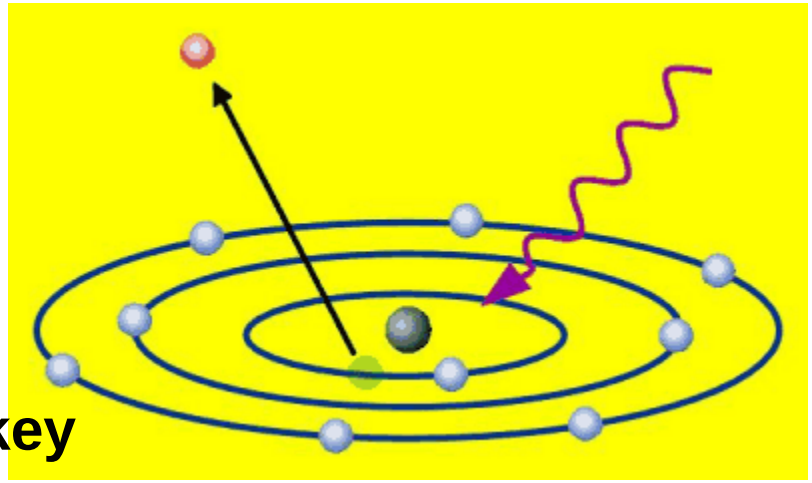
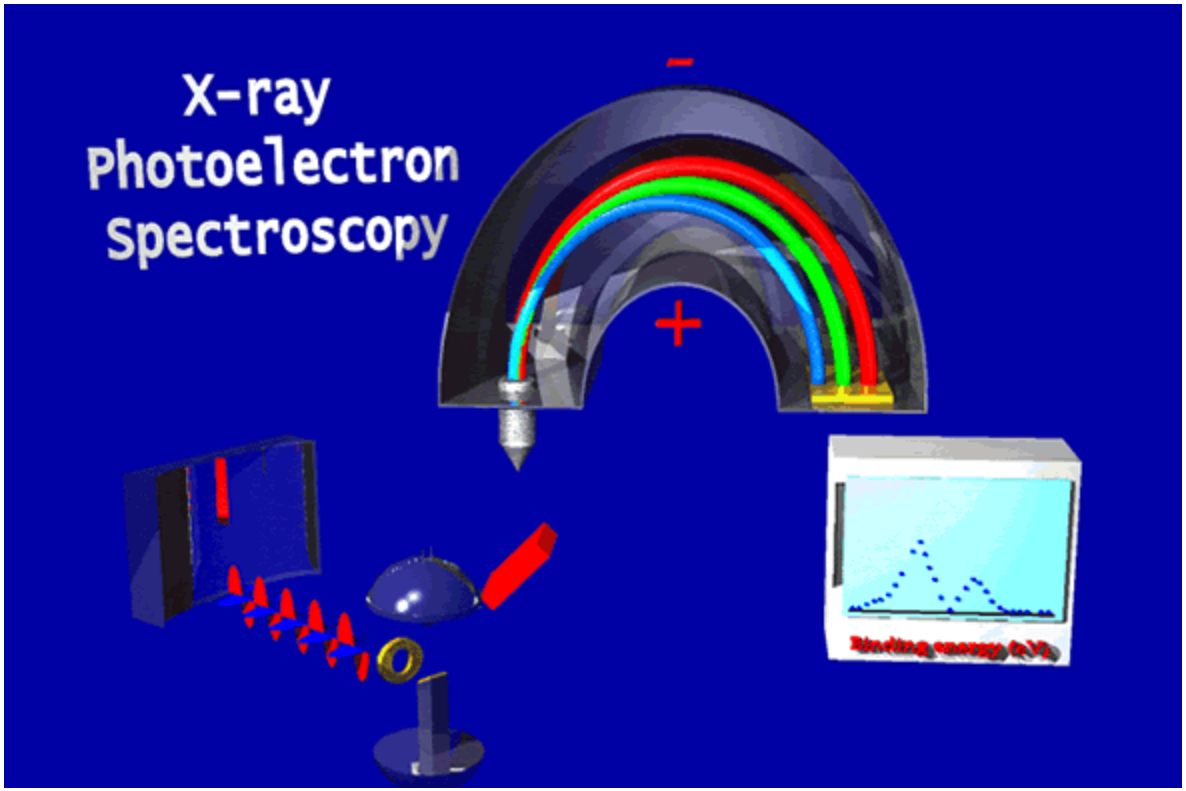
Charge Sensitive XPS
X-Ray Photoelectron Spectroscopy



Sefik Suzer, Bilkent University,
Chemistry Department, Ankara, Turkey

July 4, 2014

FU Berlin



In Honor of

David A. SHIRLEY

Beginning of Research (UC Berkeley, 1970)

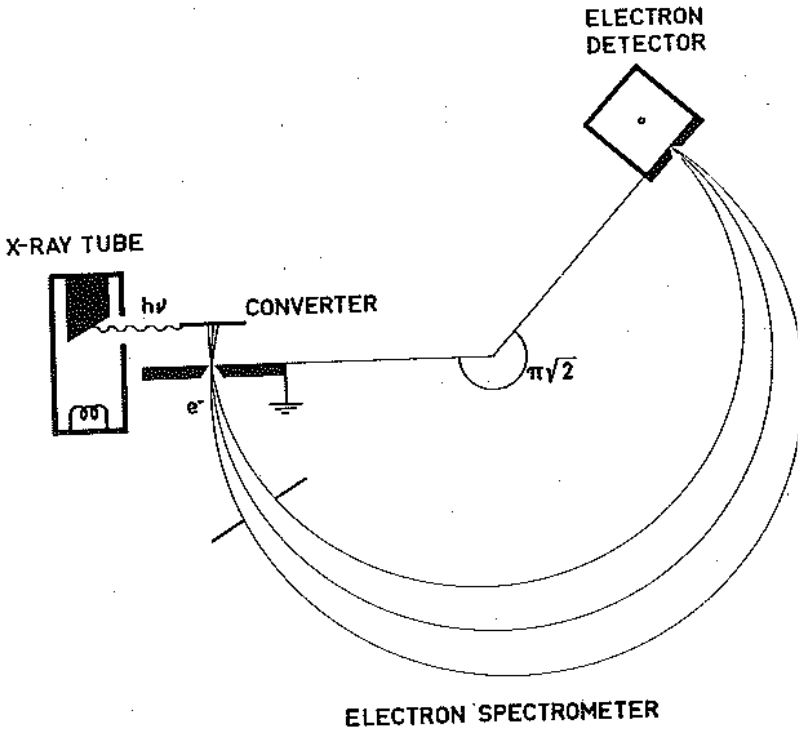


Fig. I:2. Schematic view of an ESCA arrangement for t
study of electrons expelled by X-rays.

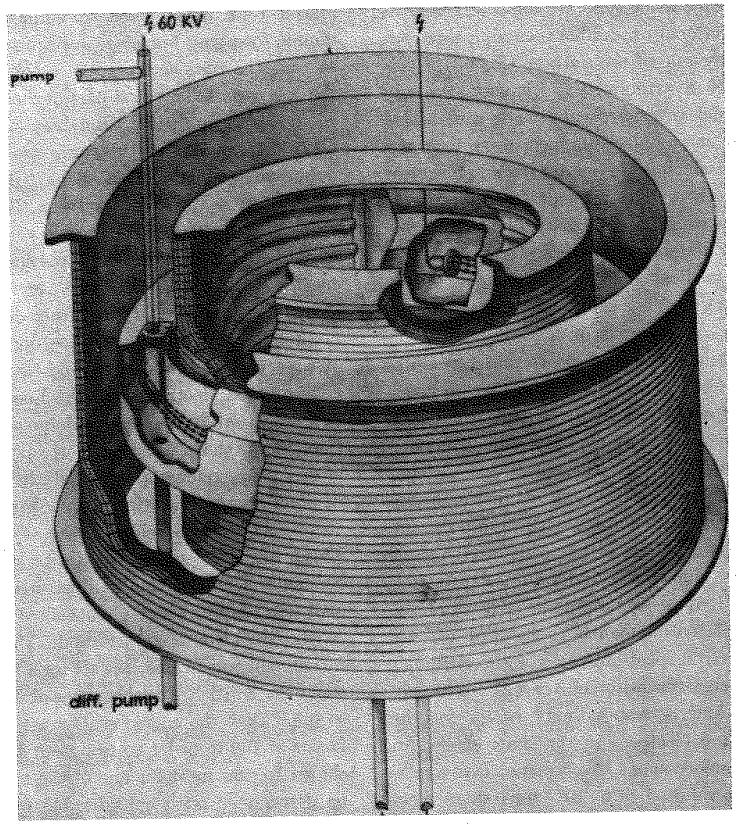


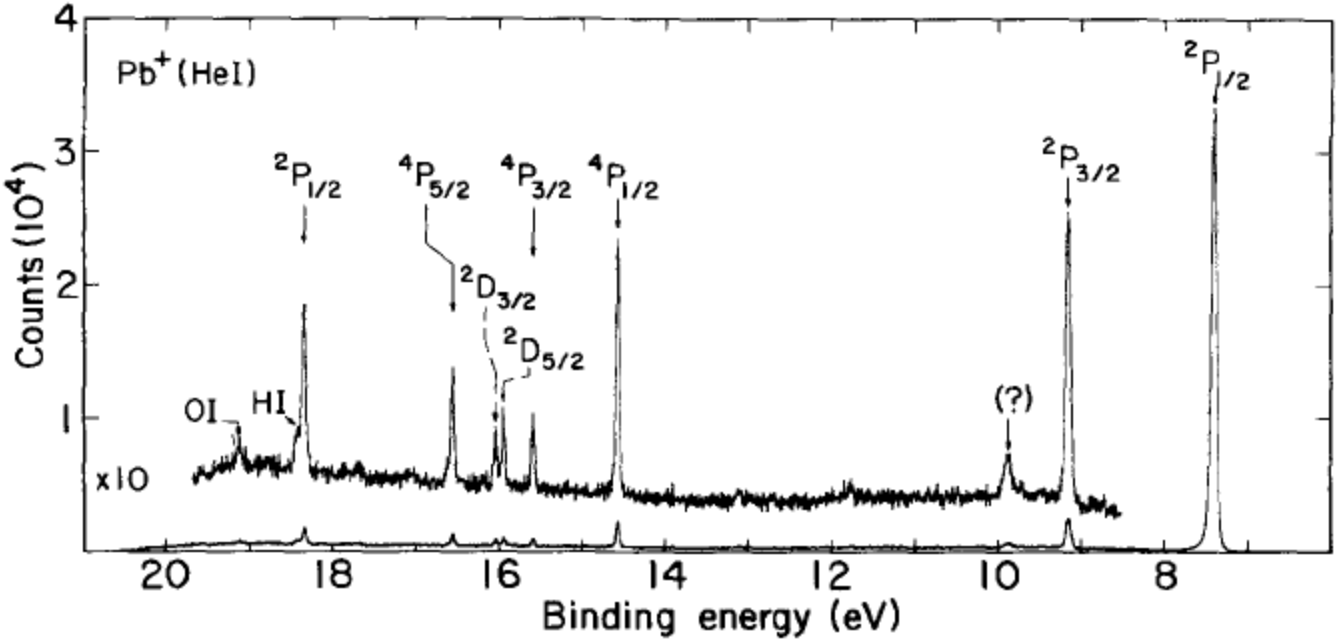
Fig. I:3. First iron-free double focussing spectrometer adapted for ESCA. The magnetic field is obtained from two co-axial coils with radii 24 cm and 36 cm, and height 48 cm.[5]

Sefik Suzer (Berkeley, 1972-75) Ultra Violet P.E.S. (Valence Electrons-MULTIPLETS)

INERT - PAIR EFFECT : Large Spin-Orbit Splitting

Pb: $6s^2 6p^2$:

L-S Coupling	50% $6p_{1/2}$ – 50% $6p_{3/2}$
Intermed. Coupling	93% $6p_{1/2}$ – 7% $6p_{3/2}$
J-J Coupling	100% $6p_{1/2}$ – 0% $6p_{3/2}$



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

ACCOUNTS OF CHEMICAL RESEARCH

VOLUME 12 NUMBER 8 AUGUST, 1979

Relativistic Effects on Chemical Properties

KENNETH S. PITZER

Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Received November 8, 1978

While it is generally recognized that a rigorous theoretical foundation for chemistry would rest on relativistic quantum theory, the great majority of quantum mechanical calculations of quantities of chemical interest are based on the nonrelativistic Schrödinger equation, or its equivalent, together with the qualitative rules related to spin and the Pauli exclusion principle. If fine structure features are of interest, spin–orbit, spin–spin, and other terms are added as perturbations, but for light atoms these terms yield very small energies that may be of spectroscopic interest but have no effect on most chemical properties.

For very heavy atoms, however, this situation changes. Certain terms which were very small compared to thermal energy for light atoms increase very rapidly with atomic number and become comparable to chemical bond energies for elements in the range gold–bismuth.

Table I
Energy Terms for Fourth Group Elements (Electronvolts)

element X	ionization potential	X_2 bond D_0	spin–orbit $^3P_2$–$^3P_0$
C	11.26	6.1	0.005
Si	8.15	3.2	.03
Ge	7.88	2.8	.17
Sn	7.34	2.0	.42
Pb	7.42	1.0	1.32

increase in atomic number.

My principal purpose in this Account is to examine the special or anomalous chemical effects that have been noted for heavy elements in relation to periodic-table trends and to determine the degree to which these are relativistic effects. To the extent that these anomalies are explained in most inorganic chemistry books, they are usually ascribed to the introduction of the 4f shell. It is found that the effects of the 4f shell

Table VII
Dirac Atomic Orbitals[a]

$s_{1/2}$, $m = +1/2$

$$\begin{bmatrix} g(r) \\ 0 \\ f(r)\cos\theta \\ f(r)\sin\theta\ e^{i\phi} \end{bmatrix}$$

$s_{1/2}$, $m = -1/2$

$$\begin{bmatrix} 0 \\ g(r) \\ f(r)\sin\theta\ e^{-i\phi} \\ -f(r)\cos\theta \end{bmatrix}$$

$p_{1/2}$, $m = +1/2$

$$\begin{bmatrix} g(r)\cos\theta \\ g(r)\sin\theta\ e^{i\phi} \\ f(r) \\ 0 \end{bmatrix}$$

$p_{1/2}$, $m = -1/2$

$$\begin{bmatrix} g(r)\sin\theta\ e^{-i\phi} \\ -g(r)\cos\theta \\ 0 \\ f(r) \end{bmatrix}$$

$p_{3/2}$, $m = +3/2$

$$\begin{bmatrix} g(r)\sin\theta\ e^{-i\phi} \\ 0 \\ f(r)\sin\theta\cos\theta\ e^{i\phi} \\ f(r)\sin^2\theta\ e^{2i\phi} \end{bmatrix}$$

$p_{3/2}$, $m = -3/2$

$$\begin{bmatrix} 0 \\ g(r)\sin\theta\ e^{-i\phi} \\ f(r)\sin^2\theta\ e^{-2i\phi} \\ -f(r)\sin\theta\cos\theta\ e^{-i\phi} \end{bmatrix}$$

$p_{3/2}$, $m = +1/2$

$$\begin{bmatrix} 2g(r)\cos\theta \\ -g(r)\sin\theta\ e^{i\phi} \\ f(r)(\cos^2\theta - 1/3) \\ f(r)\sin\theta\cos\theta\ e^{i\phi} \end{bmatrix}$$

$p_{3/2}$, $m = -1/2$

$$\begin{bmatrix} g(r)\sin\theta\ e^{-i\phi} \\ 2g(r)\cos\theta \\ f(r)\sin\theta\cos\theta\ e^{-i\phi} \\ -f(r)(\cos^2\theta - 1/3) \end{bmatrix}$$

[a] The angular factors are shown explicitly; other factors are included in $g(r)$ and $f(r)$ in each case.

In contrast, there are profound differences in angular properties for those relativistic p orbitals with z component of angular momentum $m = \pm 1/2$. Both large components are non-zero, and one component has the angular dependence of a pσ orbital whereas the other has that of a pπ orbital. If one forms a diatomic molecular orbital from $p_{1/2}$ atomic orbitals for each atom with signs appropriate for σ bonding, then the other components yield π antibonding. More exactly, if the $p_{1/2}$ orbitals are combined with g symmetry one has one-third σ-bond and two-thirds π-antibond character. Correspondingly, the combination with u symmetry yields one-third σ-antibond and two-thirds π-bond character. Thus $p_{1/2}$ orbitals do not form strong bonds. By taking linear combinations of $p_{1/2}$ and $p_{3/2}$ orbitals, the angular and bonding characteristics of Schrödinger p orbitals can be regained, but this requires substantial promotion energy in many cases.

Are elements 112, 114, and 118 relatively inert gases?

Kenneth S. Pitzer

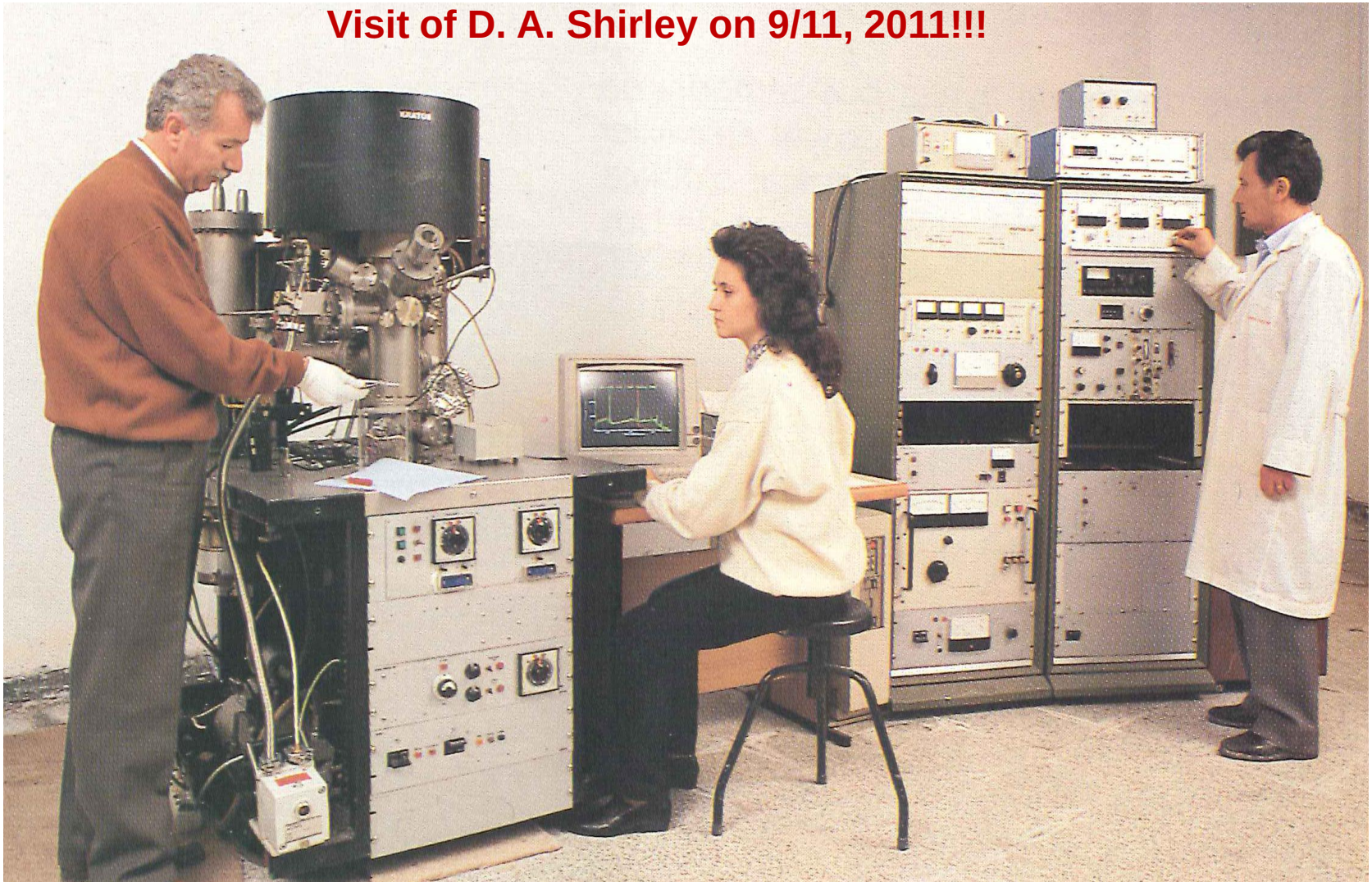
Department of Chemistry and Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720
(Received 14 April 1975)

1979-1992 METU, Ankara, Turkey

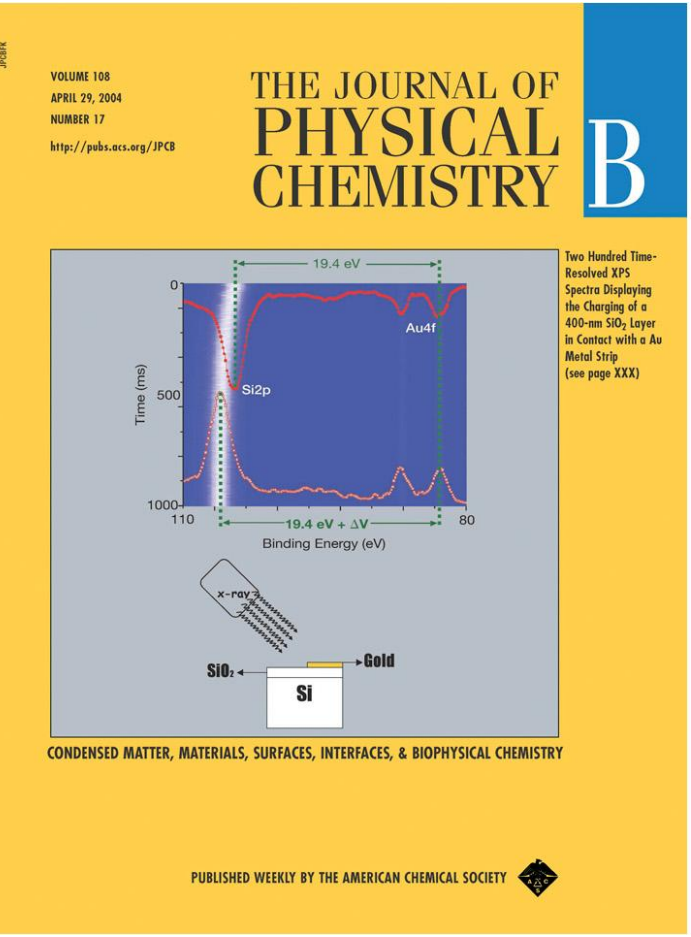
1992- Present, Bilkent, Ankara, Turkey

1994 3rd Hand KRATOS ES300 (~50 k$)

Visit of D. A. Shirley on 9/11, 2011!!!

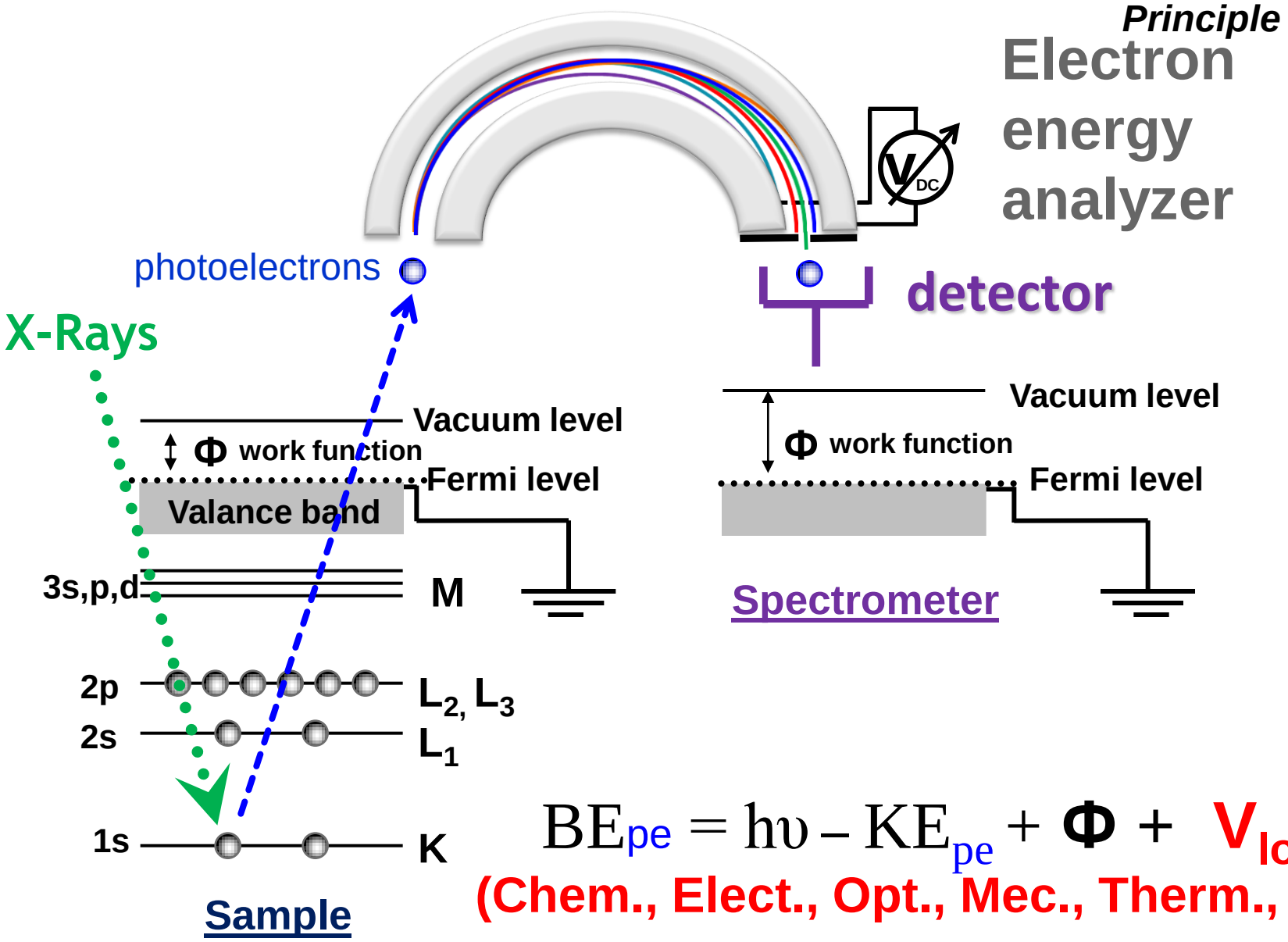


2002 `2rd Hand KRATOS ES800 (~60 k$)




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

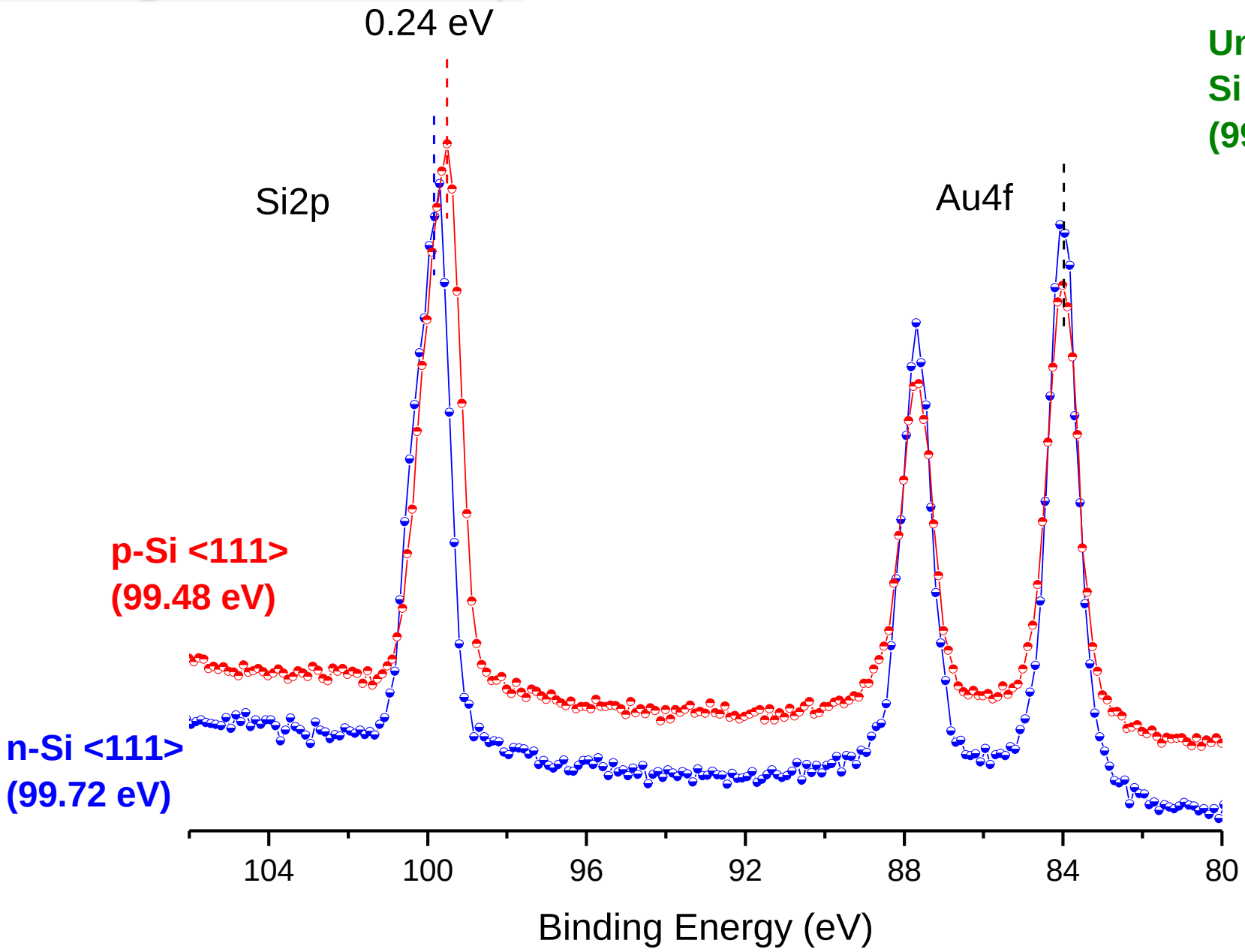
X-ray Photoelectron Spectroscopy:



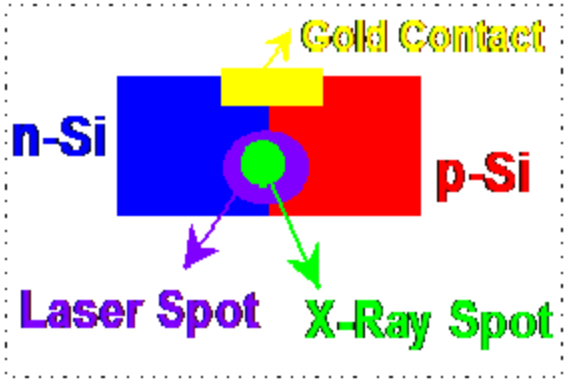
$$BE_{pe} = h\upsilon - KE_{pe} + \Phi + V_{loc}$$

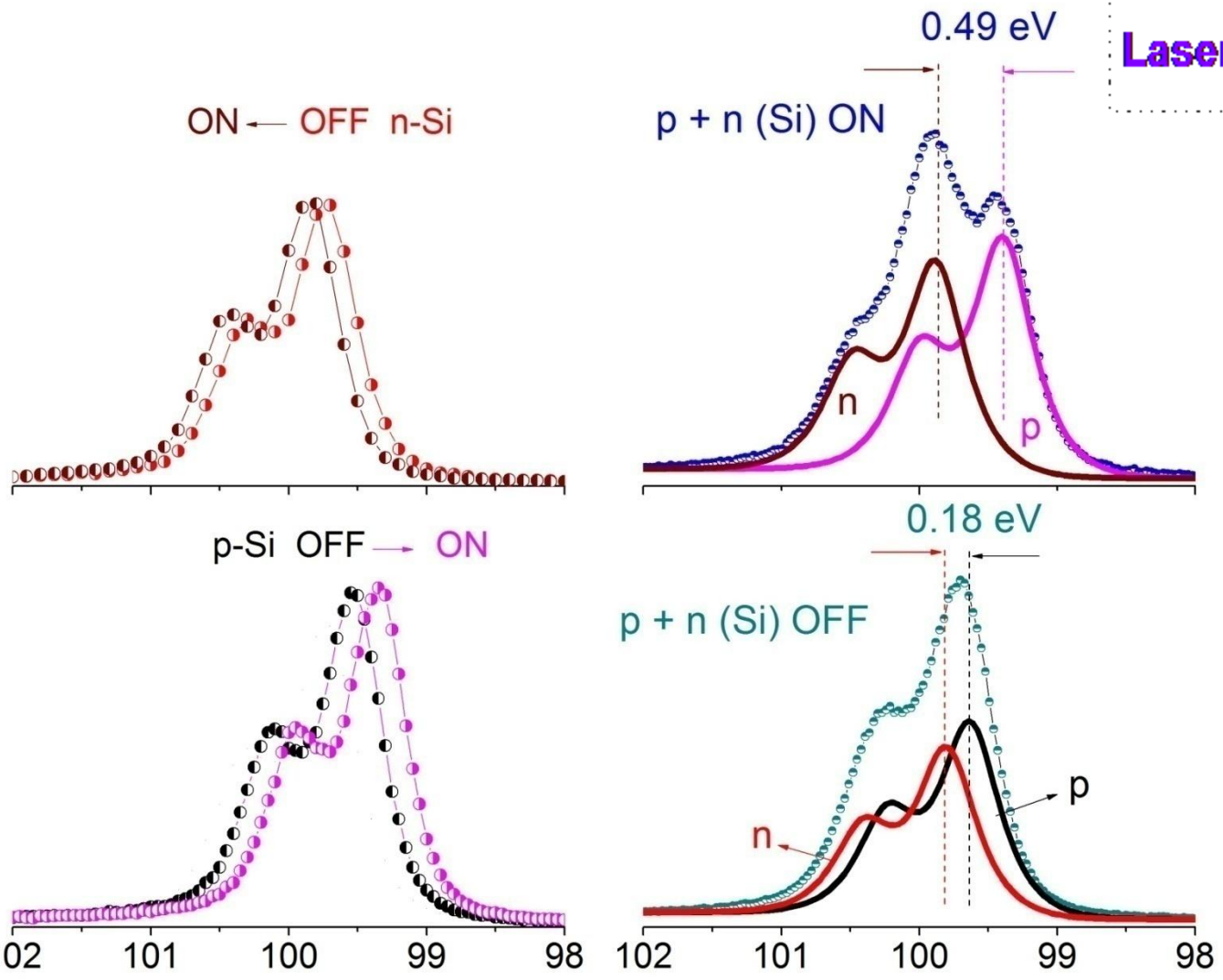
(Chem., Elect., Opt., Mec., Therm., etc.)

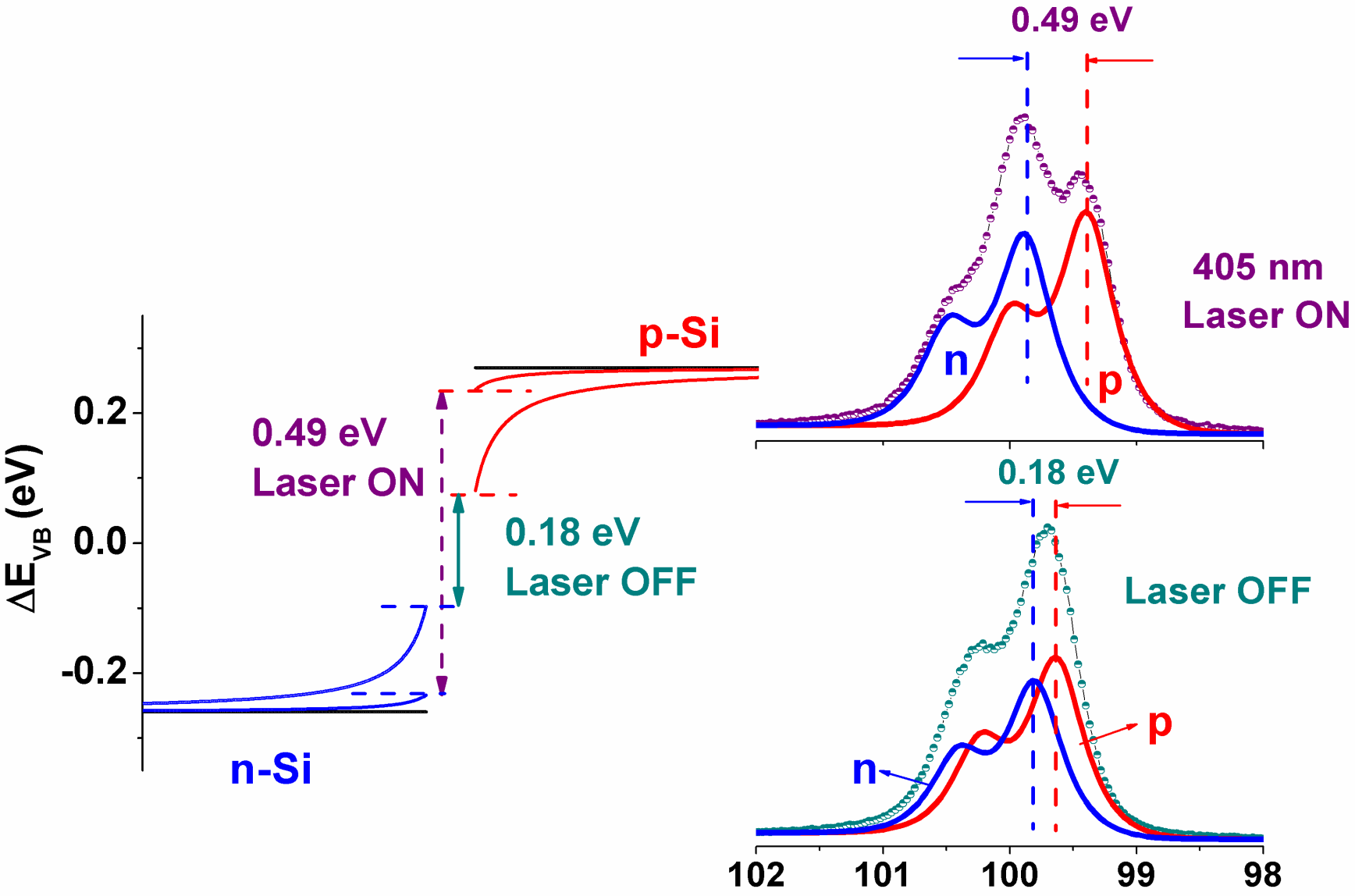
- Charge Sensitivity

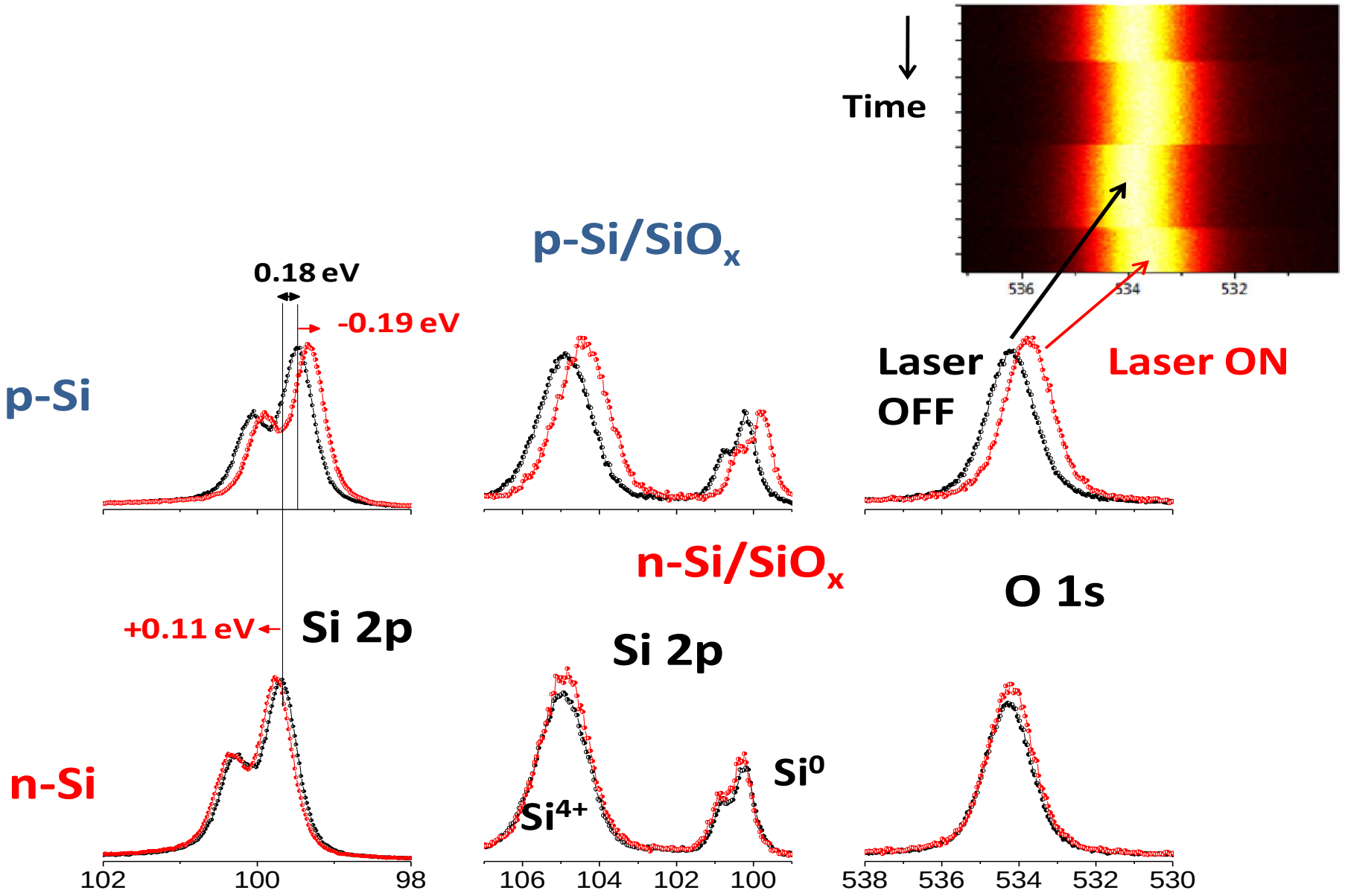


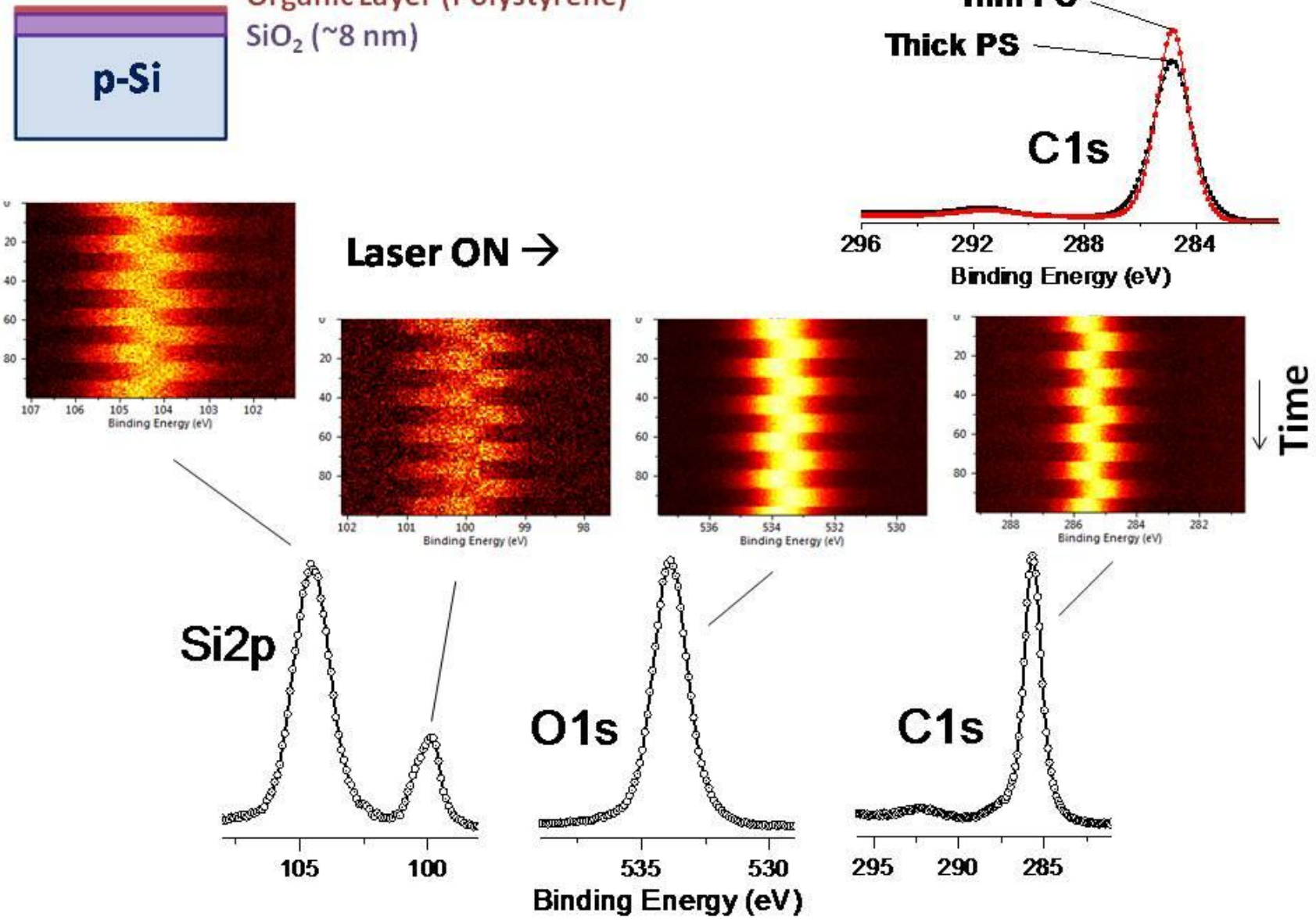
- Charge + Light Sensitivity

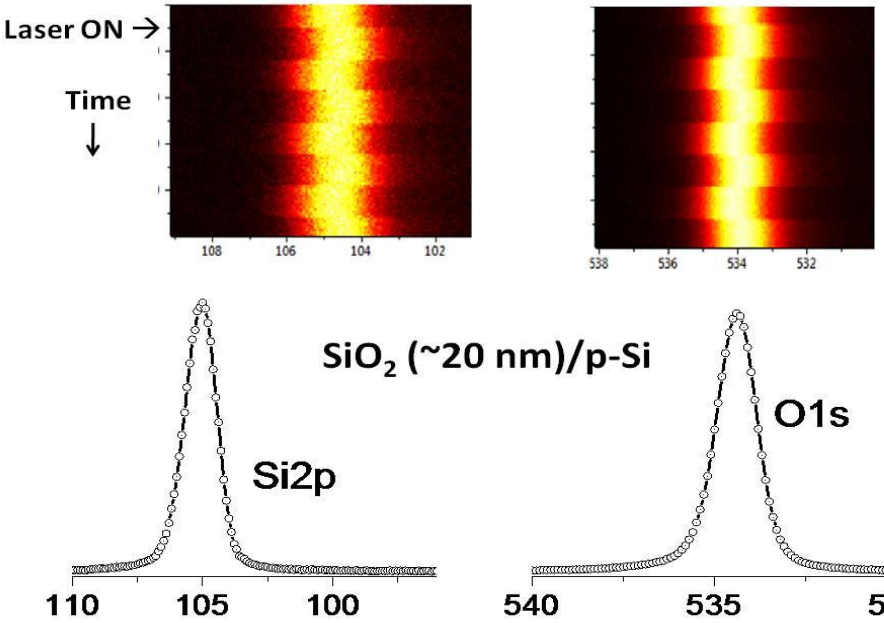


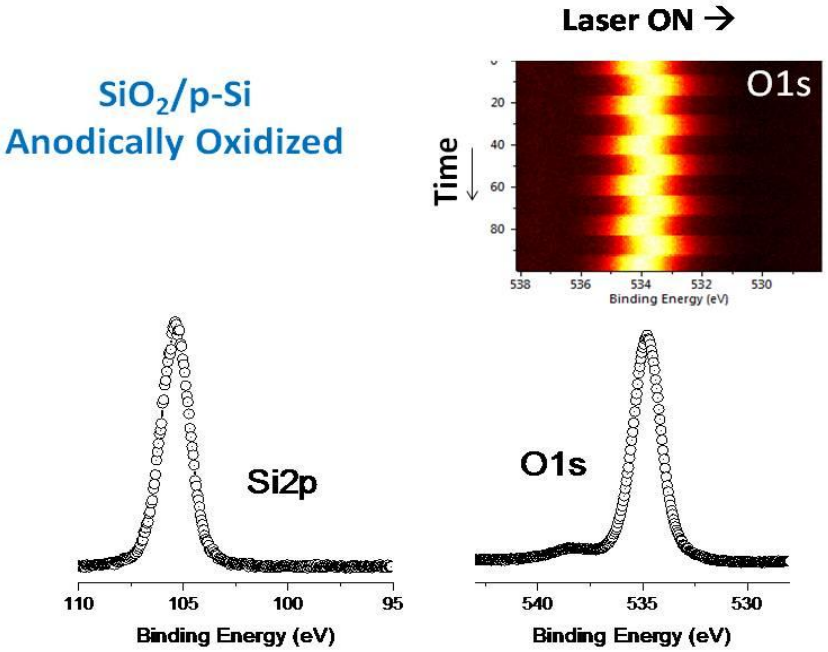


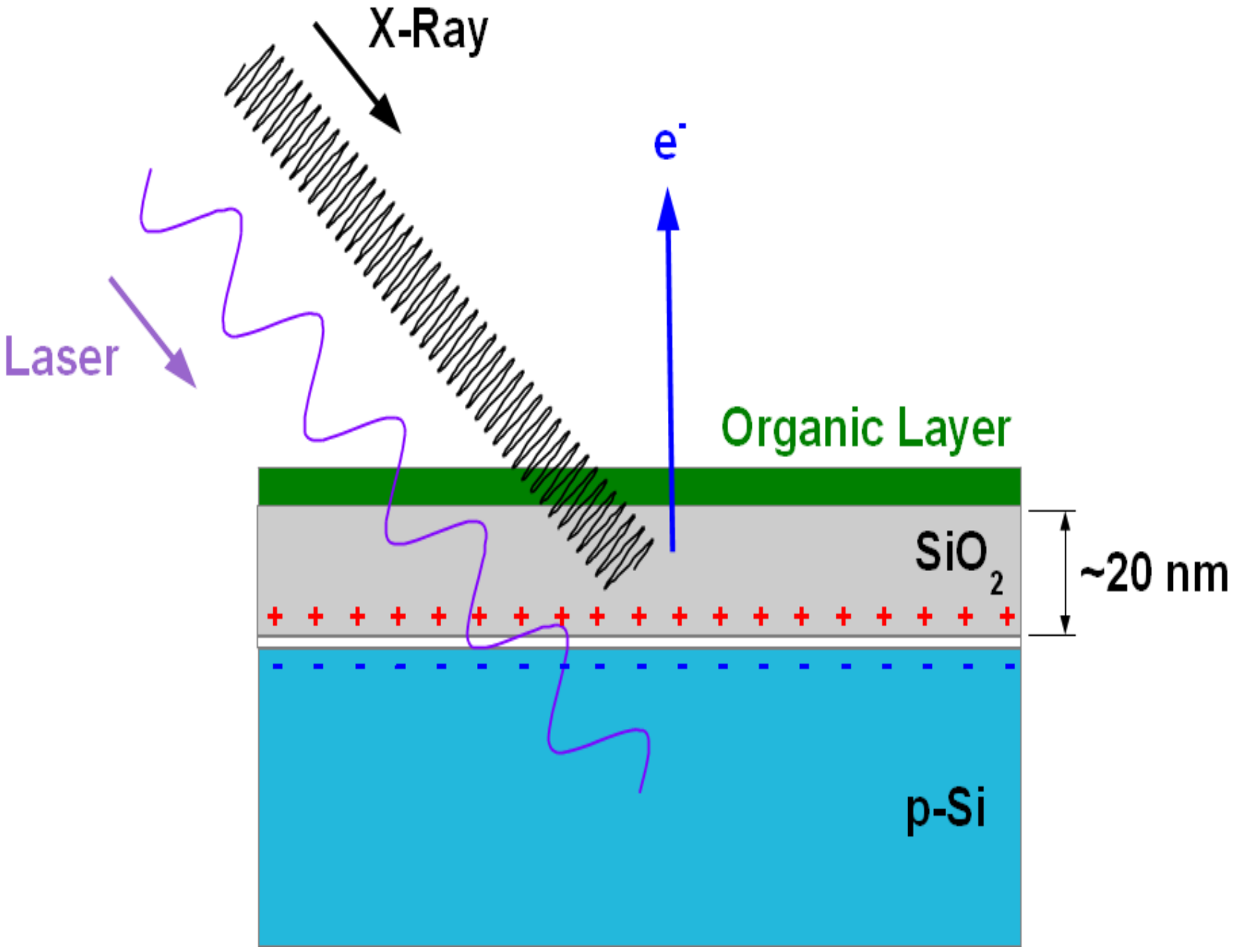

0.49 eV
405 nm
Laser ON
n
p
p-Si
0.49 eV
Laser ON
0.18 eV
Laser OFF
0.2
0.0
-0.2
ΔE_VB (eV)
n-Si
0.18 eV
Laser OFF
p
n
102
101
100
99
98


Time
536
534
532
p-Si/SiOx
0.18 eV
-0.19 eV
p-Si
Laser
OFF
Laser ON
n-Si/SiOx
O 1s
+0.11 eV
Si 2p
Si 2p
n-Si
Si4+
Si0
102
100
98
106
104
102
100
538
536
534
532
530

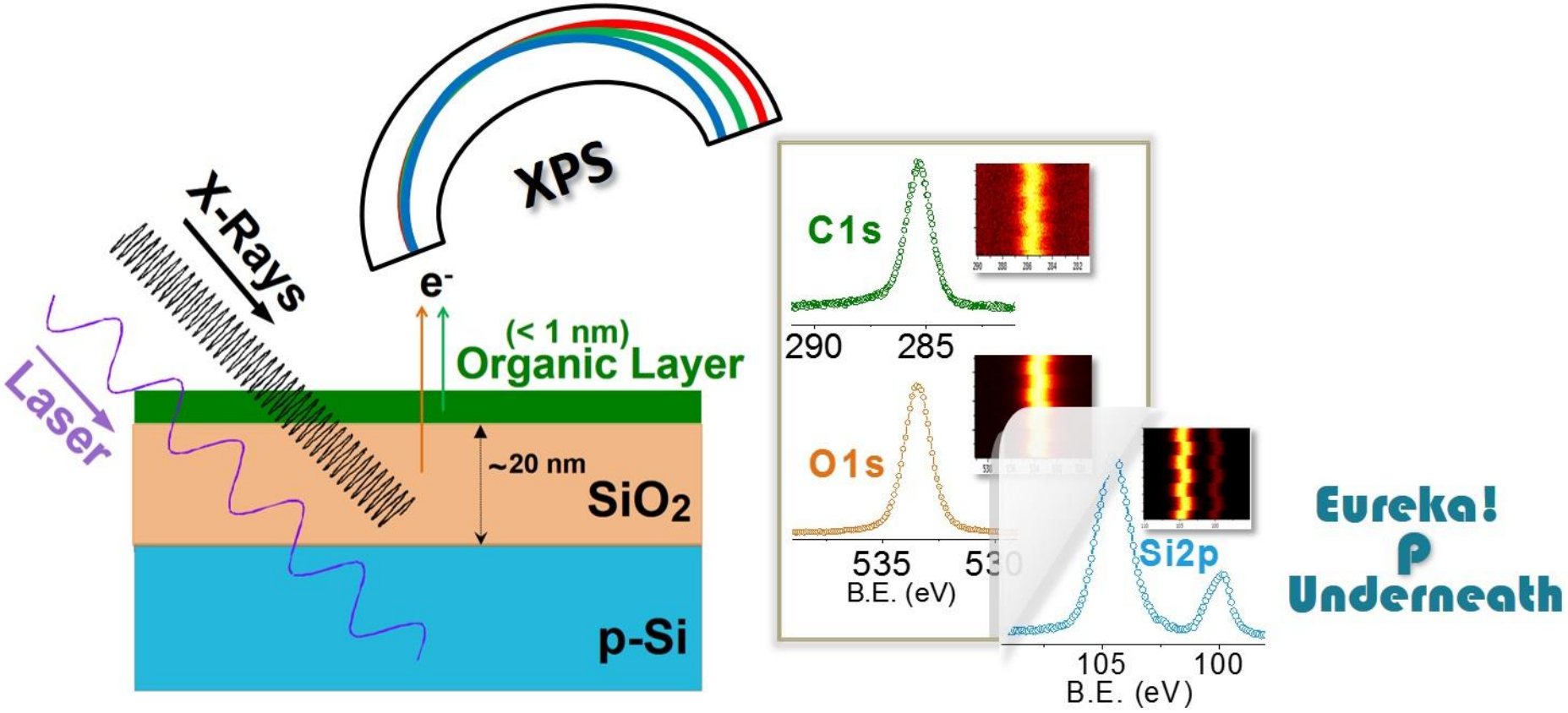

p-Si
Organic Layer (Polystyrene)
SiO2 (~8 nm)
Thin PS
Thick PS
C1s
296
292
288
284
Binding Energy (eV)
Laser ON →
Time
Si2p
O1s
C1s
105
100
535
530
295
290
285
Binding Energy (eV)

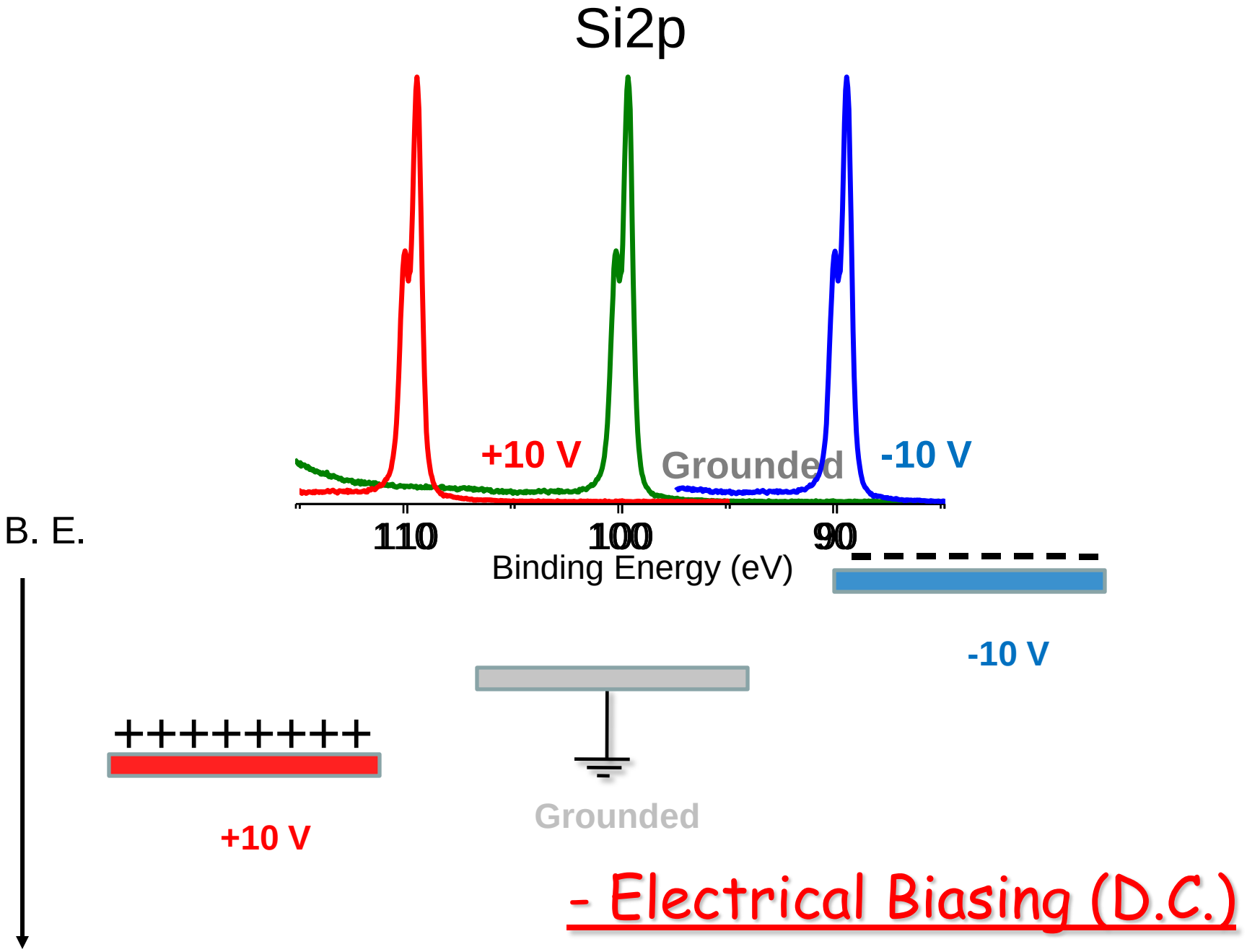

Laser ON →
Time
108
106
104
102
538
536
534
532
SiO2 (~20 nm)/p-Si
Si2p
O1s
110
105
100
540
535
530


Laser ON →
SiO2/p-Si
Anodically Oxidized
Time
O1s
20
40
60
80
538
536
534
532
530
Binding Energy (eV)
Si2p
110
105
100
95
Binding Energy (eV)
O1s
540
535
530
Binding Energy (eV)


X-Ray
e-
Laser
Organic Layer
SiO2
~20 nm
p-Si

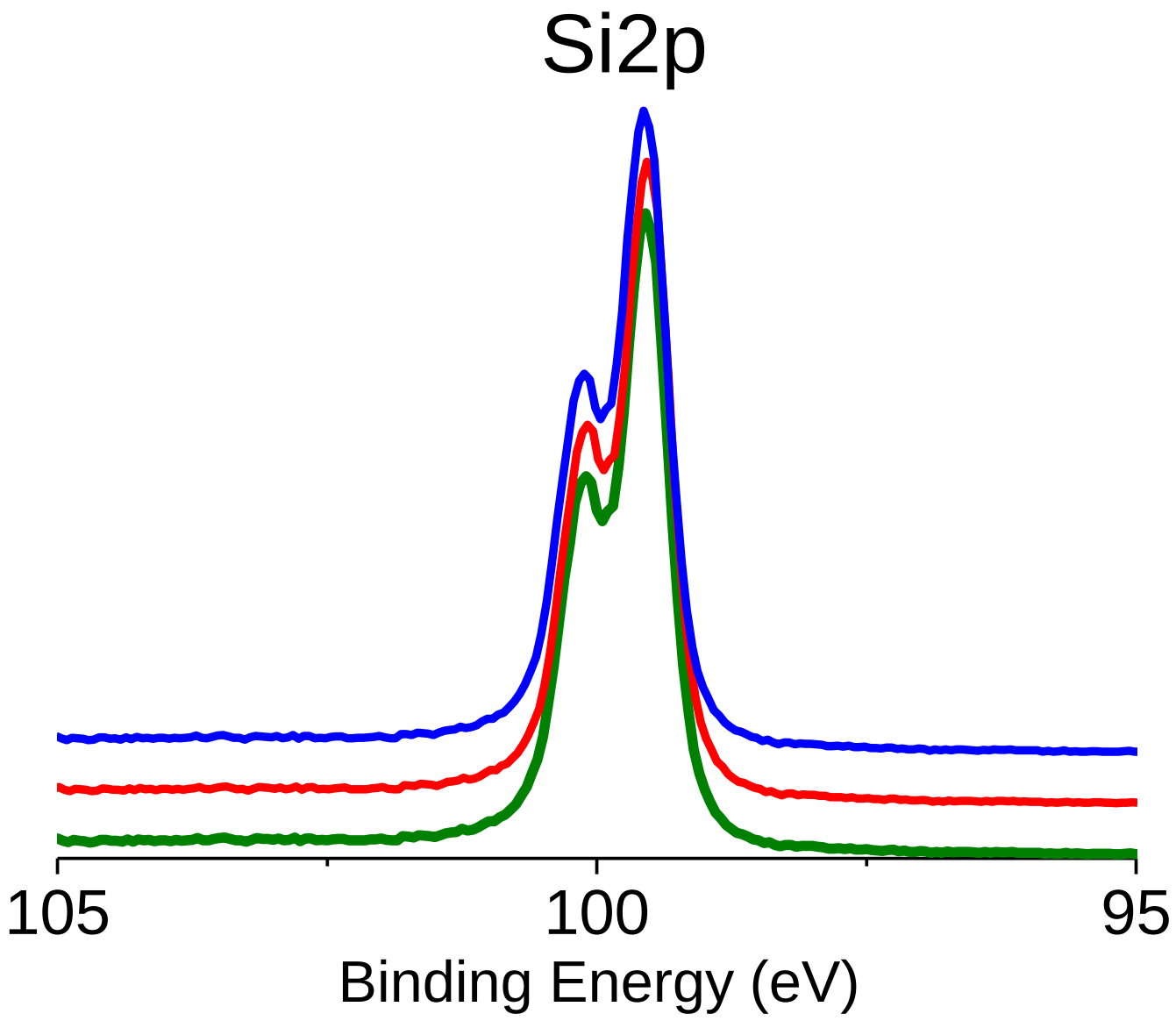
S. Suzer, *ACS Appl. Surf. Interf., 2013*

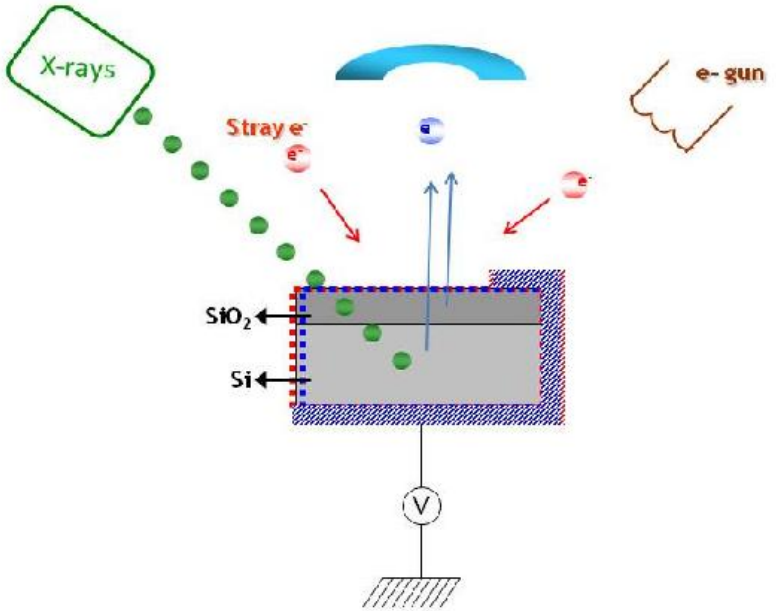


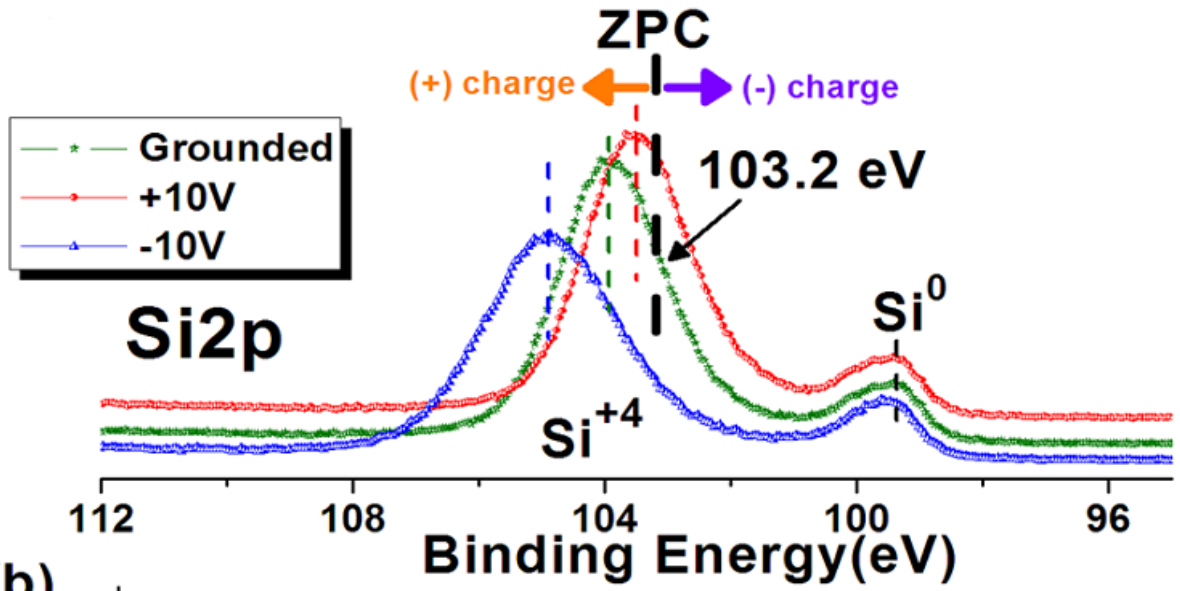


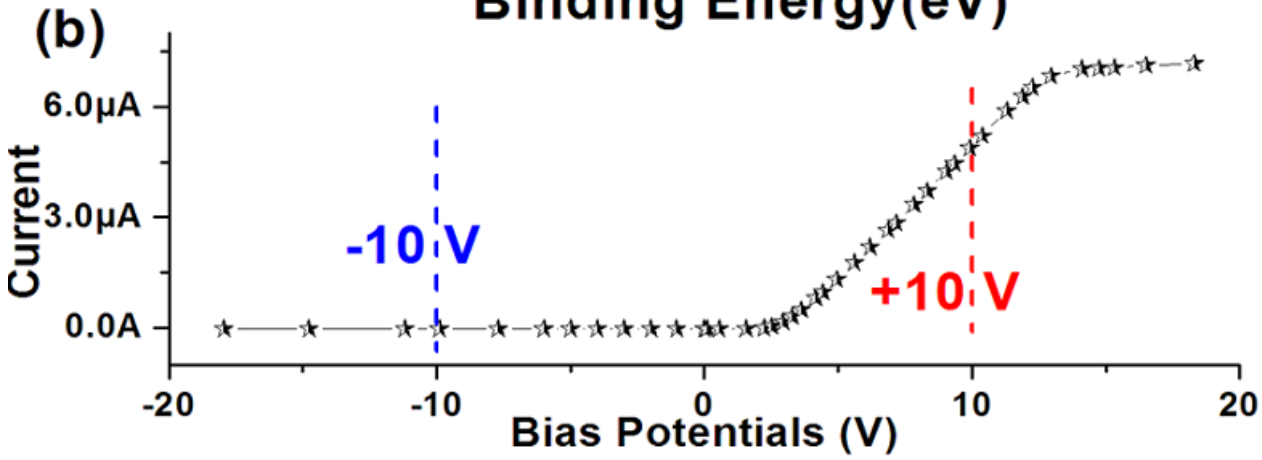
- Electrical Biasing (D.C.)

TRIVIAL SHIFTS FOR CONDUCTING MATERIALS

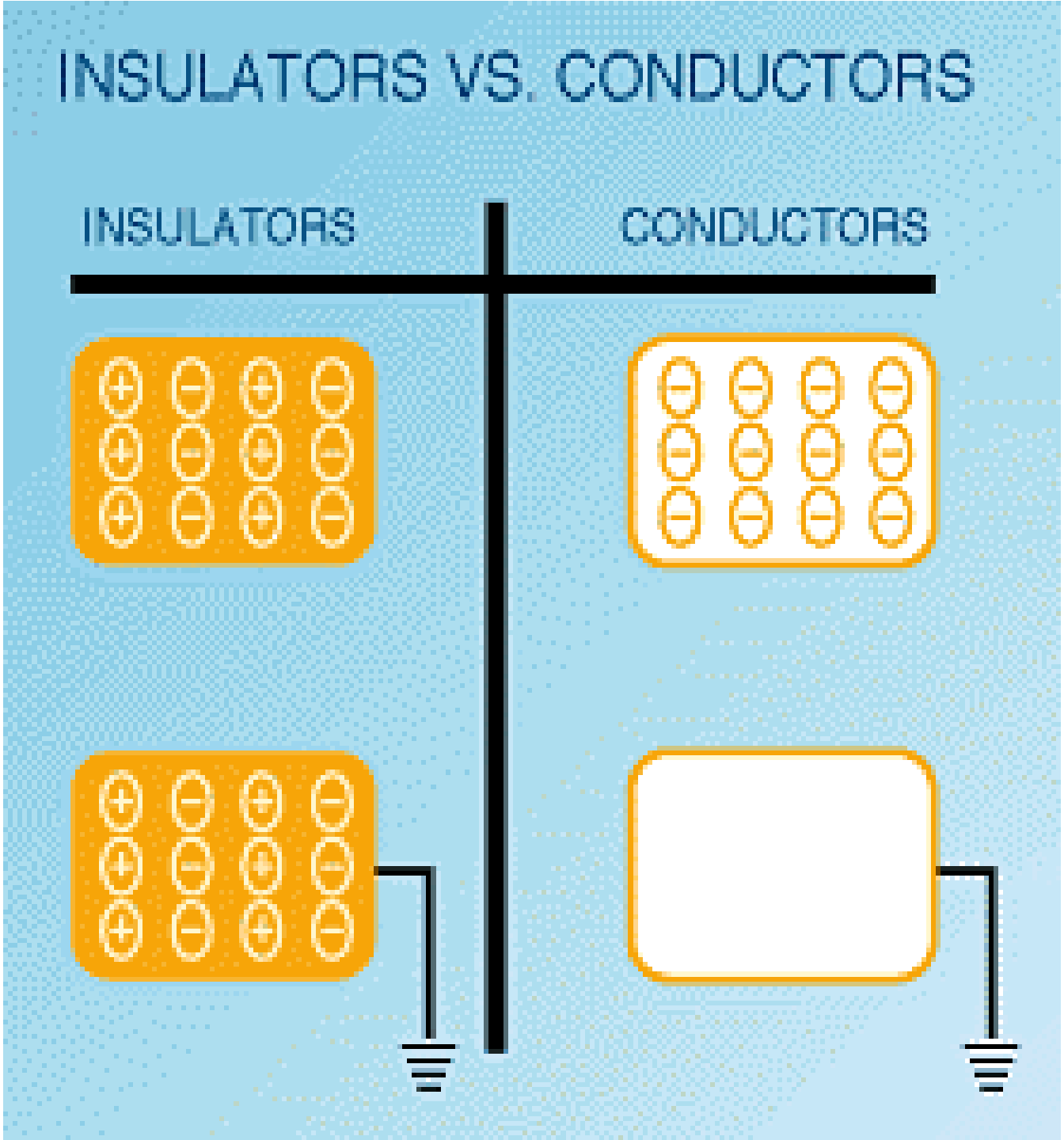


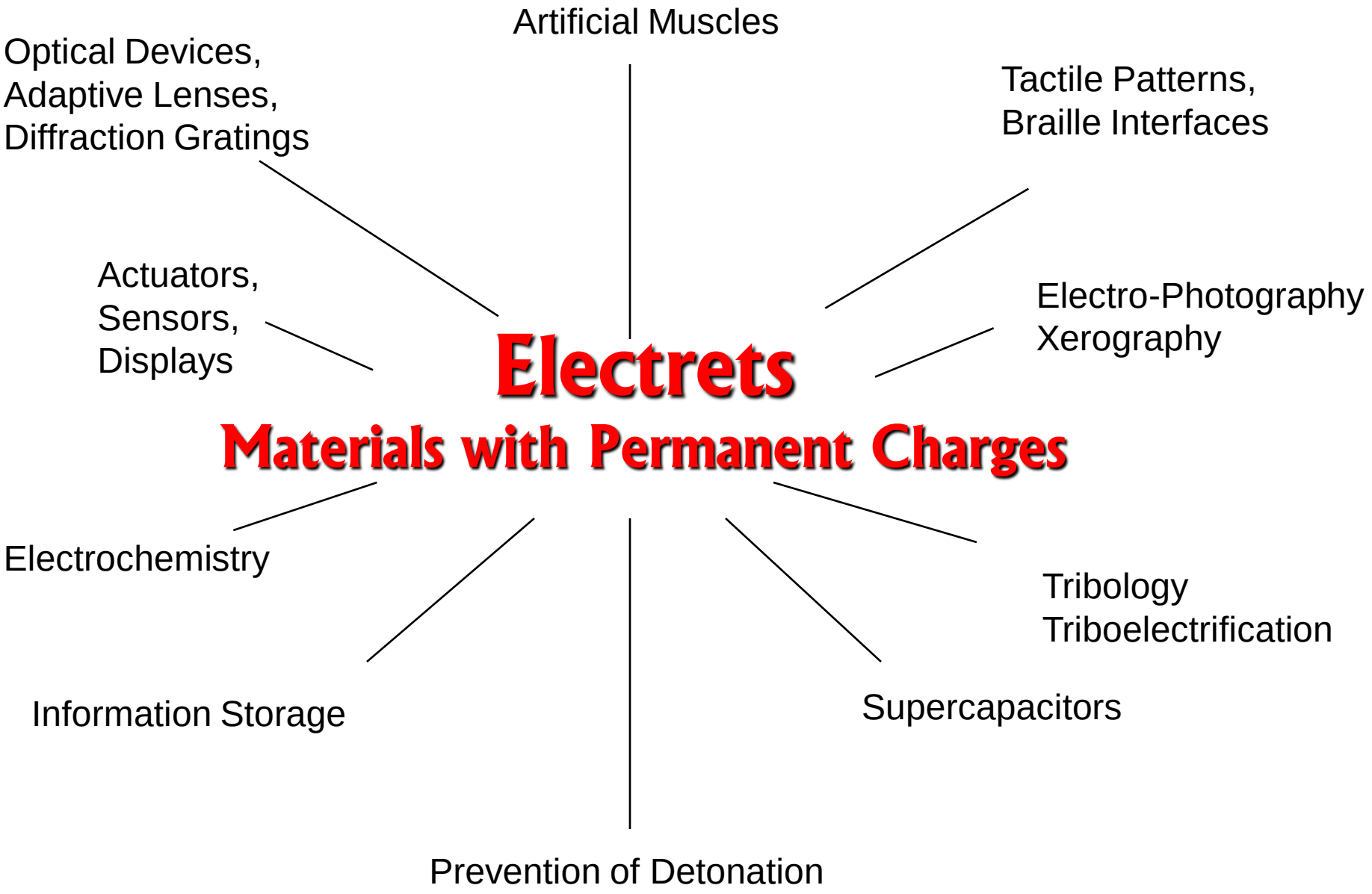

X-rays
Stray e-
e- gun
SiO2
Si
V

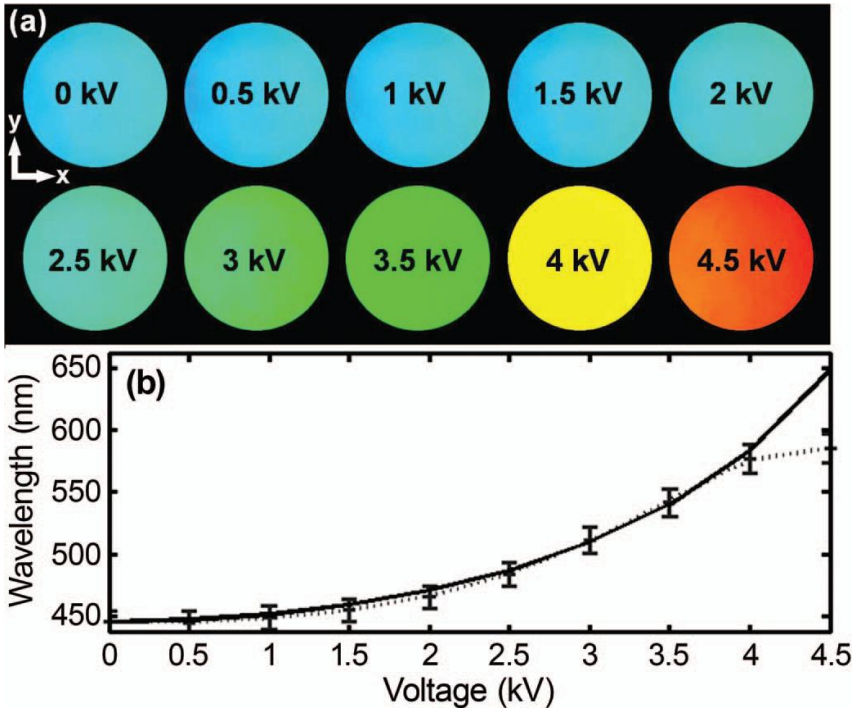

ZPC
(+) charge
(-) charge
Grounded
+10V
-10V
103.2 eV
Si2p
Si0
Si+4
112
108
104
100
96
Binding Energy(eV)


(b)
6.0μA
3.0μA
0.0A
Current
-10 V
+10 V
-20
-10
0
10
20
Bias Potentials (V)

WHY BOTHER!!

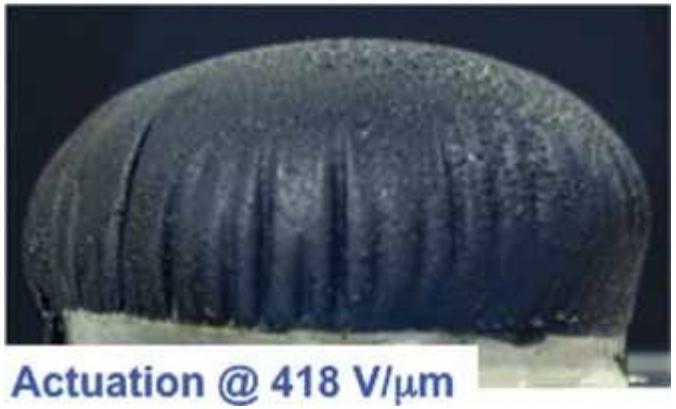

INSULATORS VS. CONDUCTORS
INSULATORS
CONDUCTORS


Artificial Muscles
Optical Devices,
Adaptive Lenses,
Diffraction Gratings
Tactile Patterns,
Braille Interfaces
Actuators,
Sensors,
Displays
Electro-Photography
Xerography
Electrets
Materials with Permanent Charges
Electrochemistry
Tribology
Triboelectrification
Information Storage
Supercapacitors
Prevention of Detonation



Polymeric, electrically tunable diffraction grating based on artificial muscles

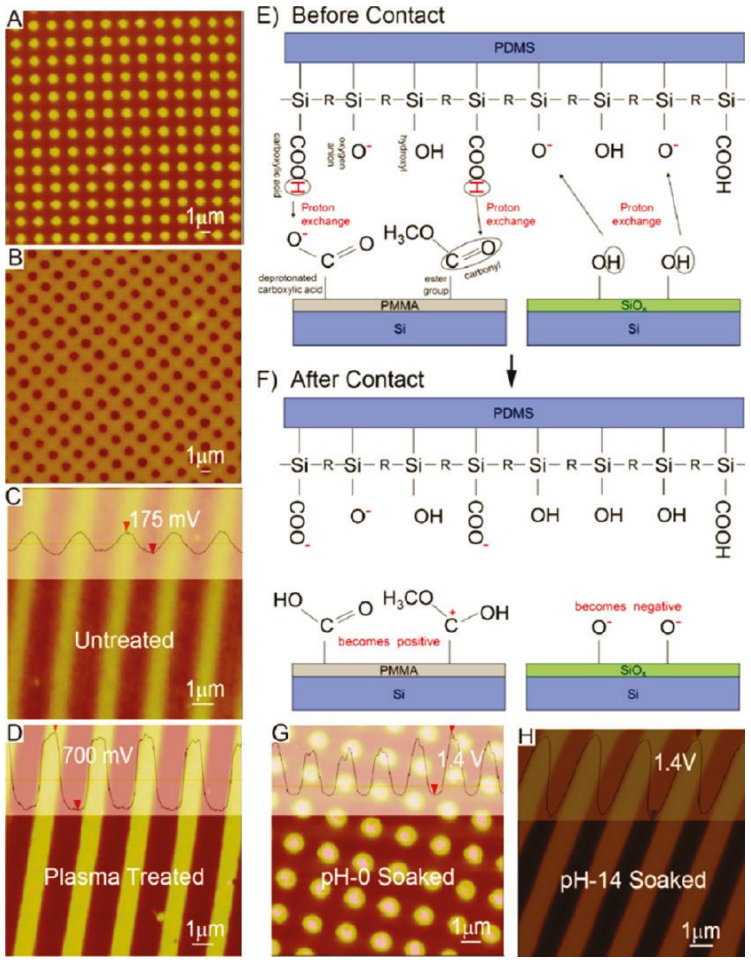
M. Aschwanden, A. Stemmer, Optics Letters, 31, 2610 (2006)

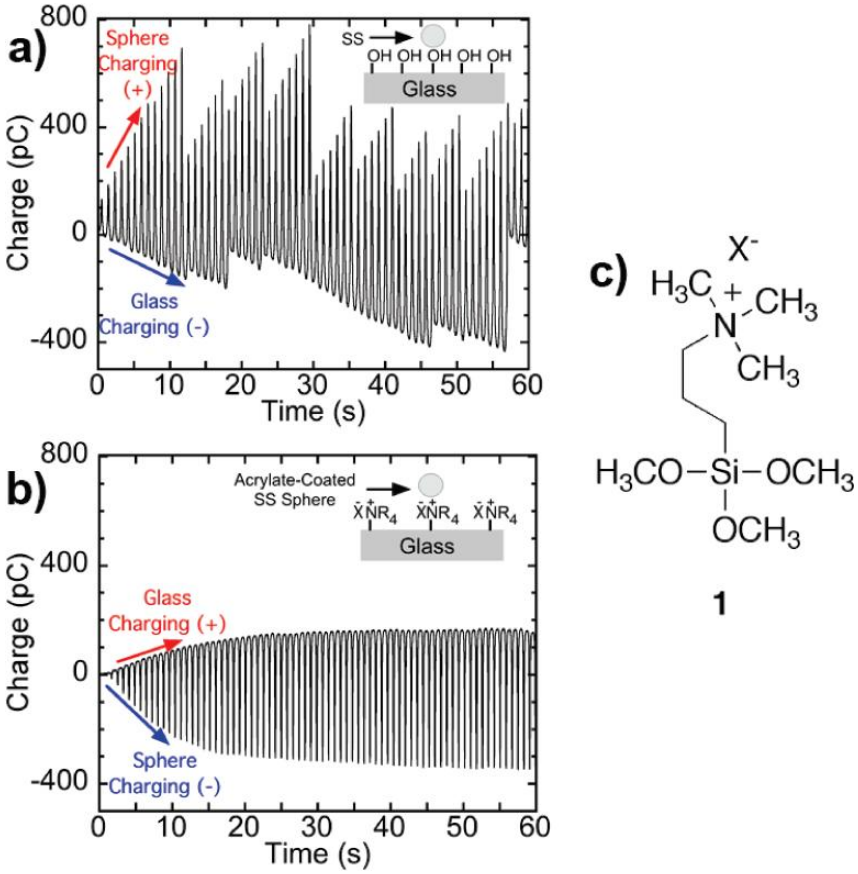


Advances in Dielectric Elastomers for Actuators and Artificial Muscles

Paul Brochu, Qibing Pei, Macromol. Rapid Commun. 31, 10 (2010)

Techniques for Detection of Charge Built-Up (AFM - KELVIN PROBE)





G. M. Whitesides et. al., JACS. 2009, *131, 8746*

H. O. Jacobs, Langmuir 27, 7321 (2011)

Elektrostatische Aufladung durch Separierung von Ionen an Grenzflchen: Kontaktelektrisierung von ionischen Elektreten

Logan S. McCarty und George M. Whitesides*

Angew. Chem. 2008, 120, 2218 – 2239

Organic Electrets

A.J. Bard
Crypto Electrons do Chemsitry ($Cu^{2+} \rightarrow Cu^0$)

Electrostatic electrochemistry at insulators

CHONGYANG LIU AND ALLEN J. BARD*

The identity of charges generated by contact electrification on dielectrics has remained unknown for centuries and the precise determination of the charge density is also a long-standing challenge. Here, electrostatic charges on Teflon polytetrafluoroethylene) produced by rubbing with Lucite (polymethylmethacrylate) were directly identified as electrons rather than ions.

Nature Materials VOL 7 JUNE 2008

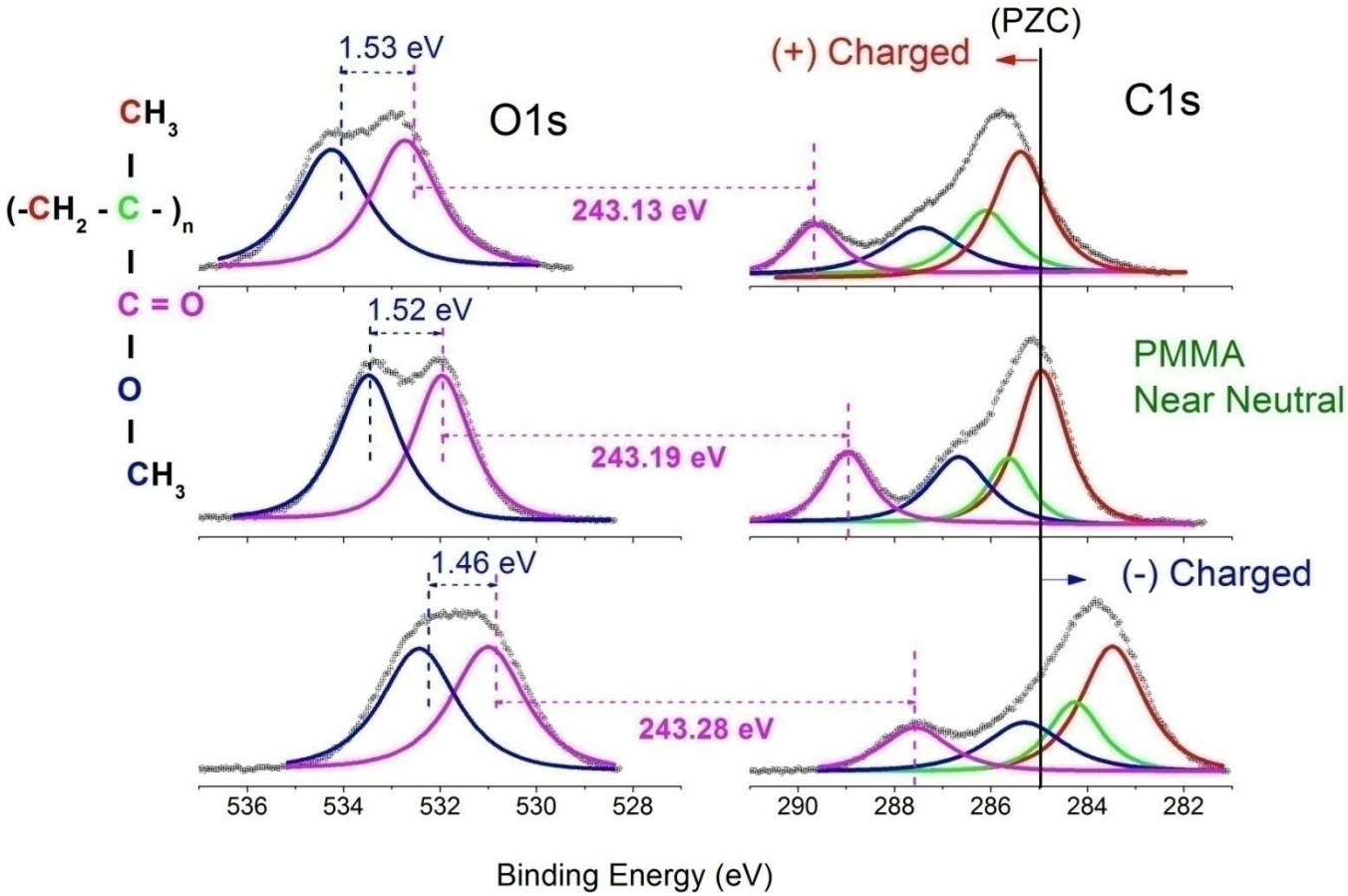
Angewandte Communications

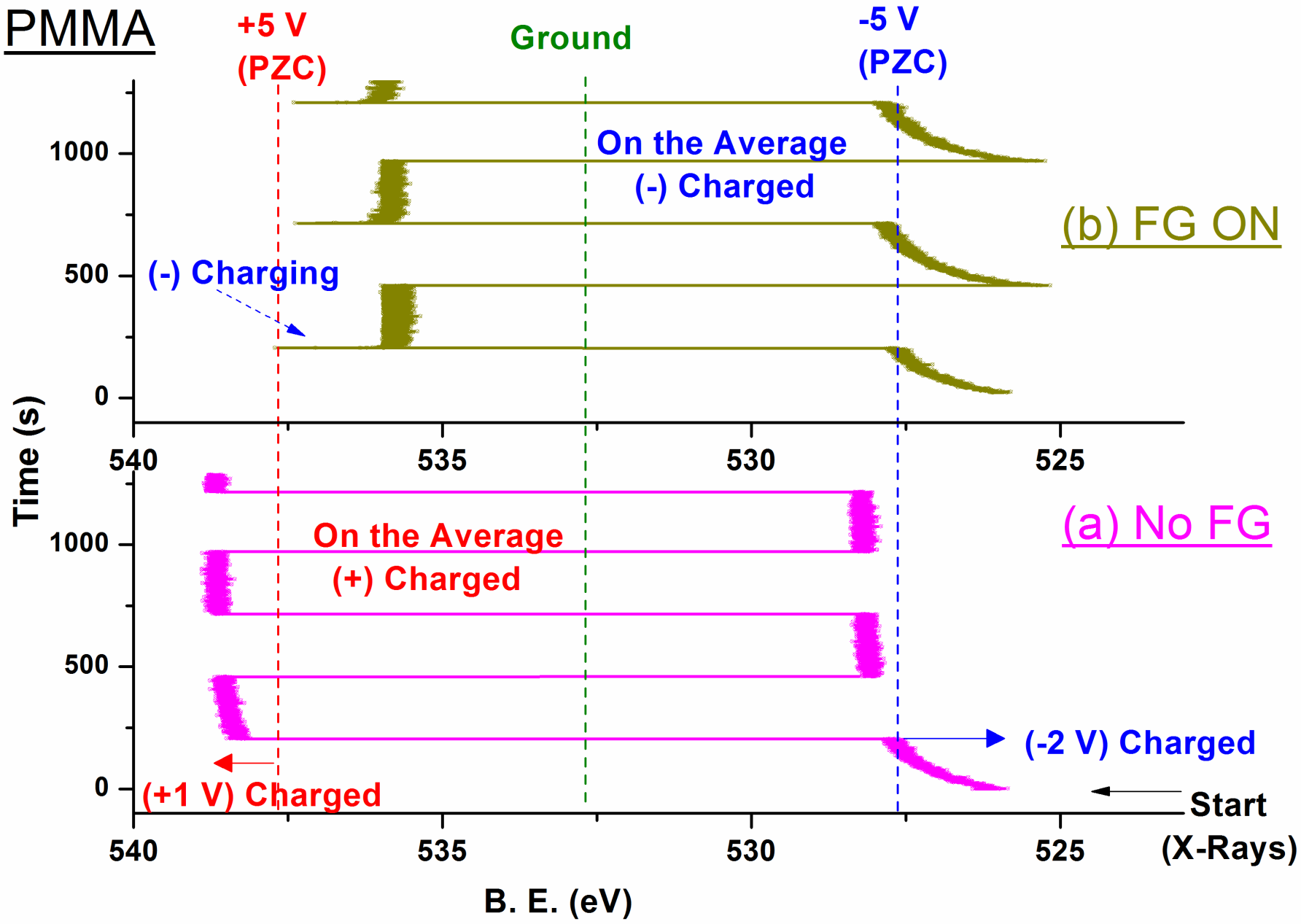
Surface Charges

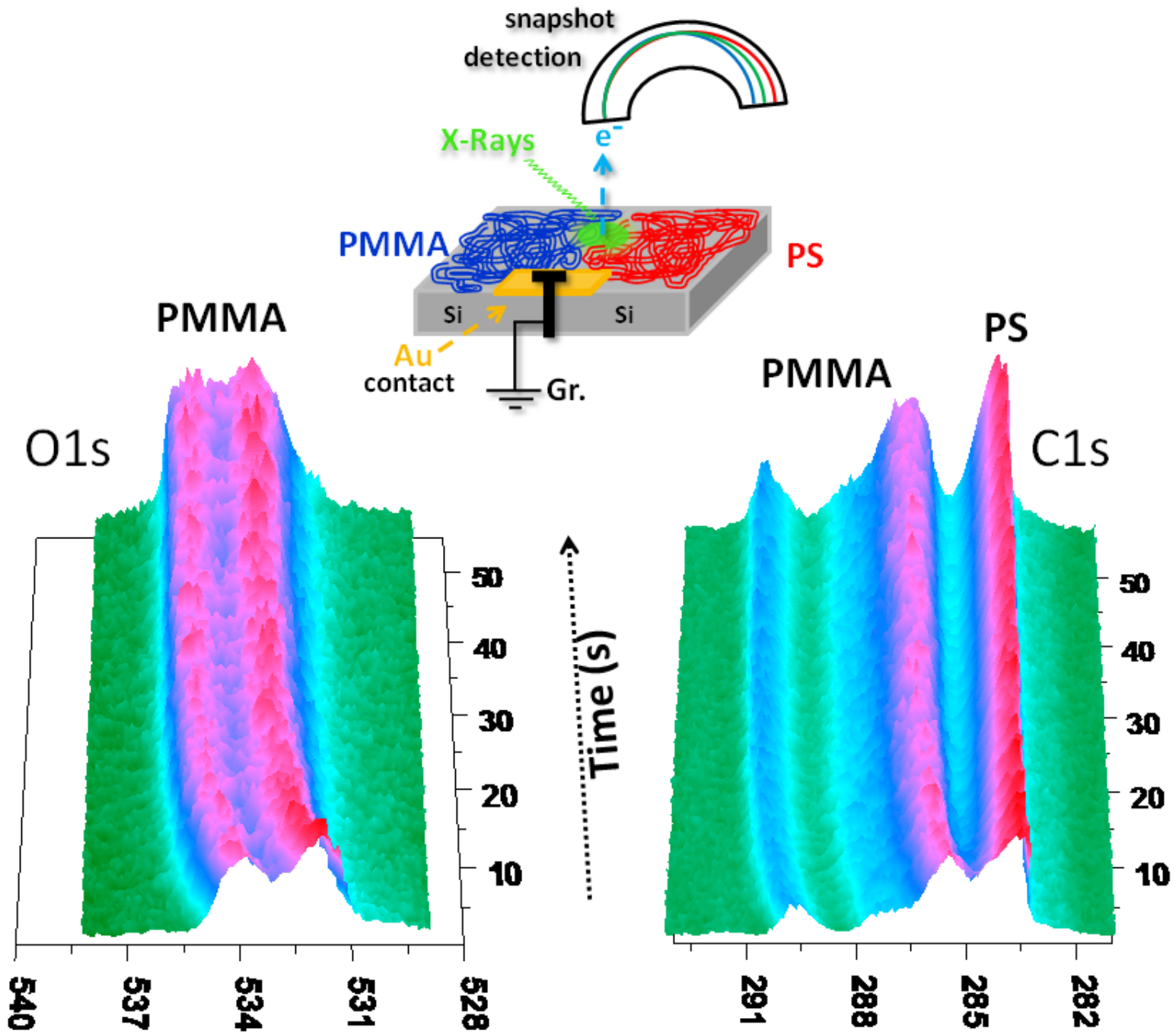
DOI: 10.1002/anie.201201351

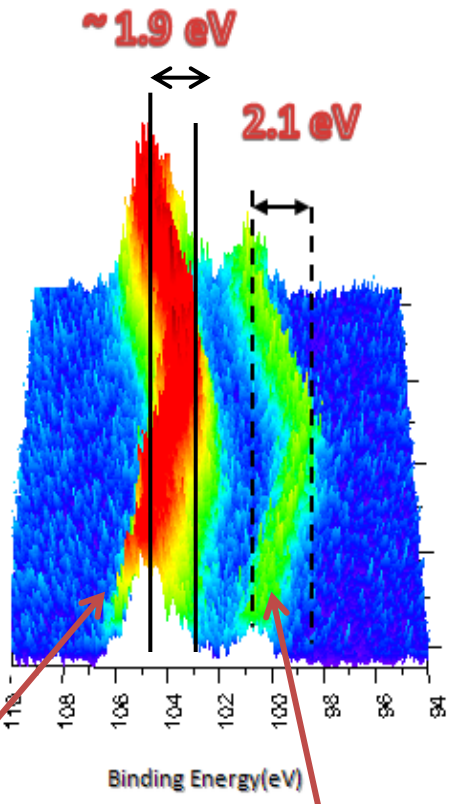
Probing the Charge Build-Up and Dissipation on Thin PMMA Film Surfaces at the Molecular Level by XPS**

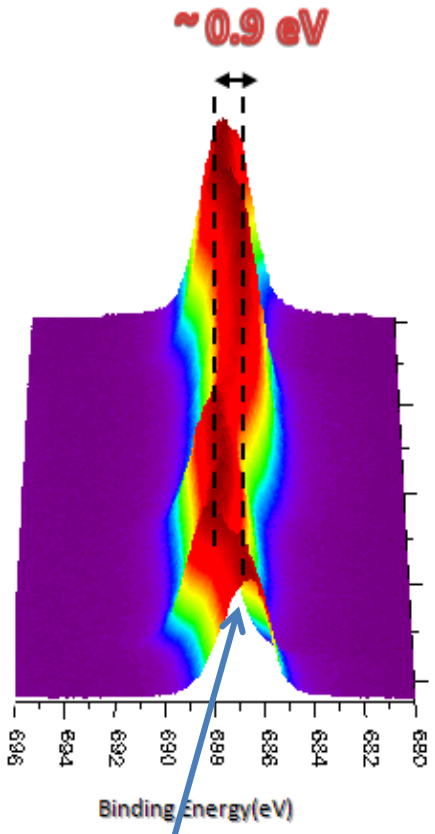
*Eda Yilmaz, Hikmet Sezen, and Sefik Suzer**

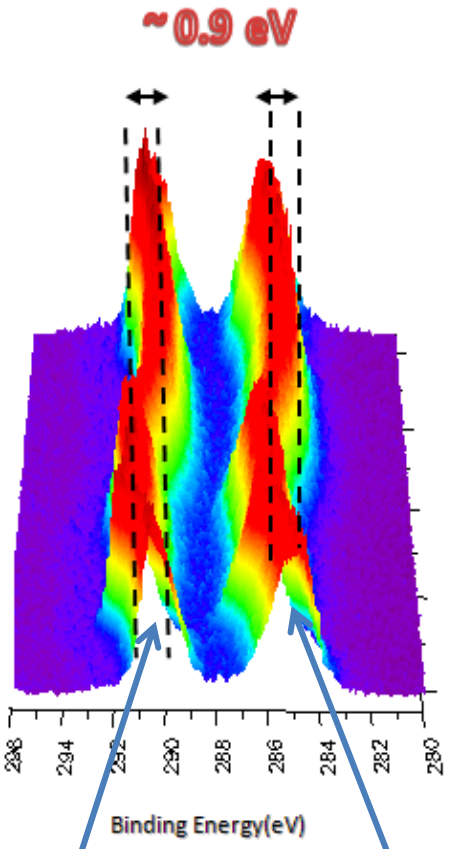



PMMA
+5 V
(PZC)
Ground
-5 V
(PZC)
On the Average
(-) Charged
(b) FG ON
(-) Charging
1000
500
0
Time (s)
540
535
530
525
On the Average
(+) Charged
(a) No FG
(-2 V) Charged
(+1 V) Charged
Start
(X-Rays)
B. E. (eV)


snapshot
detection
X-Rays
e⁻
PMMA
PS
Si
Si
Au
contact
Gr.
PMMA
O1s
PS
PMMA
C1s
Time (s)
50
40
30
20
10
540
537
534
531
528
291
288
285
282







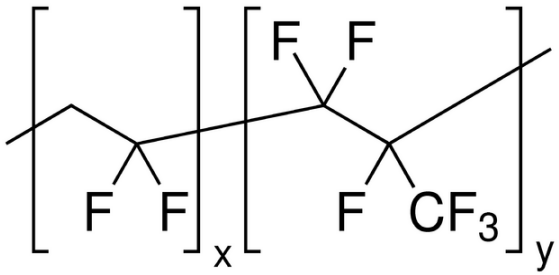
Oxidized Si($2p_{3/2}$)

Si($2p_{3/2}$)

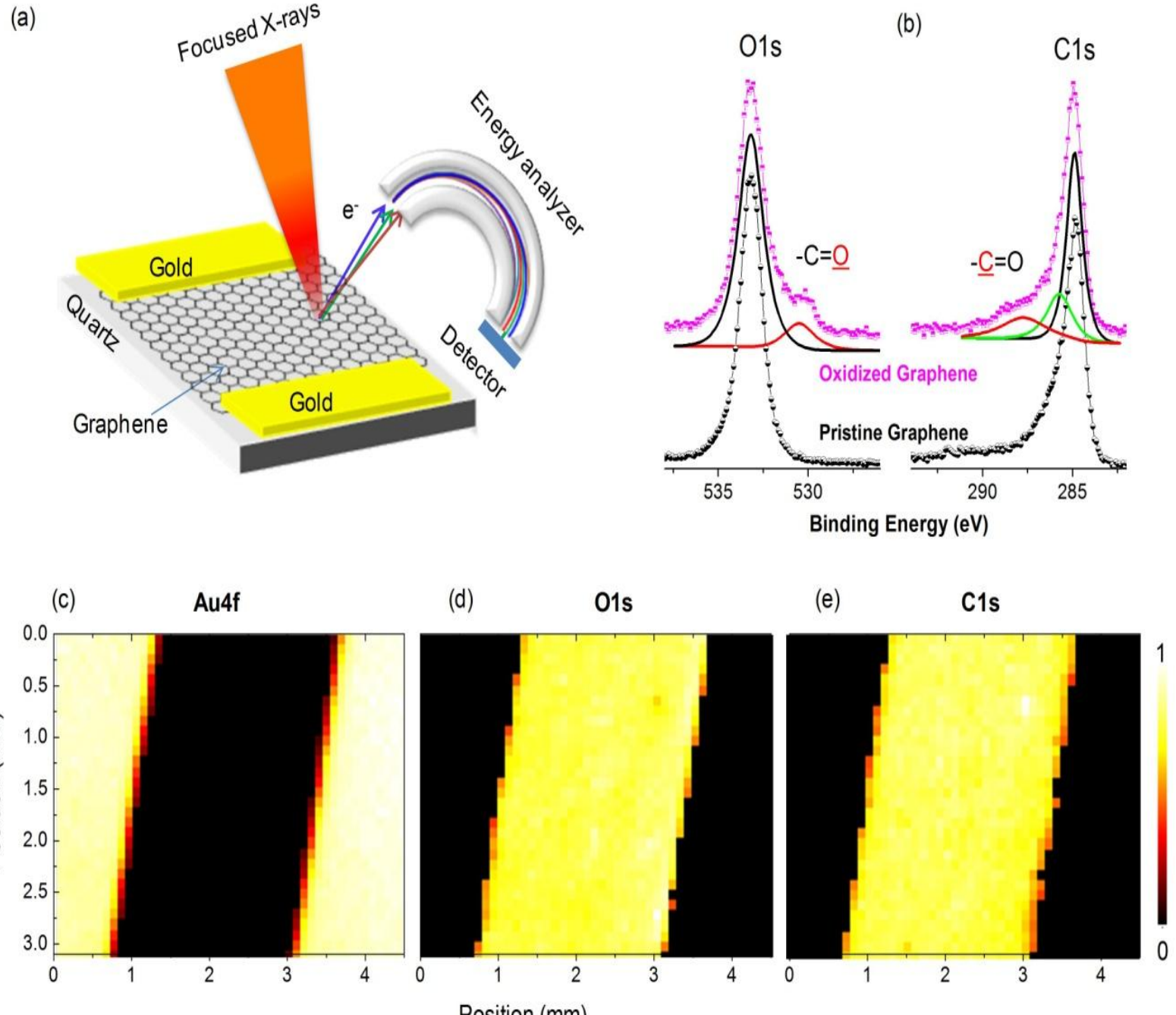
F(1s)

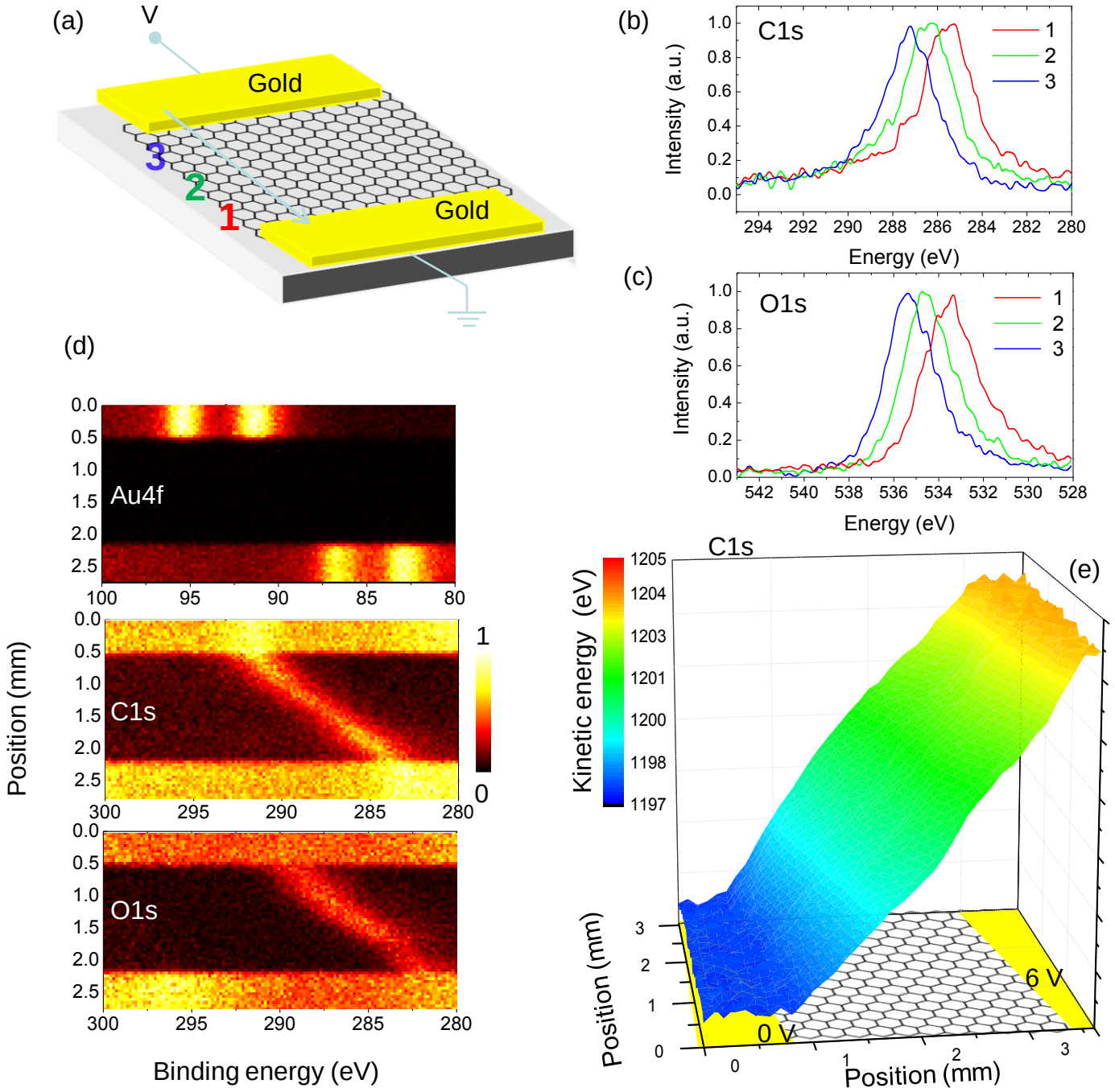
-CF_2- C(1s)

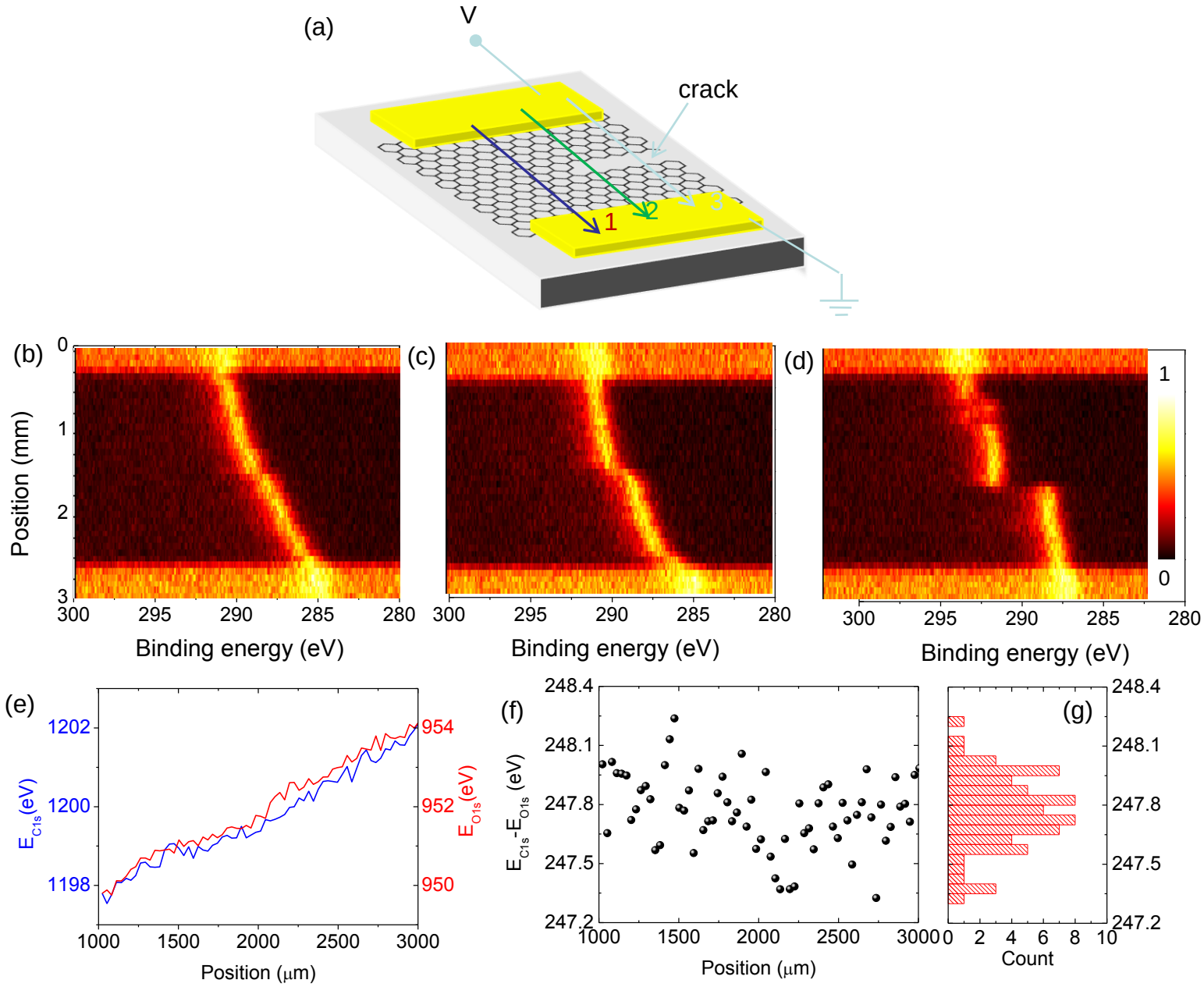
-CH_2- and organic contaminations C(1s)



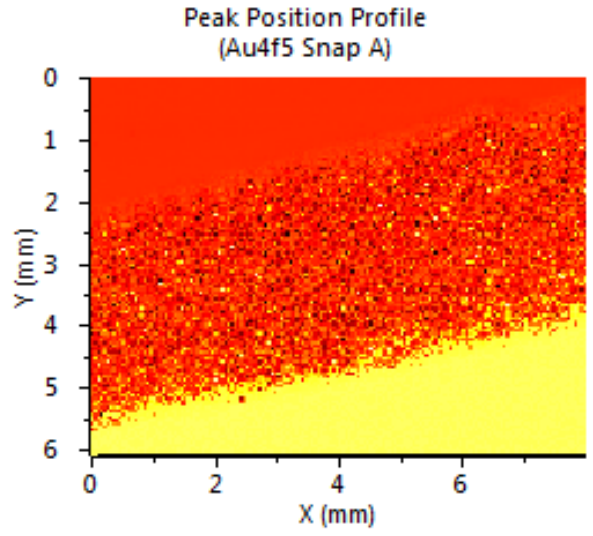
Applying Voltage Across the Sample

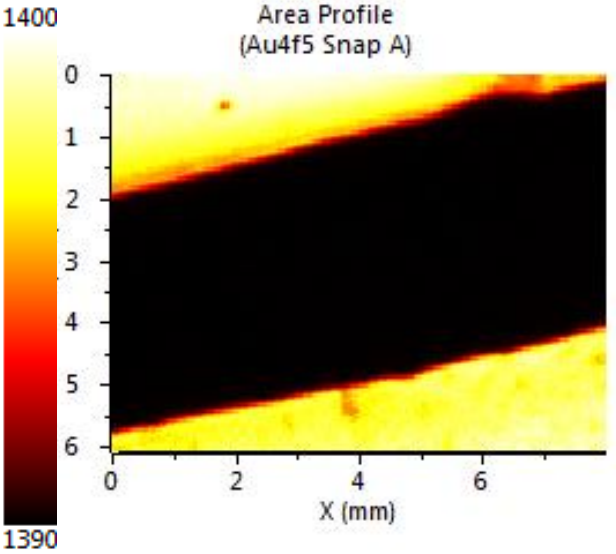



(a)
V
Gold
Gold
3
2
1
(b)
C1s
1
2
3
Intensity (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
294 292 290 288 286 284 282 280
Energy (eV)
(c)
O1s
1
2
3
Intensity (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
542 540 538 536 534 532 530 528
Energy (eV)
(d)
Au4f
C1s
O1s
Position (mm)
0.0
0.5
1.0
1.5
2.0
2.5
100 95 90 85 80
300 295 290 285 280
1
0
Binding energy (eV)
(e)
C1s
Kinetic energy (eV)
1205
1204
1203
1201
1200
1198
1197
Position (mm)
0 V
6 V
0 1 2 3
Position (mm)

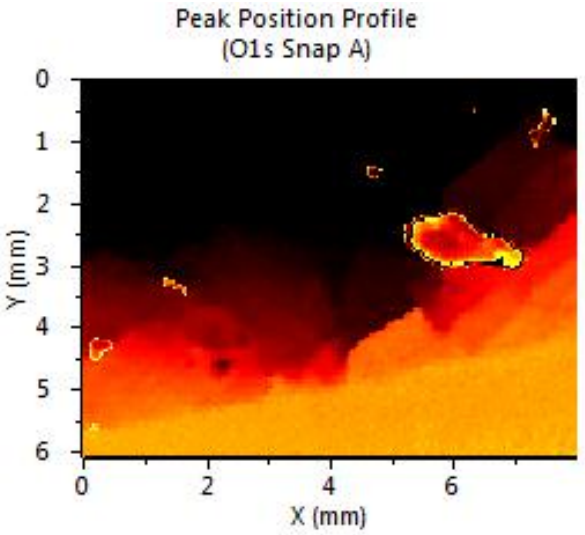


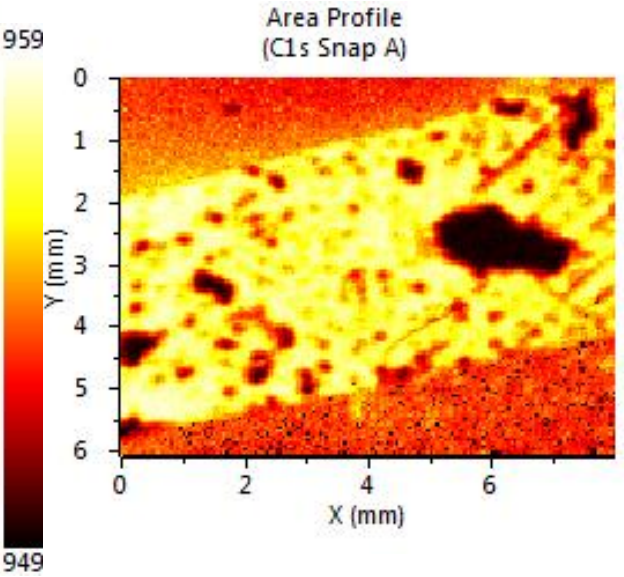
C. Kocabas, S. Suzer, *Anal. Chem.* **85**, 4172 (2013).


Peak Position Profile
(Au4f5 Snap A)
Y (mm)
X (mm)

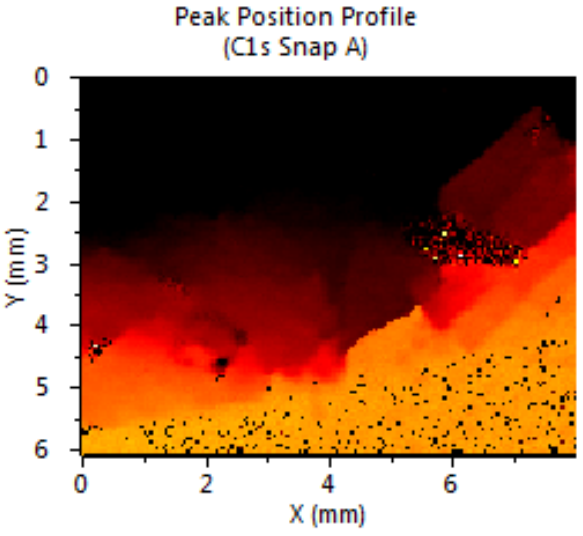

1400
1390
Area Profile
(Au4f5 Snap A)
X (mm)

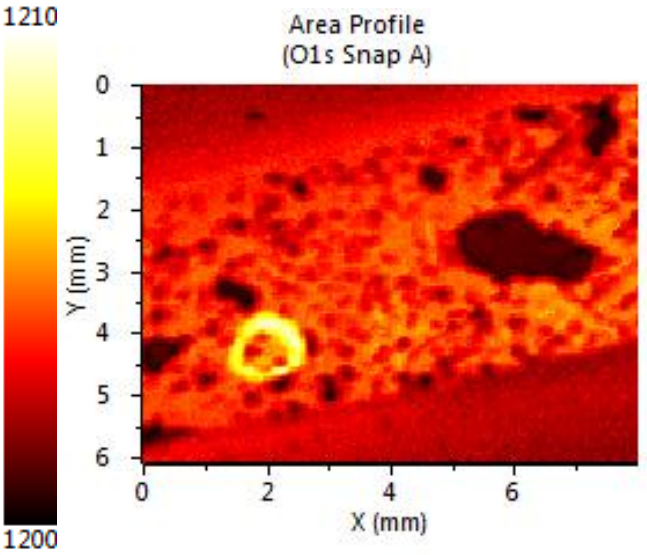

1400
0


Peak Position Profile
(O1s Snap A)
Y (mm)
X (mm)


959
949
Area Profile
(C1s Snap A)
Y (mm)
X (mm)


332
0


Peak Position Profile
(C1s Snap A)
Y (mm)
X (mm)

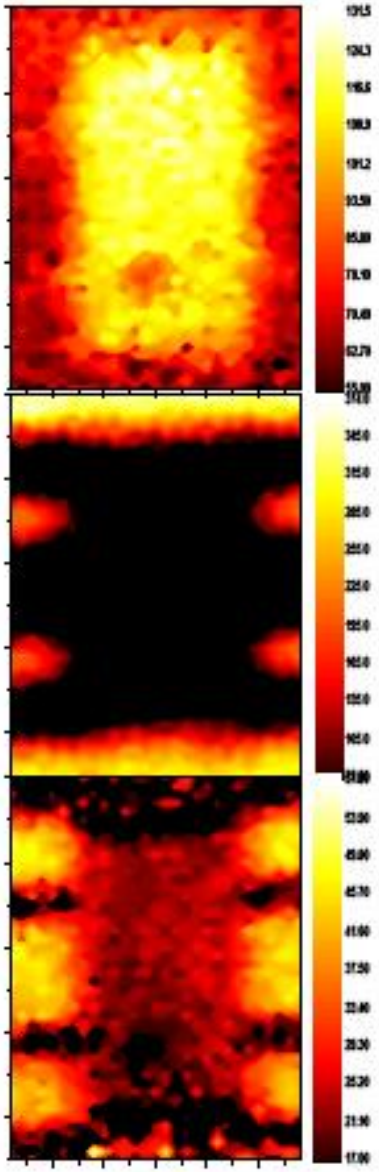

1210
1200
Area Profile
(O1s Snap A)
Y (mm)
X (mm)


735
0

C- Face (~400 Ω)

Si Face (~700 Ω)

Areal Maps of Elements' Distribution

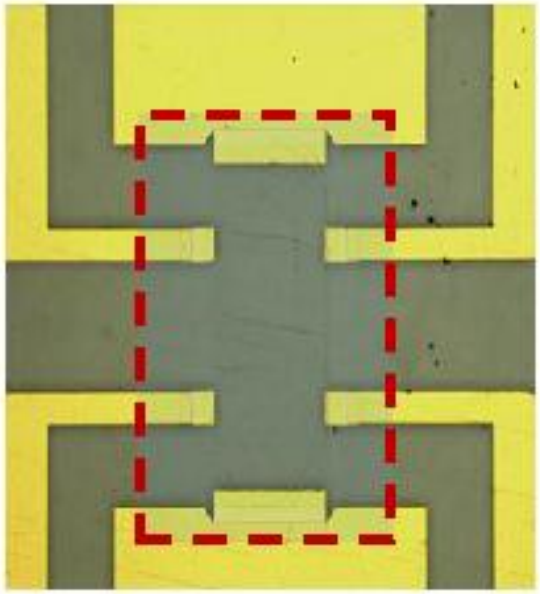


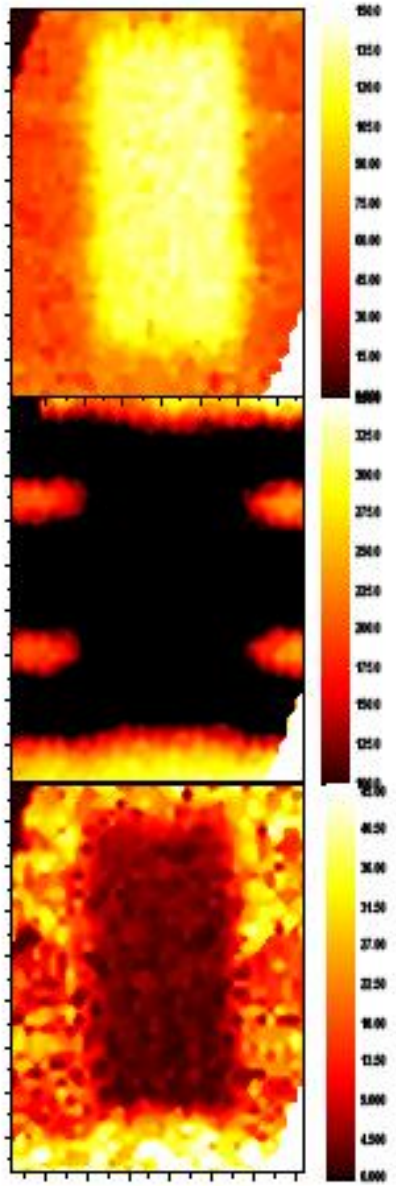
(a) C1s

(b) Au4f

(c) Si2p

(d)

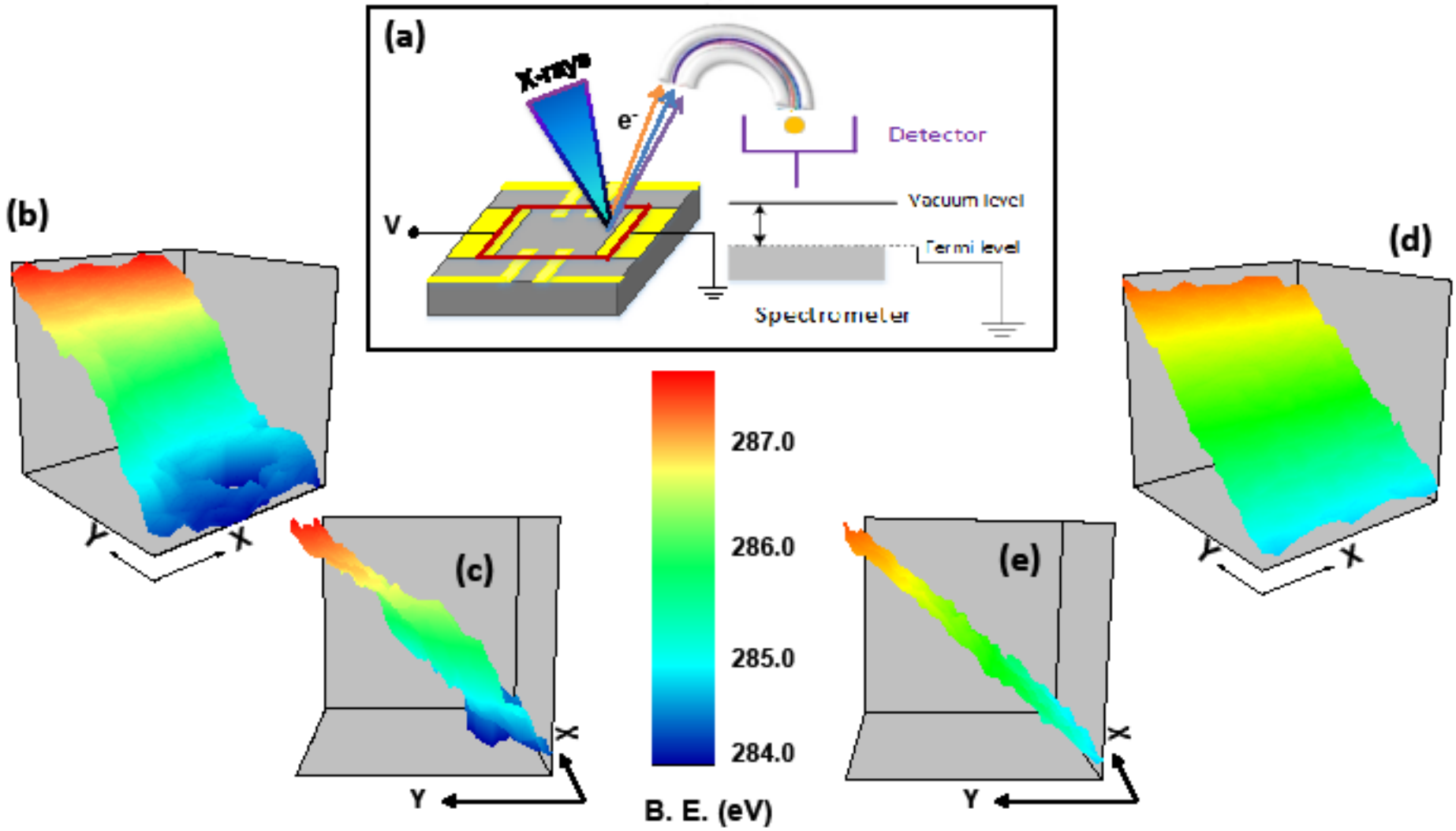




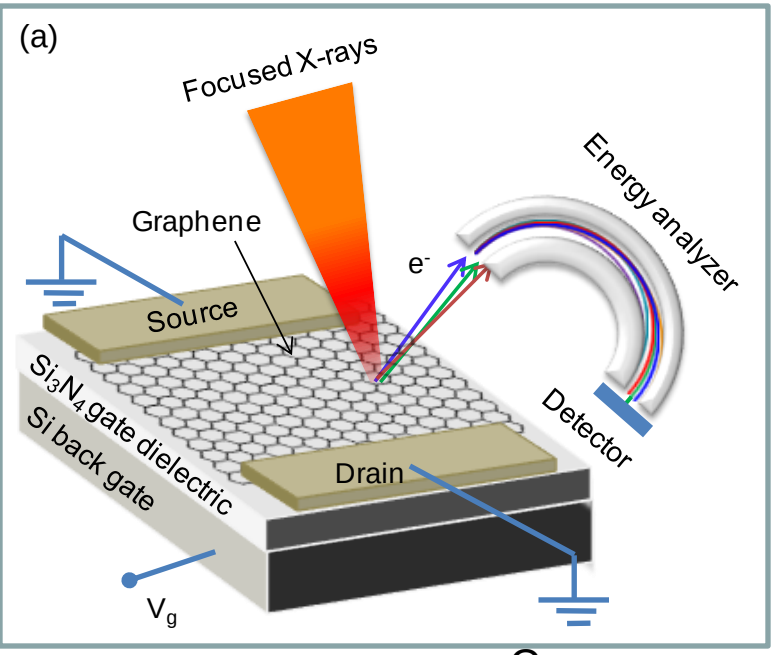
(e) C1s

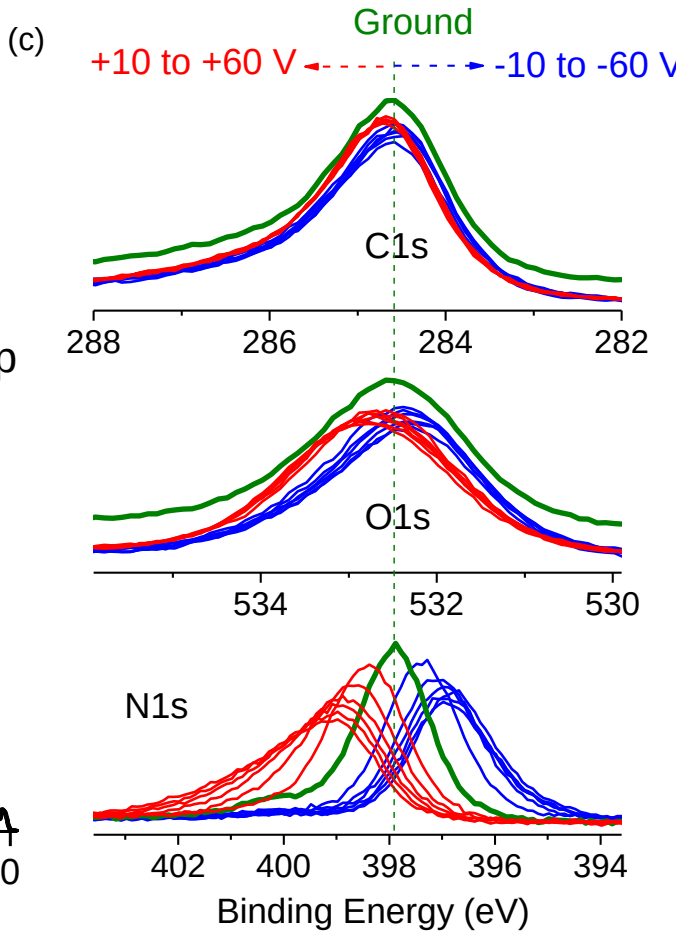
(f) Au4f

(g) Si2p


(a)
X-rays
e⁻
Detector
V
Vacuum level
Fermi level
Spectrometer
(b)
(c)
(d)
(e)
287.0
286.0
285.0
284.0
B. E. (eV)
X
Y

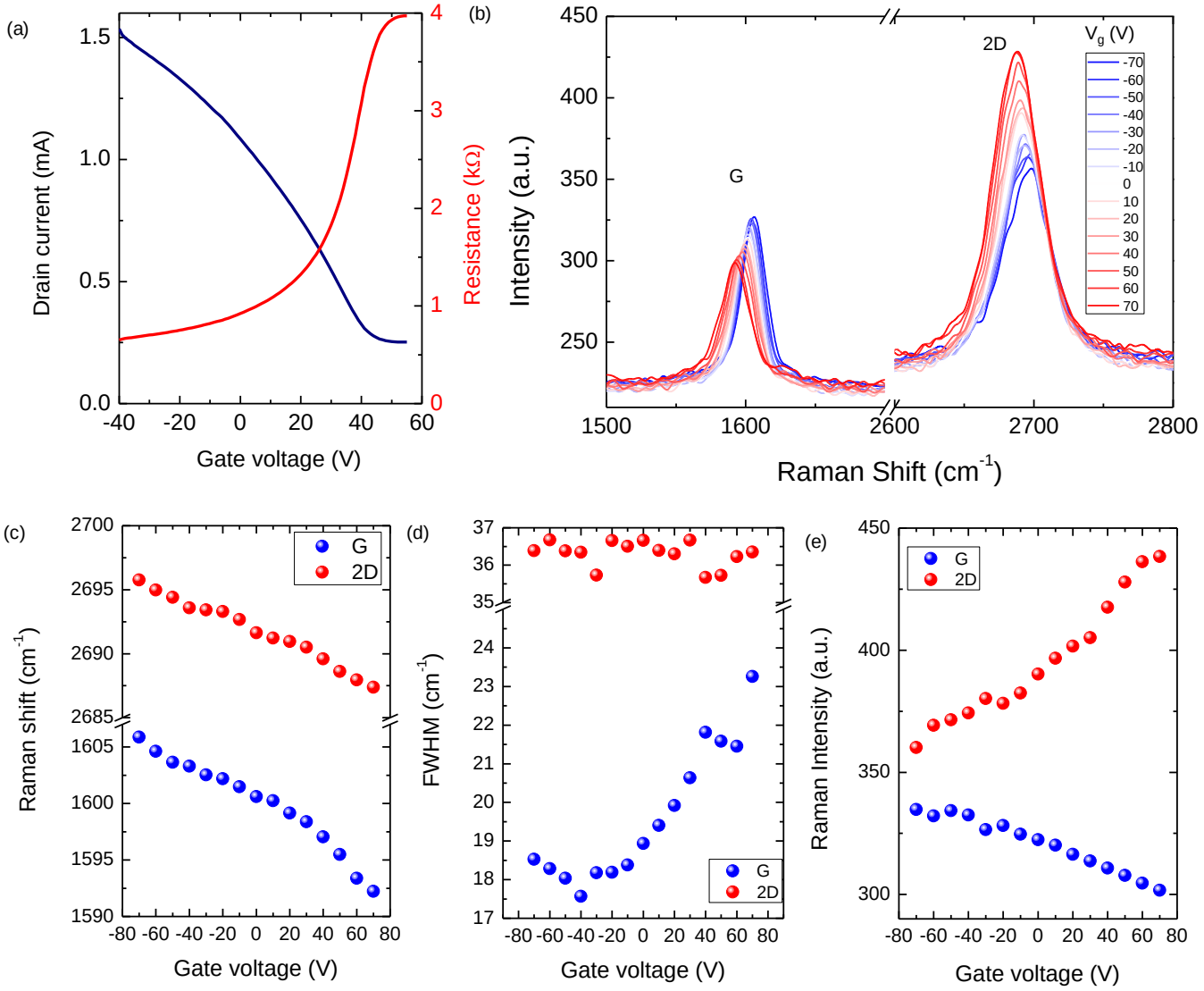
Gating

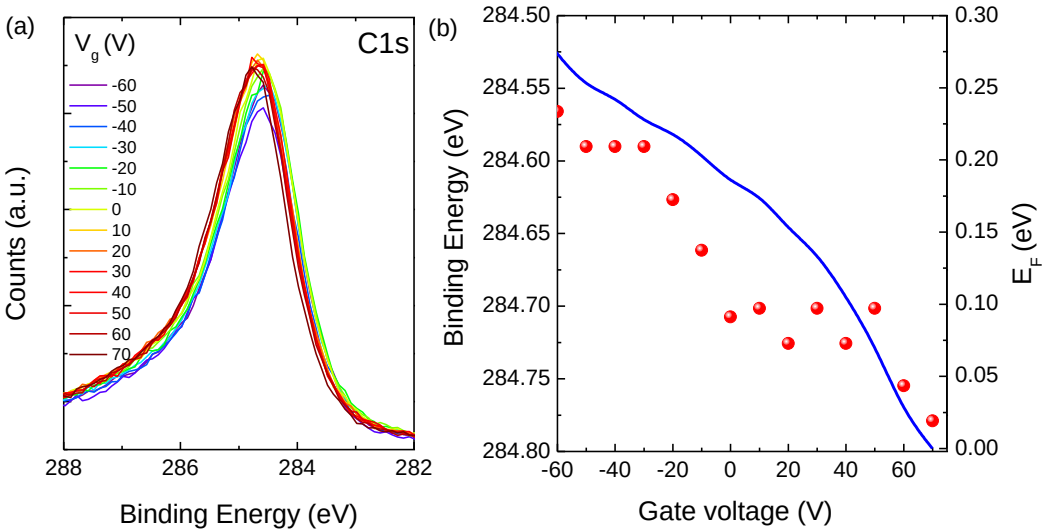


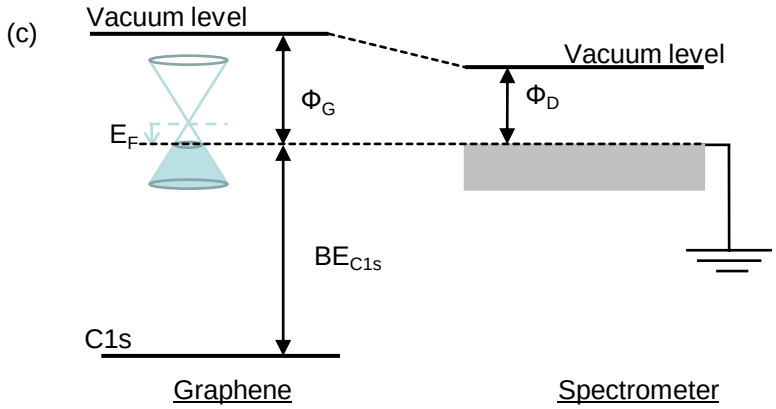


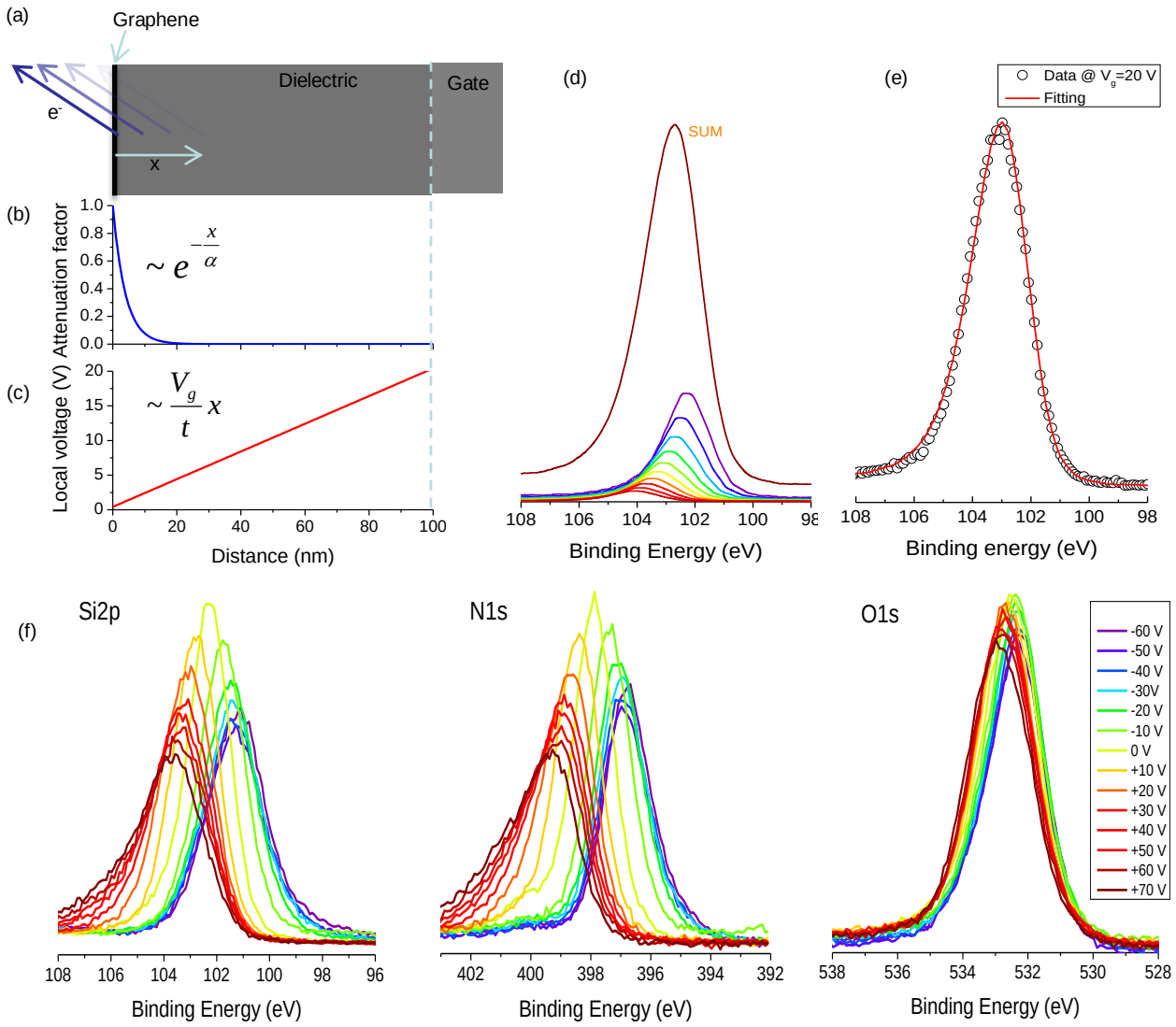
P. Aydogan, M. Copuroglu, C. Kocabas, S. Suzer, *Nano Letters* (2014).

Raman Spectroscopy

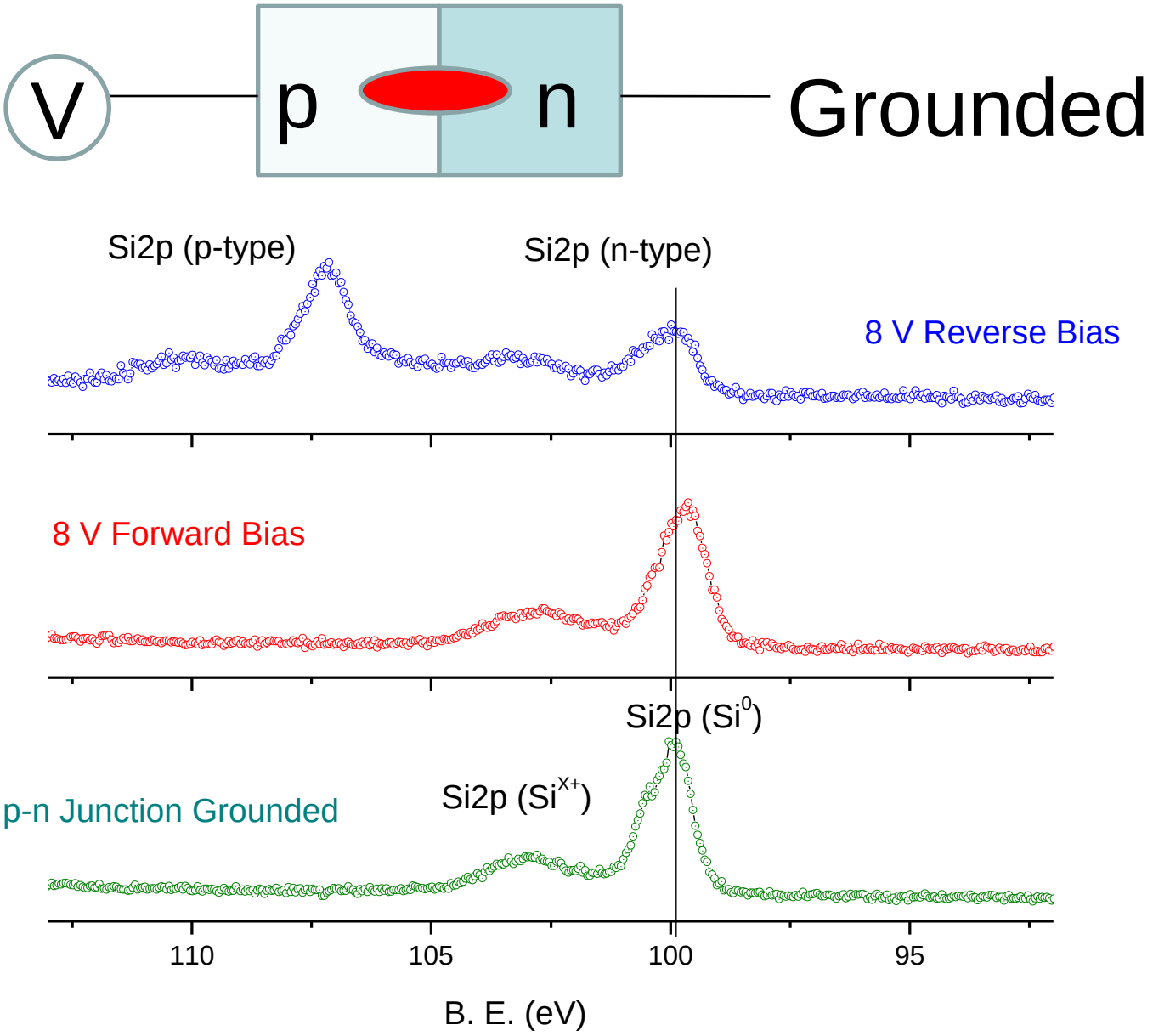


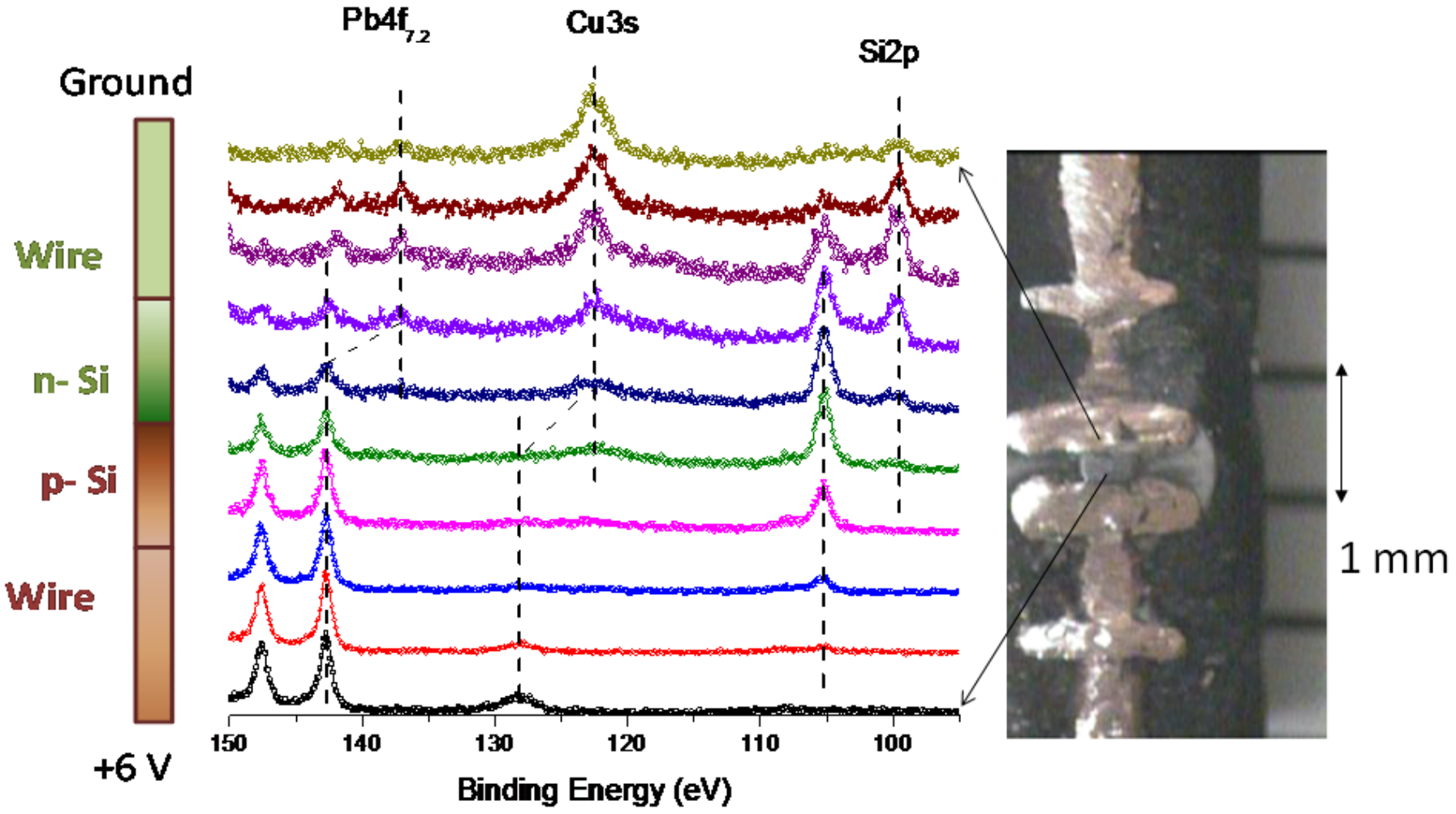

(a)
V_g (V)
C1s
-60
-50
-40
-30
-20
-10
0
10
20
30
40
50
60
70
Counts (a.u.)
288
286
284
282
Binding Energy (eV)
(b)
284.50
284.55
284.60
284.65
284.70
284.75
284.80
Binding Energy (eV)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
E_F (eV)
-60
-40
-20
0
20
40
60
Gate voltage (V)

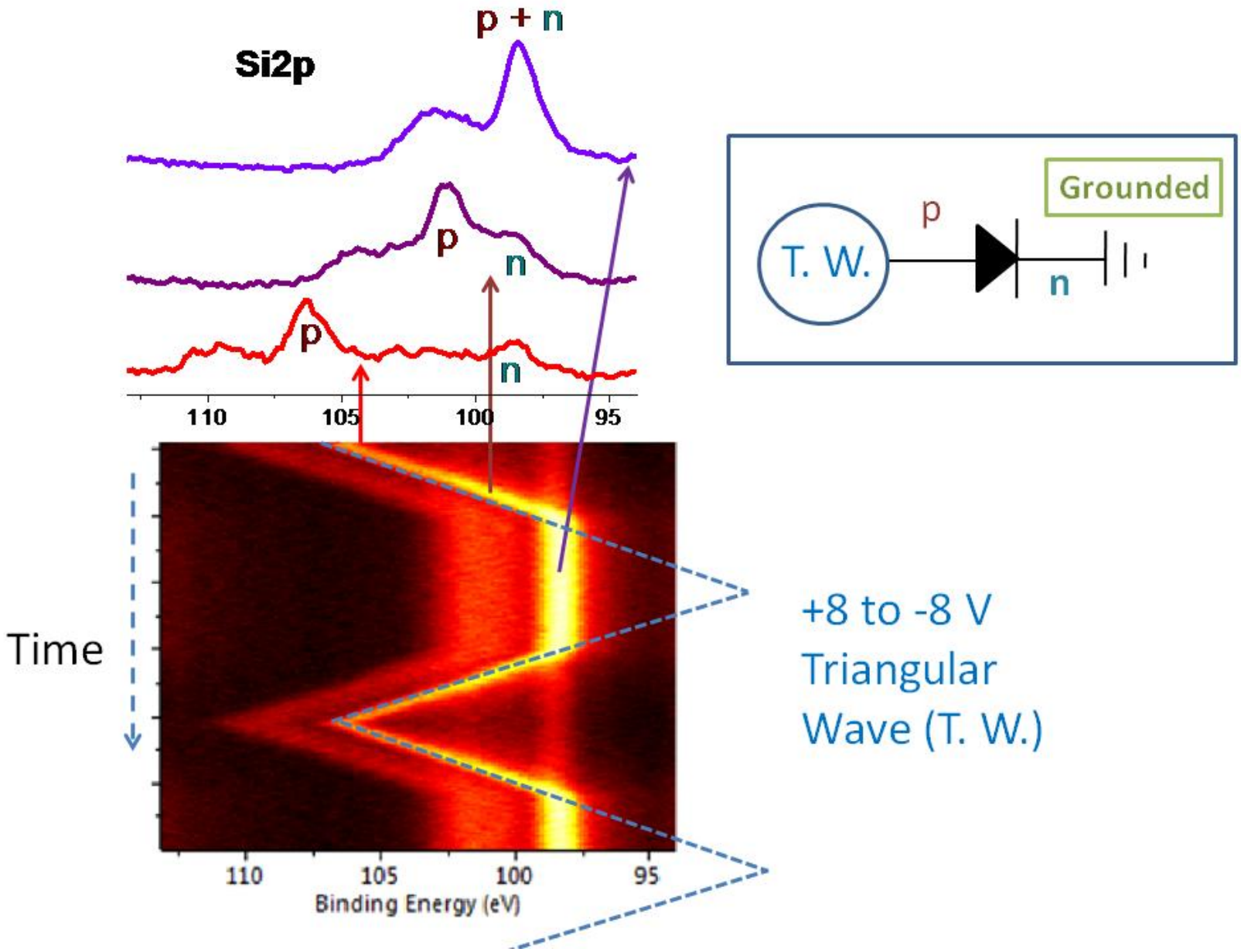

(c)
Vacuum level
Vacuum level
Φ_G
Φ_D
E_F
BE_C1s
C1s
Graphene
Spectrometer


(a)
Graphene
Dielectric
Gate
e-
x
(b)
Attenuation factor
1.0
0.8
0.6
0.4
0.2
0.0
$\sim e^{-\frac{x}{\alpha}}$
(c)
Local voltage (V)
20
15
10
5
0
$\sim \frac{V_g}{t} x$
0
20
40
60
80
100
Distance (nm)
(d)
SUM
108
106
104
102
100
98
Binding Energy (eV)
(e)
Data @ V_g=20 V
Fitting
108
106
104
102
100
98
Binding energy (eV)
(f)
Si2p
108
106
104
102
100
98
96
Binding Energy (eV)
N1s
402
400
398
396
394
392
Binding Energy (eV)
O1s
538
536
534
532
530
528
Binding Energy (eV)
-60 V
-50 V
-40 V
-30V
-20 V
-10 V
0 V
+10 V
+20 V
+30 V
+40 V
+50 V
+60 V
+70 V

A Commercial Si-Diode (Analytical Methods, 2012)




Pb4f7,2
Cu3s
Si2p
Ground
Wire
n- Si
p- Si
Wire
+6 V
150
140
130
120
110
100
Binding Energy (eV)
1 mm

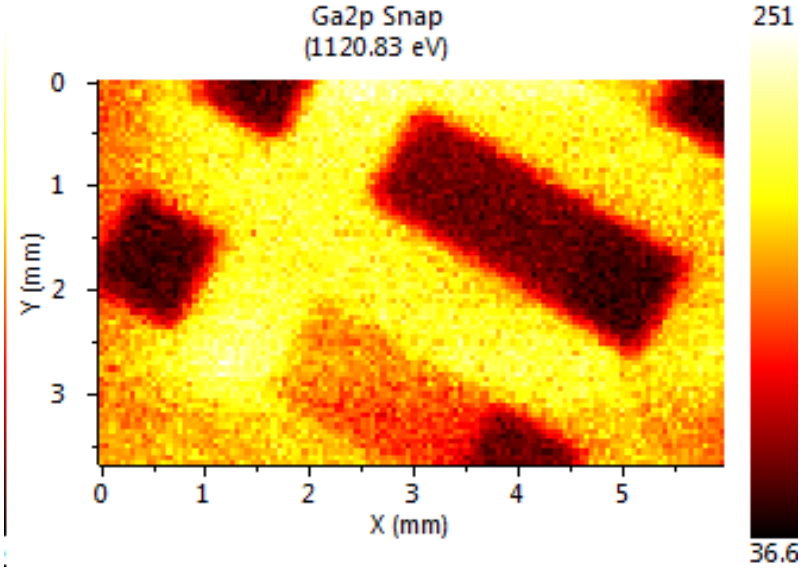


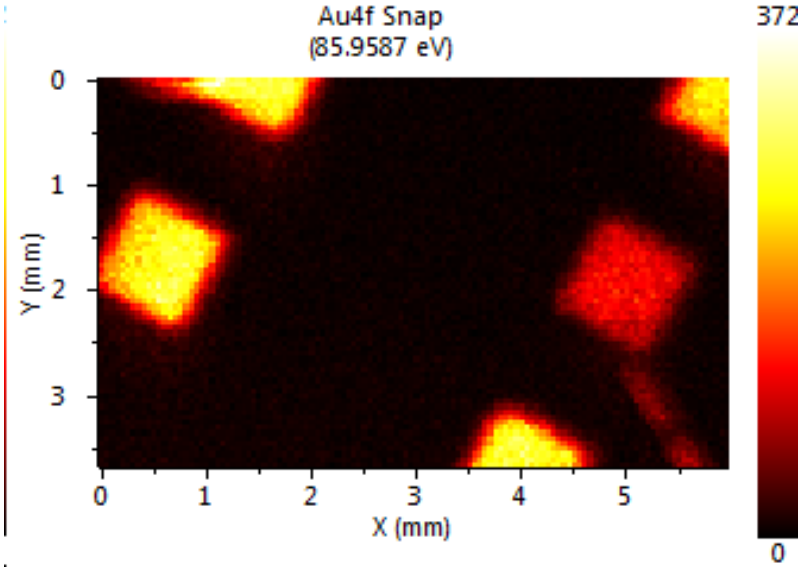
S. Suzer, *Anal. Meth.* **4,** 3527 (2012)

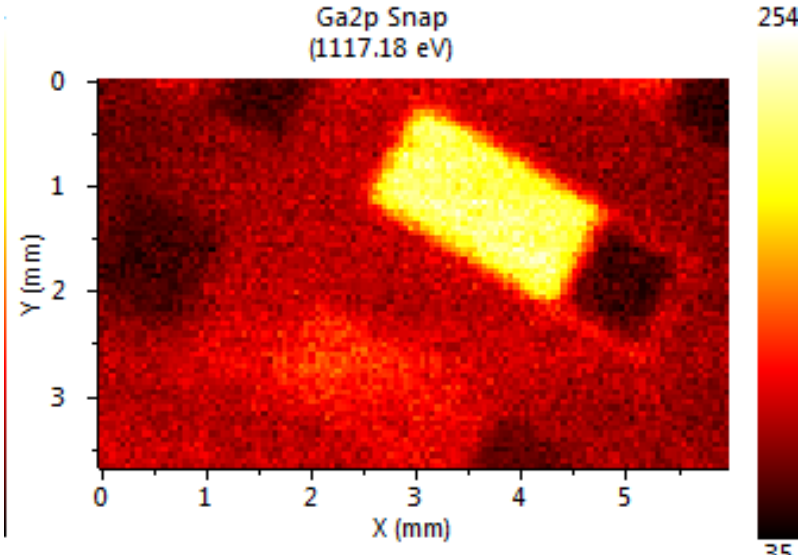
Highligthed in ***Advances in Engineering*** on March 24, 2013).

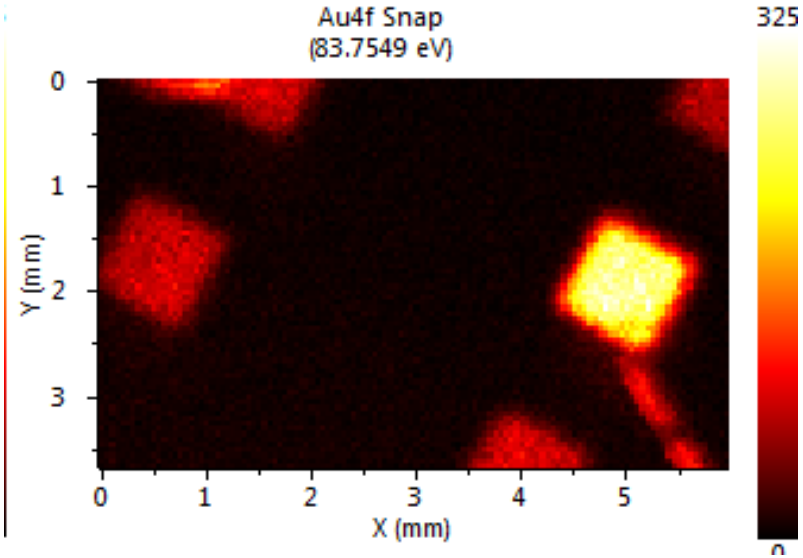
Video Clip-Ga&AuYavas.mp4

GaN p-n Junction at +2V Reverse Bias









Conclusions

XPS Can Also Detect Shifts due to

Charge Built-Up (CHEMICALLY RESOLVED)

- i- Static Fashion (R)
- ii- Dynamical Fashion to 500 kHz (R and C)
- iii- Photovoltage
- iv- Photoconductivity Changes
- v- Voltage Stress

DEFECTS, TRAPS, DEVICE PERFORMANCE

There is Still Room on the Surfaces!!!

H. Sezen S. Suzer, Thin Solid Films, 534, 1 (2013)
Critical Review Article.

-Future: Mechanical + Chemical + Thermal Stresses

Happy Birthday DAVE

İyiki Doğdun DAVE
and
Many Happy Returns

Once a Spectroscopist Always a Spectroscopist