

Personal Reflections on Utilization of XPS Over 1/2 Century



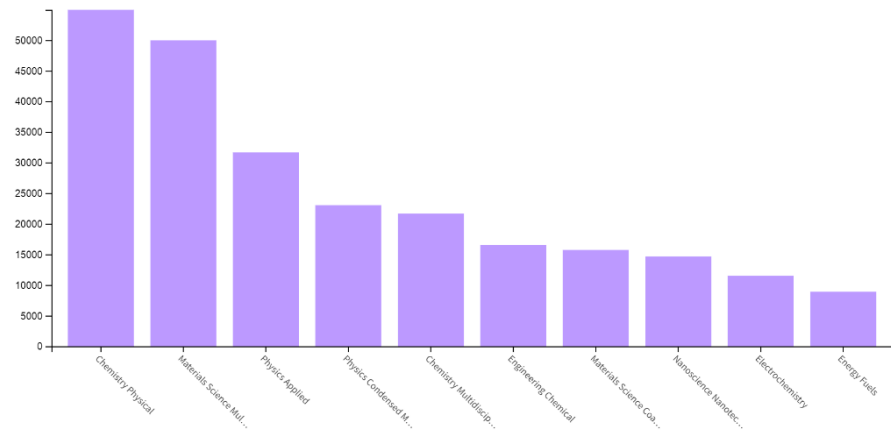
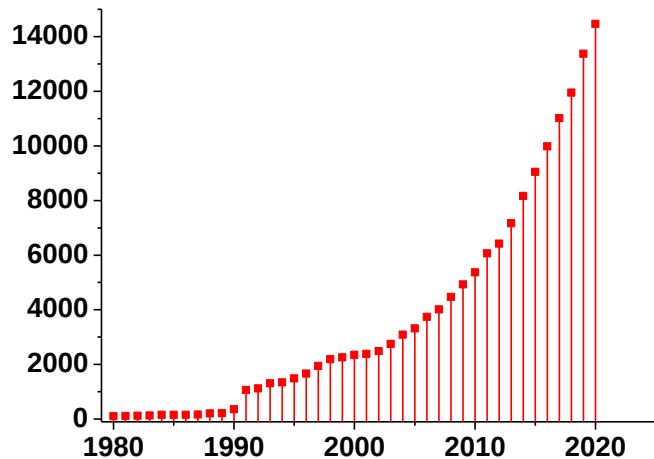
Şefik SÜZER

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Chemistry Department
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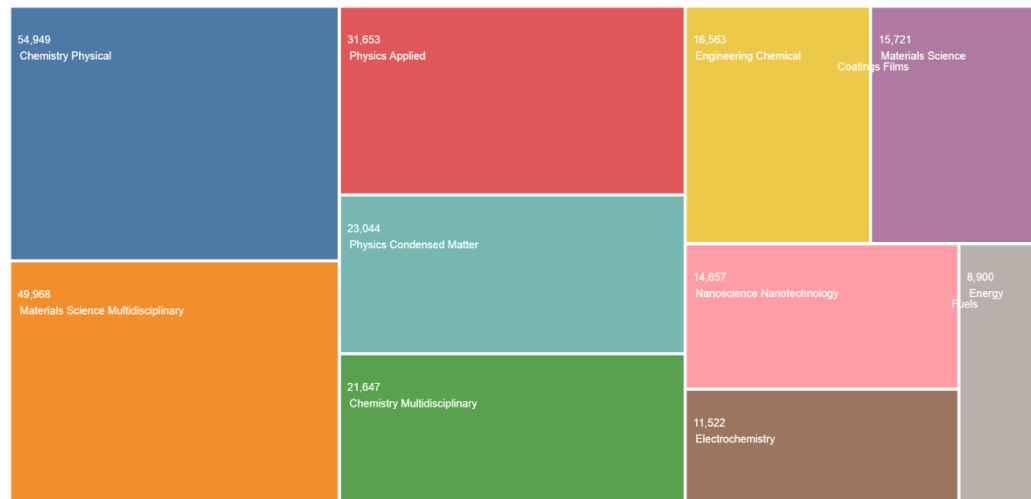
07 September 2022
HESEB - SESAME WORKSHOP
Istanbul University, Istanbul, Turkey

XPS, X-Ray Photoelectron Spectroscopy

A Surface Analysis Technique



“Web of Science”



Kai Siegbahn
Nobel Laureate 1981
ESCA

Ş. Süzer'in PES Research
(UC Berkeley, 1970-76)

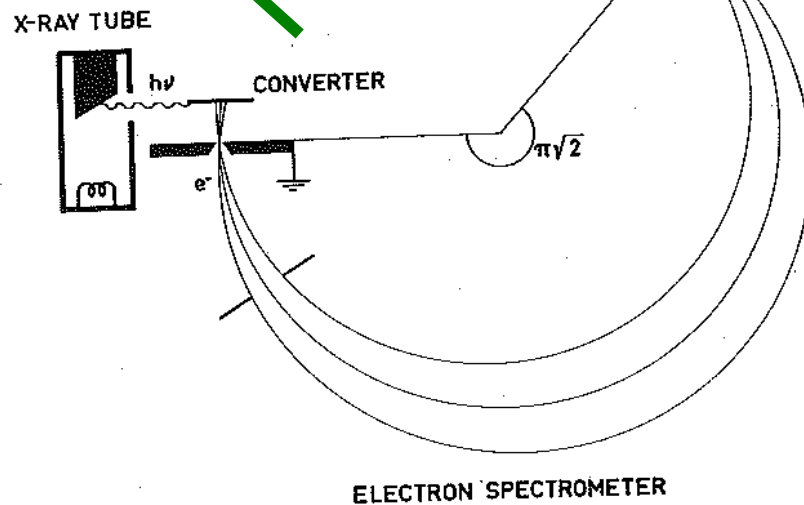


Fig. I:2. Schematic view of an ESCA arrangement for the study of electrons expelled by X-rays.

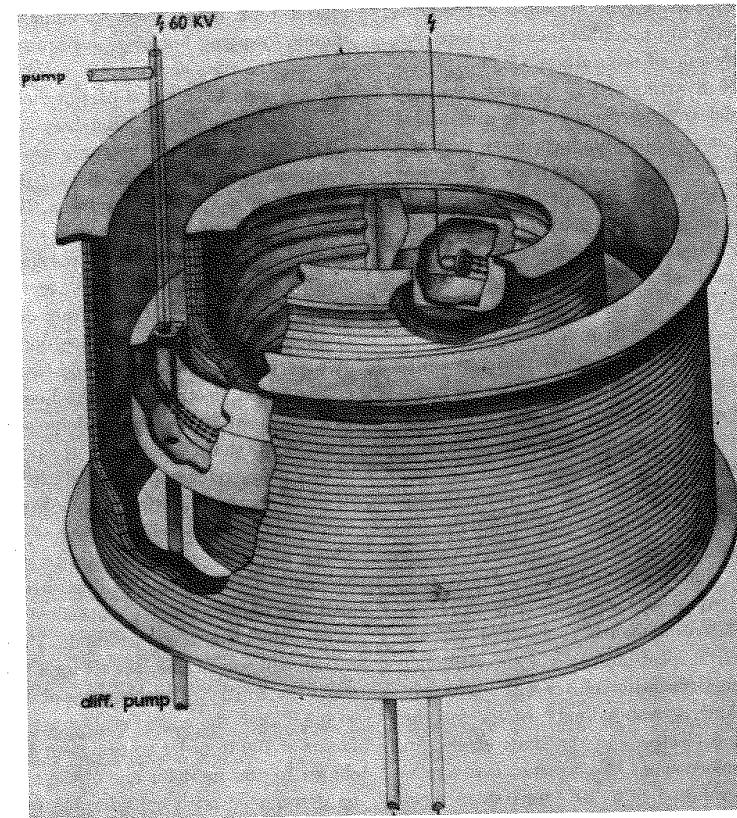


Fig. I:3. First iron-free double focussing spectrometer adapted for ESCA. The magnetic field is obtained from two co-axial coils with radii 24 cm and 36 cm, and height 48 cm.⁵

Large Spin-Orbit Splitting

Pb: $6s^2 6p^2$: L-S Coupling

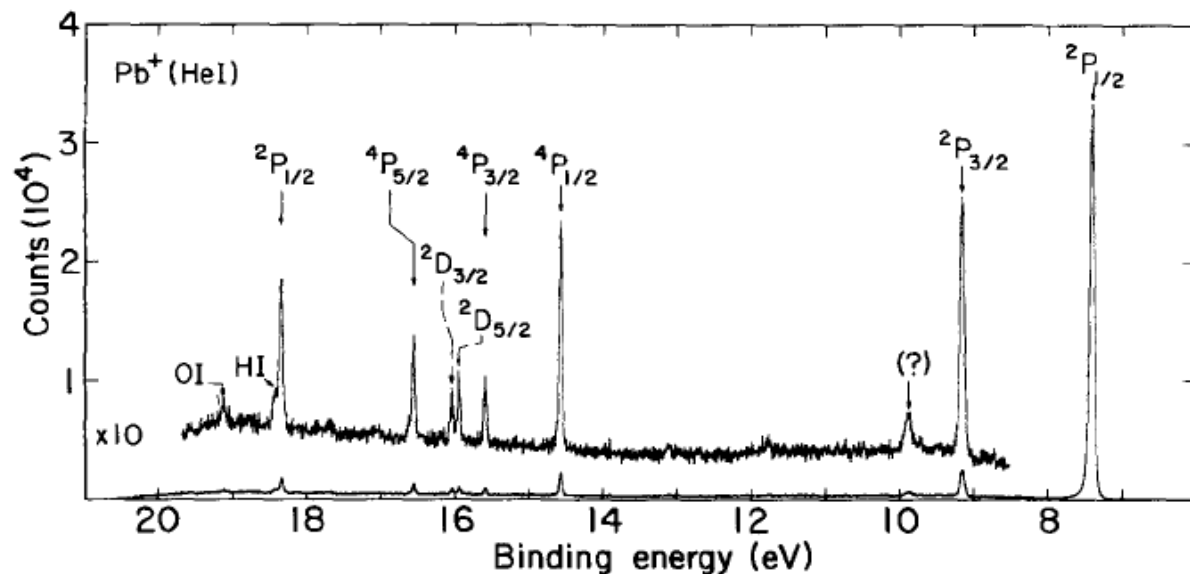
Intermed. Coupling

J-J Coupling

50% $6p_{1/2}$ - 50% $6p_{3/2}$

93% $6p_{1/2}$ - 7% $6p_{3/2}$

100% $6p_{1/2}$ - 0% $6p_{3/2}$



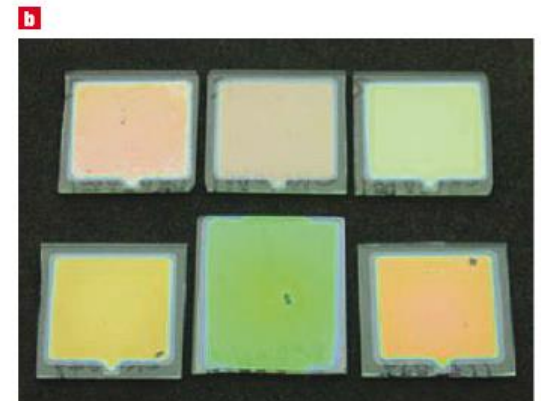
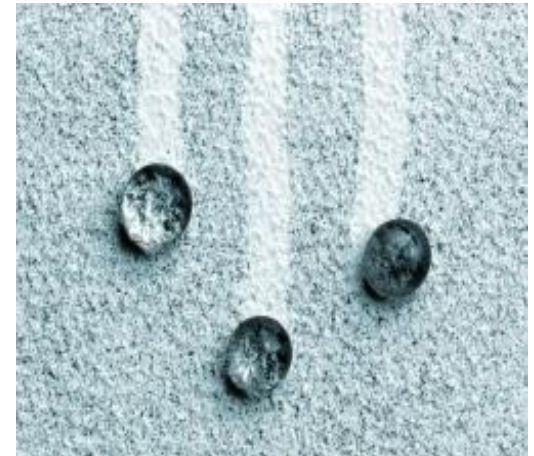
J. Chem. Phys., Vol. 63, No. 8, 15 October 1975



**INERT-PAIR EFFECT
SPIN POLARIZATION
(SPINTRONICS , MOTTTRONICS)**

Why Surface?

- Hydrophobicity x Hydrophilicity
- Wettability
- Adhesion
- Self - Cleaning
- Friction
- Corrosion, Protection, etc.
- Color – Optical Prop.



1978-1994 –GAP!!!!

3rd Hand KRATOS ES300 (~50 k\$)



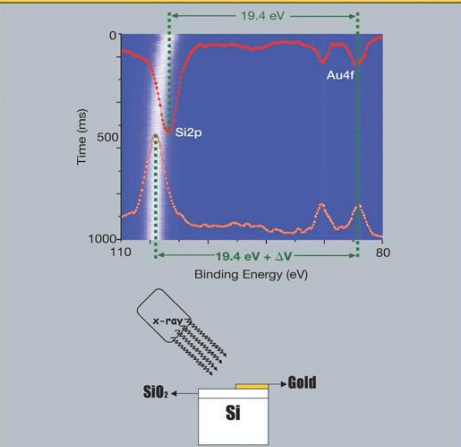
2002 2nd Hand KRATOS ES800 (~60 k\$)

JPCRD

VOLUME 108
APRIL 29, 2004
NUMBER 17
<http://pubs.acs.org/JPCB>

THE JOURNAL OF PHYSICAL CHEMISTRY

B



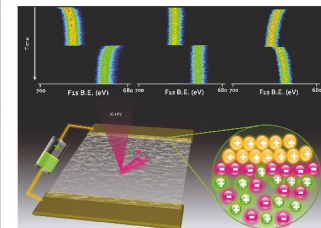
Two Hundred Time-Resolved XPS Spectra Displaying the Charging of a 400-nm SiO₂ Layer in Contact with a Au Metal Strip (see page XXX)

CONDENSED MATTER, MATERIALS, SURFACES, INTERFACES, & BIOPHYSICAL CHEMISTRY

PUBLISHED WEEKLY BY THE AMERICAN CHEMICAL SOCIETY



2009 DEMO Thermo Fisher K-Alpha (~200 k\$) – ECASIA'09 Conference



Showing research from the surface-science laboratory of Dr. S. Sauer at the Chemistry Department of Bilkent University, Ankara, Turkey.

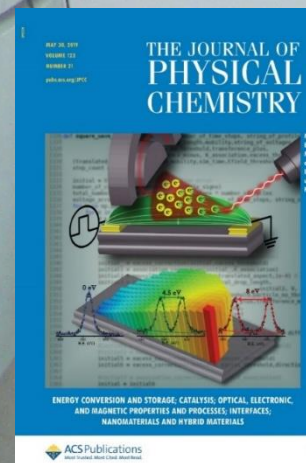
This XPS enables visualization of electrode potential screening in an ionic liquid medium with temporal and spatial resolution.

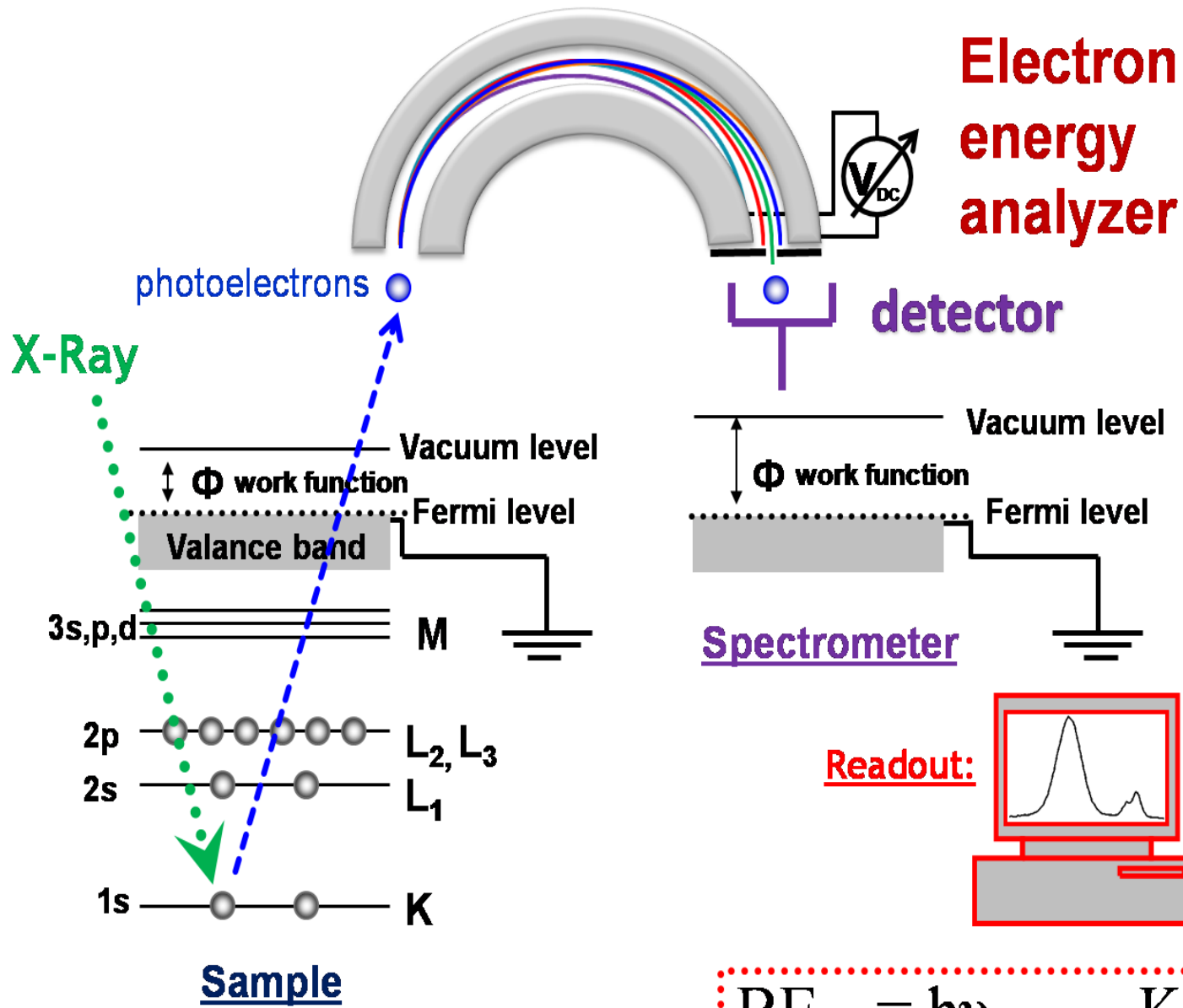
X-ray photoelectron spectroscopy is used to map local electrical potentials in a device configured as a capacitor electrode, with an ionic liquid infused polymer film between two electrodes. The screening of the electrode is mapped in voltage bias is followed by time- and position-dependent F_{1s} signals of the ionic liquid cations away from the electrodes. Shifts in the binding energy of the peaks reveal that the device has two capacitively-potential regions, each following the polarization of one of the electrodes.



2016 www.rsc.org/pccp
Representing volume 18(18)

2019

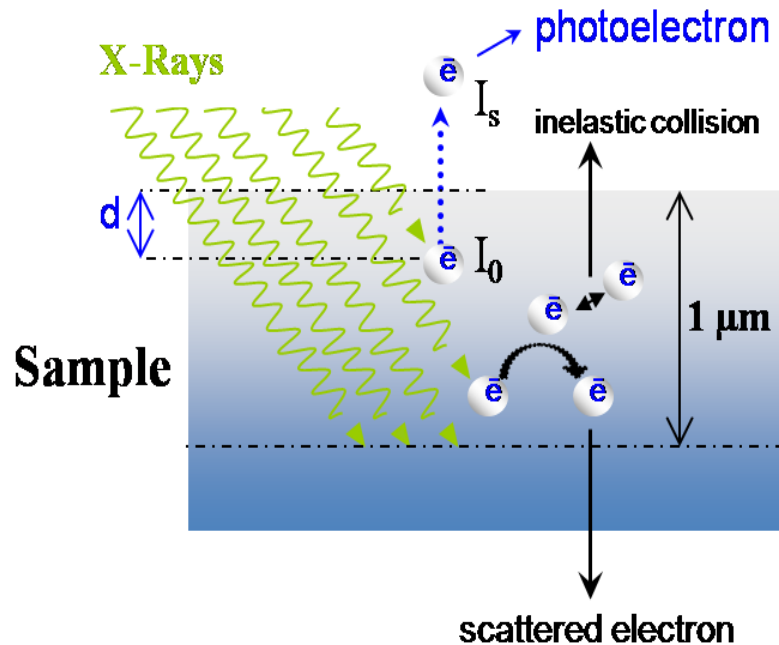




$$BE_{pe} = h\nu_{x-ray} - KE_{pe}$$

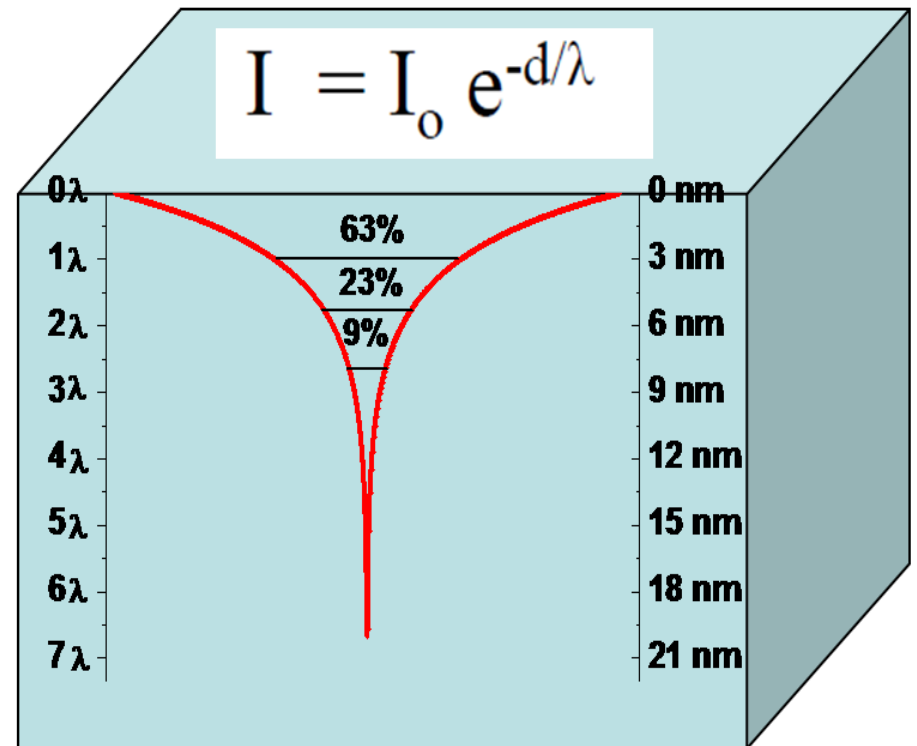
Surface Sensitive

(a)



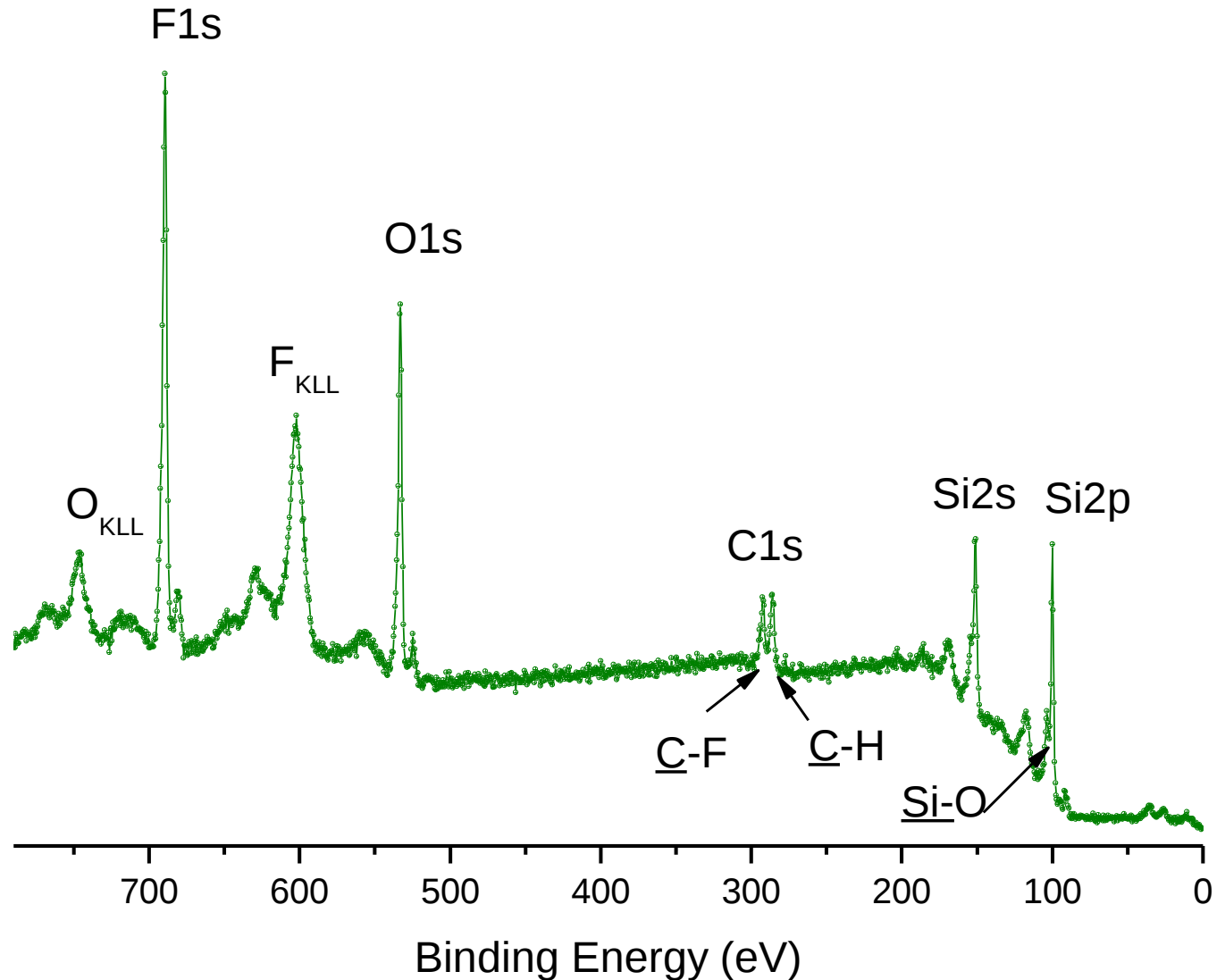
(b)

Beer-Lambert equ.:



- 1- Surface Sensitive
- 2- Element Specificity
- 3- Chemical Specificity

Hydrophobic Si (<10nm)

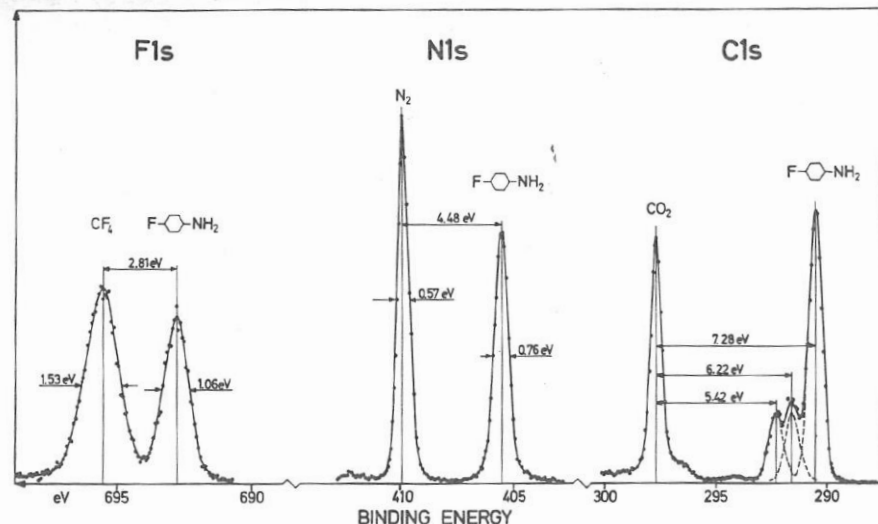


Chemical Shifts

1975

CRYSTAL
GROWTH
& DESIGN

2015



39. The core electron spectrum of *para*-aminofluorobenzene. CF_4 , N_2 and CO_2 have been used as calibration gases, mixed with the gas sample under study.

Proton Transfer, Hydrogen Bonding, and Disorder: Edge X-ray Absorption Fine Structure and X-ray Photoelectron Spectroscopy of Bipyridine–Acid Salts and Co-crystals

Joanna S. Stevens,^{*,†} Lauren K. Newton,[†] Chernio Jaye,^{||} Christopher A. Muryn,[§] Daniel A. Fischer,^{||} and Sven L. M. Schroeder^{*,†,‡,§}

[†]School of Chemical Engineering and Analytical Science, The University of Manchester, Oxford Road, Manchester M13 9PL, U.K.

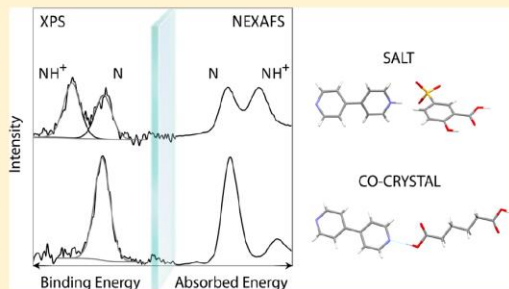
[‡]School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, U.K.

[§]School of Chemistry, The University of Manchester, Brunswick Street, Manchester M13 9PL, U.K.

^{||}National Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States

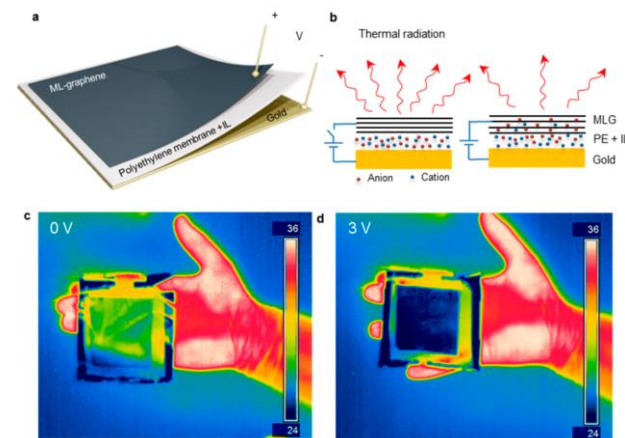
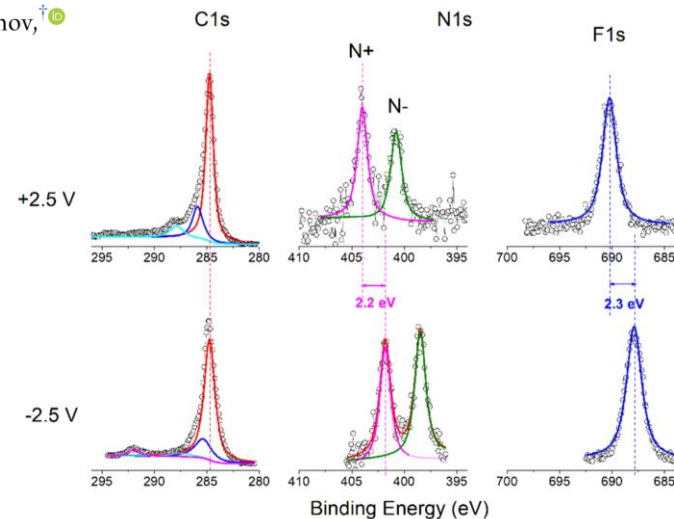
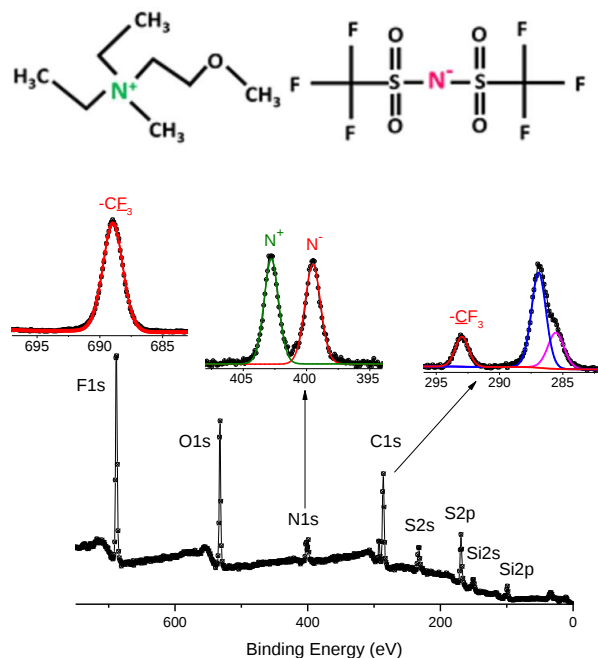
S Supporting Information

ABSTRACT: The sensitivity of near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to Brønsted donation and the protonation state of nitrogen in the solid state is investigated through a series of multicomponent bipyridine–acid systems alongside X-ray photoelectron spectroscopy (XPS) data. A large shift to high energy occurs for the $1s \rightarrow 1\pi^*$ resonance in the nitrogen K-edge NEXAFS with proton transfer from the acid to the bipyridine base molecule and allows assignment as a salt ($\text{C}=\text{NH}^+$), with the peak ratio providing the stoichiometry of the types of nitrogen species present. A corresponding binding energy shift for $\text{C}=\text{NH}^+$ is observed in the nitrogen XPS, clearly identifying protonation and formation of a salt. The similar magnitude shifts observed with both techniques relative to the unprotonated nitrogen of co-crystals ($\text{C}=\text{N}$) suggest that the chemical state (initial-state) effects dominate. Results from both techniques reveal the sensitivity to identify proton transfer, hydrogen bond disorder, and even the potential to distinguish variations in hydrogen bond length to nitrogen.



Graphene-Based Adaptive Thermal Camouflage

Omer Salihoglu,[†] Hasan Burkay Uzlu,[†] Ozan Yakar,[†] Shahnaz Aas,[†] Osman Balci,[†] Nurbek Kakenov,^{†,‡} Sinan Balci,^{‡,§} Selim Olcum,[§] Sefik Süzer,^{||,§} and Coskun Kocabas*^{*,†,||,§}



Ionic Liquid Intercalates MLC

Electrical Potentials on MLC and IL DIFFER!!!

Chemical Shift

What is it?

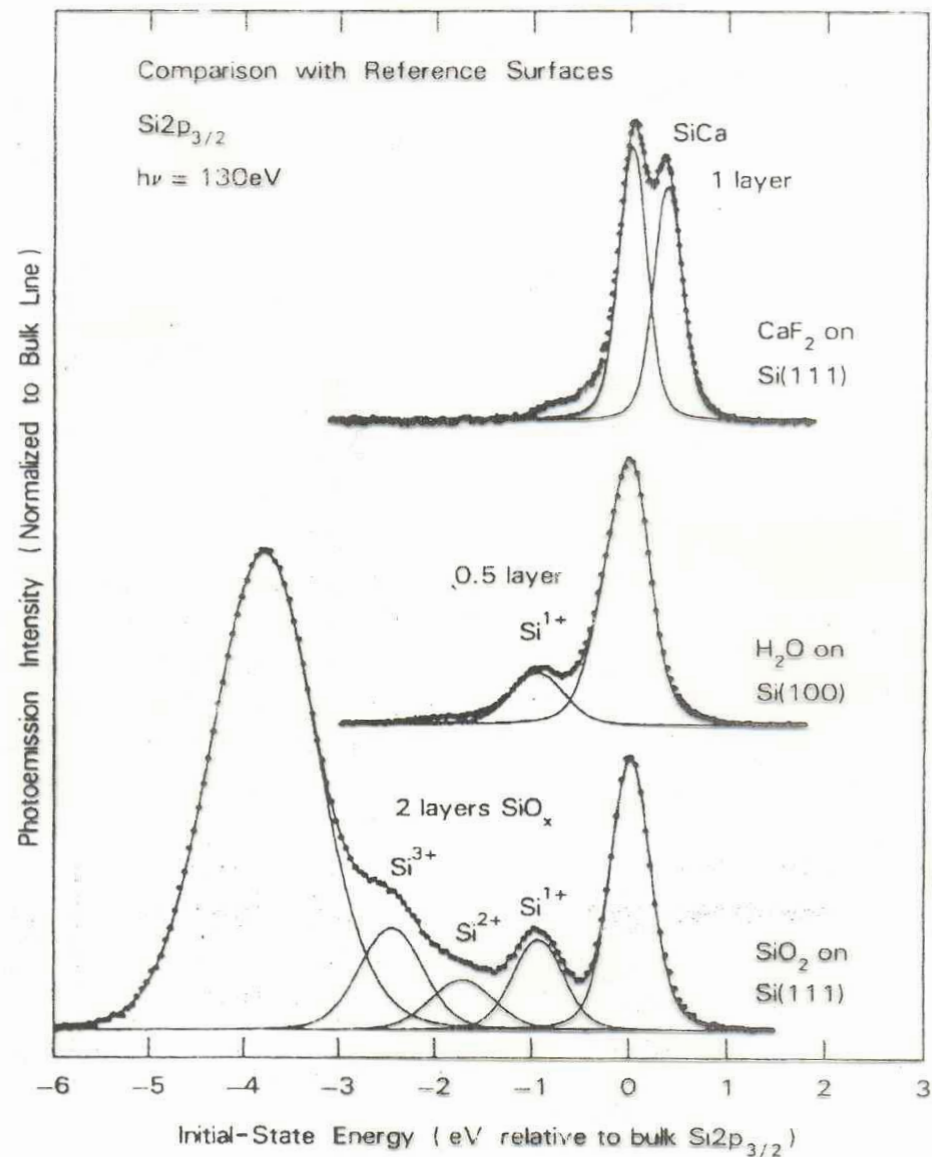
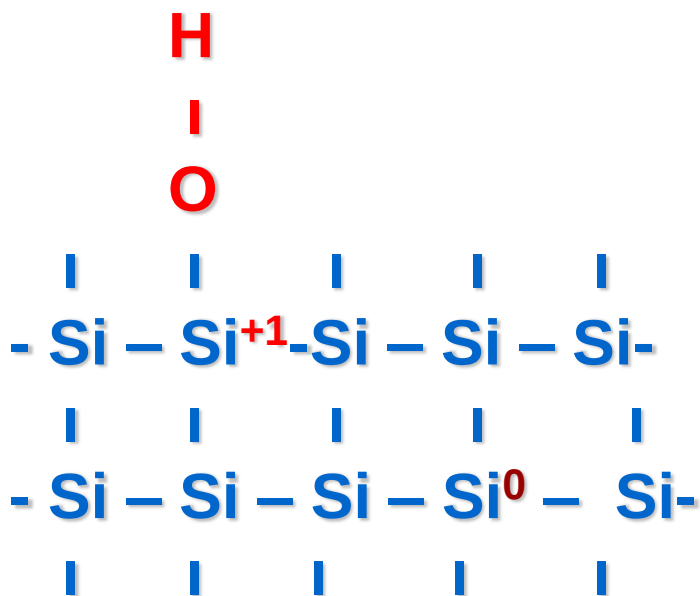
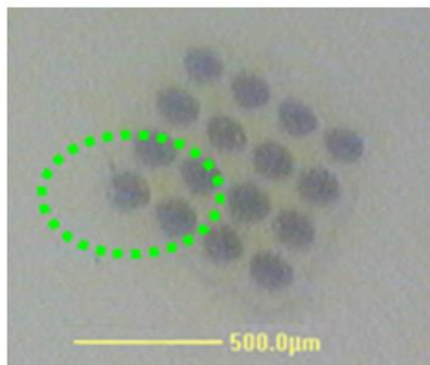


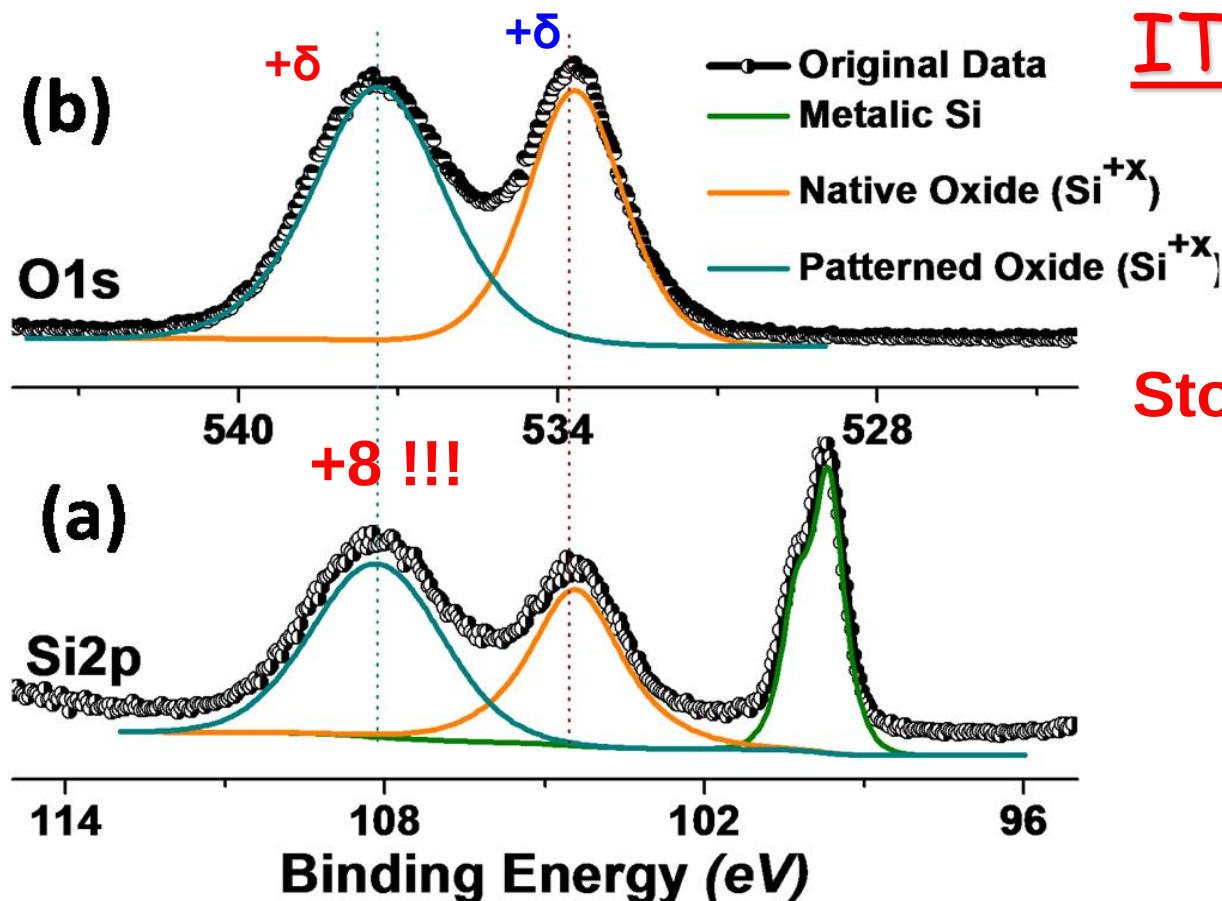
FIG. 3. Comparison of core-level spectra from SiO₂/Si(111) with the CaF₂/Si(111) interface and the H₂O-exposed Si(100)2×1 surface. A density of two Si layers is derived for the Si atoms in intermediate-oxidation states by comparing with the H₂O/Si(100) reference surface.

Elemental Characterization with XPS



Name	Peak BE	FWHM eV	At. %
Si2p metallic	99.6	0.67	10.3
Si2p native	104.02	1.63	13.4
Si2p patterned	106.91	2.84	17.3
O1s Scan native	533.51	2	26.0
O1s Scan patterned	536.58	2.93	33.1

What

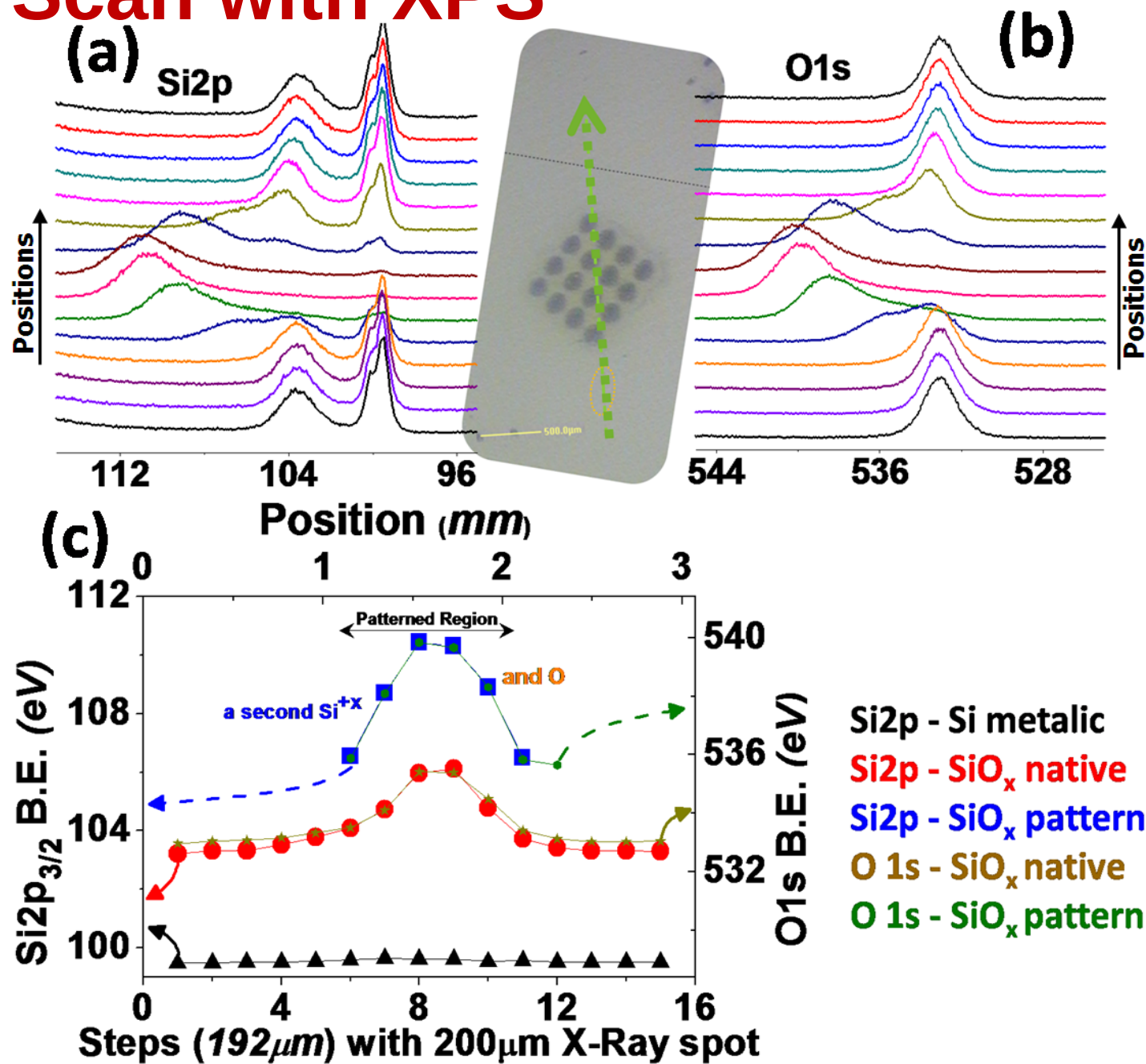


IT IS NOT?

Stoichiometric
ratio:

Si:O
~1:2

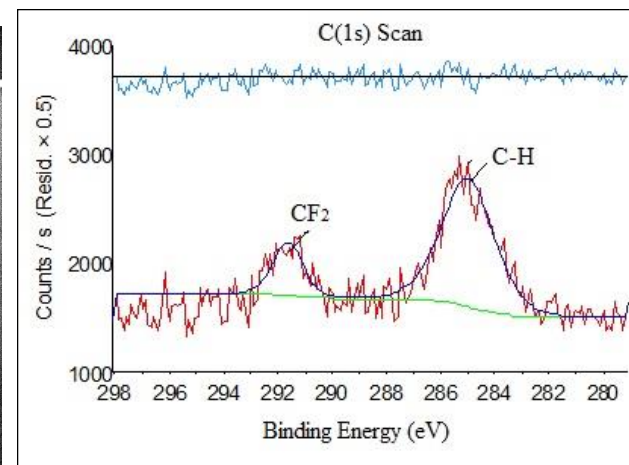
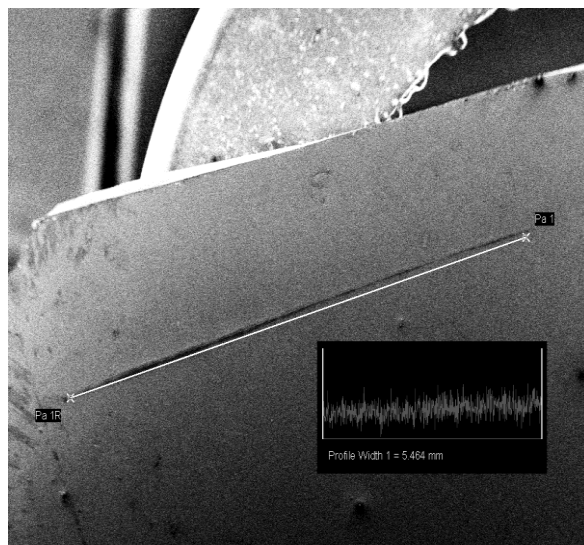
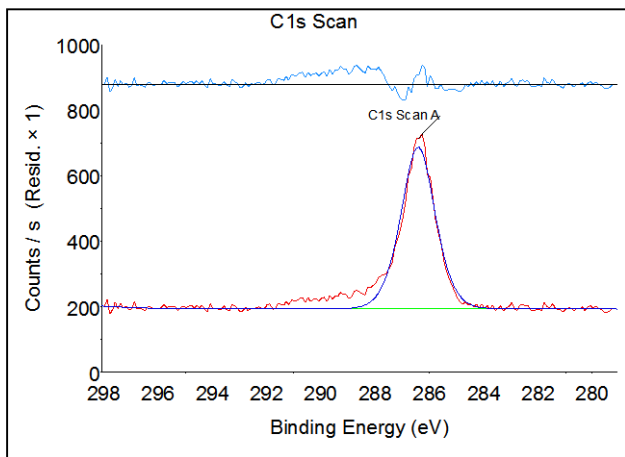
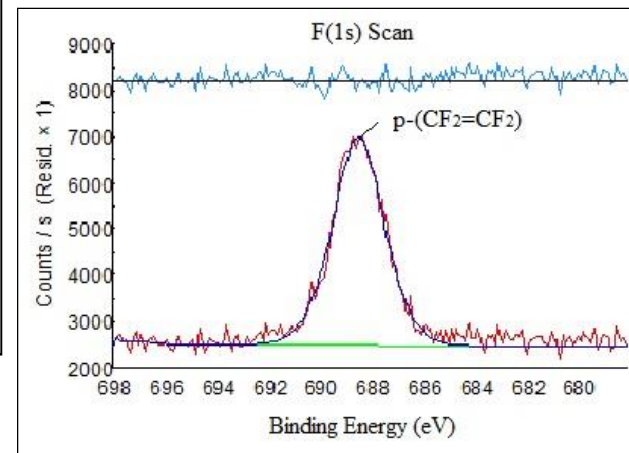
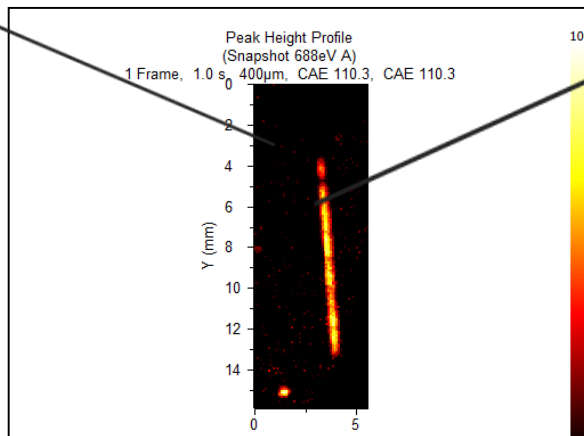
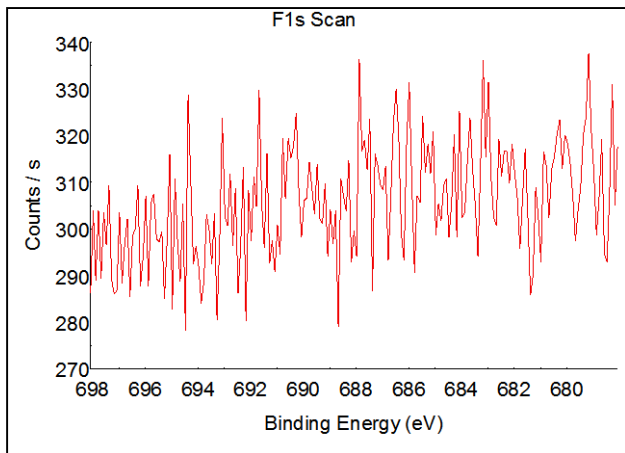
Line Scan with XPS



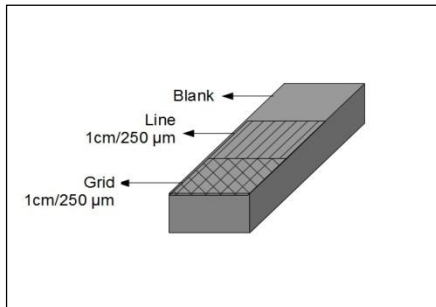
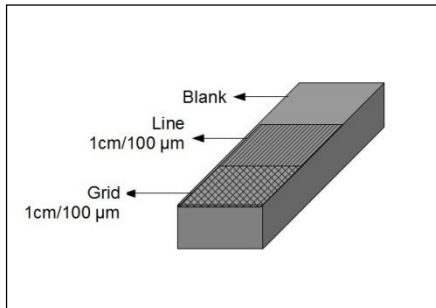
XPS-SEM RESULTS

off the line

on the line



WCA results of 'as is' surfaces – Case: Grid+Line+Blank



WCA(⁰) Results

Density of PTFE	Blank	Line	Grid
(1cm/100µm)	51	76	98
(1cm/250µm)	46	89	100

Experimental Details

-Data Gathering Modes

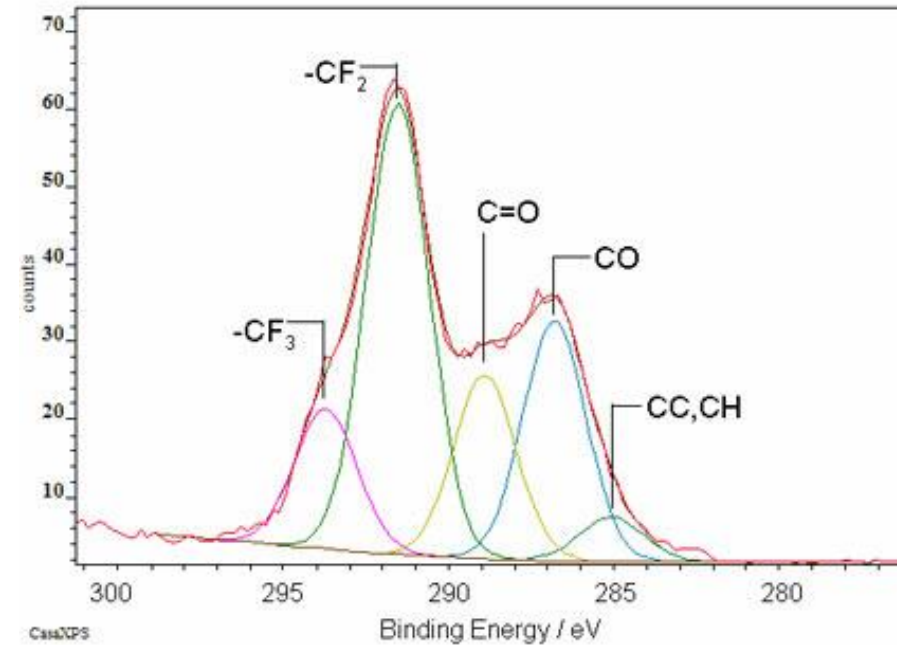
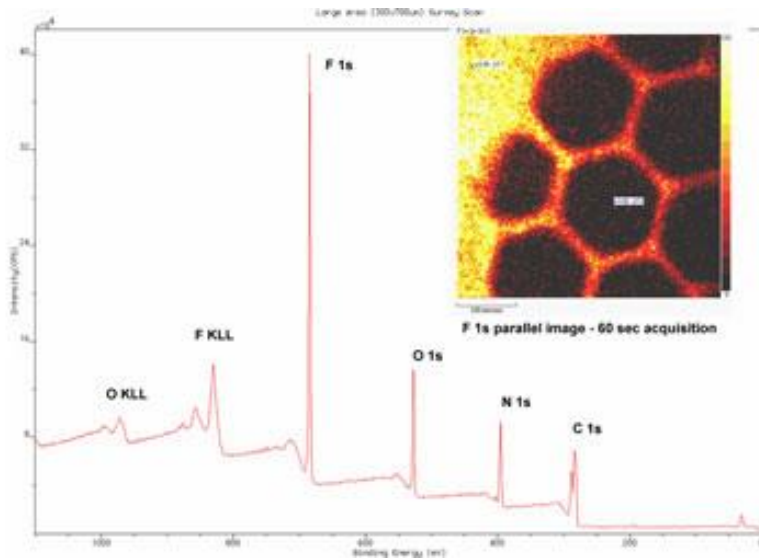
- Survey Scans (Poorer Energy Resolution)
- Regions Scans
- Line Scans
- Iterations in Snap-Shot Mode (>10 ms)
- Areal Scans and Maps

Lateral Position or Energy

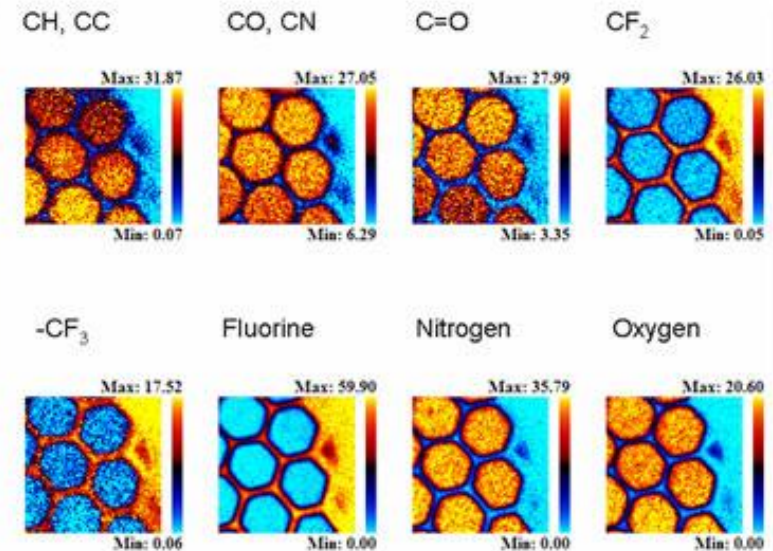
- Lateral Resolution 30-400 μm
- Time Resolution >10 ms
- Depth Information (4-6 nm, XPS)

LIMITATIONS

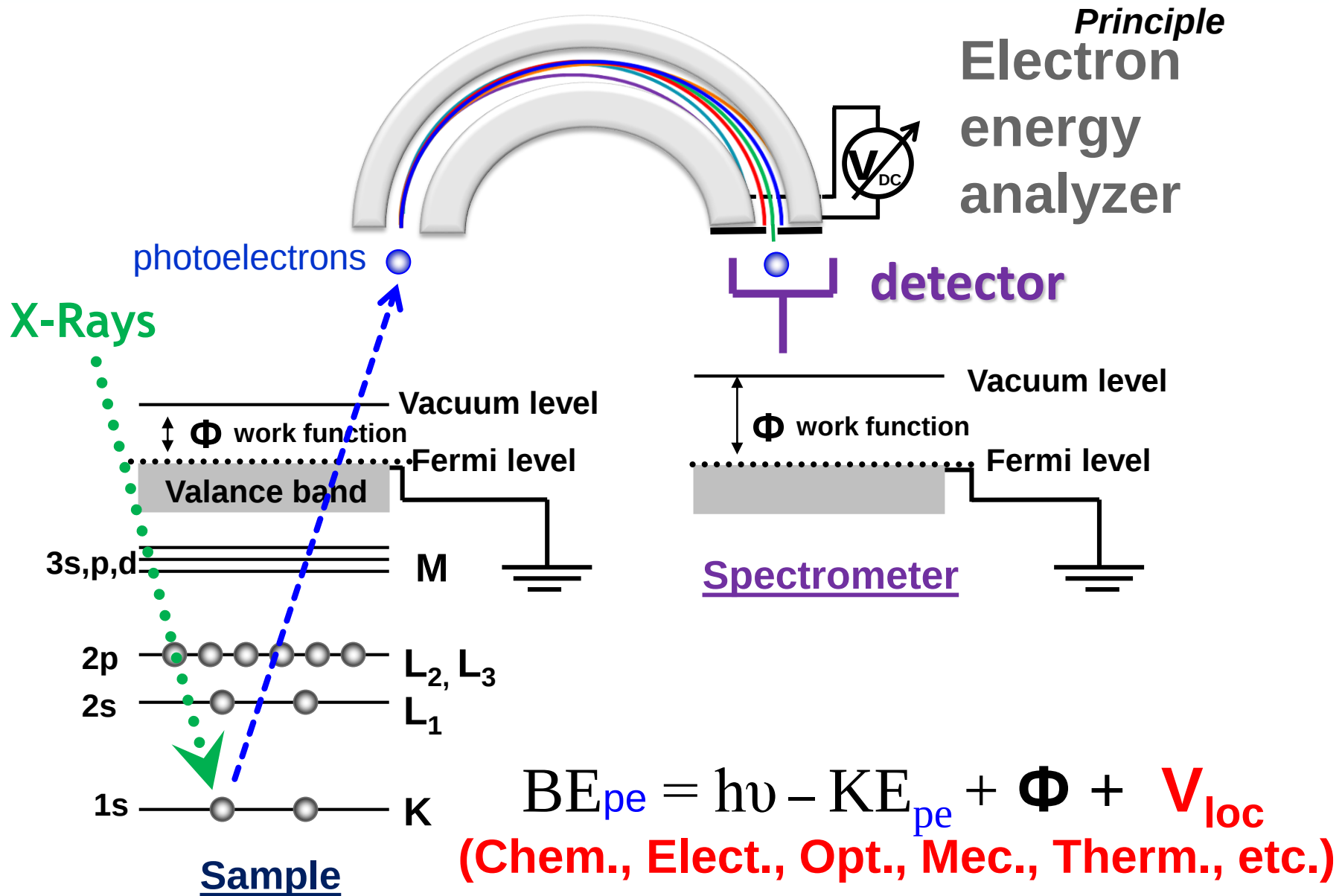
Lateral Resolution: $\sim 5 \mu\text{m}$
 Time Resolution: $\sim 10 \text{ ms}$
 Element Sensitivity: $\sim 0.5 \%$
 Chemical Sensitivity: Fair
 Physical (Phases) Sen.: Poor
 (No Way to Distinguish say
 btwn ANATASE x RUTILE !!!)



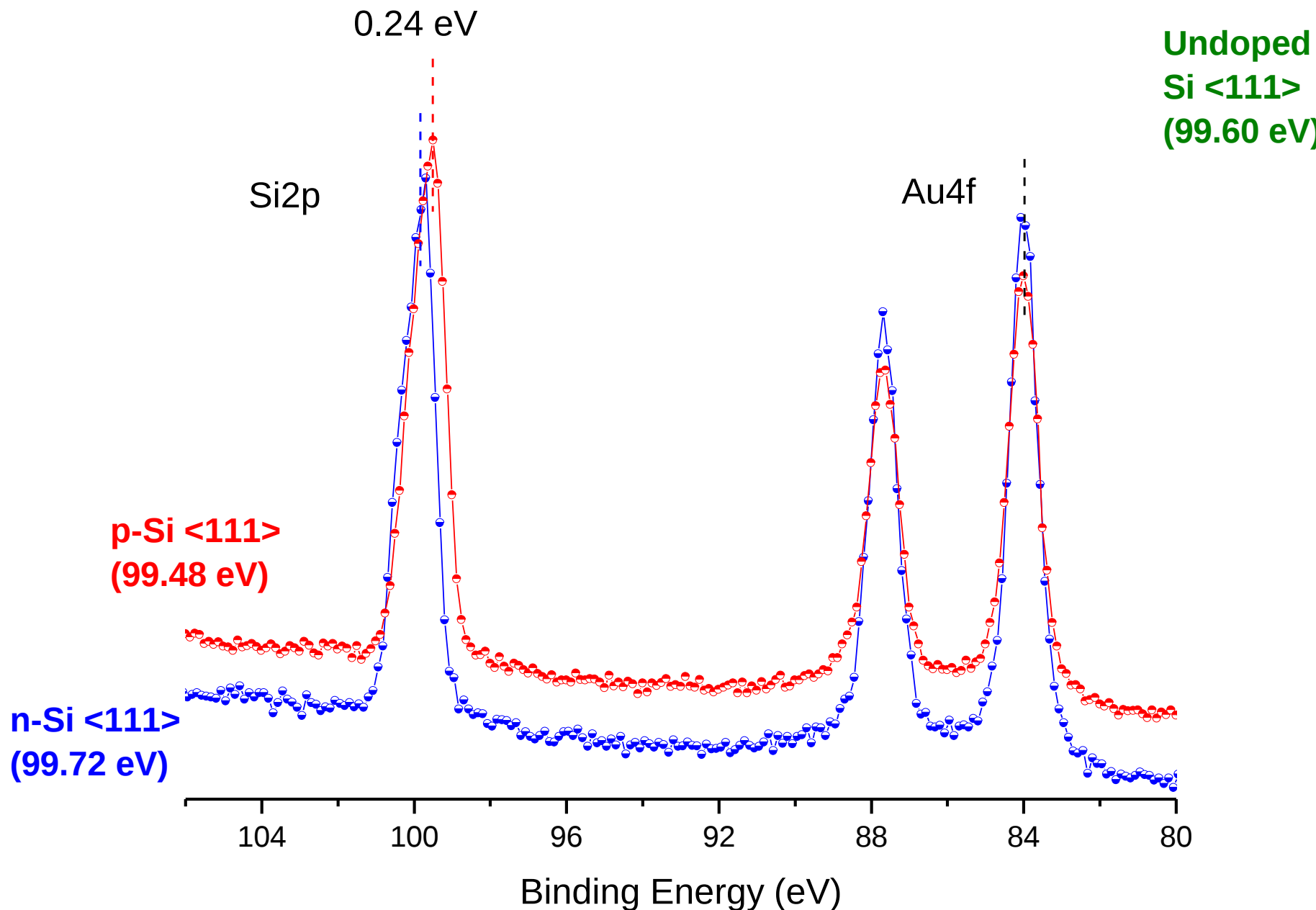
— C 1s spectrum generated from 5x5 pixels



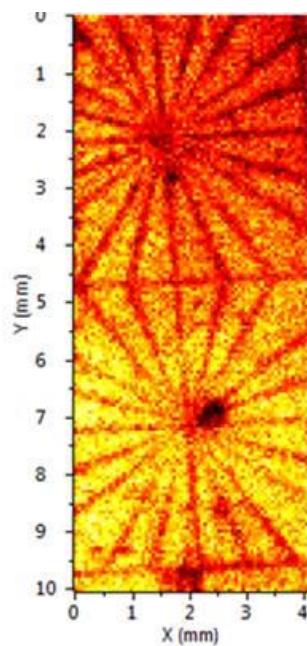
X-ray Photoelectron Spectroscopy:



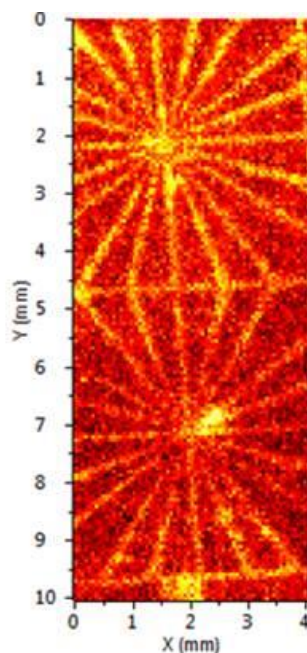
- Charge Sensitivity



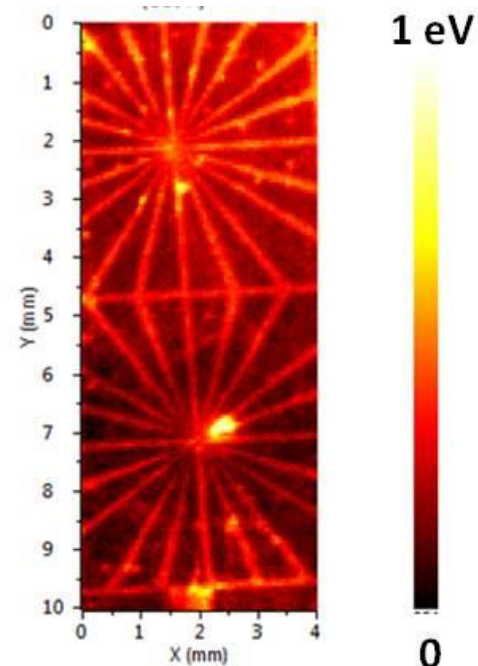
4- Charge Sensitive



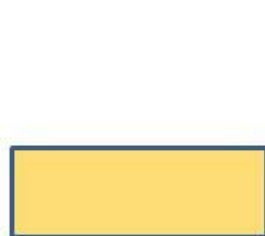
O1s at (a) 533.44 eV



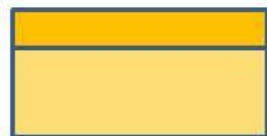
(b) 530.29 eV



(c) O1s B.E. Shift



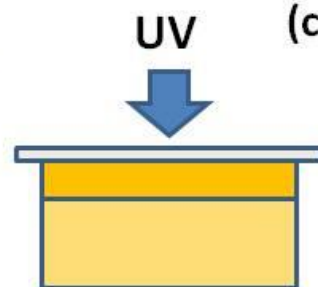
p-Si



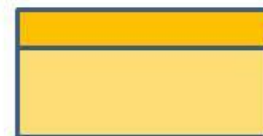
Thermal Oxide



Mask

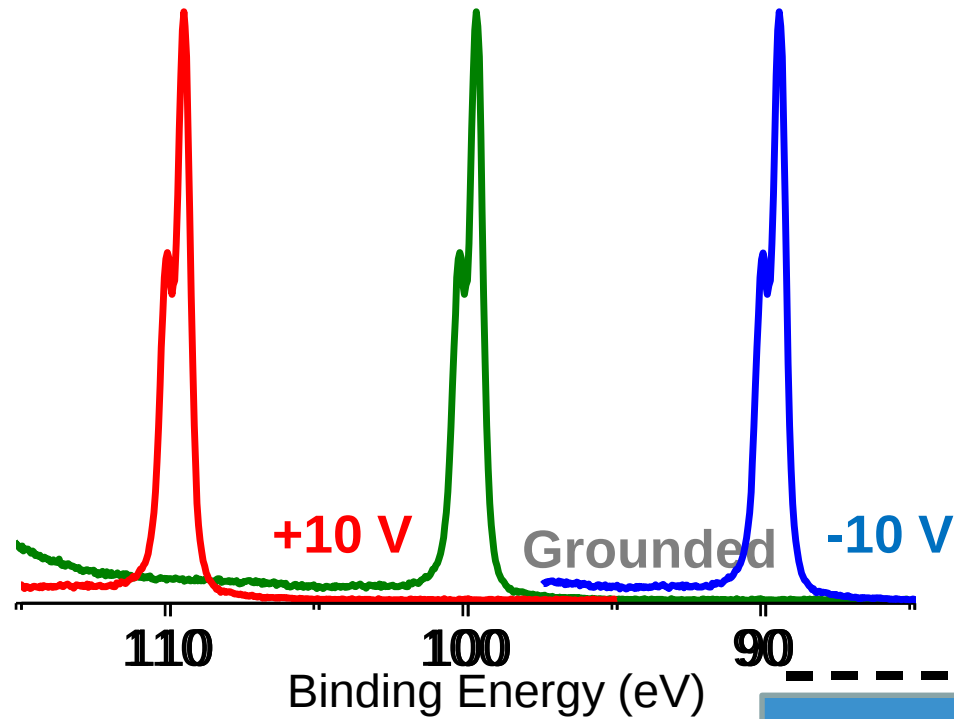


UV Exposure



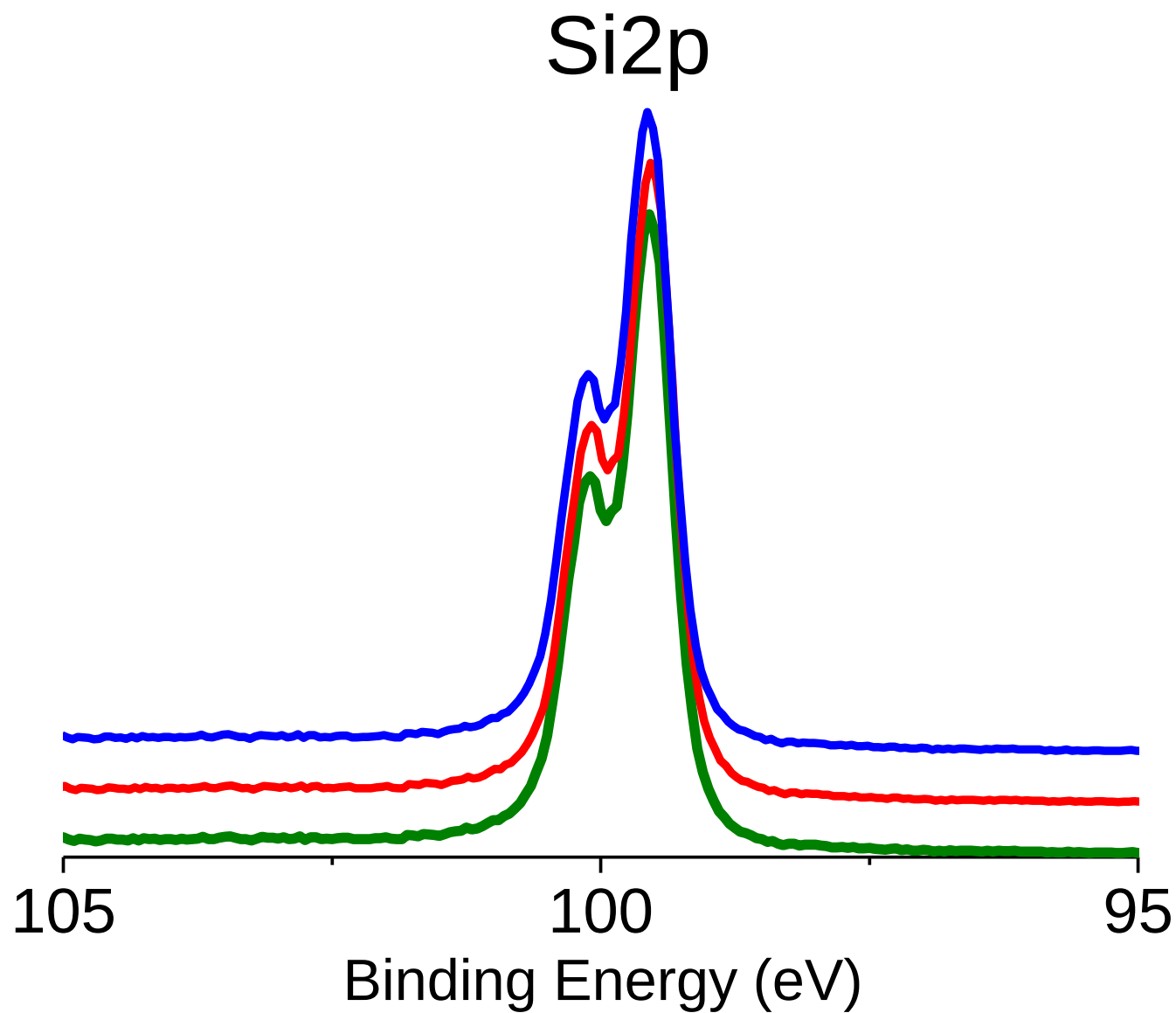
XPS Analysis

Si2p

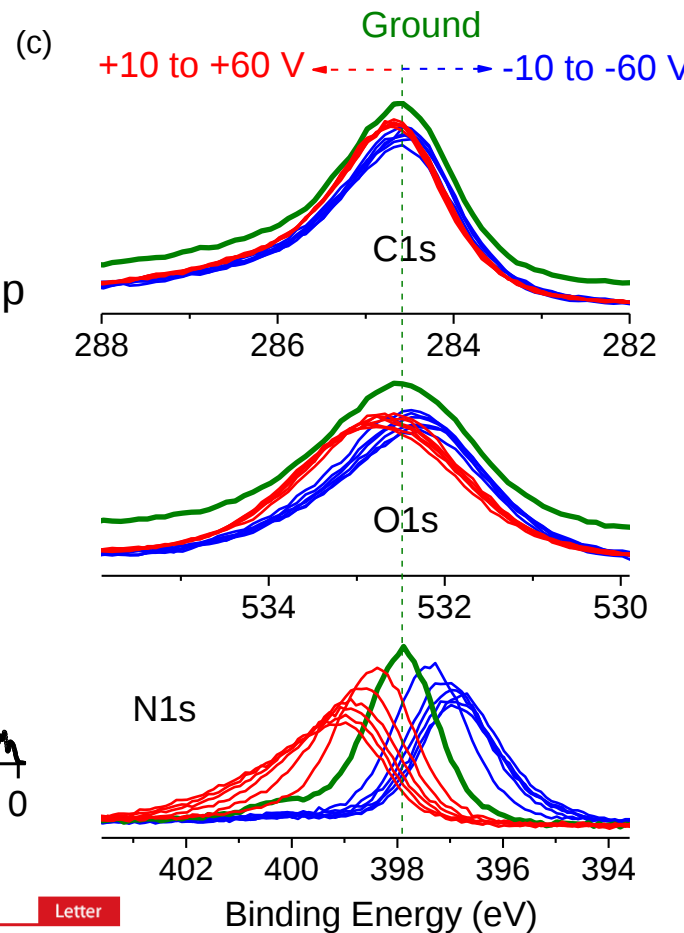
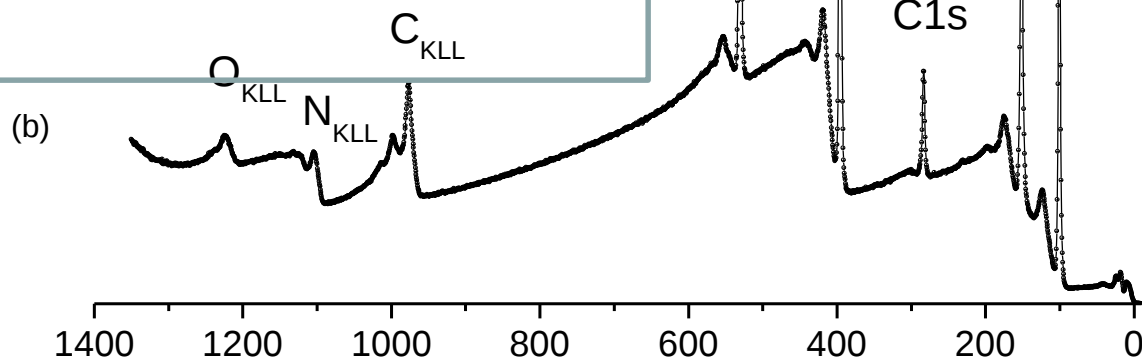
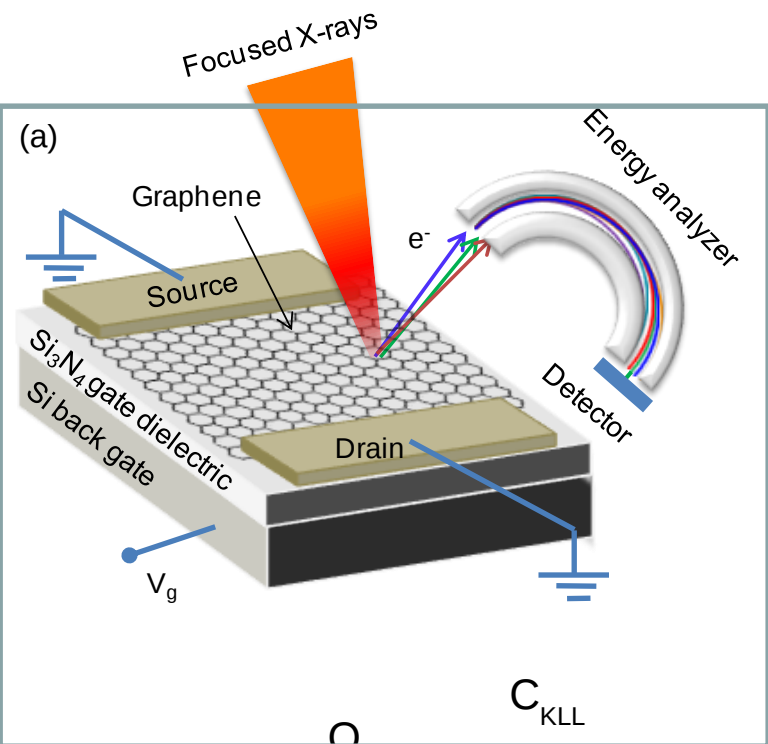


- Electrical Biasing (D.C.)

TRIVIAL SHIFTS FOR CONDUCTING MATERIALS



Gating



NANO LETTERS

Letter

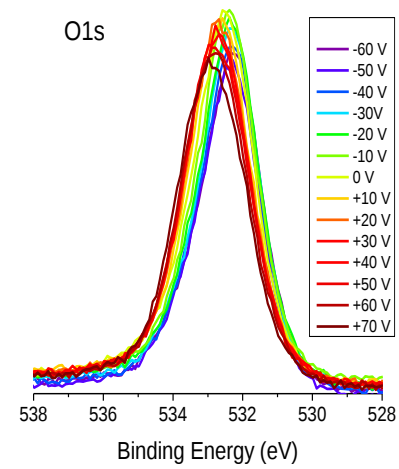
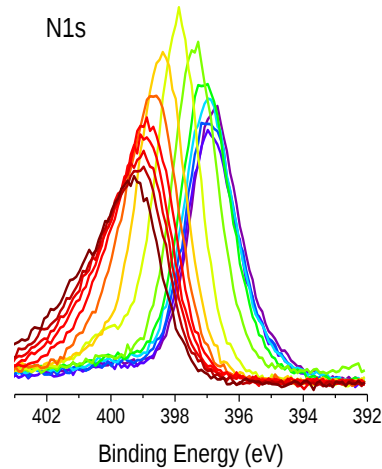
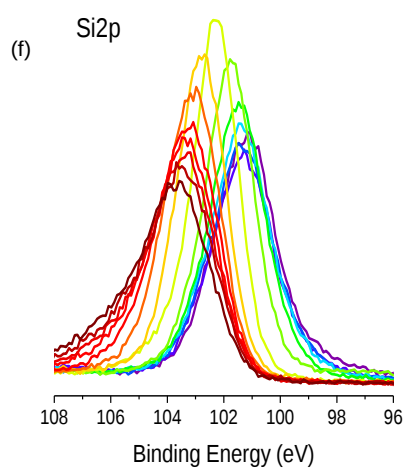
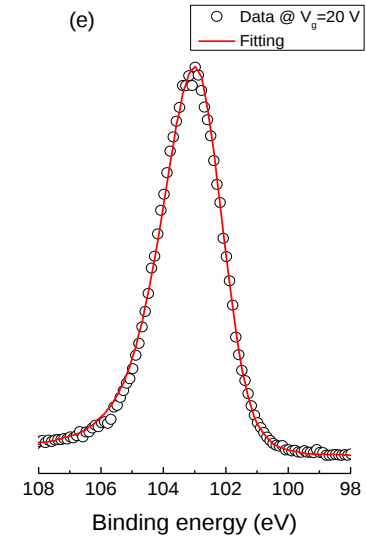
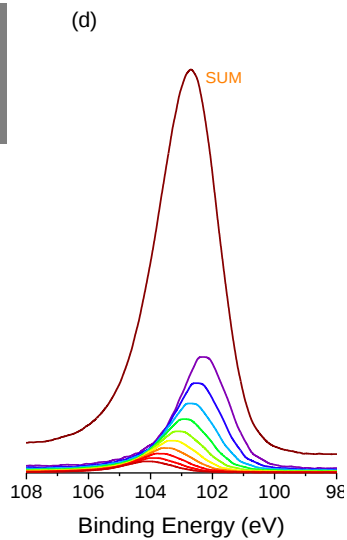
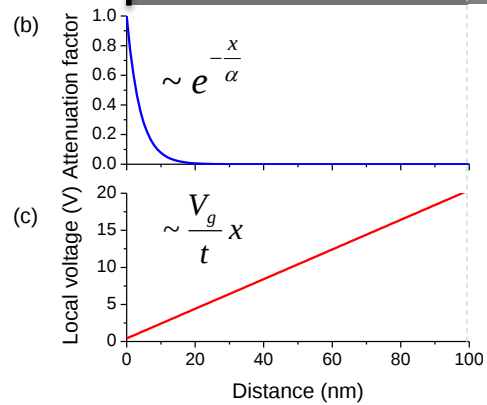
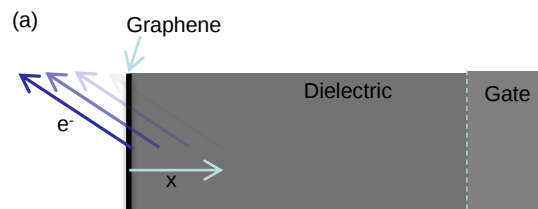
pubs.acs.org/NanoLett

dx.doi.org/10.1021/nl500842y | Nano Lett. 2014, 14, 2837–2842

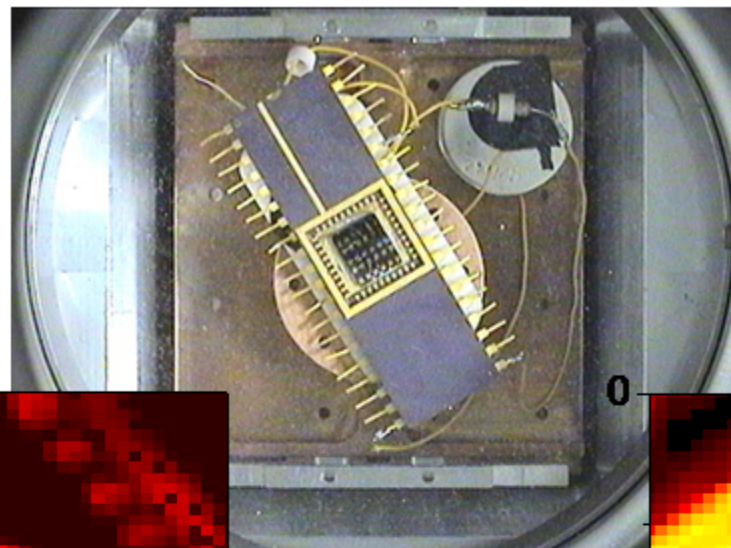
Gate-Tunable Photoemission from Graphene Transistors

Mehmet Copuroglu,[†] Pinar Aydogan,[†] Emre O. Polat,[‡] Coskun Kocabas,^{*,‡} and Sefik Sützer^{*,†}

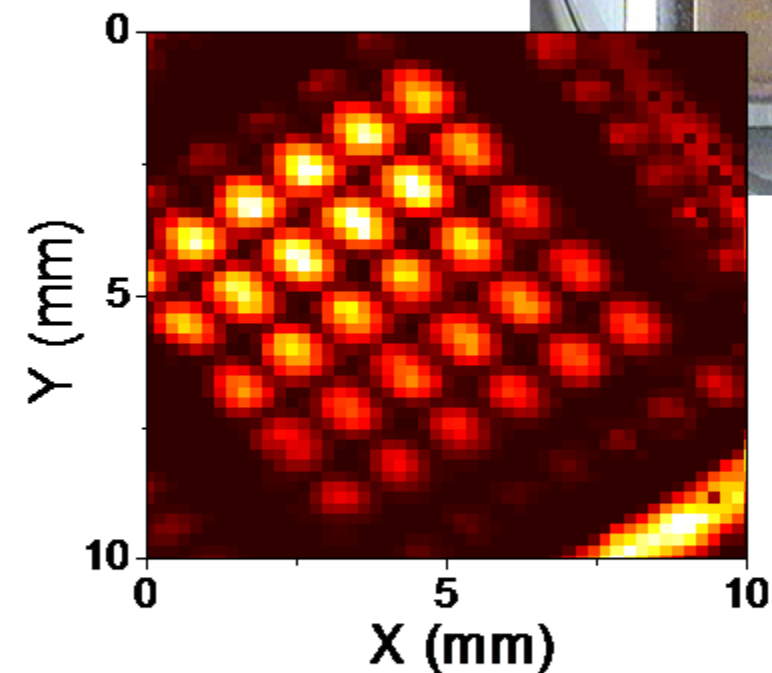
[†]Department of Chemistry and [‡]Department of Physics, Bilkent University, Ankara 06800, Turkey



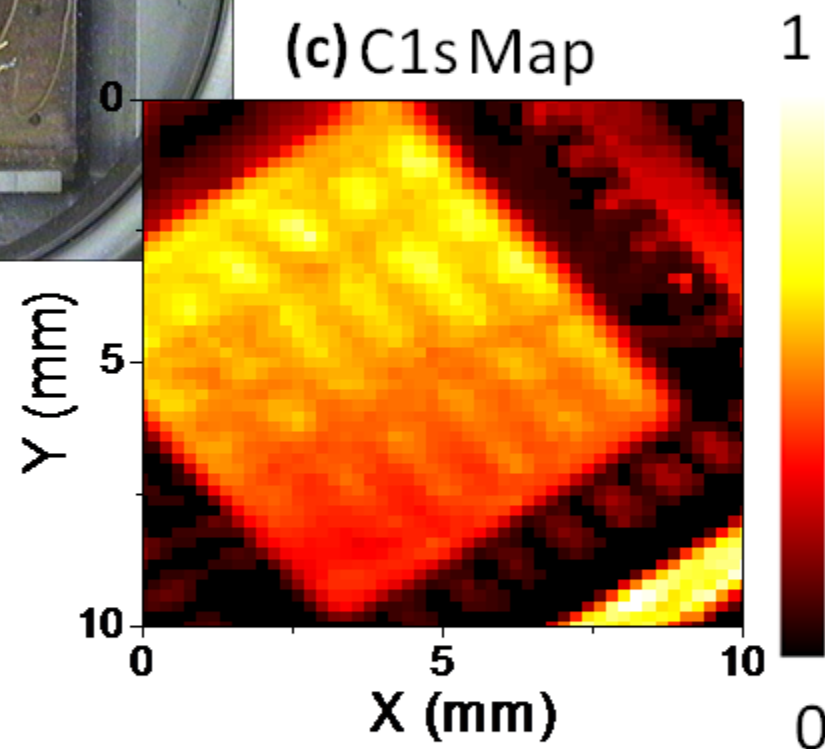
(d)



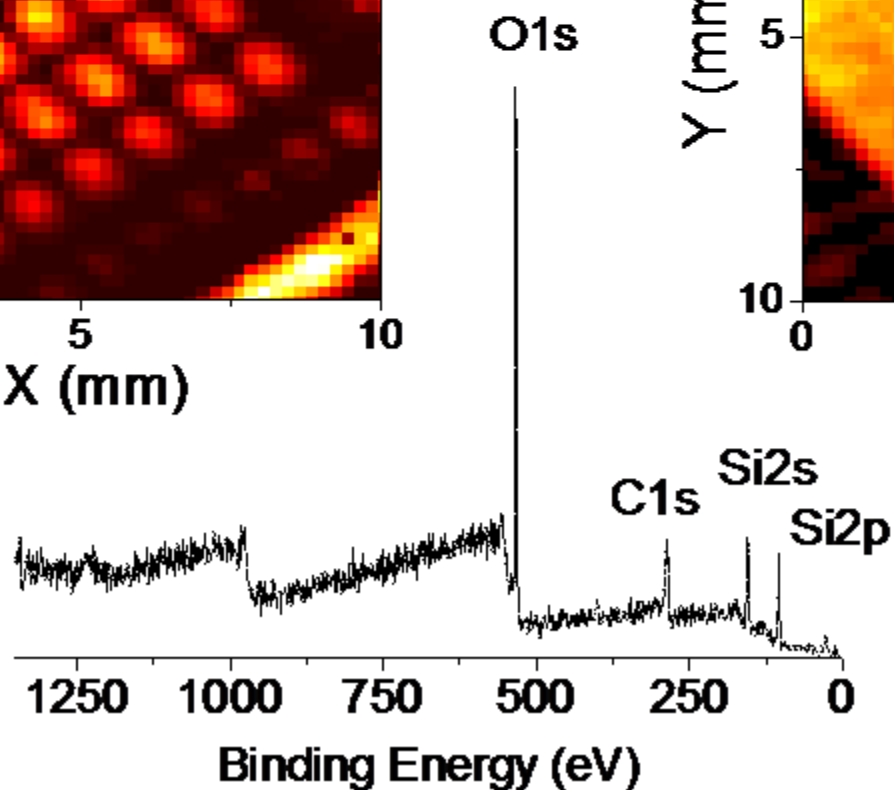
(b) Au4f Map

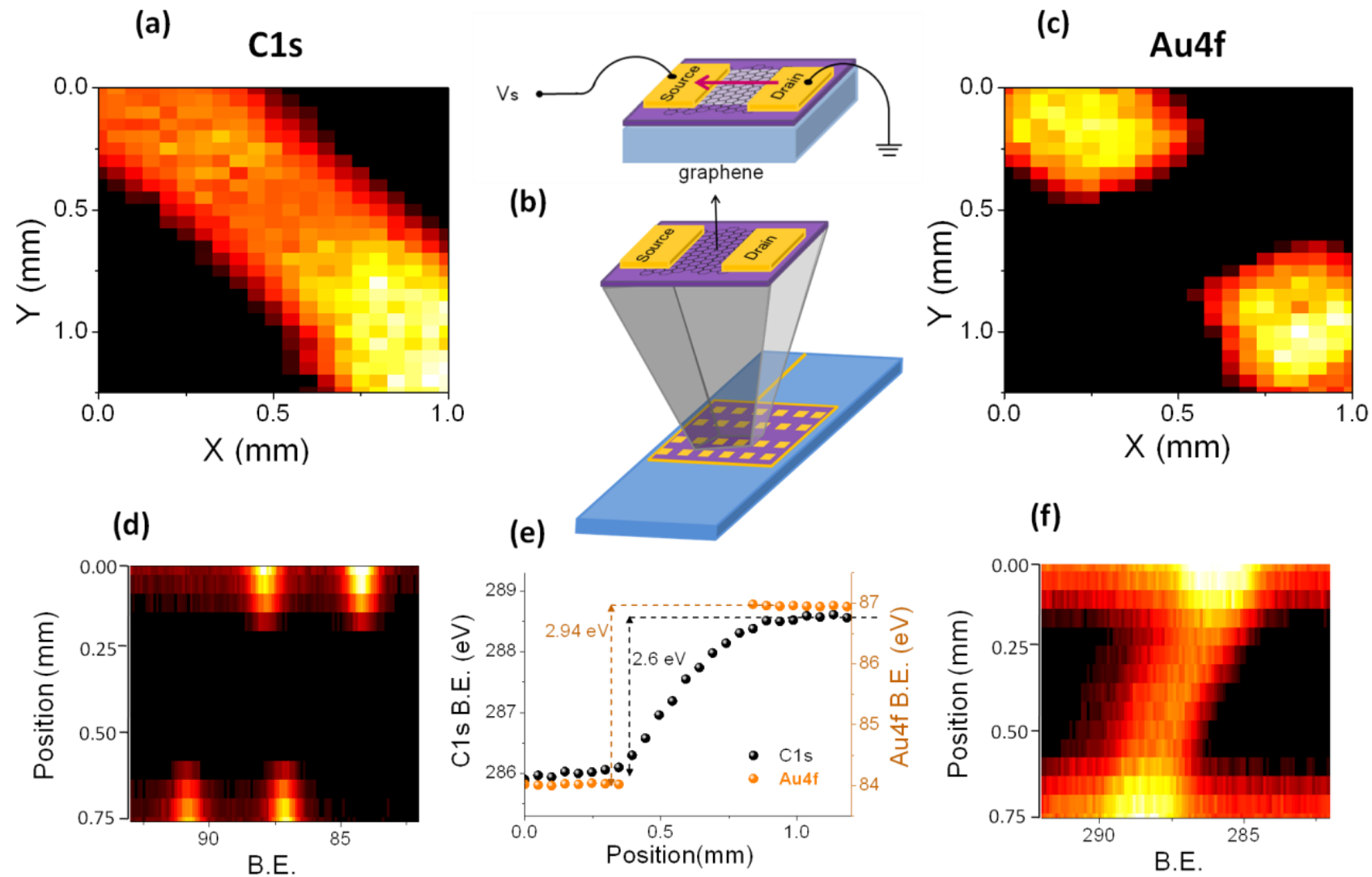


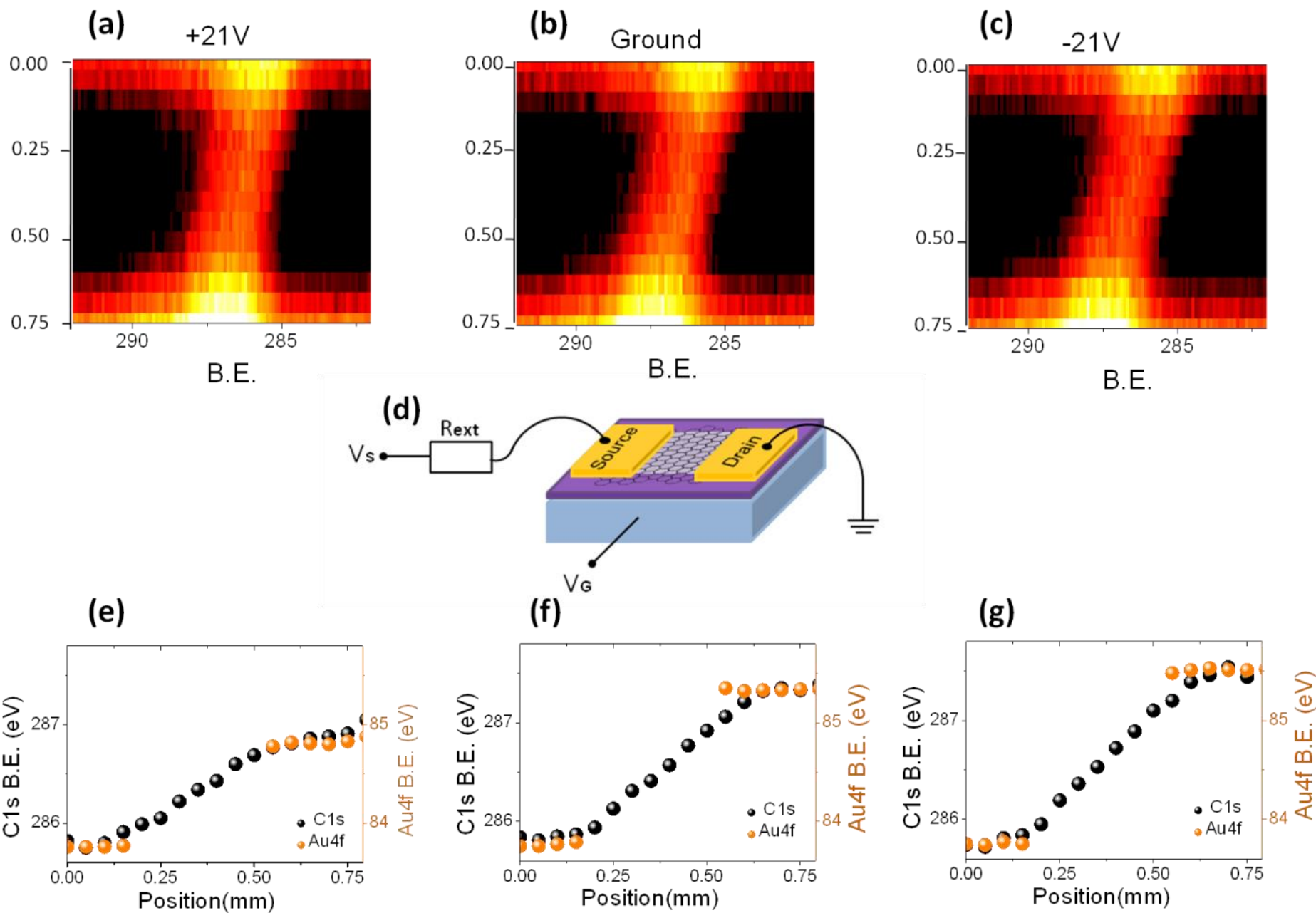
(c) C1s Map



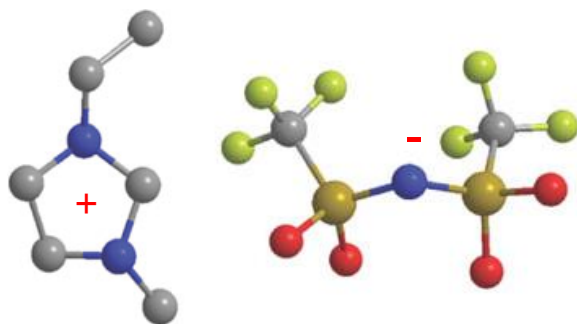
(a)







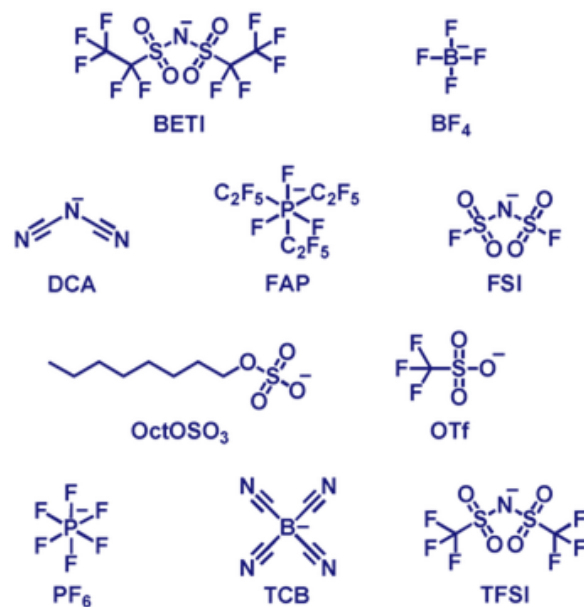
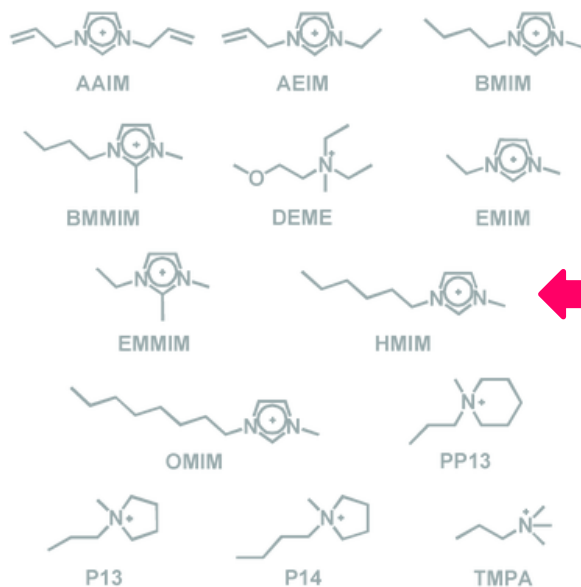
'Ionic Liquid'



Ionic Liquids (IL) is.....

Molten salt but at **Room Temperature**
composed only of large anions & cations

- ~No vapor pressure
- Designable & unlimited combinations





Electrode material–ionic liquid coupling for electrochemical energy storage

Xuehang Wang¹, Maryam Salari², De-en Jiang³, Jennifer Chapman Varela², Babak Anasori¹, David J. Wesolowski⁴, Sheng Dai⁴, Mark W. Grinstaff² and Yury Gogotsi¹

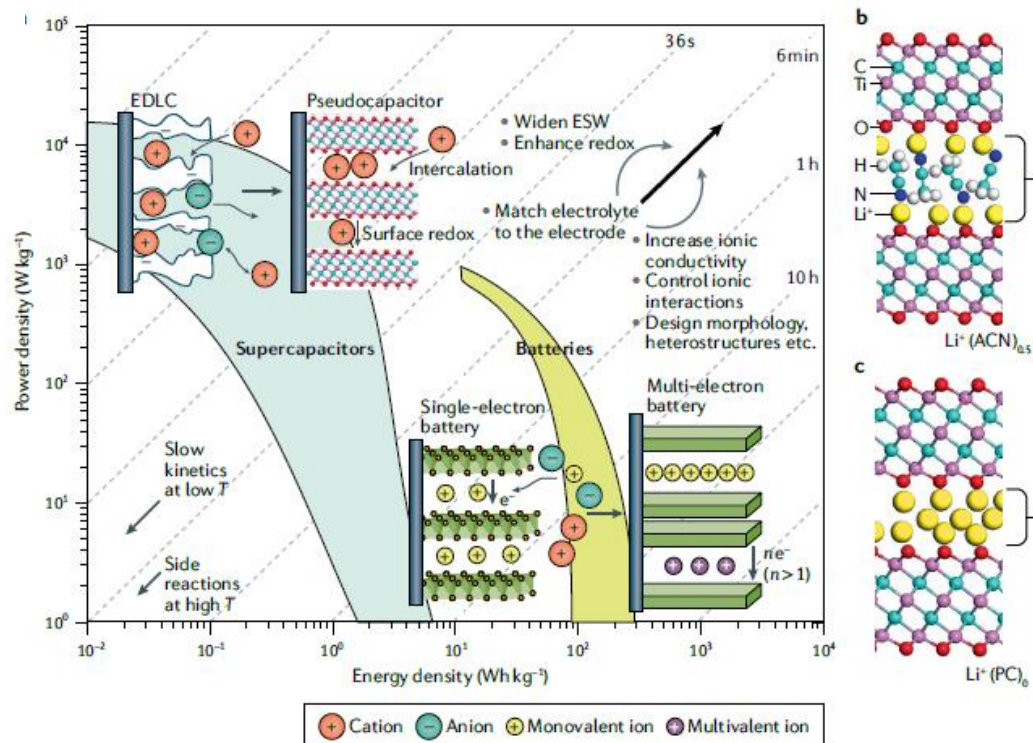
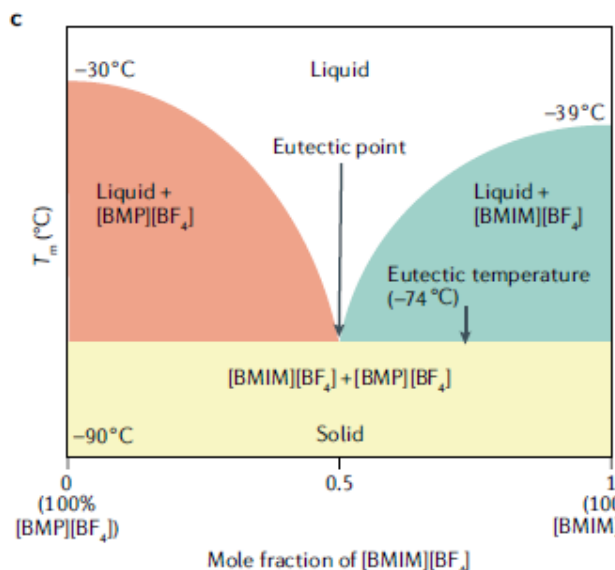


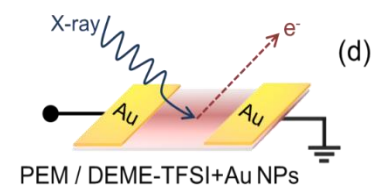
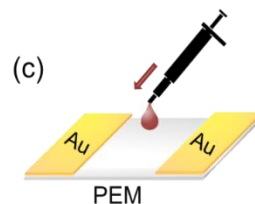
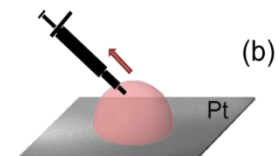
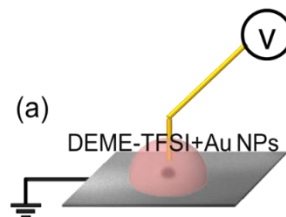
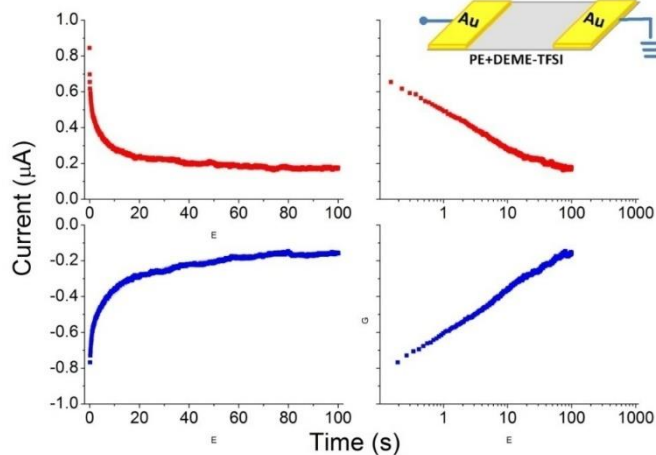
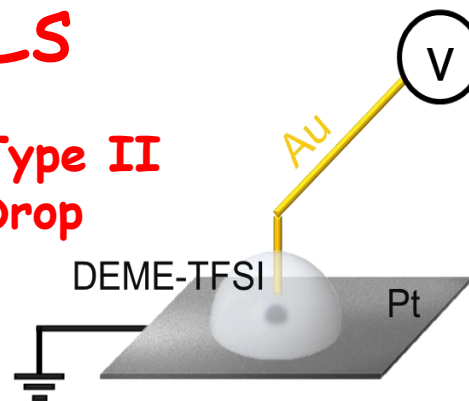
Fig. 6 | New electrolyte–electrode interfaces. **a** | A Ragone plot for electric double-layer capacitors (EDLCs) and Li-ion batteries, summarizing the key strategies to improve the energy and power density. The schematic shows that the introduction of pseudocapacitance (involving pseudocapacitive intercalation and surface redox process) and multi-electron redox processes (involving multi-phase transformations and multi-electron transfers per ion) can increase the energy density of EDLCs and batteries, respectively. The grey dashed lines indicate the time for complete charging or discharging of the device. **b** | A molecular dynamics (MD)-simulated image of a $\text{Ti}_3\text{C}_2\text{T}_x$ electrode in 1 M $\text{Li}[\text{TFSI}]$ (where $[\text{TFSI}]^-$ is bis(trifluoromethanesulfonyl)imide) in acetonitrile (ACN), showing the arrangement of ACN and Li ions confined between the charged $\text{Ti}_3\text{C}_2\text{T}_x$ layers²¹². **c** | A MD-simulated image of a $\text{Ti}_3\text{C}_2\text{T}_x$ electrode in 1 M $\text{Li}[\text{TFSI}]$ in propylene carbonate (PC), showing that the Li ions confined between the charged $\text{Ti}_3\text{C}_2\text{T}_x$ layers are fully desolvated²¹². The size of the Li ions is increased for clarity in the simulated images. ESW, electrochemical stability window; T, temperature. Panels b and c adapted from REF.²¹², Springer Nature Limited.

Devices with ILs

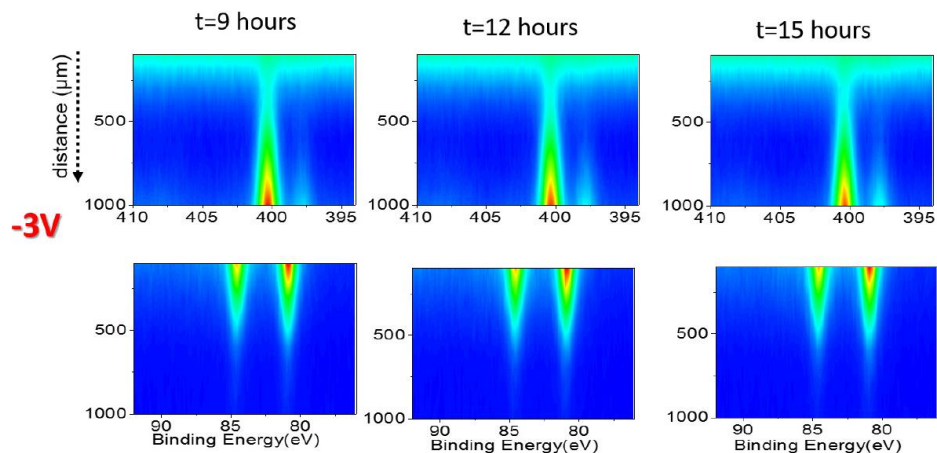
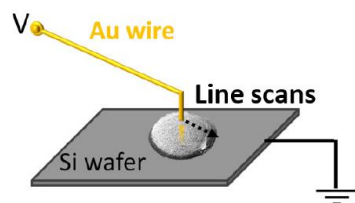
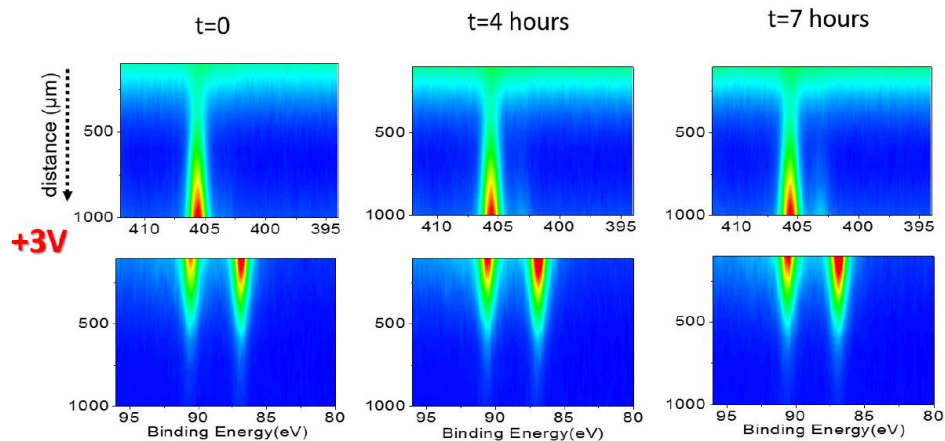
Type I
Coplanar Capacitor



Type II
Drop



- Electro-Chemical Synthesis of CARBENE



N1s

Au4f

N1s

Au4f

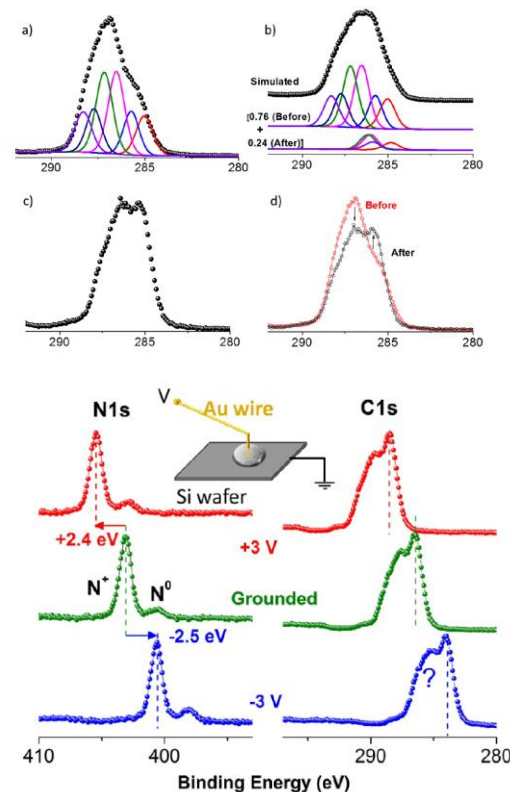
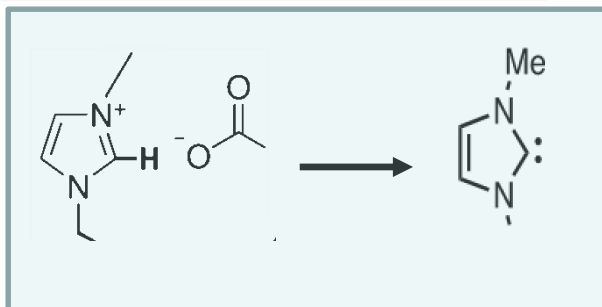
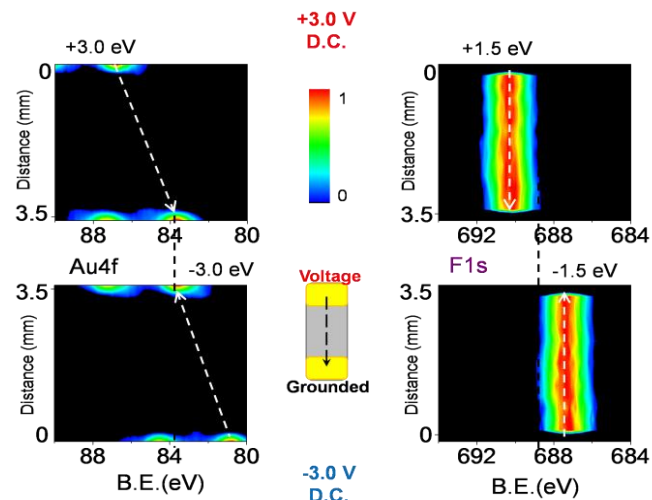
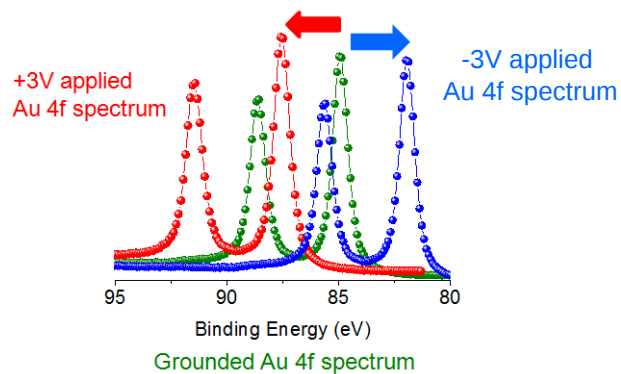
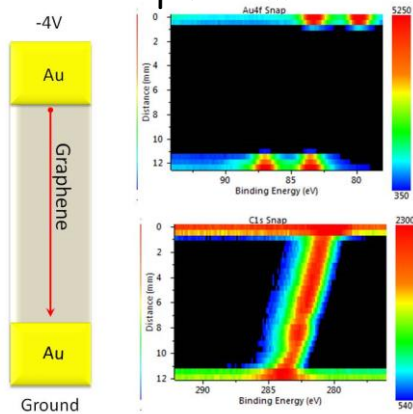


Fig. 3. XP Spectra of the N1s and Au4f regions along the line designated under +3 V and -3 V Bias and in different periods.

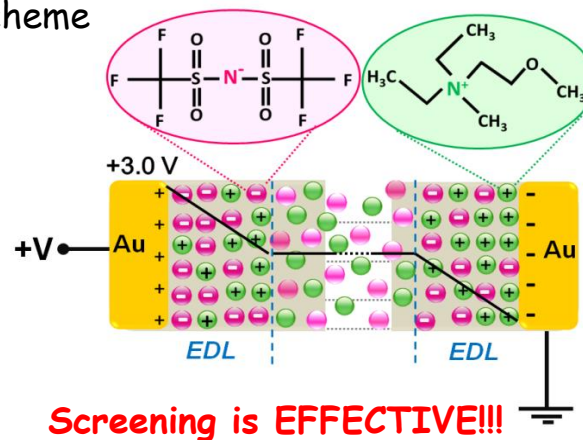
DC BIASING



Graphene !!!

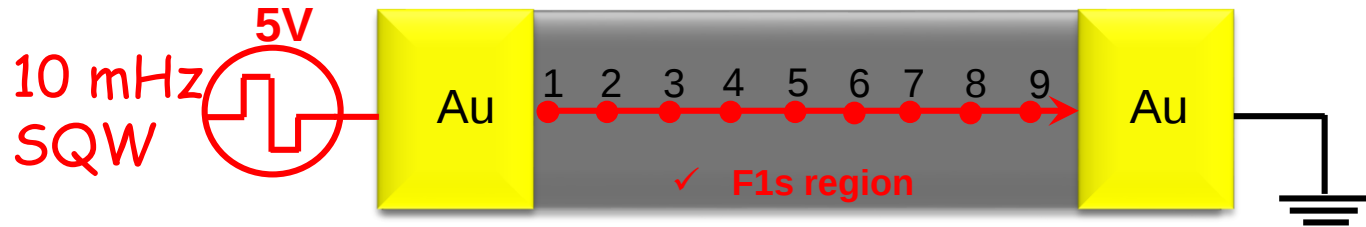


Scheme



Dynamics of Ionic-Liquids

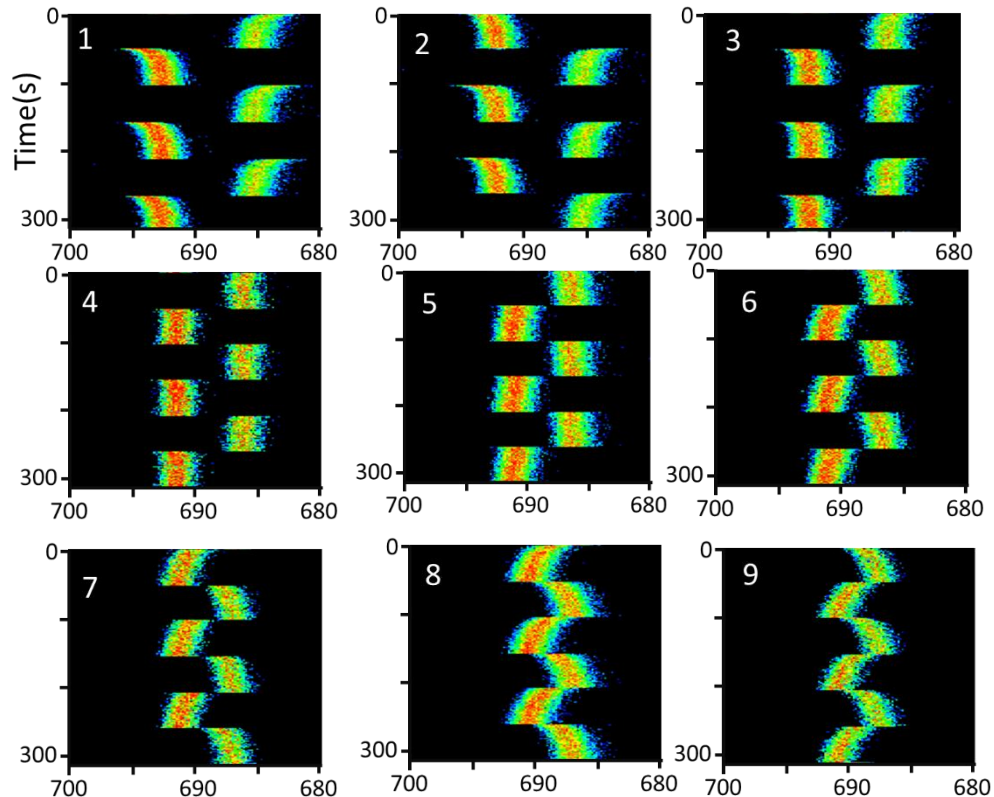
COPLANAR CAPACITOR



Line Scan Mode
Step size:
800 μ m

➤ Position
dependent
information
across the
electrodes.

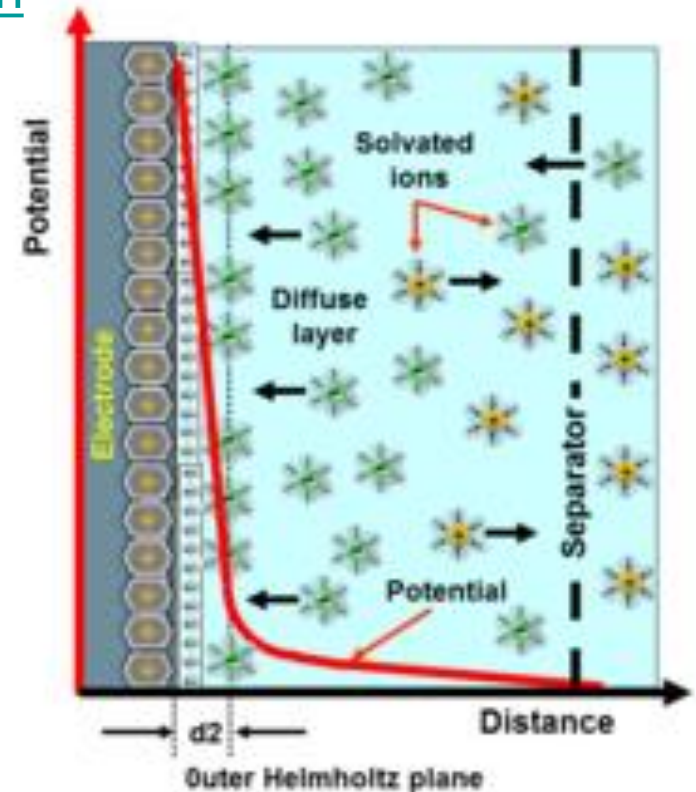
**EXTREMELY
SLOW!!!
and
LONG
RANGE!!!**



Double layer (surface science)

From Wikipedia, the free encyclopedia

When an *electronic* conductor is brought in contact with a solid or liquid *ionic* conductor (electrolyte), a common boundary ([interface](#)) among the two [phases](#) appears. [Hermann von Helmholtz](#)^[1] was the first to realize that [charged](#) electrodes immersed in electrolyte solutions repel the co-ions of the charge while attracting counterions to their surfaces. Two layers of opposite [polarity](#) form at the interface between electrode and electrolyte. In 1853 he showed that an electrical double layer (DL) is essentially a [molecular](#) dielectric and stores charge electrostatically.^[2] Below the electrolyte's decomposition voltage, the stored charge is linearly dependent on the voltage applied.



Note That DEBYE LENGTH and TIME 1-10 nm and ~1-10 ns !

Diffuse-charge dynamics in electrochemical systems

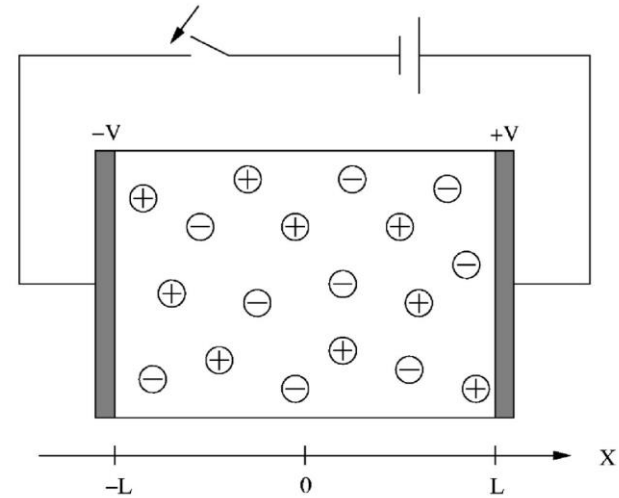
Martin Z. Bazant,^{1,2} Katsuyo Thornton,³ and Armand Ajdari²

We describe the concentrations of the charged ions by continuum fields $C_{\pm}(X, \tau)$ which satisfy the Nernst-Planck equations,

$$\frac{\partial C_{\pm}}{\partial \tau} = - \frac{\partial}{\partial X} \left(-D \frac{\partial C_{\pm}}{\partial X} \mp \mu z e C_{\pm} \frac{\partial \Phi}{\partial X} \right) \quad (11)$$

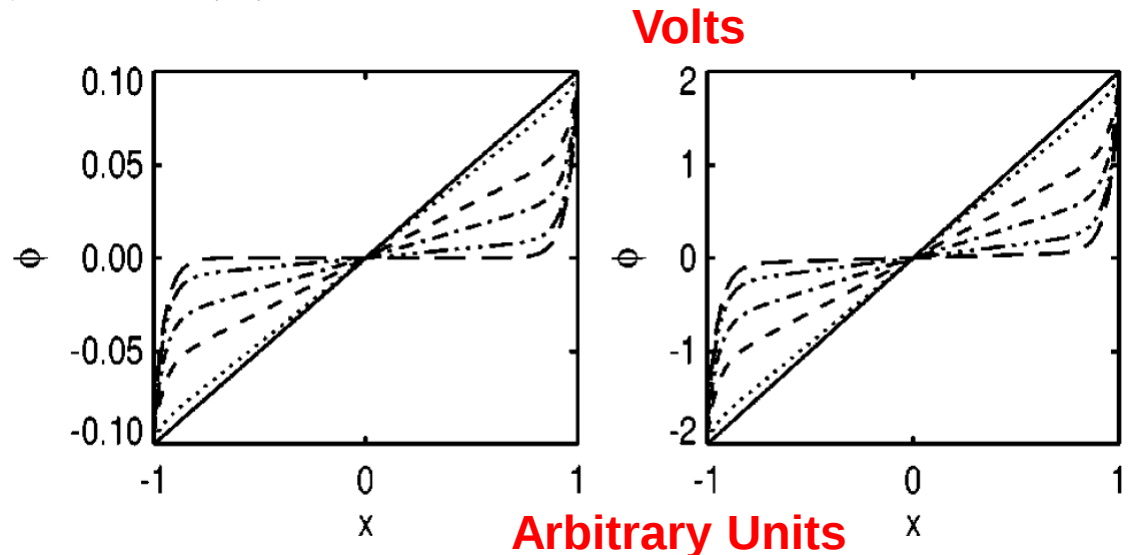
from the Einstein relation, $\mu = D/kT$. The total ionic charge density ρ_e controls the spatial variation of the potential Φ through Poisson's equation,

$$-\varepsilon \frac{\partial^2 \Phi}{\partial X^2} = \rho_e = z e (C_+ - C_-), \quad (12)$$

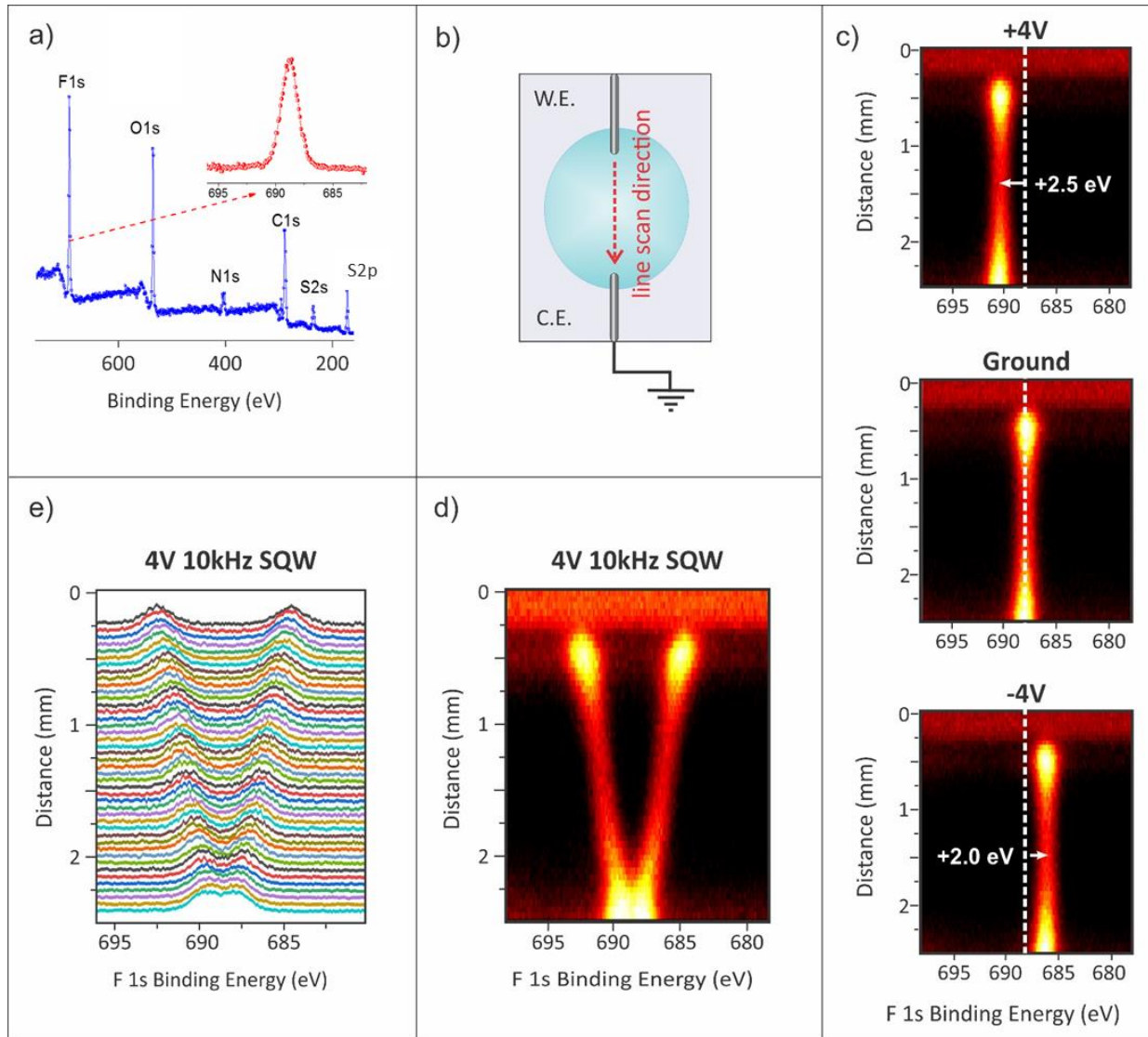


Defined A New Length and Time Scales

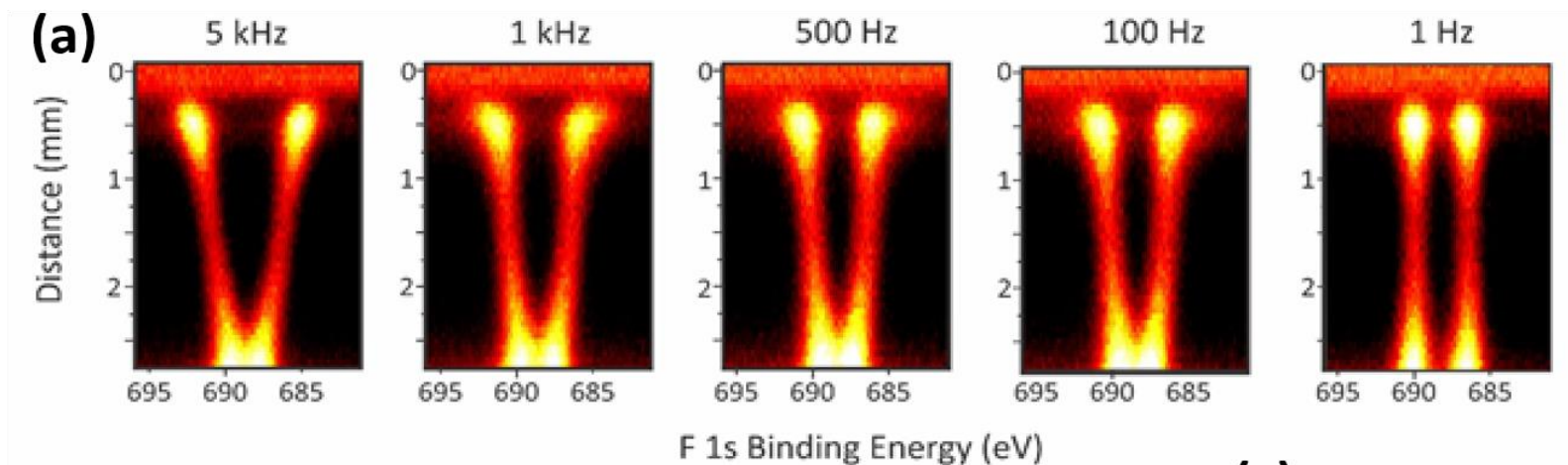
$$\tau_{\rho} \sim \left(\frac{\lambda_D L}{D} \right) - \frac{\lambda_D^2}{D}$$



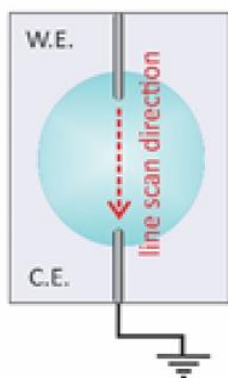
AC BIASING – SQUARE WAVES



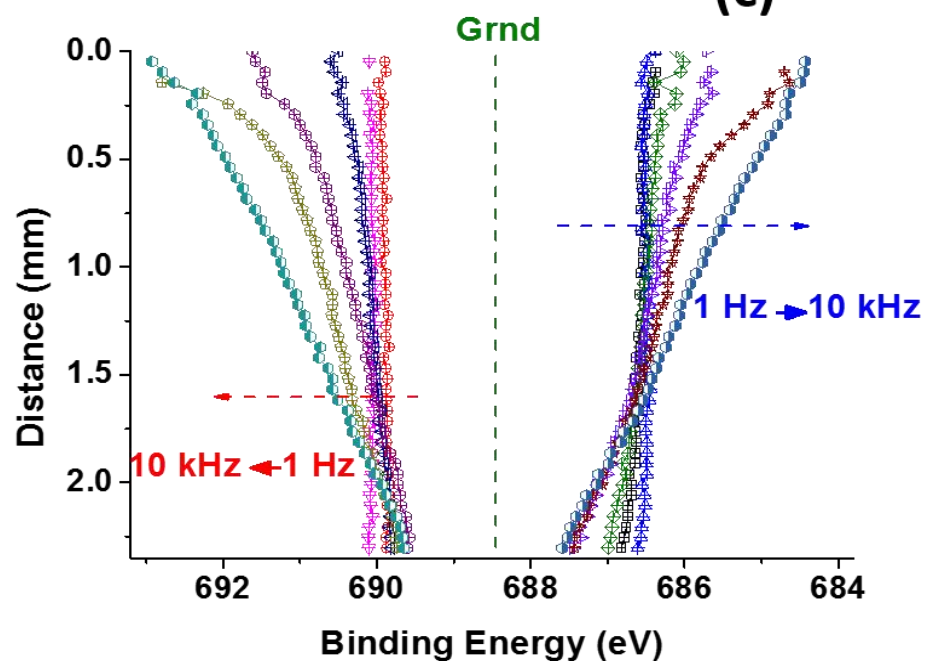
Line-Scans: 1-Dimensional Potential Profiles



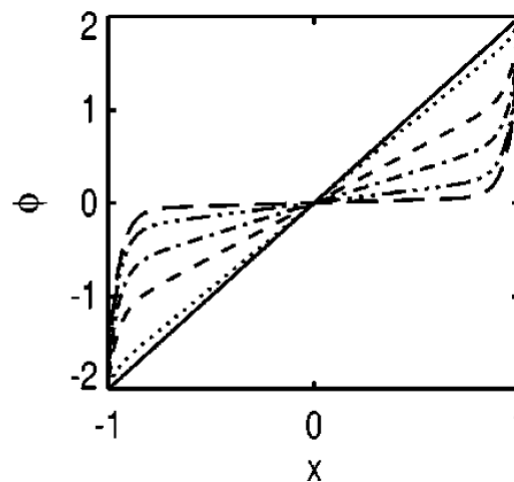
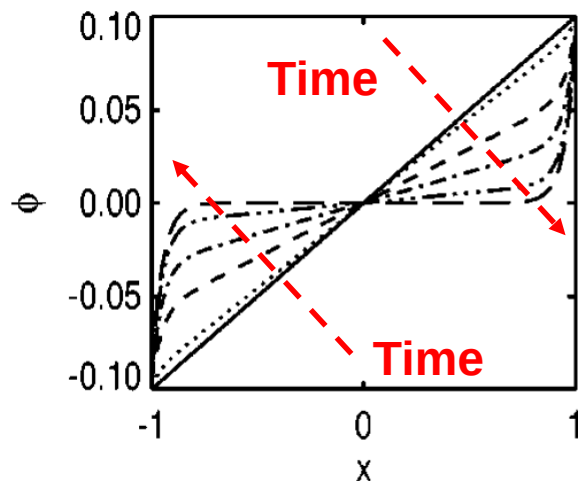
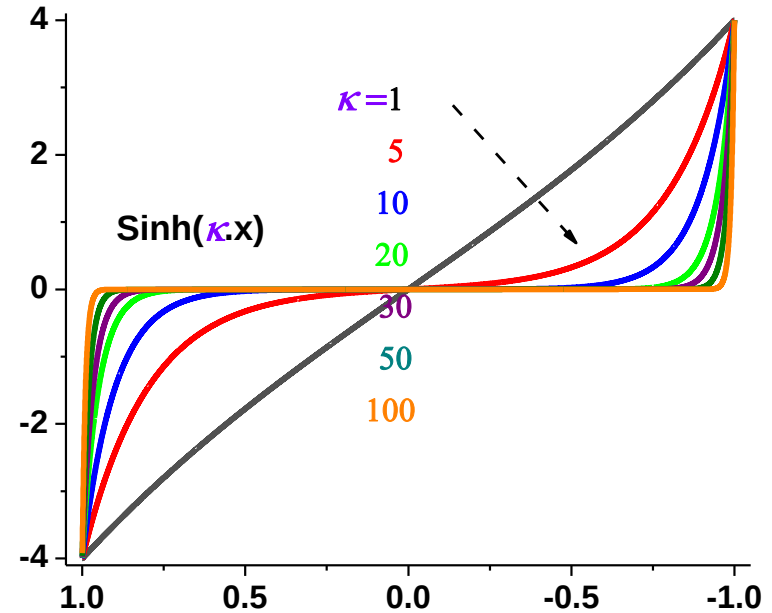
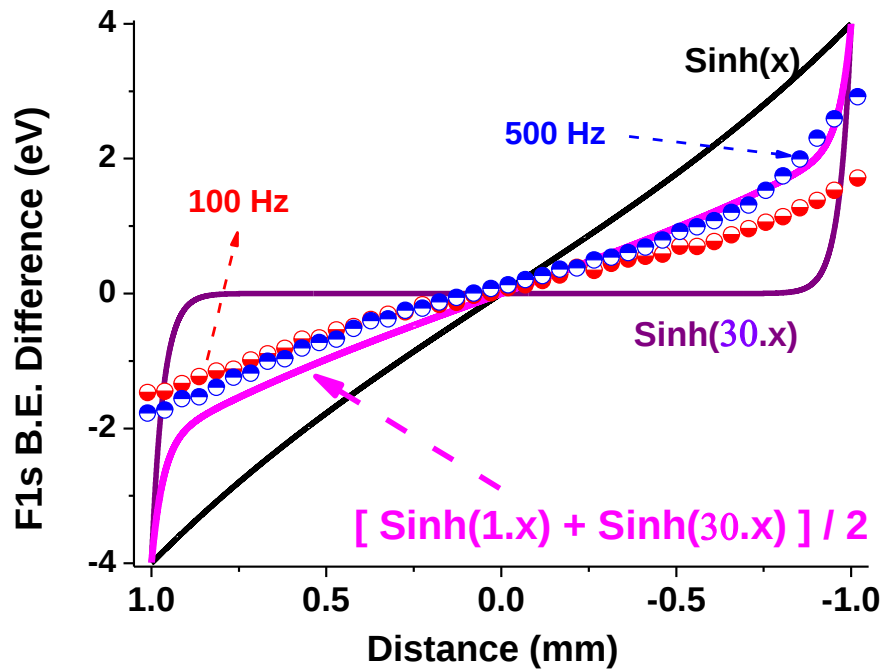
(b)



(c)



1st Ever Experimental Verification



2 Widely Different

Time-Constants

~1:1000 Ratio

$\kappa = 1$ and 30

$\tau = 1^2$ and 30^2

$\tau_c = \lambda_D \cdot L/D =$

10 nm $\times$ 1 mm /

$2 \times 10^{-11} \text{ m}^2/\text{s} = 0.5 \text{ s}$

Double Layer in Ionic Liquids: Overscreening versus Crowding

Martin Z. Bazant,¹ Brian D. Storey,² and Alexei A. Kornyshev³

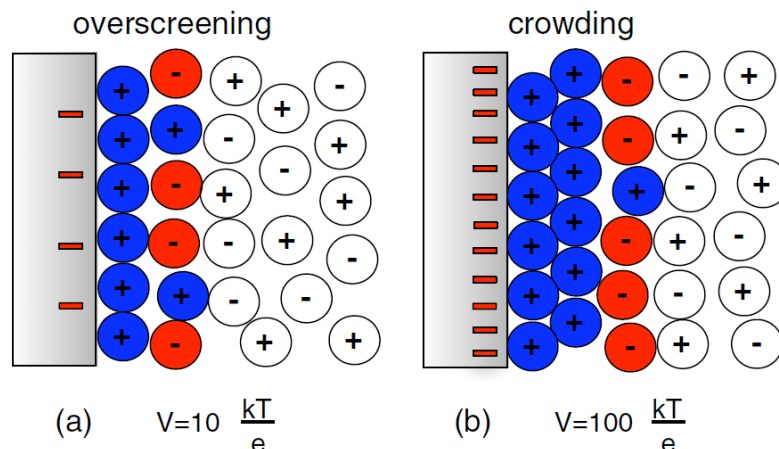
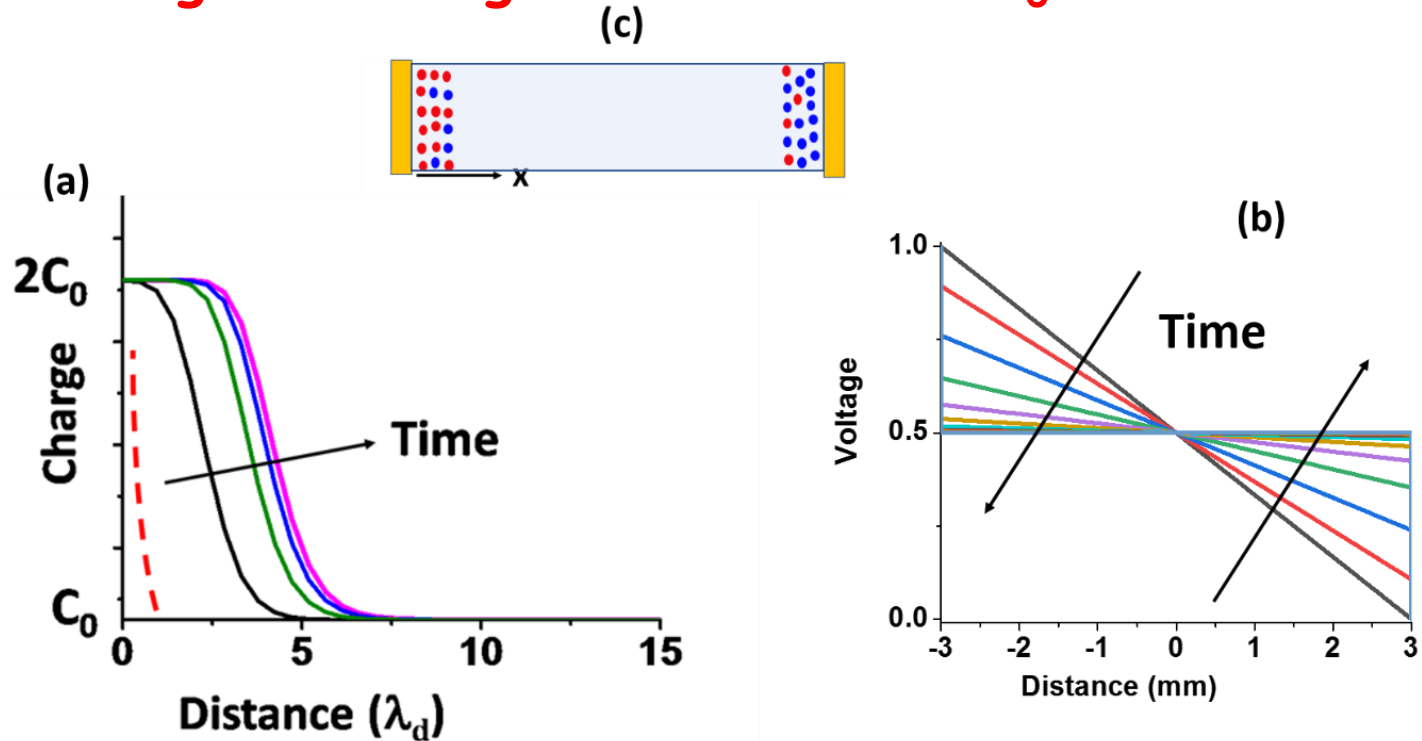


FIG. 1 (color online). Structure of the ionic-liquid double layer (in color) predicted by our theory and molecular dynamics simulations [19] [Figs. 2 and 3]. (a) At a moderate voltage, $V = 10k_B T/e$ (0.26 V), the surface charge is overscreened by a monolayer of counterions, which is corrected by an excess of coions in the second monolayer. (b) At a high voltage, $V = 100k_B T/e$ (2.6 V), the crowding of counterions extends across two monolayers and dominates overscreening, which now leads to a coion excess in the third monolayer. Because of electrostriction, the diffuse double layer (colored ions) is more dense than the quasineutral bulk liquid (white ions).

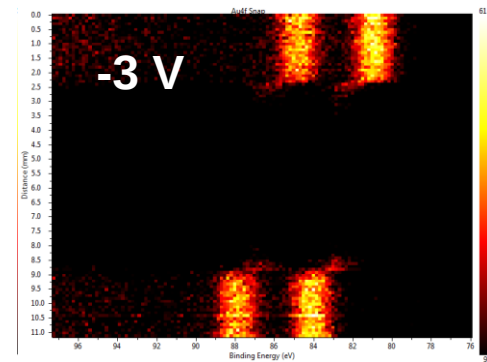
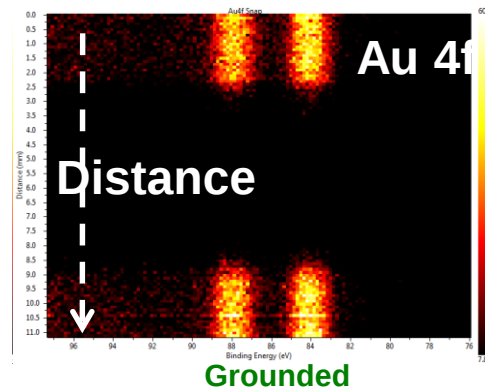
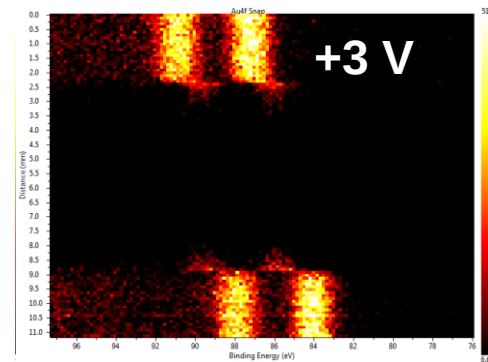
Parallel-Plate Capacitor

1-D COMSOL SIMULATION RESULTS

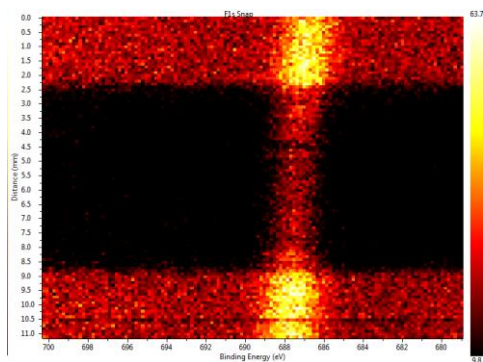
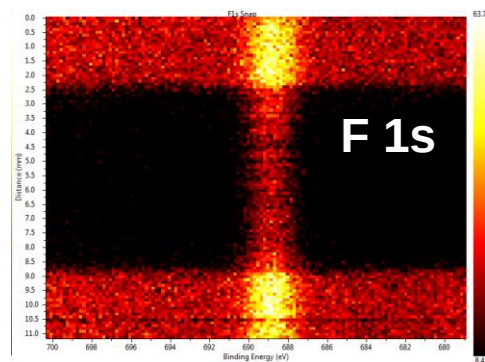
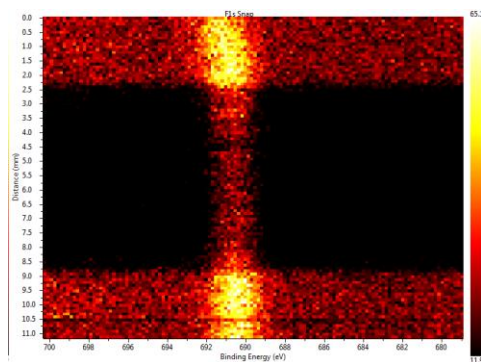
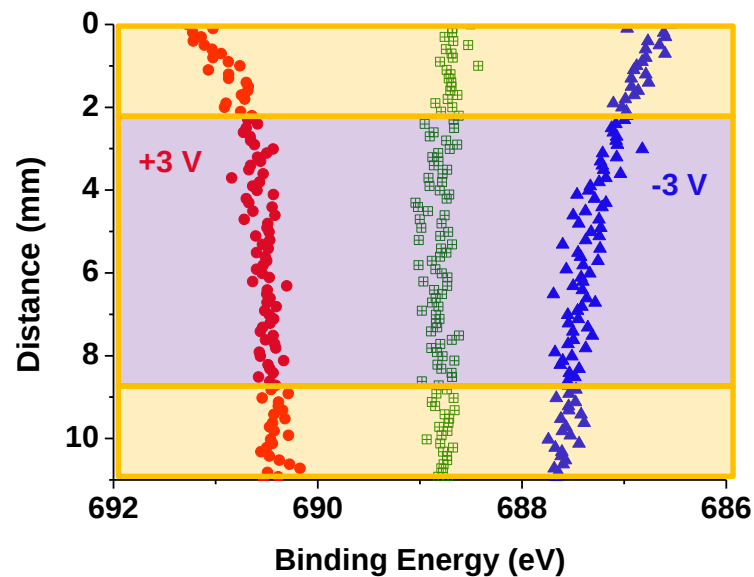
Restricting the Charge Accumulation: $C_0 = 3.3 \text{ M}$

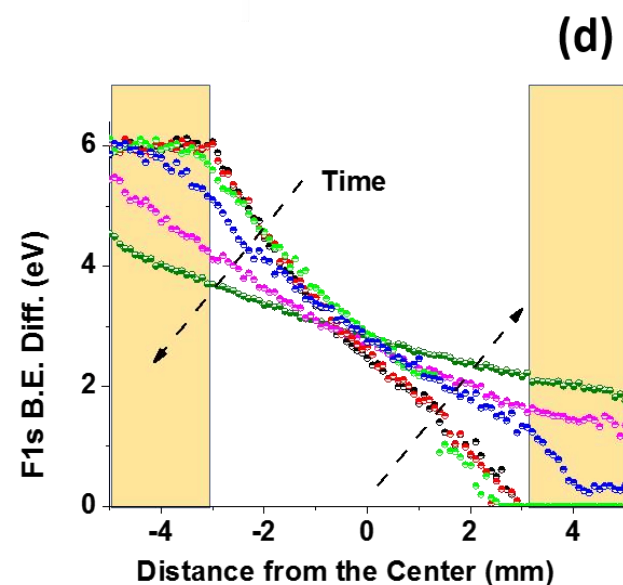
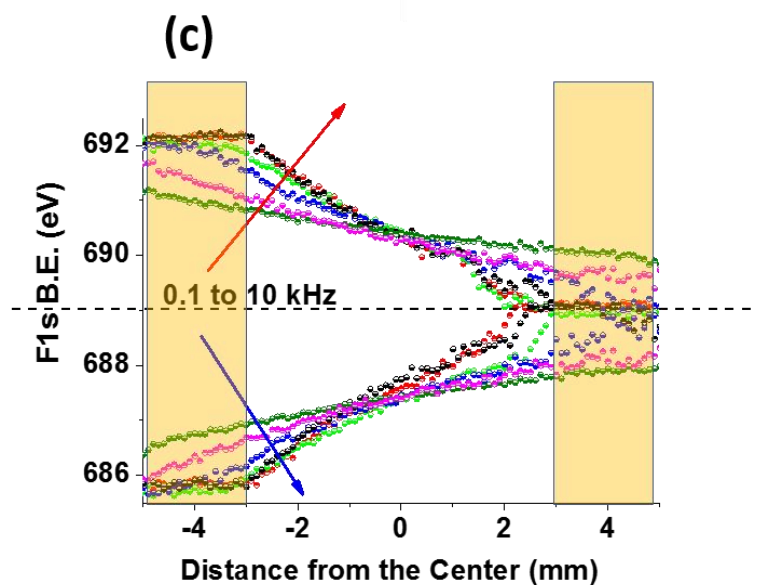
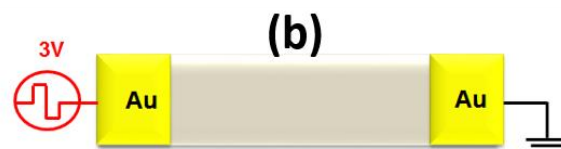
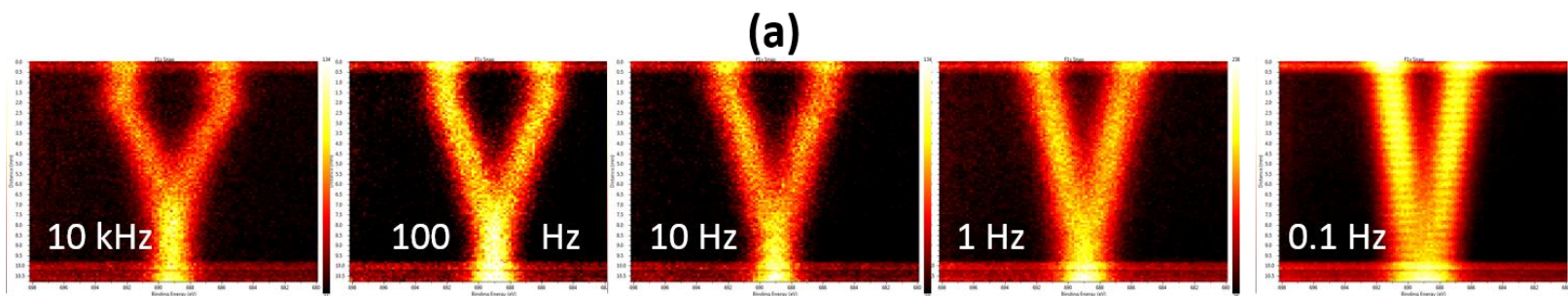


Leads to Increase in the DL thickness:
0.1 nm to maybe 1 nm
Still TOO SMALL!!!!

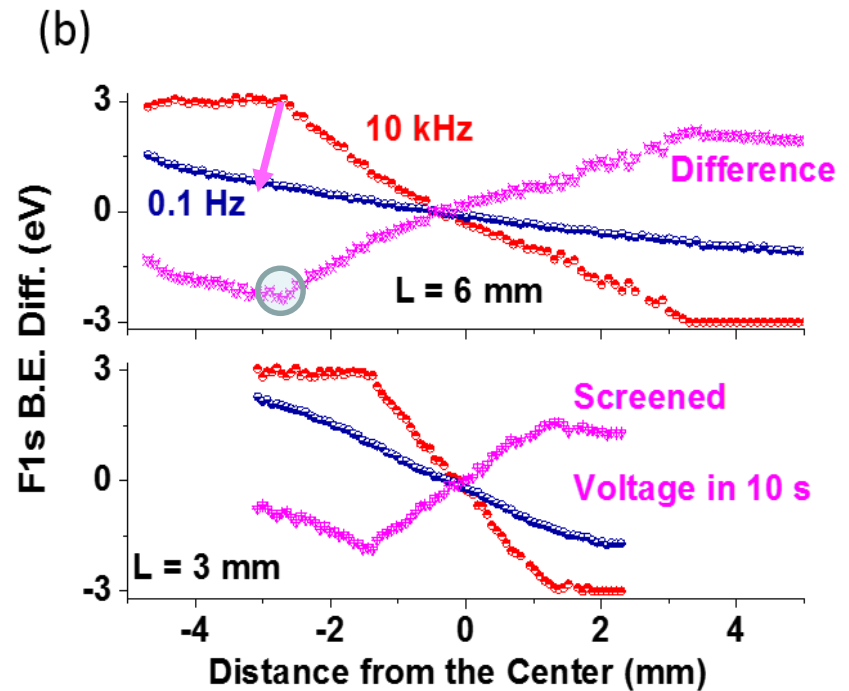
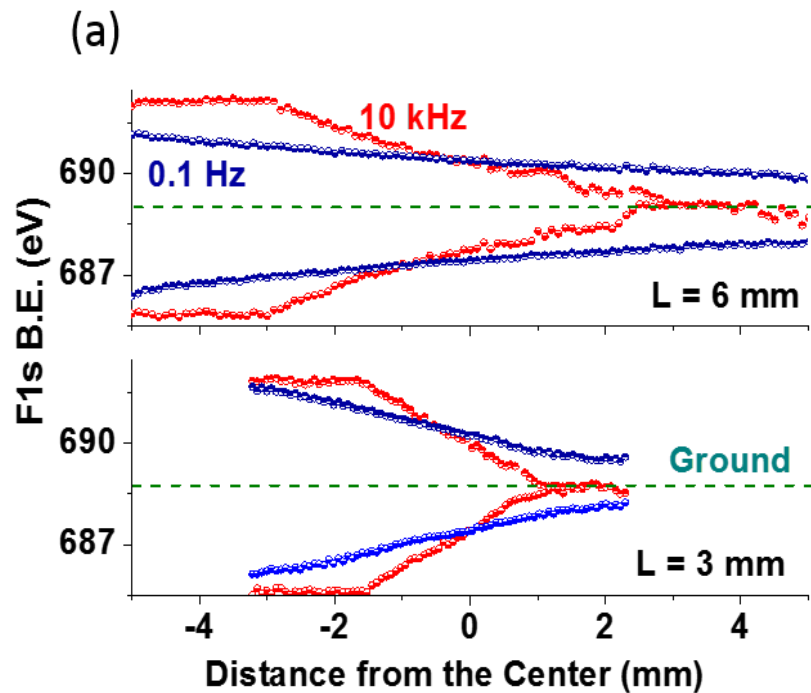


Co-Planar
Capacitor





2 Different Devices

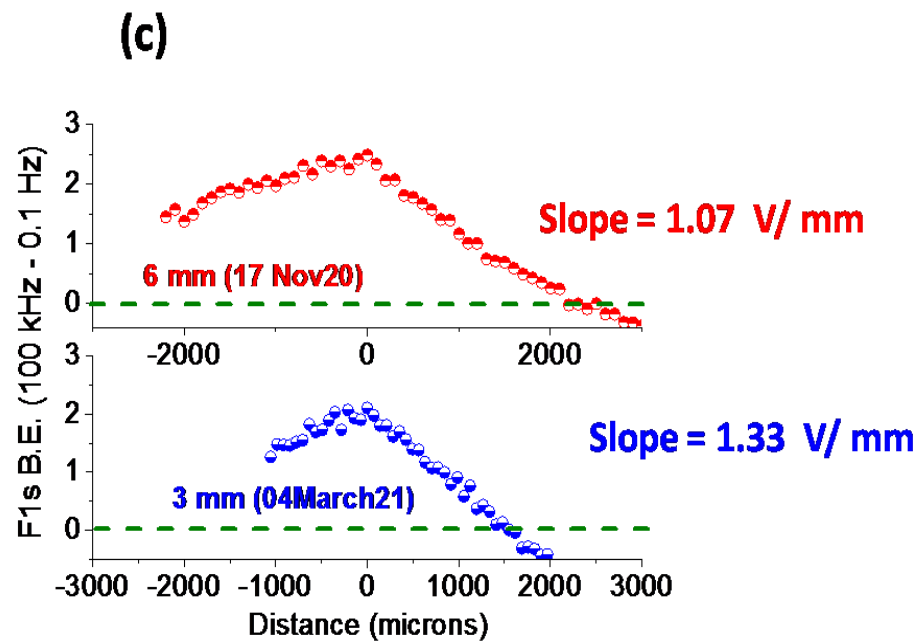
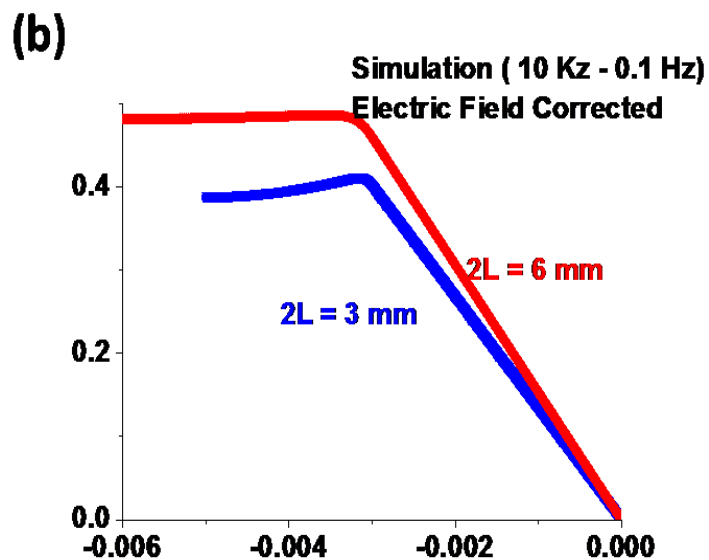
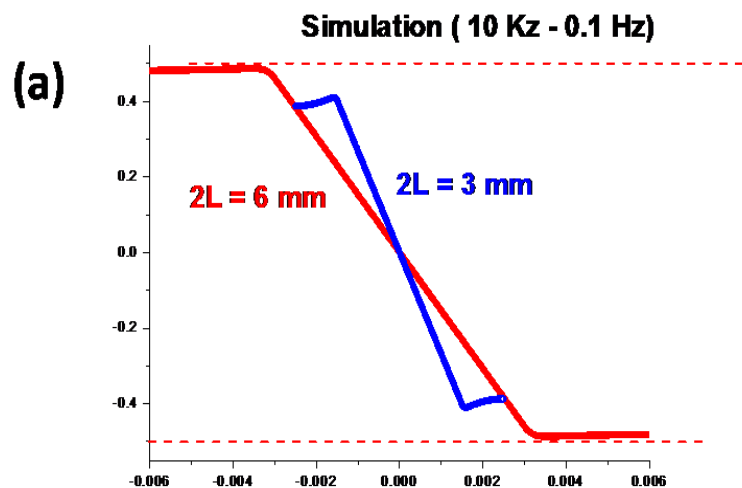


-Using Simple Diffusion Model:

$$\text{Distance} = (D \cdot \Delta t)^{1/2} = [10^{-11} \text{ (m}^2/\text{s)} \times 10 \text{ s}]^{1/2} = 10^{-5} \text{ m}$$

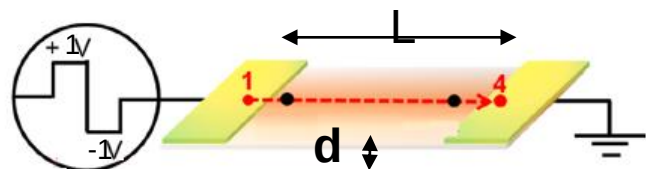
- Drift Velocity (using known viscosity values) = $\sim 3 \text{ } \mu\text{m/s}$

Again both are TOO SMALL!!!!



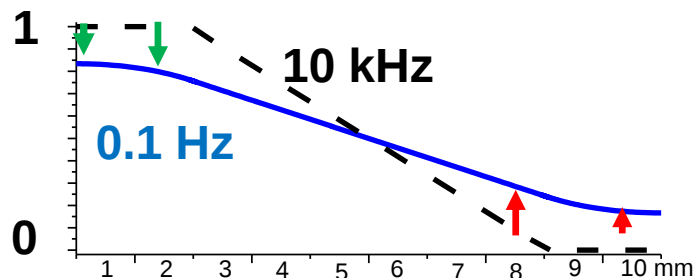
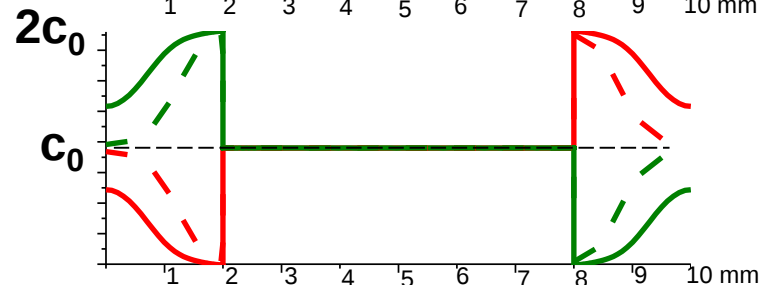
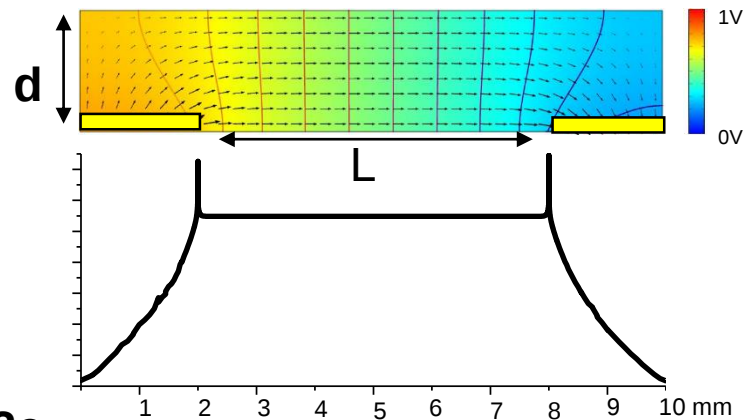
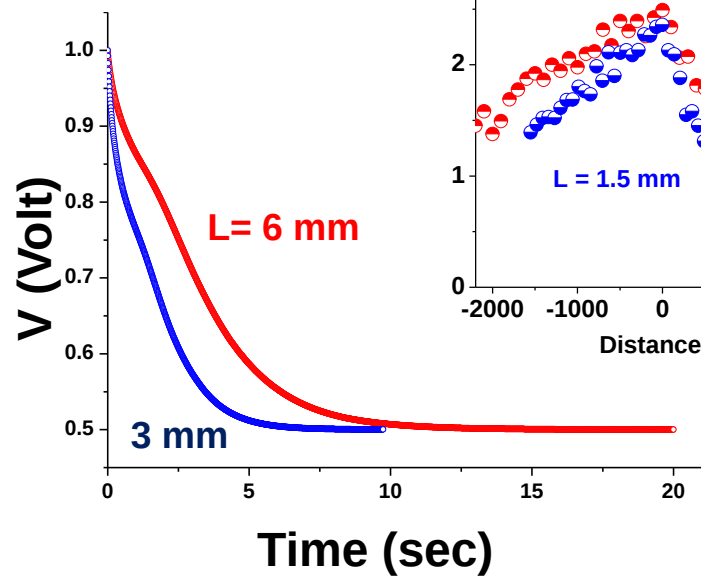
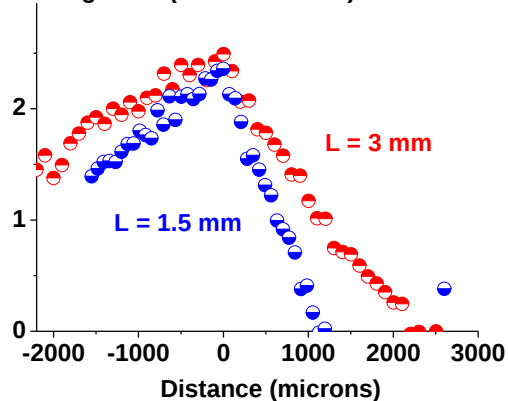
SIMULATIONS USING 2-D COMSOL

Geometric Effects and Nonuniform Double Layer



$$\tau \approx RC \approx L/d$$

Screening in eV (10 kHz - 0.1 Hz)



Slow response time $\tau = 5$ sec
for XPS measurements

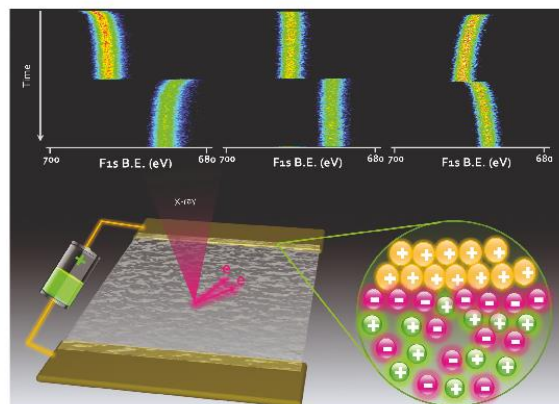
Conclusions

- ✓ D.C. or A.C. Biased XPS
- ✓ Chemical Processes and/or Reactions,
- ✓ Frequency Dependence (Impedance-Like) of Different Liquids on Types of Bonding (Dipolar, and/or Ionic),
- ✓ Validation of Different Models, EDL Formation, etc.,

Can be monitored in a Chemically Resolved Fashion with A BIG HELP from COMSOL

- ✓ There is Still Room for INNOVATIVE UTILIZATION of the Old-Lab-Based XPS Technique

2016



Showcasing research from the surface-science laboratory of Dr Sefik Suzer at the Chemistry Department of Bilkent University, Ankara, Turkey.

Title: XPS enables visualization of electrode potential screening in an ionic liquid medium with temporal- and lateral-resolution

As featured in:



PCCP

PAPER

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Cite this: *Phys. Chem. Chem. Phys.*,
2016, 18, 28434

XPS enables visualization of electrode potential screening in an ionic liquid medium with temporal- and lateral-resolution†

M. T. Camci,^a P. Aydogan,^a B. Ulgut,^a C. Kocabas^b and S. Suzer^{a*}



OUR HOLY GRAIL

LIQUID/SOLID INTERFACES be represented by SOLID STATE ELEMENTS ONLY??

CATIONS & ANIONS VS ELECTRONS & HOLES

2018

LANGMUIR

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Article

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DC Electrowetting of Nonaqueous Liquid Revisited by XPS

Pinar Aydogan Gokturk,^a Burak Ulgut,^a and Sefik Suzer^{a*}

Department of Chemistry, Bilkent University, 06800 Ankara, Turkey

2019

LANGMUIR

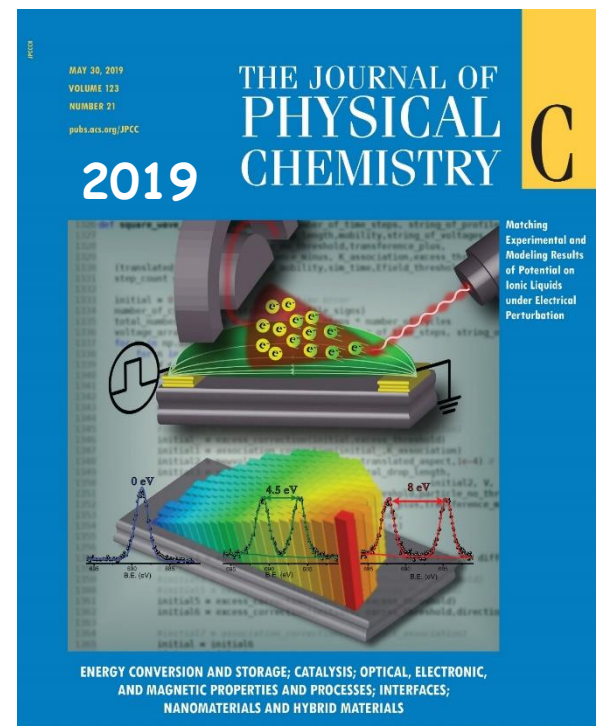
Cite This: *Langmuir* 2019, 35, 3319–3326

Article

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AC Electrowetting Modulation of Low-Volatile Liquids Probed by XPS: Dipolar vs Ionic Screening

Pinar Aydogan Gokturk,^a Burak Ulgut,^a and Sefik Suzer^{a*}



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