dewetting



$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \quad (\text{Young equation})$$

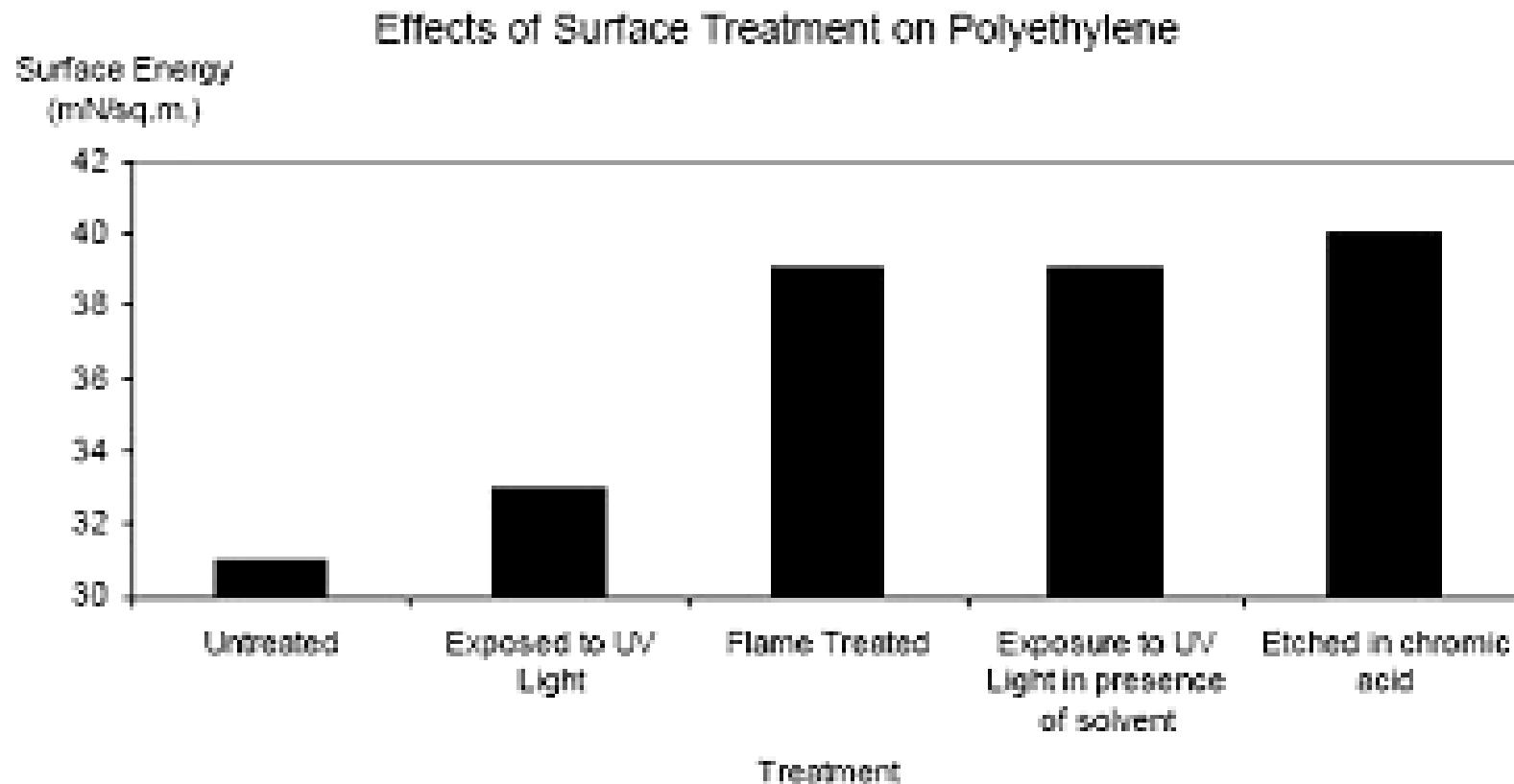
γ_{LV} = liquid-vapor interfacial tension or surface tension

γ_{SV} = solid-vapor interfacial tension, not true surface energy

γ_{SL} = solid-liquid interfacial tension

θ = contact angle (angle liquid makes with solid surface)

Surface Treatments and Surface Energy



Surface chemistry changes → Surface energy changes

Surface & Interface Physics

5. Surface Characterization Methods

Amare B. Belay

5. Surface Characterization Methods

- 5.1. Thin Films Characterizations
- 5.2. Microscopy methods
- 5.3. Spectroscopy methods
- 5.4. Diffraction Methods
- 5.5. Contact angle and other methods

Why Thin Films are Characterized?

- ❑ Materials are processed for a desired property
 - ➔ Make sure that the required property of a material/film is attained
E.g., desired structure, optical, electrical, chemical property ...
- ❑ Material component/s fail → Device failure
 - ➔ Materials careful characterization for efficient device
E.g., chemically stability of a material for possible oxidation and/or fade
- ❑ To predict new applications
- ❑ To find a solution for a device failure (caused by material property)
- ❑ Study source of a material change (in time) by different exposures
 - E.g., Change in chemical property of a film by sun light, heat, oxygen and the like

Why Thin Films are Characterized?

What Changes the Defined Property of a Material?

A) Chemistry

E.g., Si vs. SiO_2 (Semiconductor vs. Insulator, respectively)

B) Structure

E.g., Diamond vs. graphite (made of the same material, carbon)

→ Tough and shiny that can cut a metal vs. black and fragile conductor, resp.

C) Morphology of the film

E.g., Smooth vs. rough surface (of the same material)

→ Rough surface less light reflection and higher rate of chemical reaction
(with chemical surrounding) than smooth surface

Chemistry of a material as major reason for materials to change in property

→ Change in material property (physical/electrical)

→ Desired device/instrument property degraded

What to Characterize?

Key Elements of Thin Films Characterization

A) Surface

- Chemical property
 - Purity, composition and contamination ...
- Optical property
 - Absorption, transmission, reflection ...
- Electrical property
 - Conductivity, resistivity, dielectric constant ...
- Morphological (surface topography)
 - Micro/nano size analysis, film thickness, defects (physical) ...
- Magnetic property
- Mechanical property

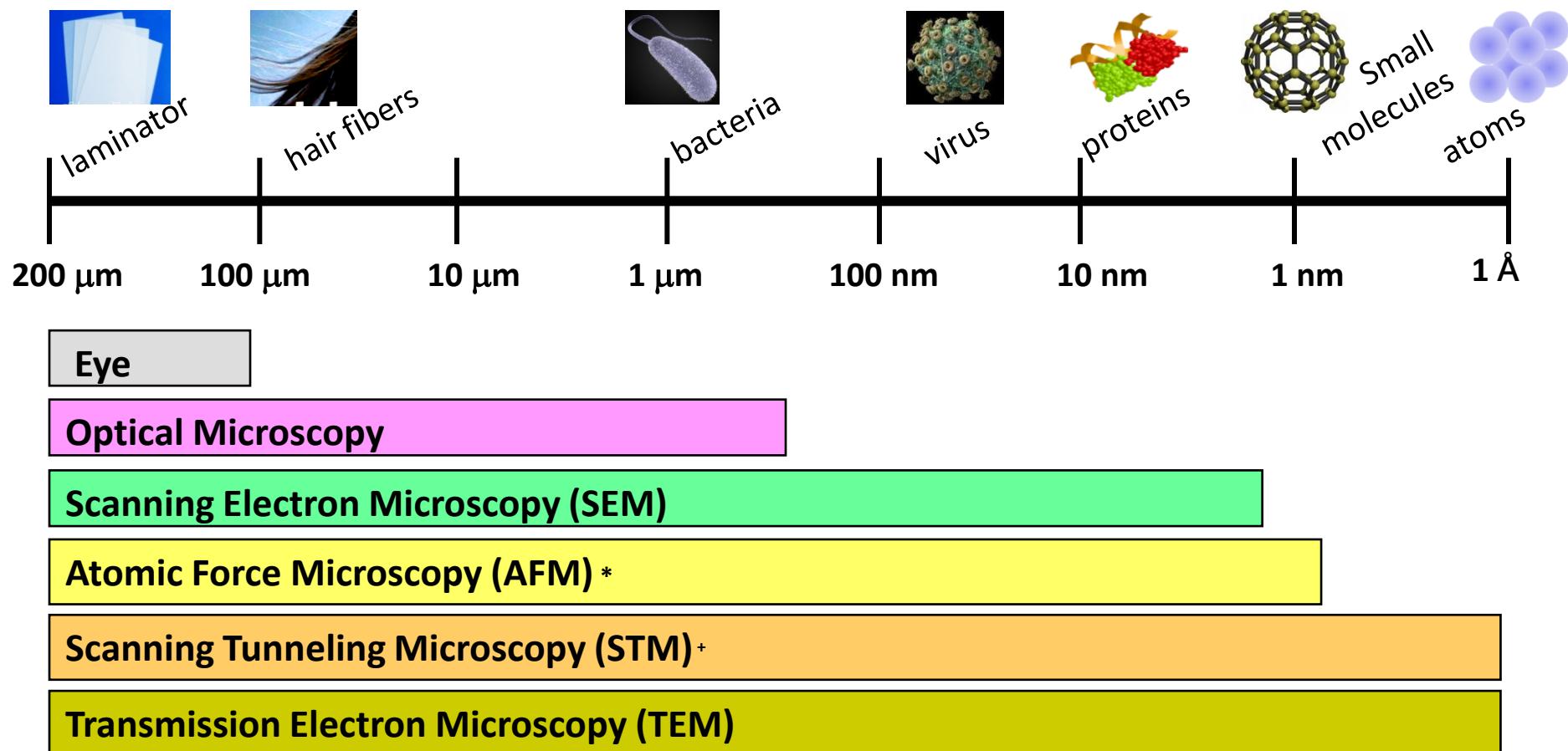
B) Interface

- Film/substrate interface → diffusion or reaction between film and substrate
- Interfaces of multilayered films → films thickness, diffusion and/or reaction

Imaging Techniques (Microscopy)

- Light Microscopy
- Scanning Electron Microscopy, **SEM**
- Scanning Tunneling Microscopy, **STM**
- Transmission Electron Microscopy, **TEM**
- Atomic/Scanning Force Microscopy, **AFM/SFM**

Resolution of Optical and Electron Microscopy



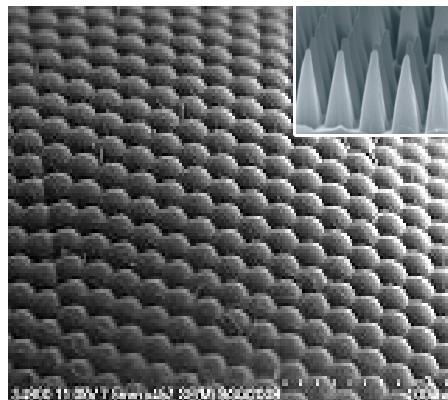
* AFM – lateral/vertical resolution $\sim 1\text{nm}/0.1\text{nm}$

+STM - lateral/depth resolution $\sim 0.1\text{nm}/0.01\text{nm}$

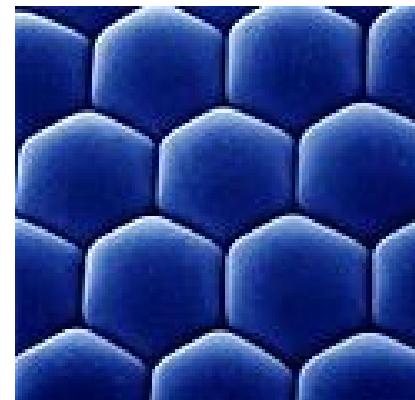
Sample Requirements in SEM

- High vacuum condition instrumentation and final 2D image
- Sample surface needs to be conductive → limitation of SEM
- If sample is conductive:
 - sample should be in small size (e.g., 1 cm x 1 cm) to be in vacuum chamber
- If sample is insulator (in addition to small size):
 - For topology study, sample surface coated by carbon, Au, Ag, ... (by evaporation to have uniform thickness over the surface).
 - If EDS is made, care must be taken to exclude any X-ray peaks generated in the deposited material

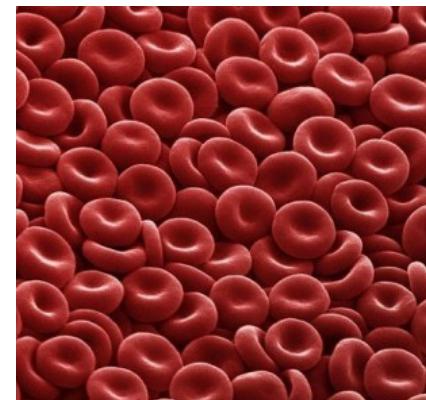
Examples of SEM images



(a)



(b)



(C)



(d)

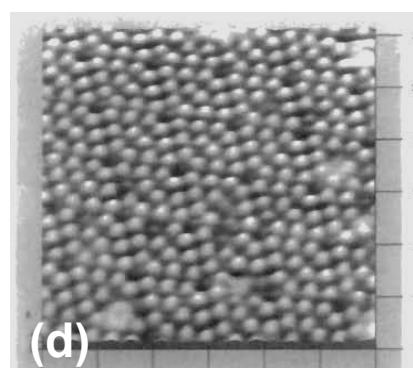
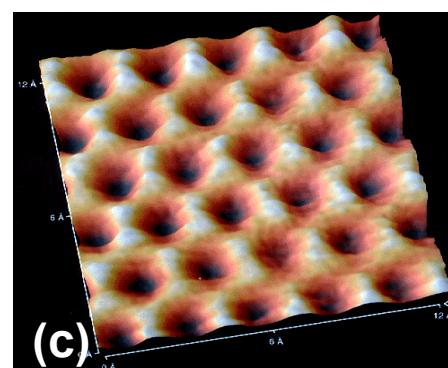
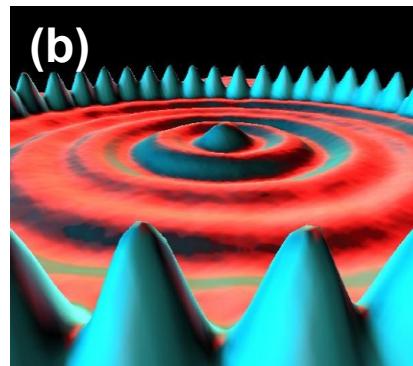
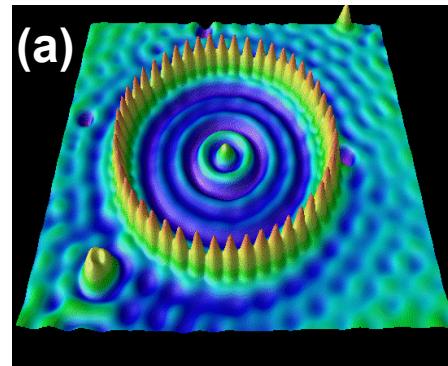
SEM images:

- A house fly compound eye surface at $450\times$ magnification and a magnification of single hexagonal structure of the eye (inset)
- Ommatidia of Antarctic krill eye
- Human blood
- Soybean cyst nematode and egg

Sample requirements in STM

- ❑ Ultrahigh vacuum condition instrumentation
- ❑ Proper sizing for entire surface final 3D image
- ❑ STM requires a conducting surface to establish the tunneling current
- ❑ Surfaces of lower conductivity may require a conductive coating
- ❑ SFM require **solid surfaces** that are somewhat rigid; otherwise the probes will deform the surfaces while scanning.
- ❑ Such deformation is easily **diagnosed by repeatedly scanning** the same area and noting changes

Examples of STM images



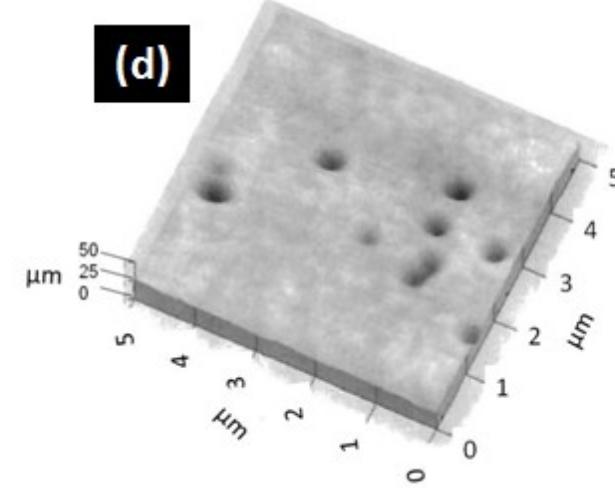
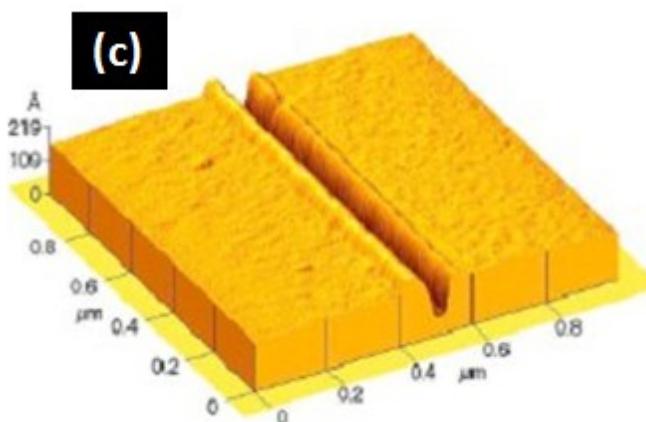
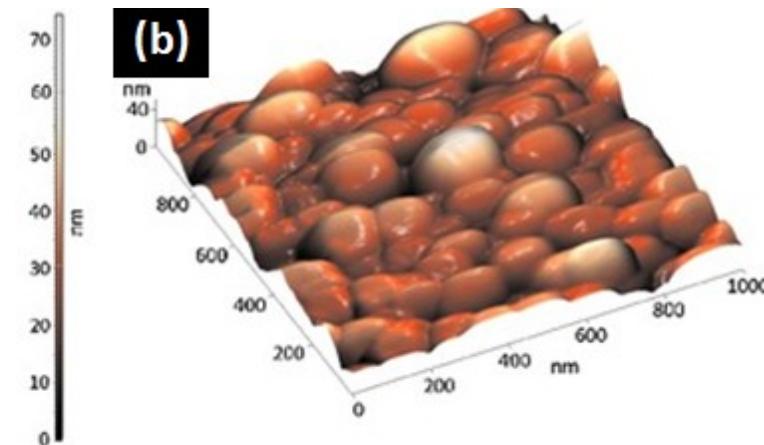
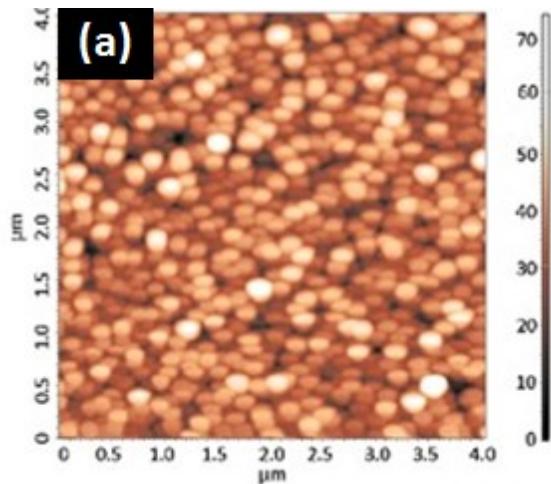
STM images of 48 iron atoms into a circular ring (a), zoomed view of the tips of the iron atoms (b) graphite surface (c) and ultrahigh-vacuum STM image of Si (111) (d)

- STM has been established as an instrument for forefront research in surface physics.
- **Atomic resolution** work in ultrahigh vacuum includes studies of metals, semimetals and semiconductors.
- Surface oxide or other contaminant (insulators) will complicate operation under ambient conditions

Sample Requirements and Remarks in AFM

- ❑ No need of vacuum condition for the instrument
- ❑ Change of cantilever → disadvantage of AFM
- ❑ SFM can image any surfaces (conductor or insulator)
- ❑ Proper sizing for entire surface final 3D image
- ❑ For specific application conductive AFM (C-AFM) is used
- ❑ Contact mode and non cont modes of AFM depending on the sample type

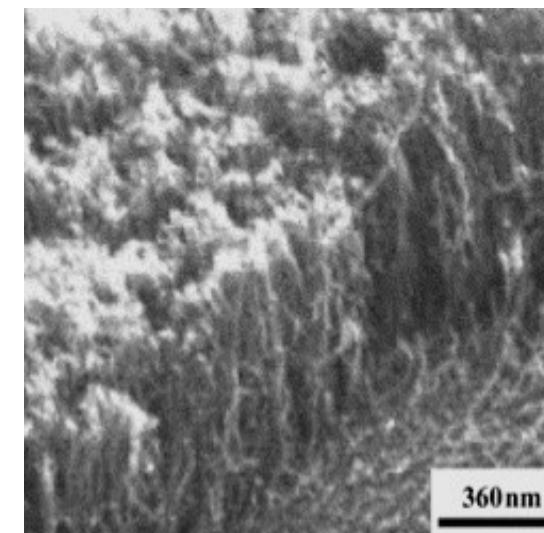
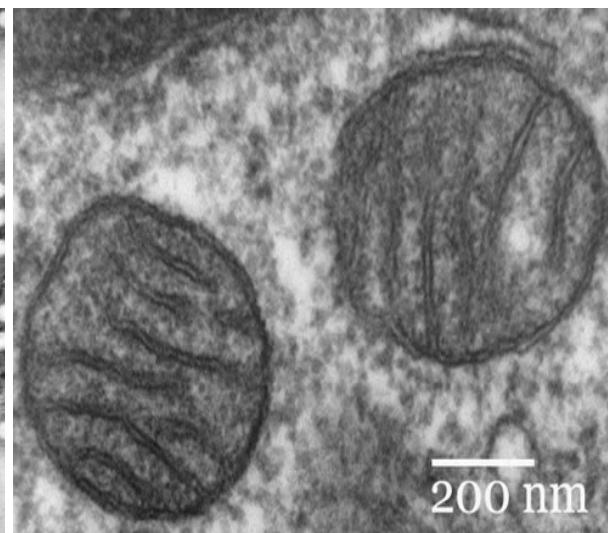
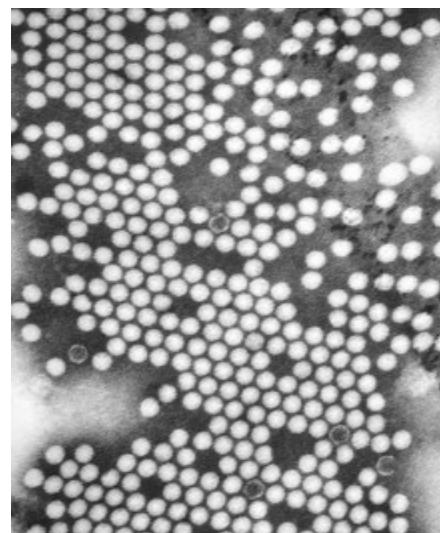
Examples of AFM images



AFM image of a 2D (a) and b 3D (b) AFM images of ellipsoid aggregates of Au nanoparticles, AFM-scratch in p-type Si (c), and oxidized Si wafer showing pinhole defects 20 Å (d)

Sample Requirements and Examples of TEM images

- Used to study all variety of materials
 - metals, ceramics, semiconductors, polymers, and composites
- Study crystal structure and microstructure
- Preparation of high-quality thin foils for observation is very difficult



A TEM image of the polio virus with 30 nm in size(a), mammalian mitochondria (b) , and carbon nanotubes grown at 400 °C (c).

Structure Determination by Diffraction and Scattering

- ❑ X-Ray Diffraction, **XRD**
- ❑ Extended X-Ray Absorption Fine Structure, **EXAFS**
- ❑ Surface Extended X-Ray Absorption Fine Structure, **SEXAFS**
- ❑ Near Edge X-Ray Absorption Fine Structure, **NEXAFS**
- ❑ Auger Electron Diffraction, **AED**
- ❑ X-Ray Photoelectron Diffraction, **XPD**
- ❑ Low-Energy Electron Diffraction, **LEED**
- ❑ Reflection High-Energy Electron Diffraction, **WEED**

Electron Emission Spectroscopies

- X-Ray Photoelectron Spectroscopy, **XPS**
- Ultraviolet Photoelectron Spectroscopy, **UPS**
- Auger Electron Spectroscopy, **AES**
- Reflected Electron Energy-loss Spectroscopy, **REELS**

X-Ray Emission Techniques

- X-Ray Fluorescence, **XRF**
- Total Reflection X-Ray Fluorescence Analysis, **TXRF**
- Particle-Induced X-Ray Emission, **PIXE**

Vibrational Spectroscopies and NMR

- Fourier Transform Infrared Spectroscopy, **FTIR**
- Raman Spectroscopy
- High-Resolution Electron Energy Loss Spectroscopy, **HREELS**
- Solid State Nuclear Magnetic Resonance, **NMR**

Visible/UV Emission, Reflection, and Absorption

- Photoluminescence, **PL**
- Modulation Spectroscopy
- Variable Angle Spectroscopic Ellipsometry, **VASE**

Ion Scattering Techniques

- ❑ Rutherford Backscattering Spectrometry, **RBS**
- ❑ Elastic Recoil Spectrometry, **ERS**
- ❑ Medium-Energy Ion Scattering with Channeling and Blocking, **MEIS**
- ❑ Ion scattering Spectroscopy, **ISS**

Mass and Optical Spectroscopies

- ❑ Dynamic Secondary Ion Mass Spectrometry, **Dynamic SIMS**
- ❑ Static Secondary Ion Mass Spectrometry, **Static SIMS**
- ❑ Surface Analysis by Laser Ionization, **SALI**
- ❑ Sputtered Neutral Mass Spectrometry, **SNMS**
- ❑ Laser Ionization Mass Spectrometry, **LIMS**
- ❑ Spark Source Mass Spectrometry, **SSMS**
- ❑ Glow-Discharge Mass Spectrometry, **GDMS**
- ❑ Inductively Coupled Plasma Mass Spectrometry, **ICPMS**
- ❑ Inductively Coupled Plasma-Optical Emission Spectroscopy, **ICP-OES**

Analytical Techniques Employed in Thin-Film Science and Technology

Primary Beam	Energy Range	Secondary Signal	Acronym	Technique	Application
Electron	20–200 eV	Electron	LEED	Low-energy electron diffraction	Surface structure
	300–30,000 eV	Electron	SEM	Scanning electron microscopy	Surface morphology
	1 keV–30 keV	X-ray	EMP (EDX)	Electron microprobe	Surface region composition
	500 eV–10 keV	Electron	AES	Auger electron spectroscopy	Surface layer composition
	100–400 keV	Electron	TEM	Transmission electron microscopy	High-resolution structure
	100–400 keV	Electron, X-ray	STEM	Scanning TEM	Imaging, X-ray analysis
	100–400 keV	Electron	EELS	Electron energy loss spectroscopy	Local small area composition
Ion	0.5–2.0 keV	Ion	ISS	Ion-scattering spectroscopy	Surface composition
	1–15 keV	Ion	SIMS	Secondary ion mass spectroscopy	Trace composition vs. depth
	1–15 eV	Atoms	SNMS	Secondary neutral mass spectrometry	Trace composition vs. depth
	1 keV and up	X-ray	PIXE	Particle-induced X-ray emission	Trace composition
	5–20 keV	Electron	SIM	Scanning ion microscopy	Surface characterization
Photon	> 1 MeV	Ion	RBS	Rutherford backscattering	Composition vs. depth
	> 1 keV	X-ray	XRF	X-ray fluorescence	Composition (μm depth)
	> 1 keV	X-ray	XRD	X-ray diffraction	Crystal structure
	> 1 keV	Electron	ESCA, XPS	X-ray photoelectron spectroscopy	Surface composition
	Laser	Ions	—	Laser microprobe	Composition of irradiated area
	Laser	Light	LEM	Laser emission microprobe	Trace element analysis

Milton Ohring , The Materials Science of Thin Films

A Summary of Selected Film Thickness Measurement Techniques

Method	Range	Accuracy or Precision	Comments
Multiple-beam FET	30–20,000 Å	10–30 Å	A step and reflective coating required
Multiple-Beam FECO	10–20,000 Å	2 Å	A step, reflective coating, and spectrometer required; accurate but time-consuming
VAMFO	800 Å–10 µm	0.02–0.05 %	For transparent films on reflective substrates; Nondestructive
CARIS	400 Å–20 µm	10 Å–0.1 %	For transparent films; Nondestructive
Step gauge	500–15,000 Å	~ 200 Å	Values for SiO ₂ on Si
Ellipsometry	A few Å to a few µm	1 Å	Transparent films; complicated mathematical analysis
Stylus	20 Å to no limit	A few Å to < 3 %	Step required; simple and rapid
Weight measurement	< 1 Å to no limit		Accuracy depends on knowledge of film density
Crystal oscillator	< 1 Å to a few µm	< 1 Å to a few %	Nonlinear behavior at larger film thicknesses

Summary of Major Chemical Characterization Techniques

Method	Detection			
	Elemental Sensitivity	Limit (at %)	Lateral Resolution	Effective Probe Depth
Scanning Electron microscope-energy dispersive x-ray (SEM/EDX)	Na-U	~ 0.1	~ 1 μm	~ 1 μm
Auger Electron spectroscopy (AES)	Li-U	~ 0.1-1	500 \AA°	~ 15 \AA°
X-Ray Photoelectron spectroscopy (XPS)	Li-U	~ 0.1-1	~ 100 μm	~ 15 \AA°
Rutherford Backscattering (RBS)	He-U	~ 1	1 mm	~ 200 \AA°
Secondary ion mass spectrometry (SIMS)	H-U	~ $10^{-4}\%$	~ 1 μm	15 \AA°

Summary of Major Chemical Characterization Techniques

AES, XPS, and SIMS are true surface analytical techniques, since the detected electrons and ions are emitted from surface layers less than $\sim 15 \text{ \AA}$ deep. Provision is made to probe deeper, or depth profile, by sputter-etching the film and continuously analyzing the newly exposed surfaces.

EDX and RBS generally sample the total thickness of the thin film ($\sim 1 \mu\text{m}$) and frequently some portion of the substrate as well. Unlike RBS with a depth resolution of $\sim 200 \text{ \AA}$, EDX has little depth resolution capability. AES, XPS, and SIMS are broadly applicable to detecting, with few exceptions, all of the elements in the periodic table.

EDX can ordinarily only detect elements with $Z > 11$, and RBS is restricted to only selected combinations of elements whose spectra do not overlap.

Summary of Major Chemical Characterization Techniques

The detection limits for AES, XPS, EDX, and RBS are similar, ranging from about ~ 0.1 to 1 at%. On the other hand, the sensitivity of SIMS is much higher and parts per million can be detected. Even lower concentration levels ($\sim 10^{-6}$ at%) are detectable in certain instances.

Quantitative chemical analysis with AES and XPS is problematical with composition error bounds of several atomic percent. EDX is better and SIMS significantly worse in this regard. Composition standards are essential for quantitative SIMS analysis.

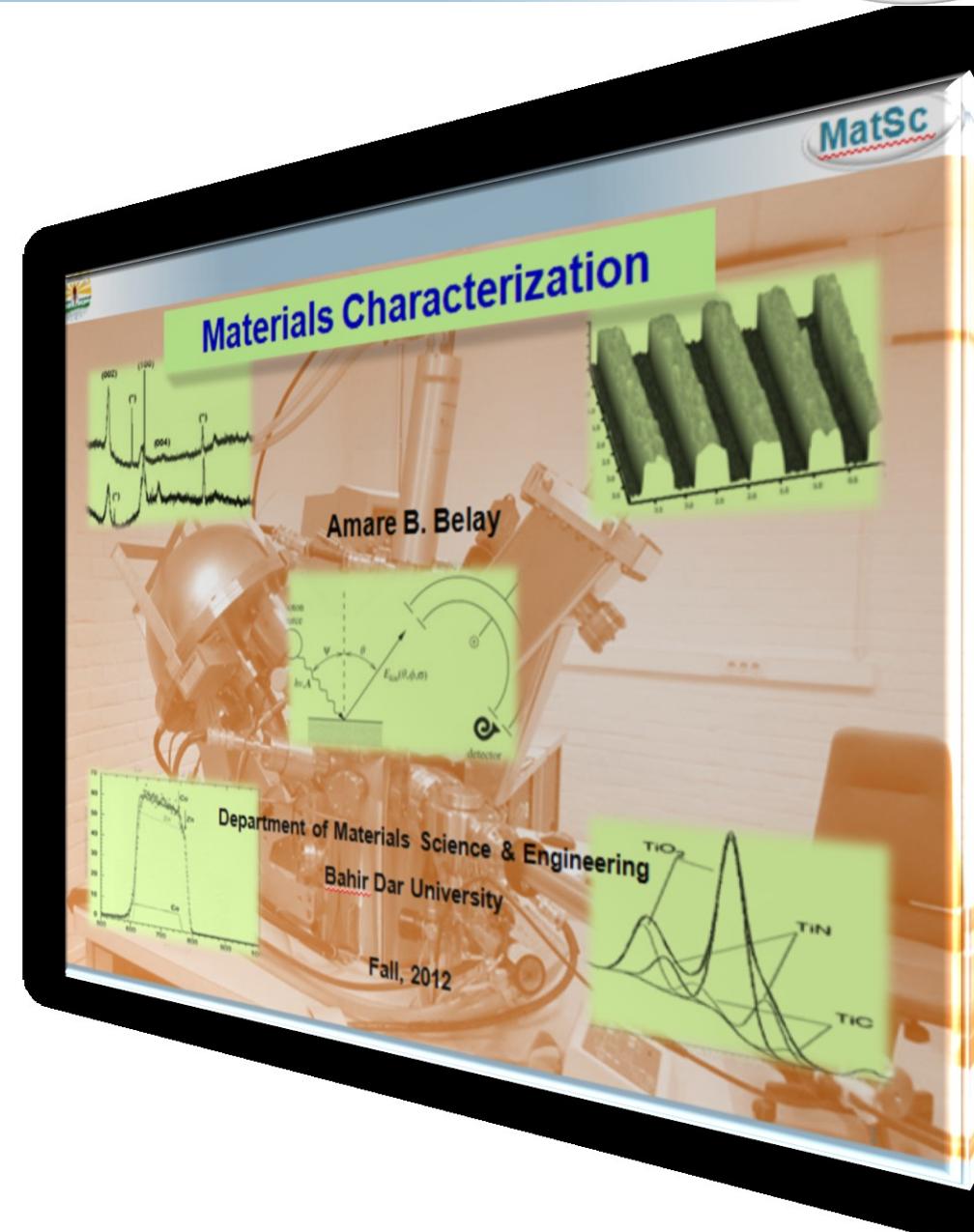
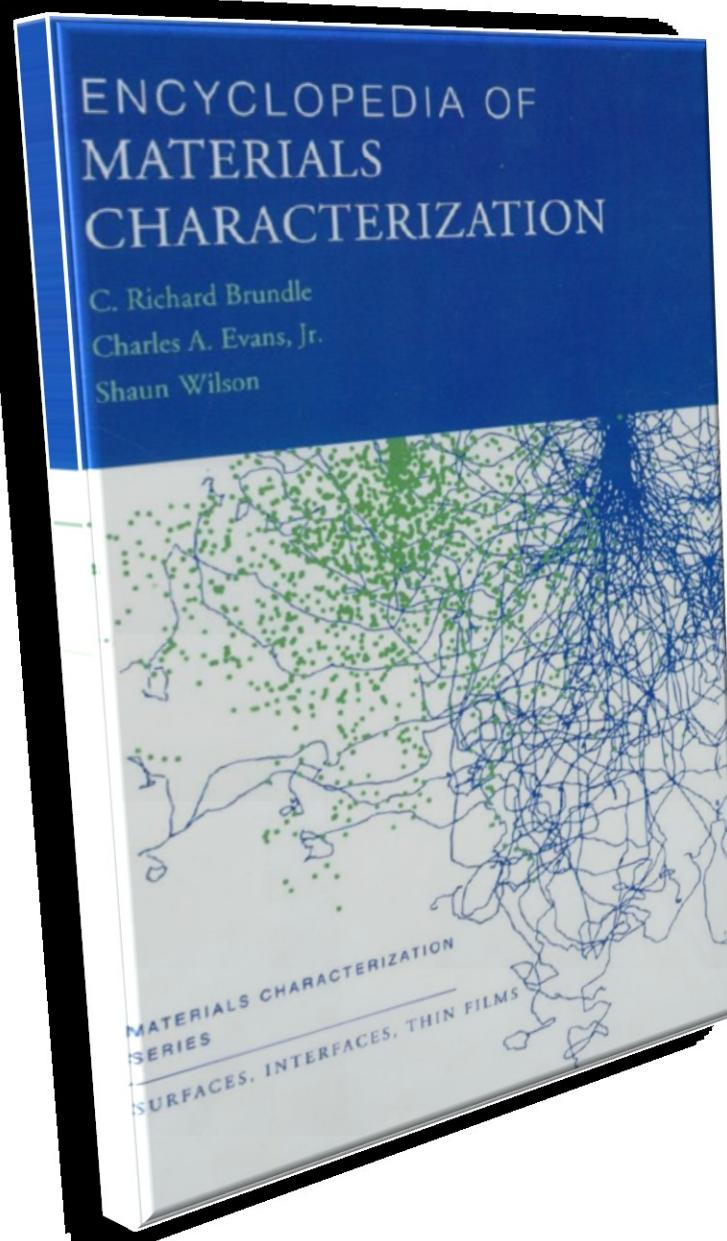
Only RBS is quantitatively precise to within an atomic percent or so from first principles and without the use of composition standards. It is the only nondestructive technique that provides simultaneous depth and composition information.

The lateral spatial resolution of the region over which analyses can be performed is highest for AES (~ 500 Å) and poorest for RBS (~ 1 mm). In between are EDX (~ 1 μ m), SIMS (several μ m), and XPS (~ 0.1 mm). AES has the distinction of being able to sample the smallest volume for analysis.

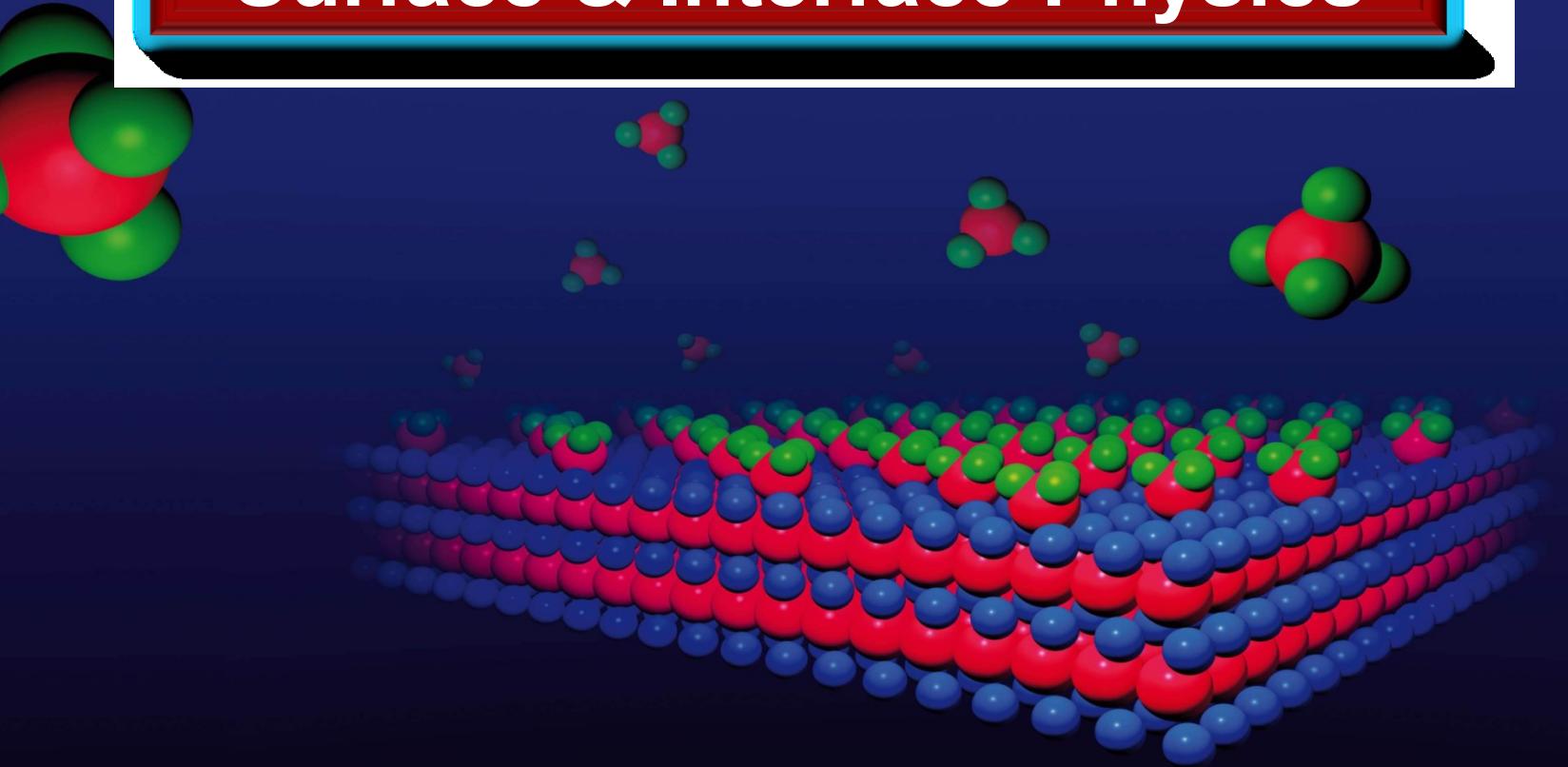
Only XPS, and to a much lesser extent AES, are capable of readily providing information on the nature of chemical bonding and valence states.

Applications of Surface Analytical Techniques in Thin Films

Application	Information Obtained, Comments	Technique
1. Nucleation and growth	Distinctions among island, layer and S.K. growth modes (p. 220)	AES
2. Diffusion in metal films	Diffusion coefficients are obtained by sputter sectioning, and surface accumulation methods	AES, SIMS. RBS
3. Doped semiconductors	Diffused and ion-implanted depth profiles in Si and GaAs	SIMS
4. Compound formation	Stoichiometry of intermetallic and silicide compounds, growth kinetics	RBS, AES
5. Investigation of surface residues, stains, haze, and discoloration after processing	Identification of elemental contaminants Identification of compound valence and bonding states	AES, SIMS. XPS XPS
6. Contamination of surfaces by organic materials	Identification of elements	AES, SIMS XPS XPS
7. Interfacial analysis	Identification of compounds Cause of adhesion failure, segregation of impurities at grain boundaries and interfaces	AES, RBS, SIMS, XPS
8. Multilayer films and coatings, superlattices	Stoichiometry, layer thickness, interfacial impurities	AES, RBS, SIMS
9. Determination of crystalline perfection	Channeling spectra distinguish between single-crystal and amorphous Si films	RBS
10. Fracture of coatings	Segregation of impurities at fracture surfaces	AES, SIMS
11. Metal-Semiconductor contacts	Adhesion, contact reactions in Si and GaAs	AES, XPS, SIMS, RBS
12. Dielectric films on metals and semiconductor	Surface contamination, impurity diffusion, and segregation at interfaces (e.g., SiO_2 -Si)	AES, SIMS, XPS
13. Molecular-beam epitaxy	Assessment of surface cleanliness prior to deposition, detection of C and O contaminants	AES, XPS



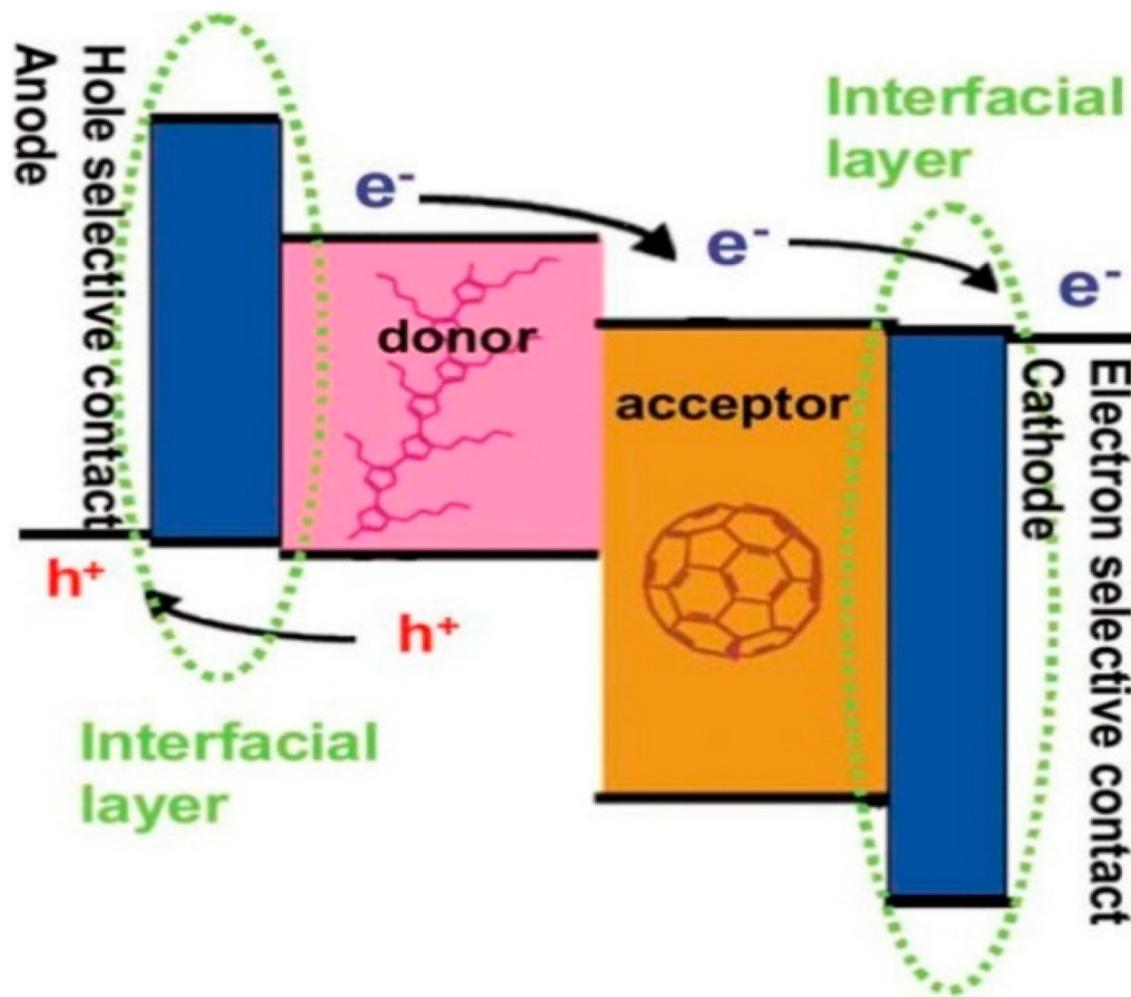
Surface & Interface Physics



5. Interface Engineering in Semiconductor Devices

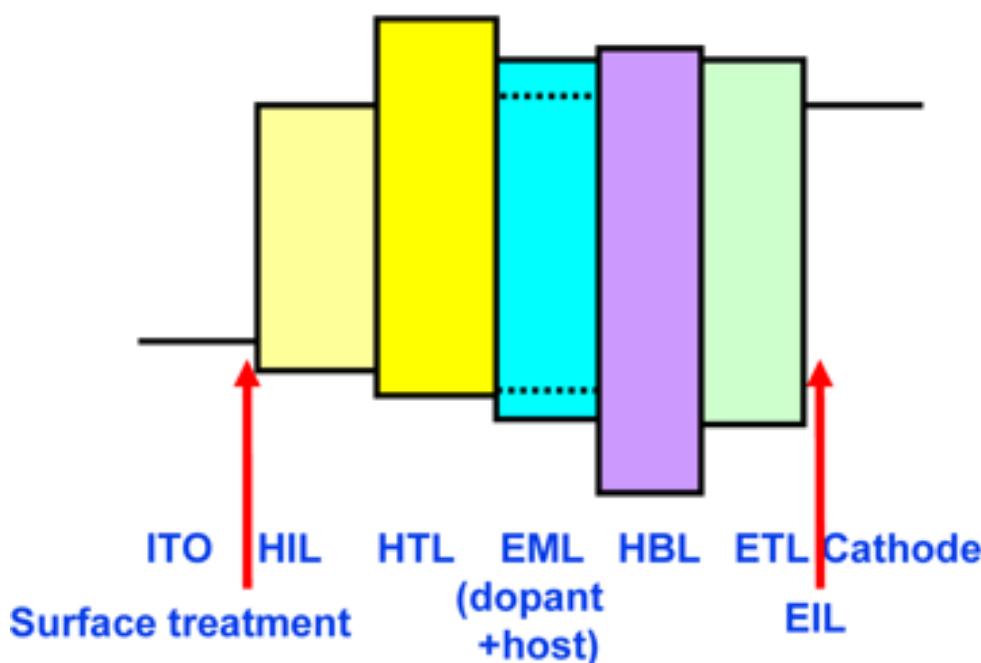
Amare B. Belay

Interface Engineering in Organic Semiconductors

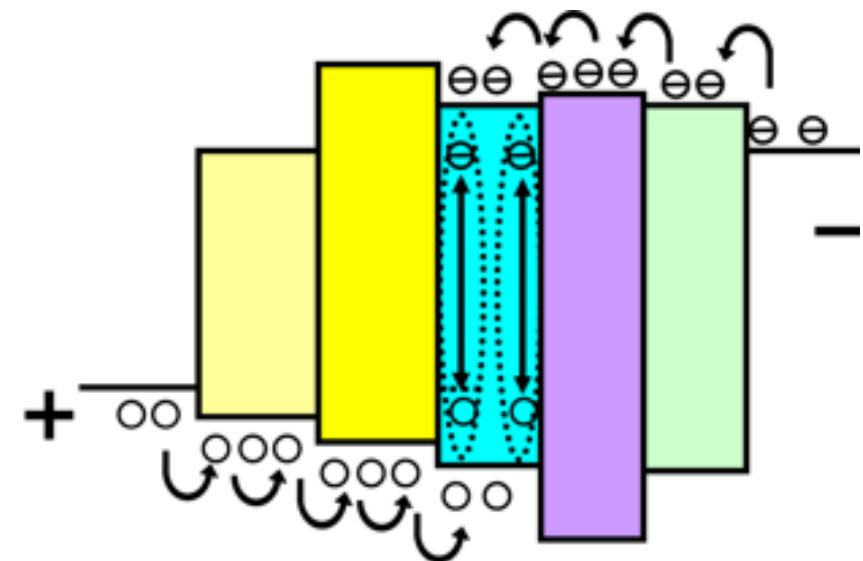


Schematic illustration of a polymer solar cell in extraction mode (Solar cells).

Interface Engineering in Organic Semiconductors



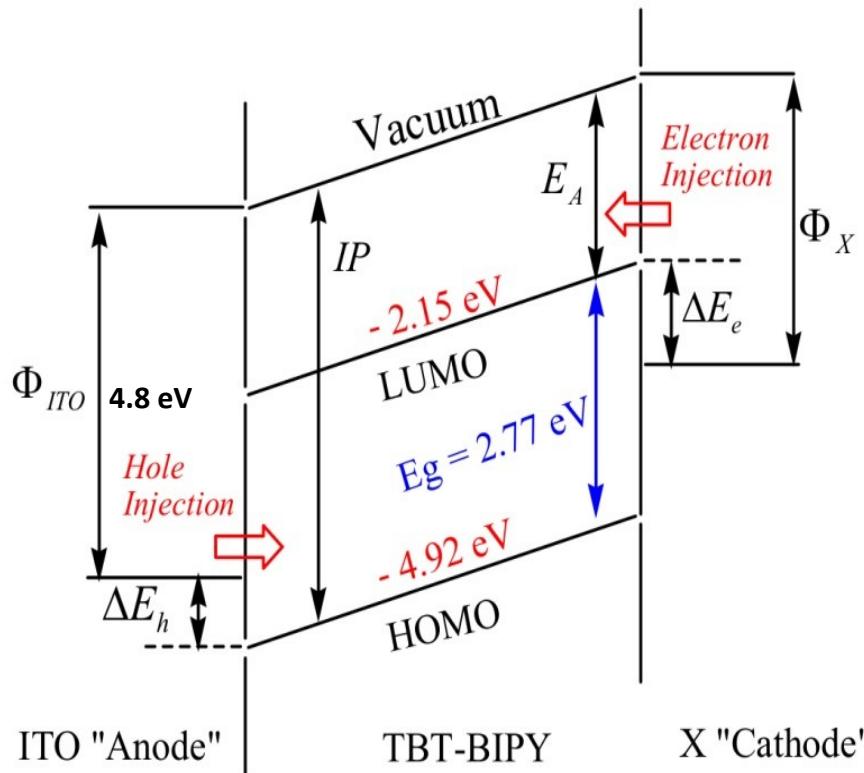
(a)



(b)

Schematic illustration of a polymer/organic in injection mode (LEDs) with layers (a) and injection (b)

Interface Engineering in Organic Semiconductors



Energy-level diagrams of a single-layer PLED (ITO/TBT-BIPY/Al, Mg or Ca), with the ionization potentials (IP) and electron affinity (E_A) of the materials and Φ_X is the work function.

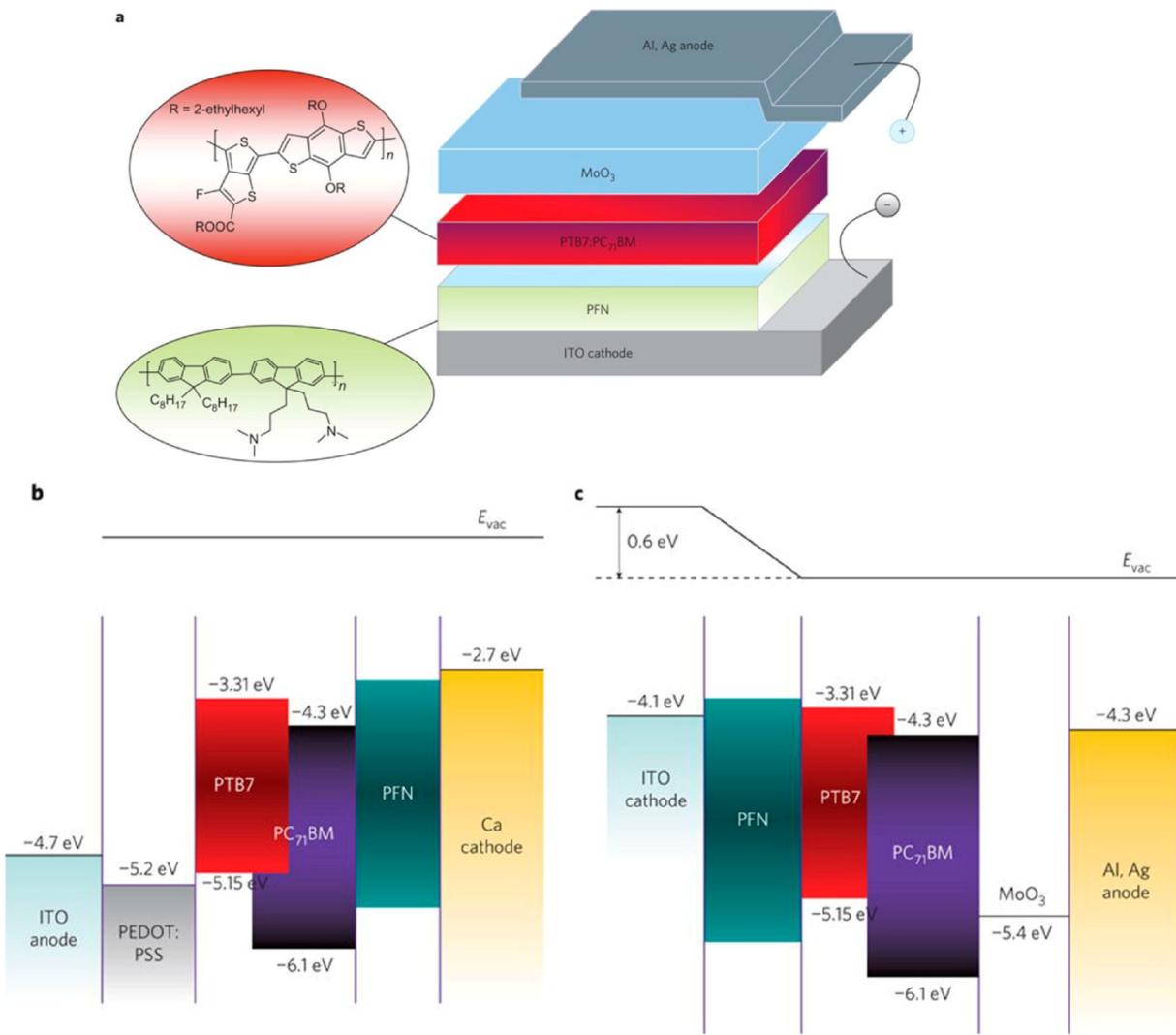
X	ϕ_x (eV)	ΔE_h (eV)	ΔE_e (eV)	$\Delta E_e - \Delta E_h$ (eV)
Al	4.2	0.12	2.05	1.93
Mg	3.6	0.12	1.45	1.33
Ca	2.8	0.12	0.65	0.53

Parameters to evaluating the balance in electron and hole injections in PLED.

hole-injection barrier is $\Delta E_h = E_{HOMO} - 4.8$ eV,
electron-injection barrier is $\Delta E_e = \phi_x - E_{LUMO}$,

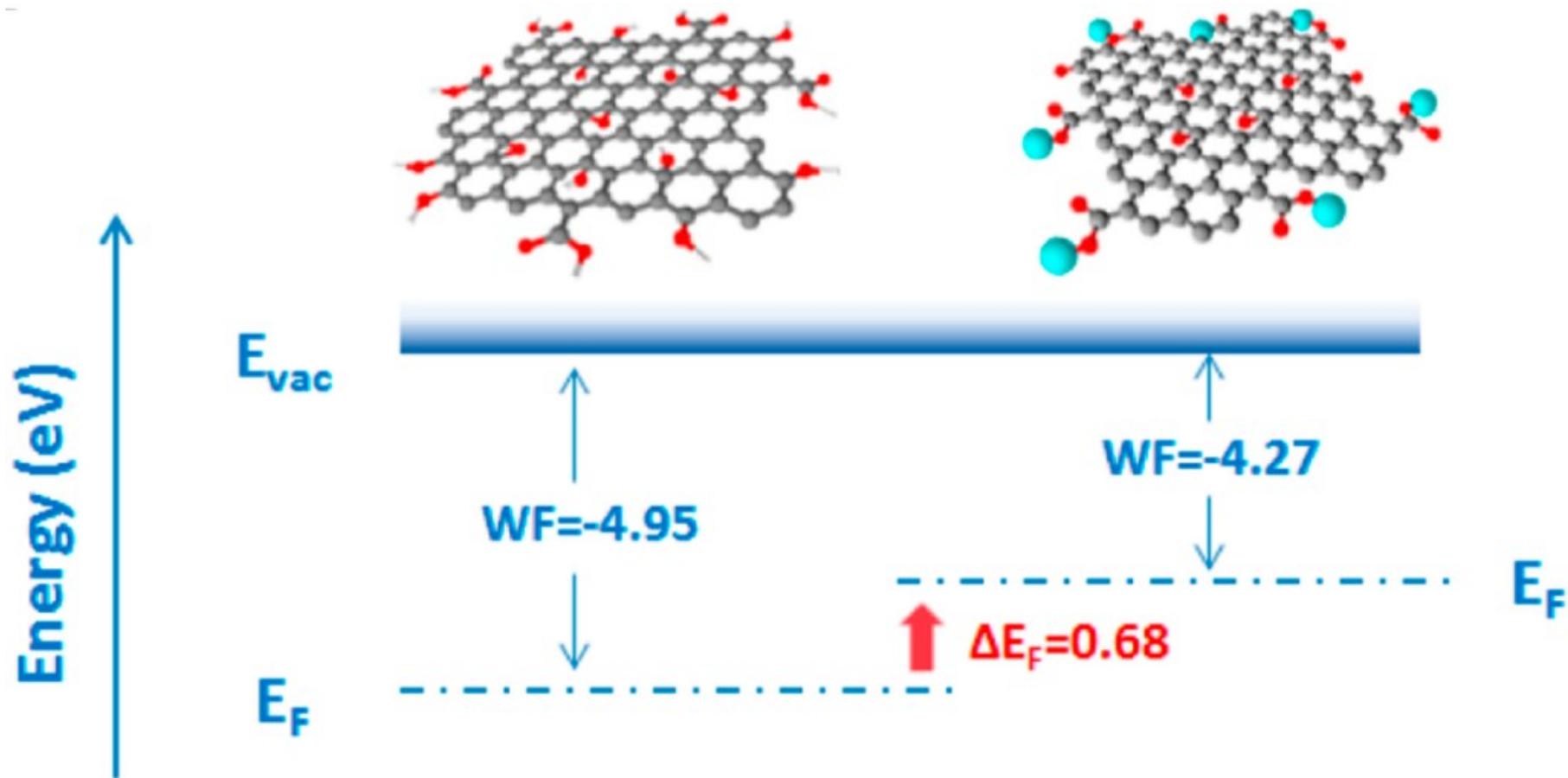
$(\Delta E_e - \Delta E_h)$ is a useful parameter to evaluate the balance in electron and hole injection
→ Needs to be minimized!

Interface Engineering in Organic Semiconductors



PFN-modified ITO cathode and an Al, Ag-based top anode (a). Schematic energy levels of the conventional (b) and inverted (c) devices under flat band conditions. Note that the formation of a positive interface dipole moment (taking the dipole moment directed outwards to be positive) is presented in the inverted cells

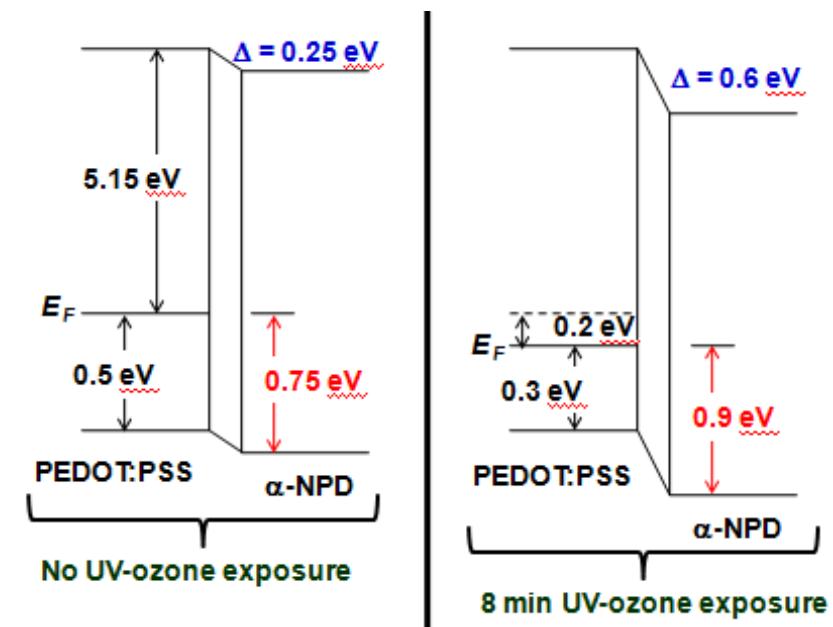
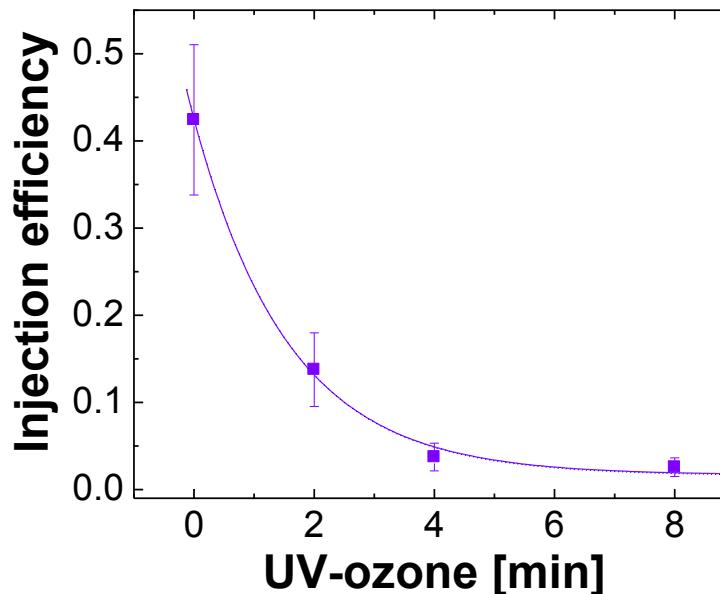
Interface Engineering ...



Energy diagram showing the Fermi level of pristine graphene oxide (GO; left) and lithium-neutralized graphene oxide (GO-Li; right).

Charge Carrier Balance in OLEDs (Cont.)

Tuning holes injection by UV-Ozone Exposure

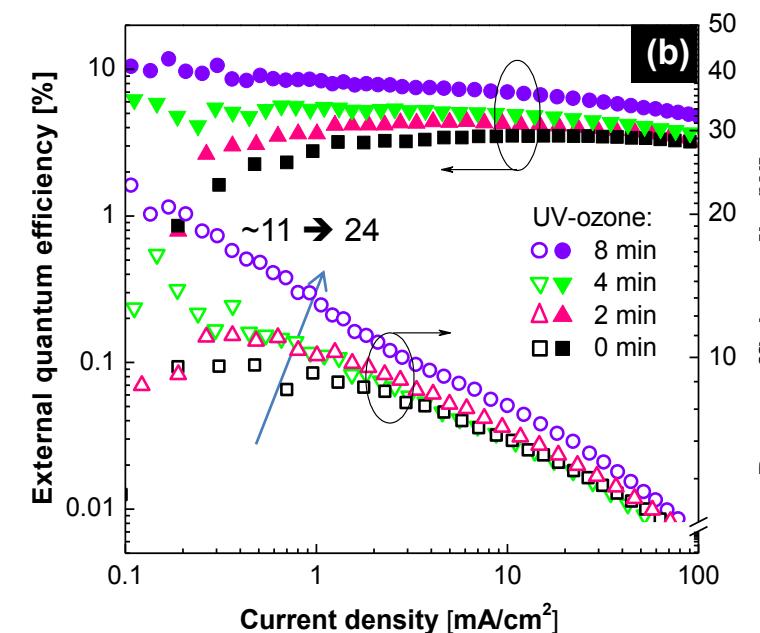
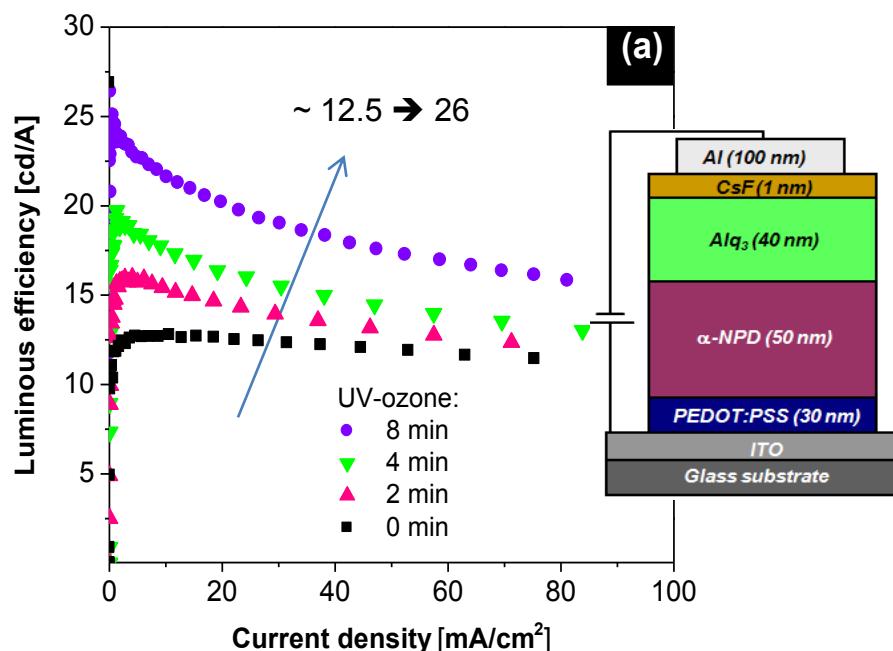


Effect of UV-Ozone on: dipole barrier (Δ) and work function

- Change of energy barrier (holes), $\Delta\phi = 0.15 \text{ eV}$ ($0.75 \rightarrow 0.9 \text{ eV}$)
- Tuning charge injection efficiency

Efficiency Improvement in OLEDs (Cont.)

Efficiency Improvement Using UV-Ozone Exposure

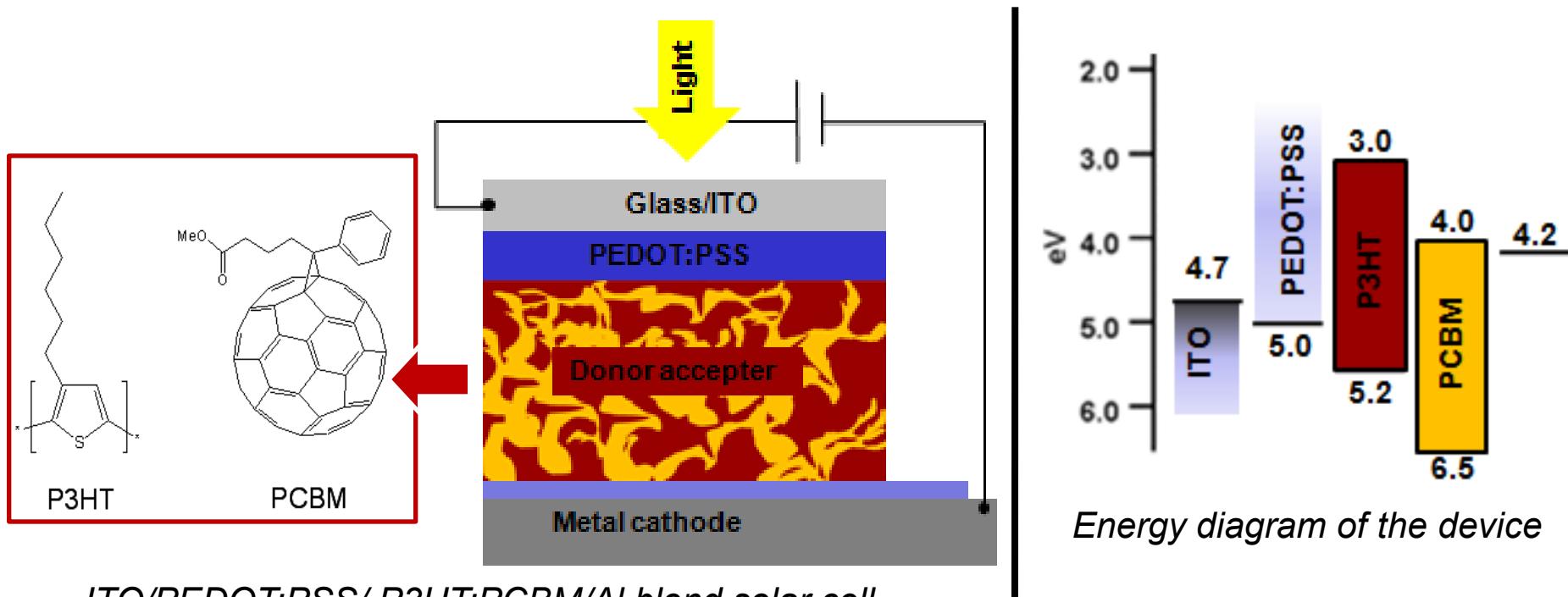


Luminous efficiency-current density characteristics of device I at 0, 2, 4, and 8 min of UV-ozone exposure

EQE improvements by the exposure: From 3.5% at 0 min to 10.5% at 8 min \rightarrow 3 fold improve !

Improved Charge Extraction in Organic Solar Cells

UV-Ozone Exposure of PEDOT:PSS

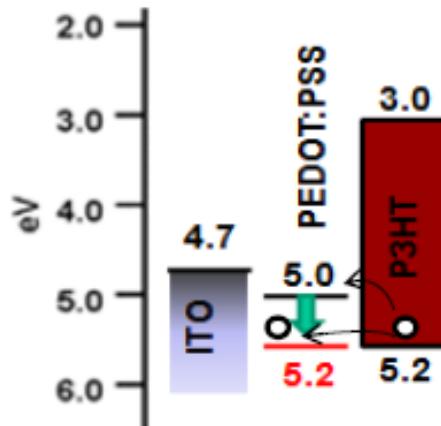


Energy barrier crucial issue in charge extraction!

- Improved surface roughness required
- Work function of PEDOT:PSS ?

Improved Charge Extraction in Organic Solar Cells

UV-Ozone Exposure of PEDOT:PSS



UV-Ozone exposure of PEDOT:PSS:

- Improved surface roughness
- Increased conductivity
- Work function of PEDOT:PSS increased

Effect on the solar cell:

- Good contact or reduced contact resistance
 - Changes the hole injection barrier
 - Increase in short-circuit current (I_{sc})
- **Improved Efficiency (from 3.07 % to 3.62%)**

UV-Ozone exposure:

I_{sc} changes: 9 → 10.2 mA/cm²

V_{sc} changes: 0.58 → 0.6 V

UV-ozone exposure can improve the device efficiency!

Other interface control and device efficacy improvement:

UV-Ozone treatment of ITO, gold → TO/PEDOT and god/organic surface

The background of the image is a vibrant sunset or sunrise over a body of water. The sky is filled with warm colors, transitioning from deep orange at the horizon to bright yellow and white near the sun. A large, dark silhouette of a tree stands prominently on the right side of the frame, its branches reaching towards the top. The water in the foreground has a textured, slightly grainy appearance.

The End