# *Hard X-ray Photoelectron Spectroscopy Research at NIST beamline X24A*

Joseph C. Woicik
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# *Outline*

- *Introduction to hard x-ray photoelectron spectroscopy (HAXPES)*
- *Semiconductor gate stacks on silicon*
- *Epitaxial, room temperature feroelectric $SrTiO_3$ on silicon*
- *Site Specific XPS and the nature of the solid state chemical bond:* Cu, GaAs, $TiO_2$
- *N doping of $TiO_2$*

# Hard X-ray Photoelectron Spectroscopy (HAXPES)

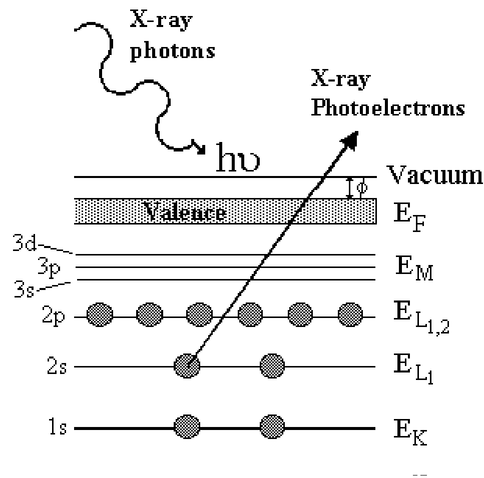
**Synchrotron Tool**

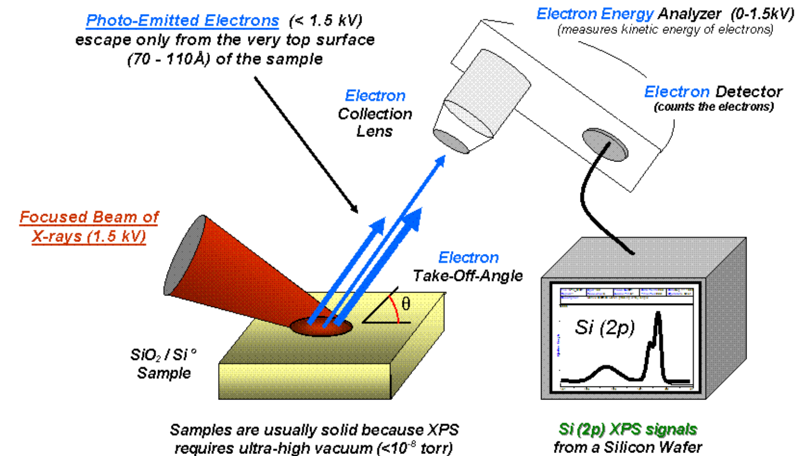
## Variable Kinetic Energy HAXPES

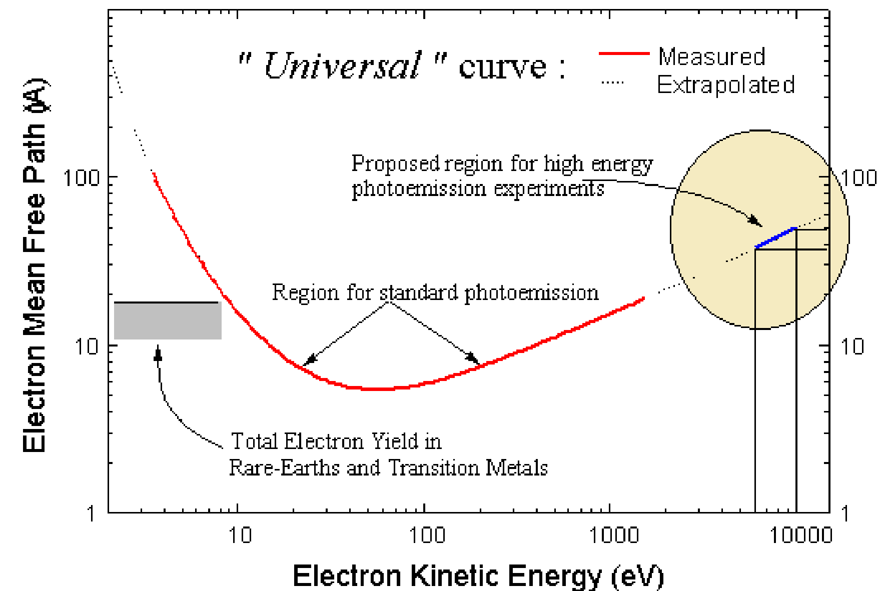
- Tune the HAXPES depth sensitivity (photoelectron kinetic energy) by tuning the X-ray excitation energy using a synchrotron X-ray beamline
- The U7A and X24A endstations form a unique measurement suite for surface to near bulk HAXPES by spanning X-ray excitation energy from 0.2 to 5 keV

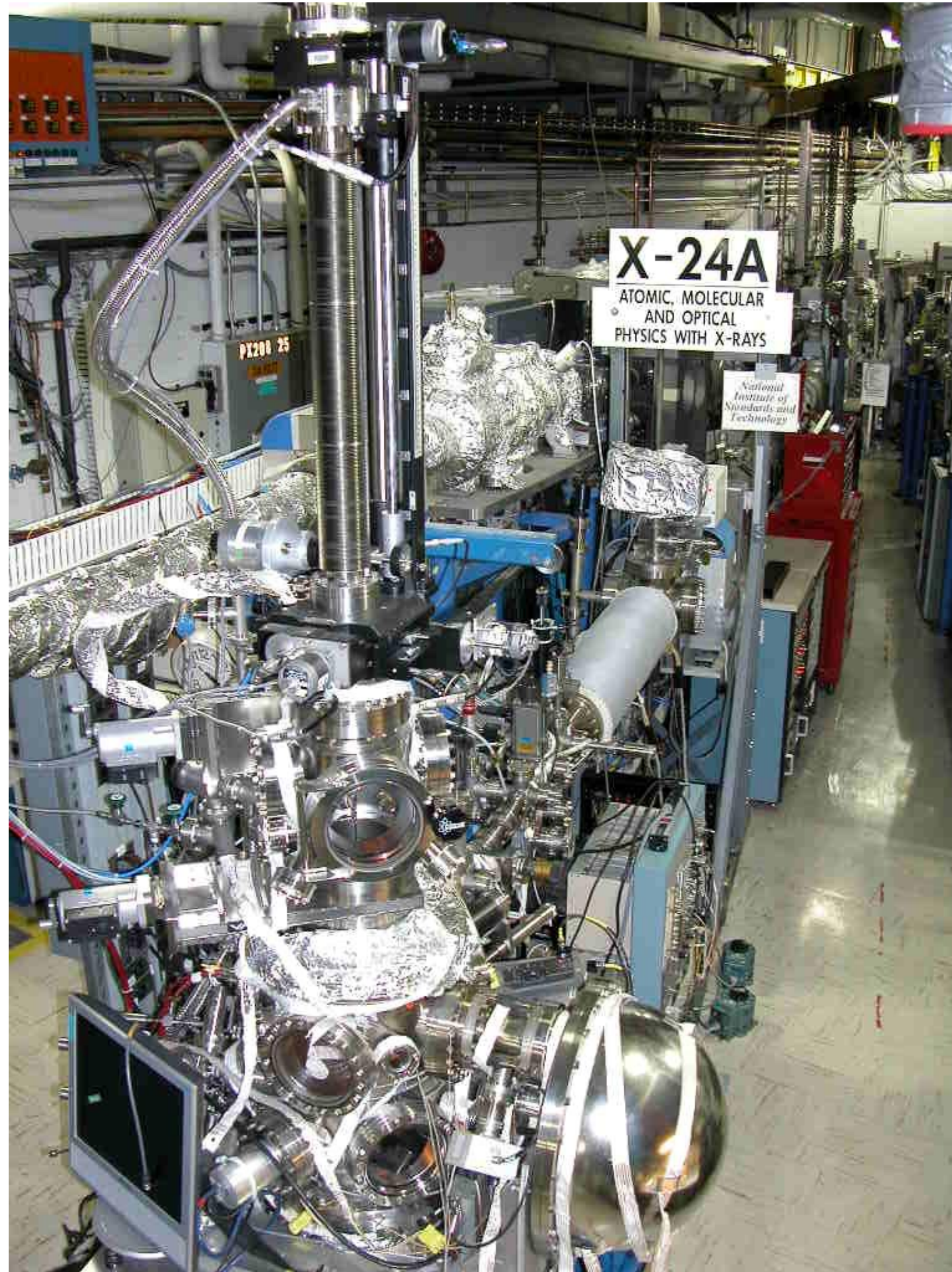
Example: Si electron binding energy 2p ~99 eV and 1s ~1840 eV, surface to bulk sensitivity (Lab source has fixed energy Al K$\alpha$)

**Photoelectron Kinetic Energy = h$\upsilon$ – Binding Energy**




X-24A
ATOMIC, MOLECULAR AND OPTICAL PHYSICS WITH X-RAYS
National Institute of Standards and Technology

# *Advantages of HAXPES*

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- *Study samples from air*

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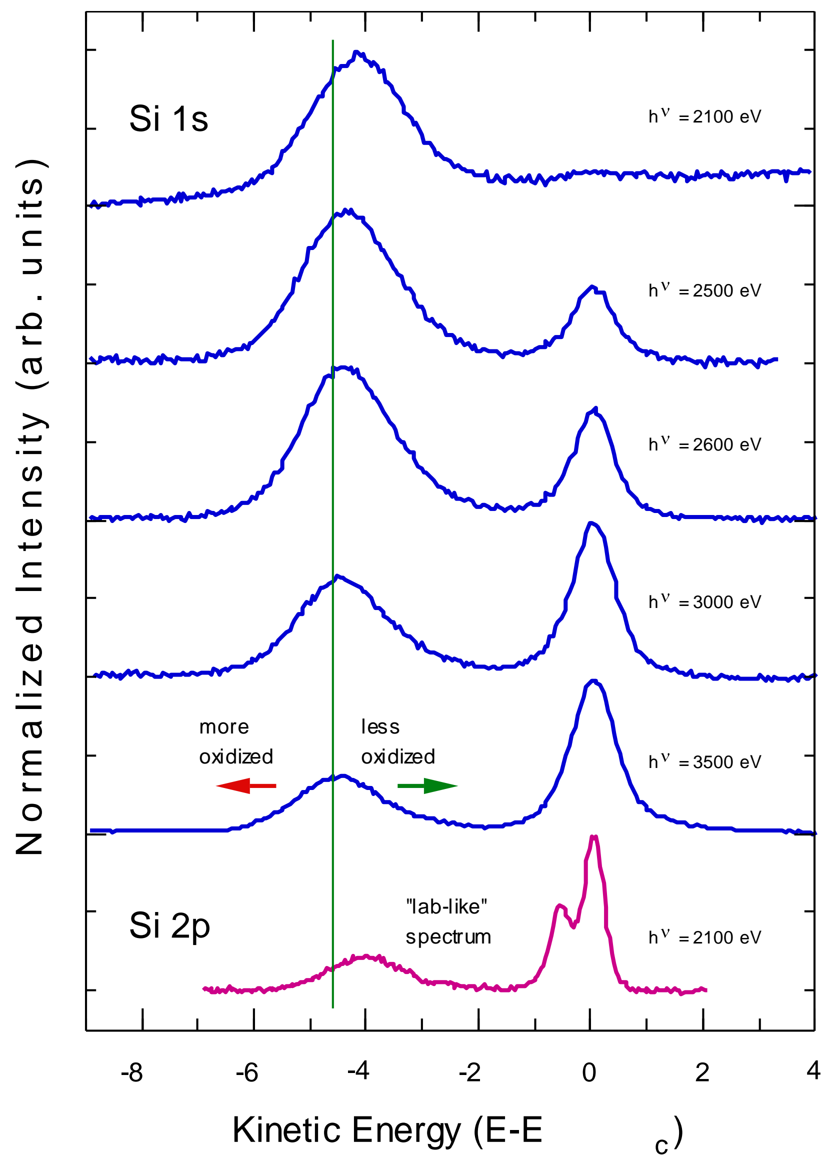
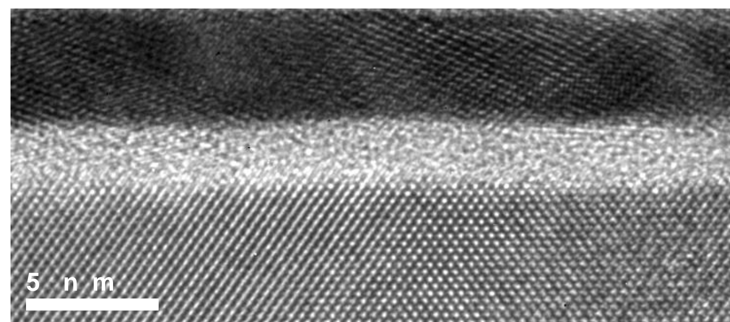
# *Depth Sensitive VKE-XPS*




P.S. Lysaght, J. Barnett, G.I. Bersuker, J.C. Woicik, D.A. Fischer, B. Foran, H.-H. Tseng, and R. Jammy

# *Advantages of HAXPES*

- *Study samples from air; i.e., real samples!*
- *Tune λ for experimental system*
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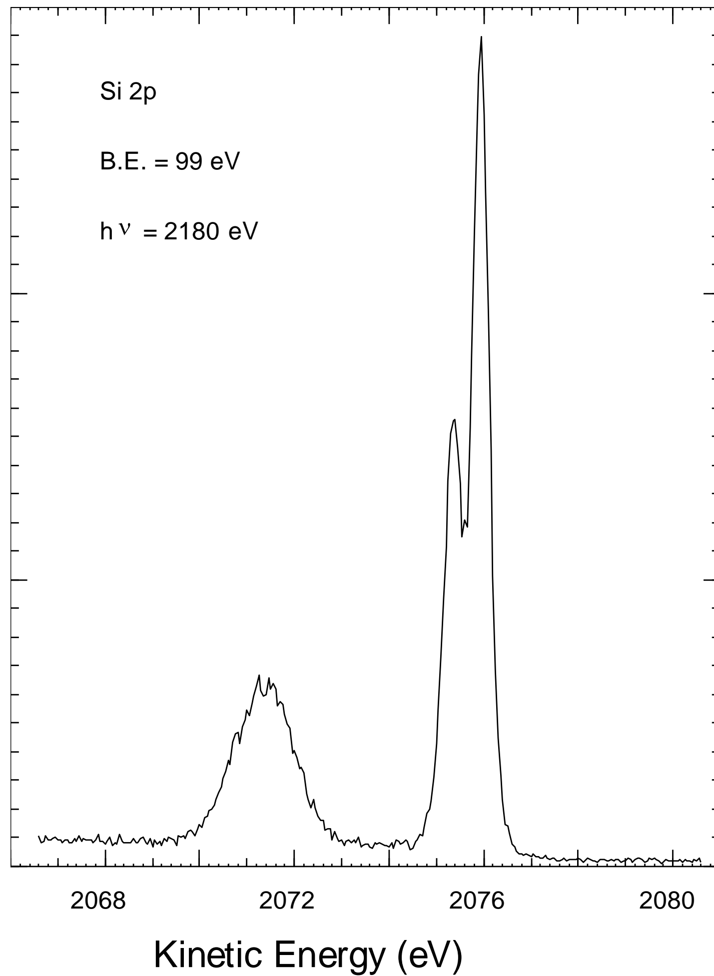
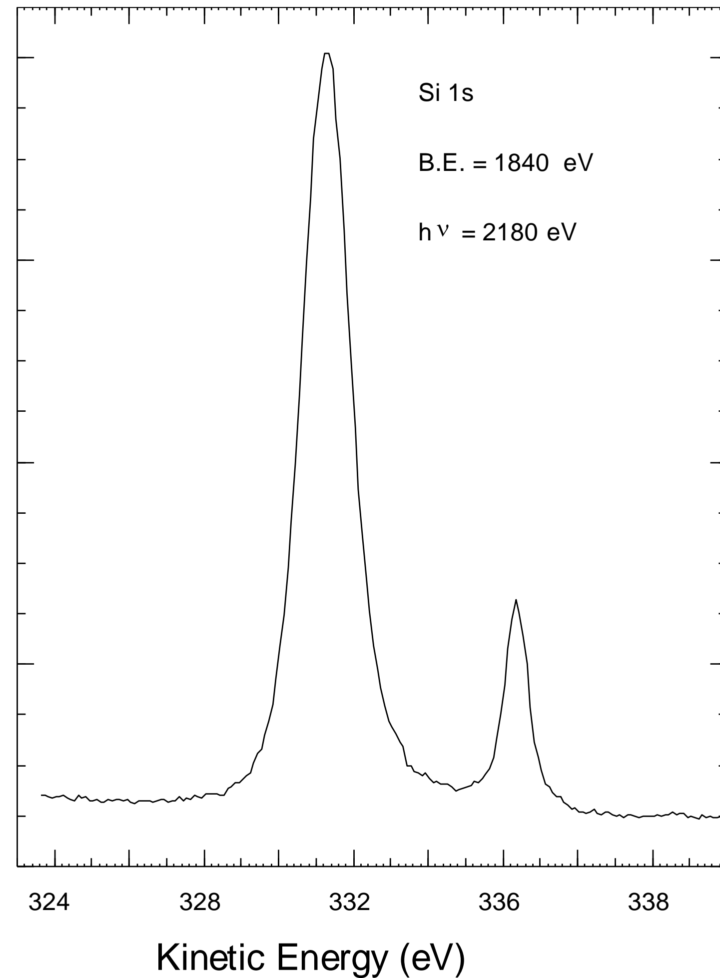
- *Bulk and surface sensitive core lines accessible for same element*

# *Surface and Bulk Sensitive Core Lines*



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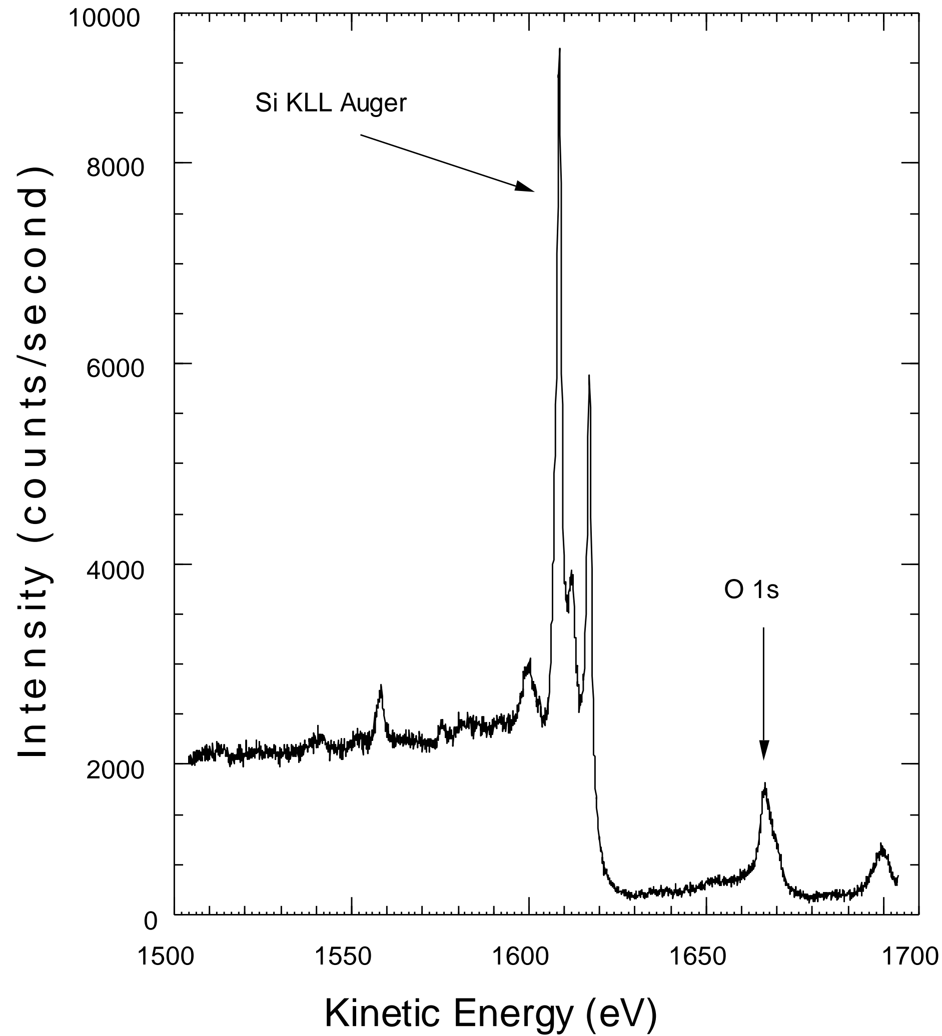
- *Eliminate Auger interference*

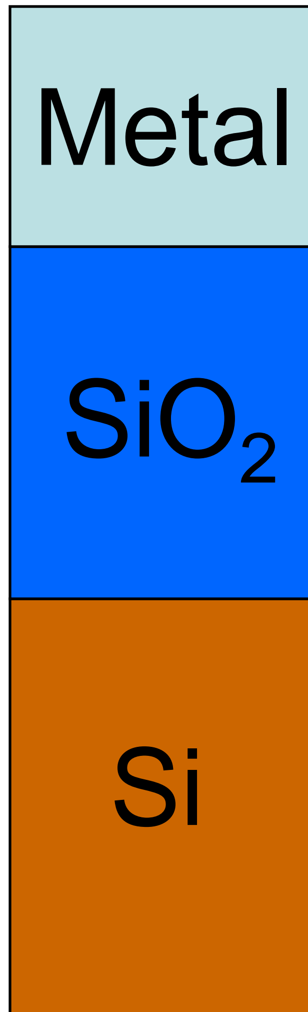
# *Auger Interference*



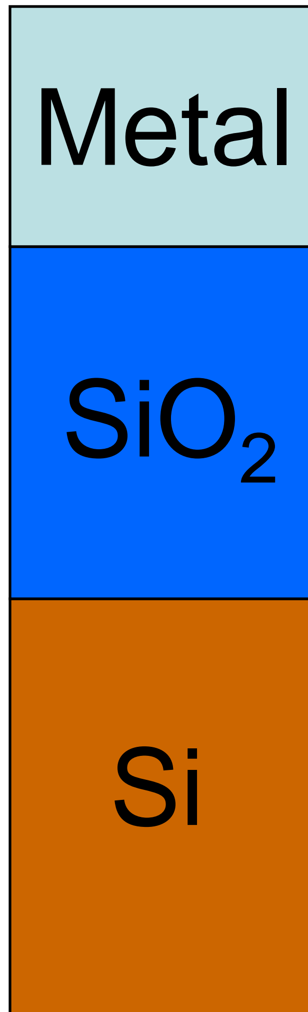
# ***Advantages of HAXPES***

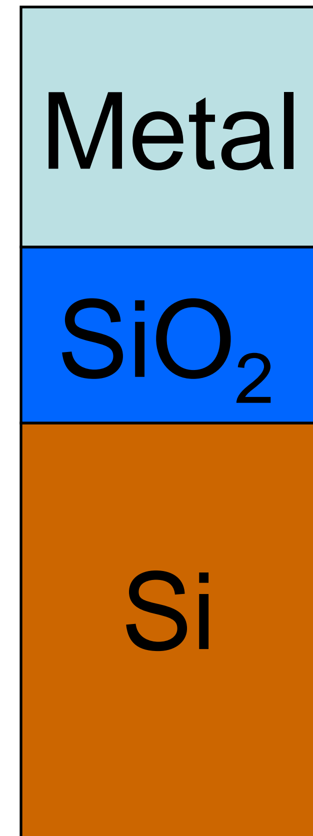
- *Study samples from air; i.e., real samples!*
- *Tune λ for experimental system*
- *Variable kinetic energy XPS (VKE-XPS) for depth profiling*
- *Bulk and surface sensitive core lines accessible for same element*
- *Eliminate Auger interference*
- *Photoemission and other techniques (SSXPS)*

# *What is a “gate stack?”*



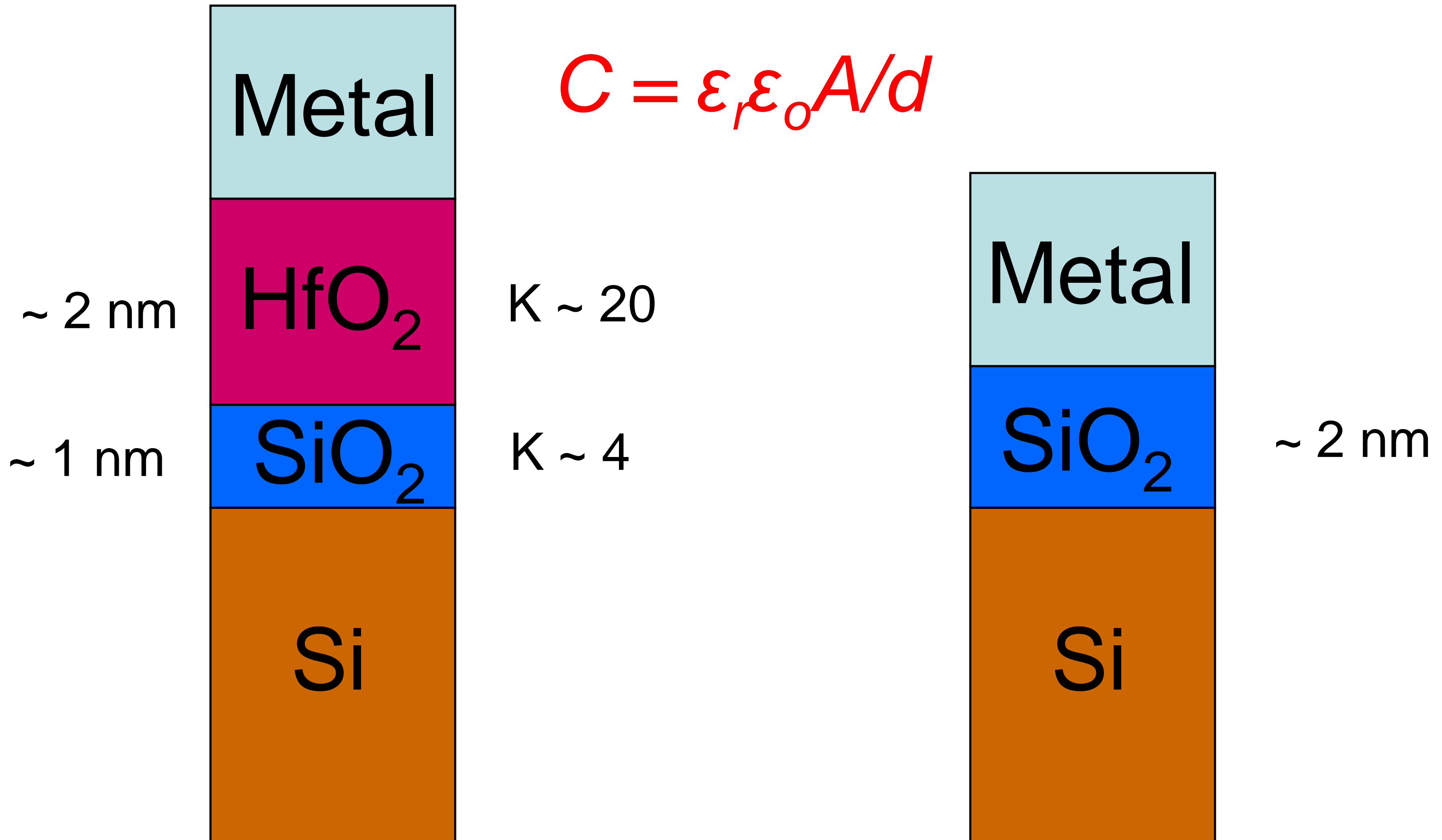
# *What is a "gate stack?"*



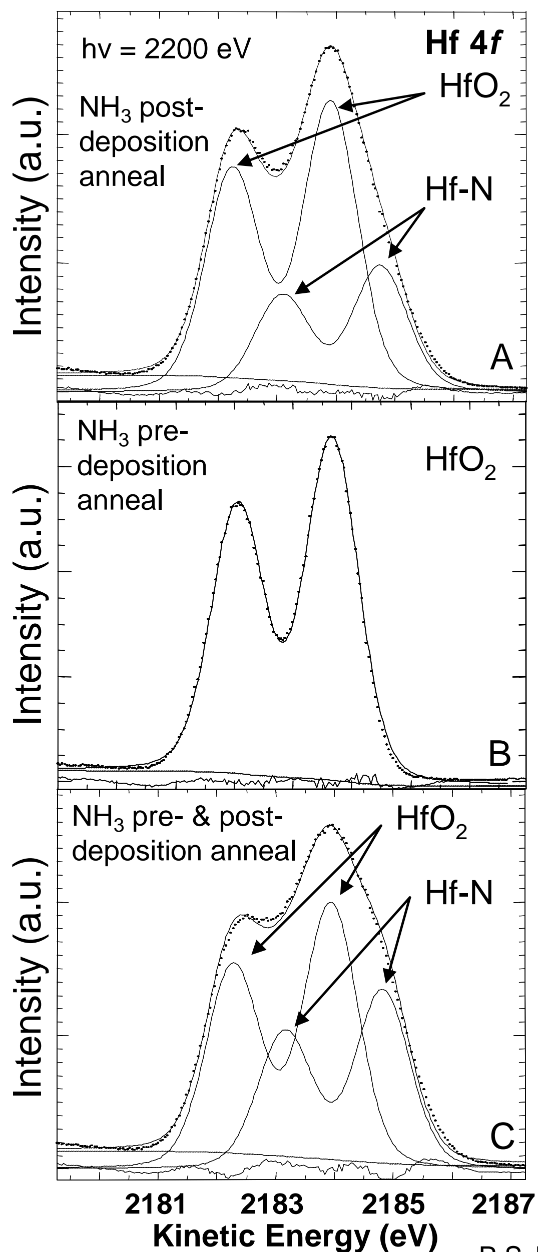



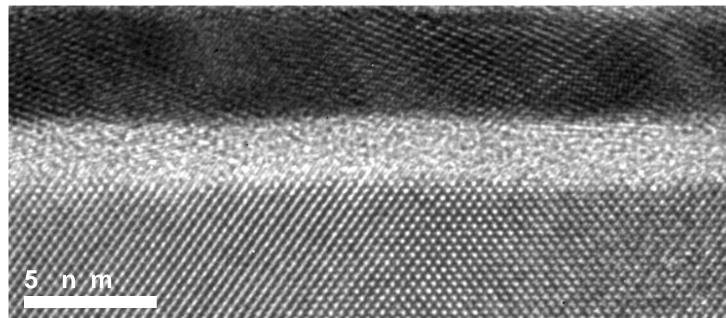

~ 2 nm

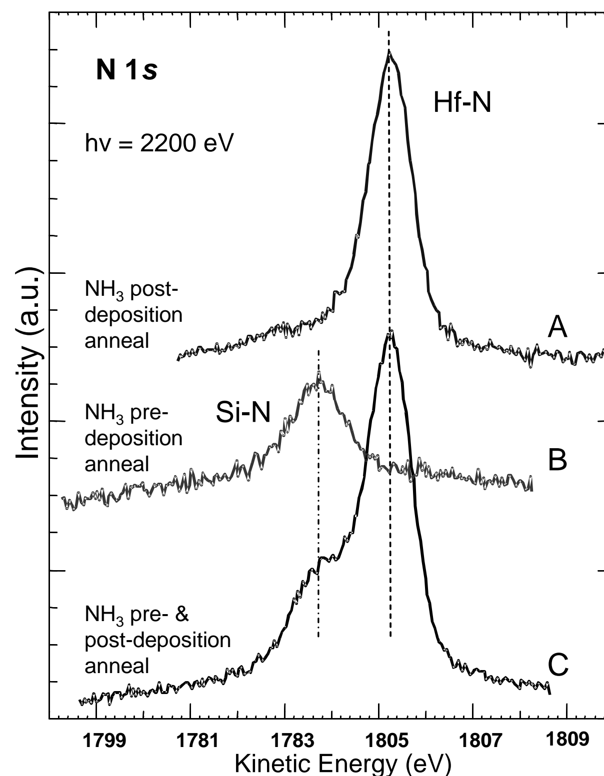
# *What is a "gate stack?"*



# SEMATECH: $HfO_2/SiO_2/Si$ Gate Stacks

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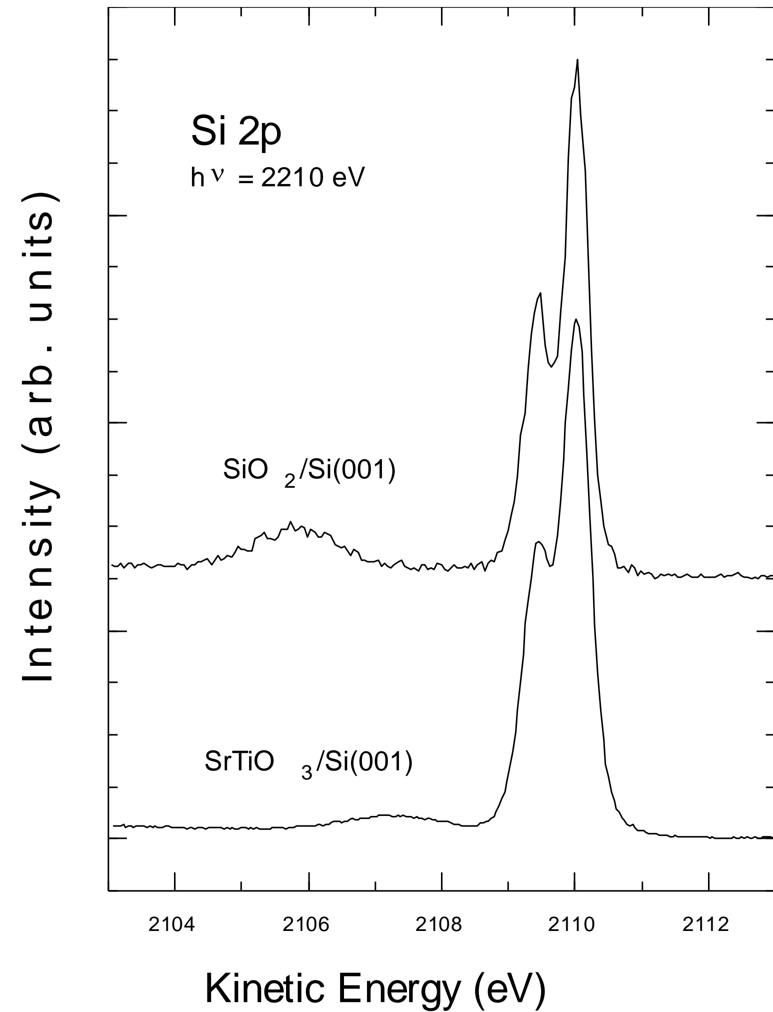
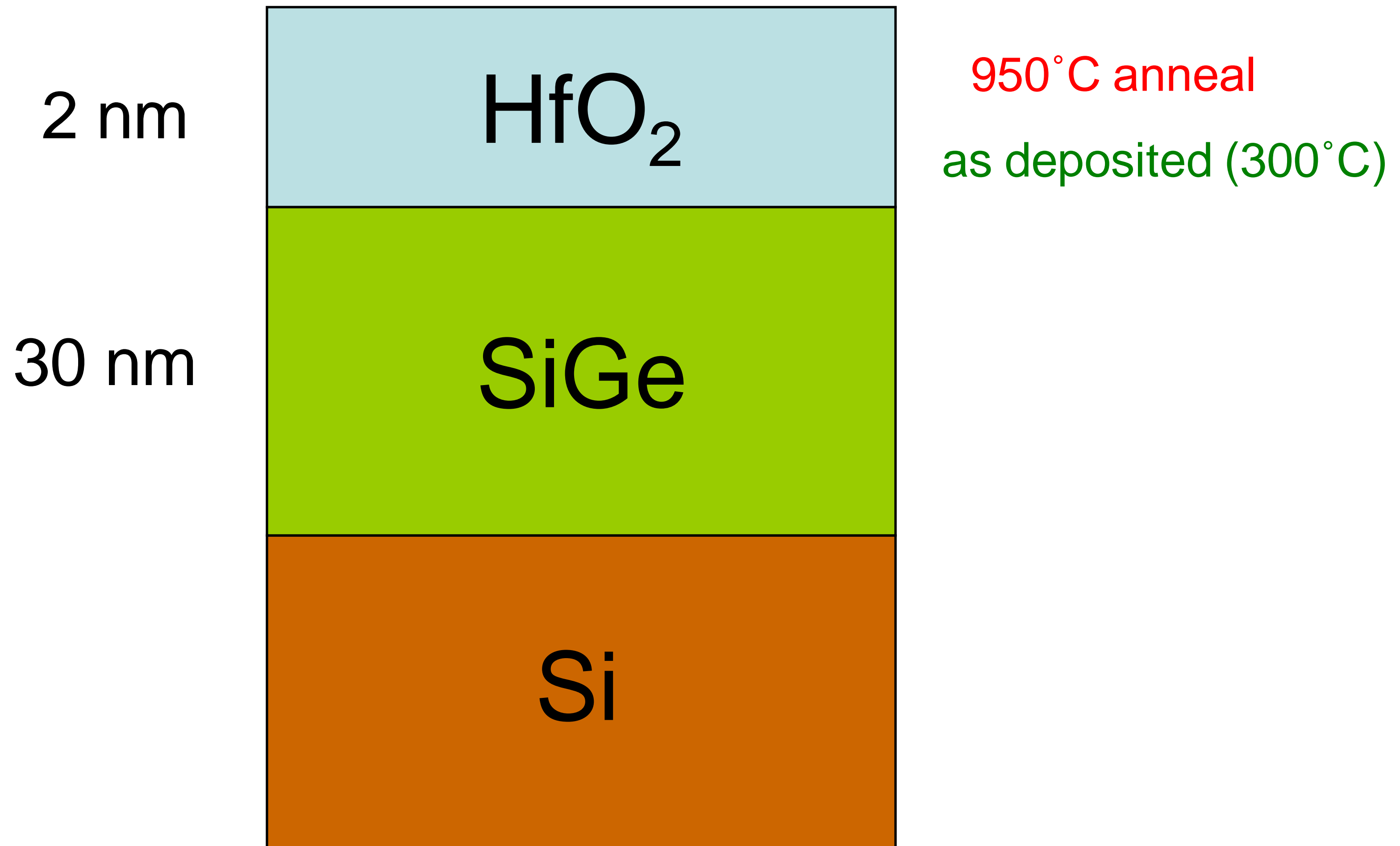
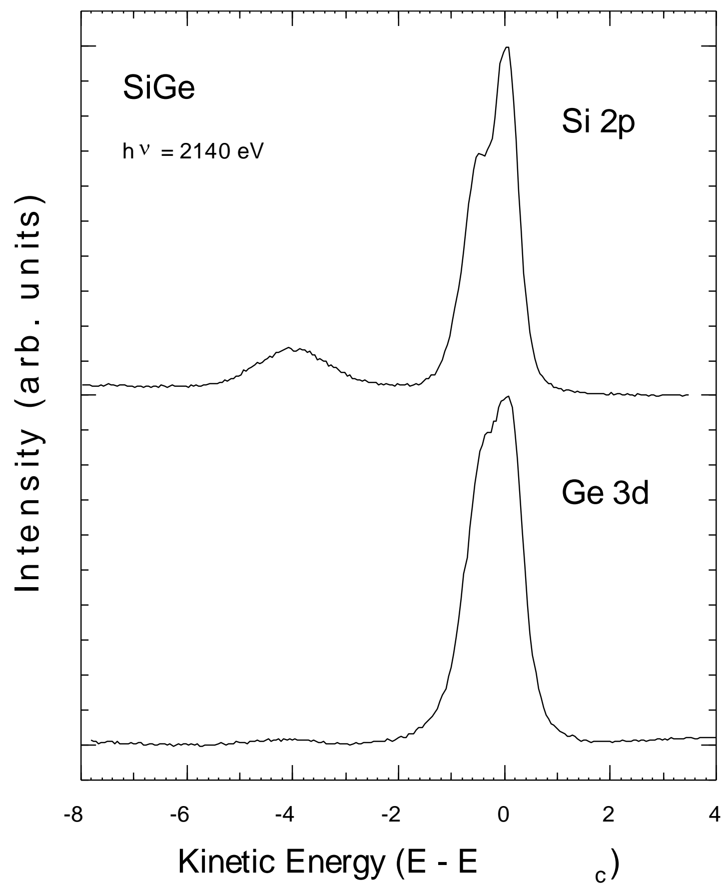
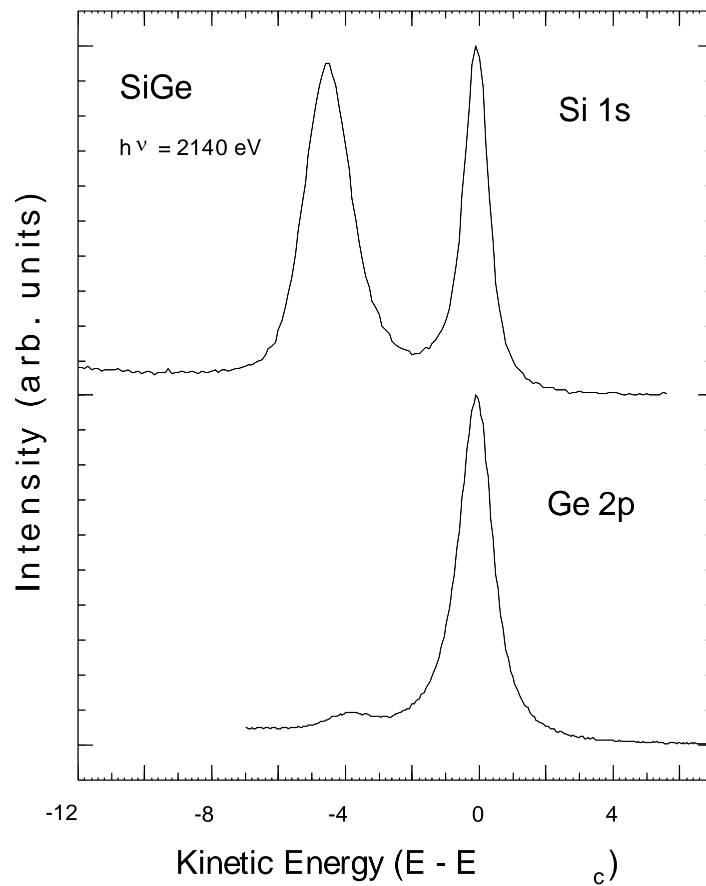
# *Motorola: 5 ML (20 Å) $SrTiO_3$ films on Si(001)*

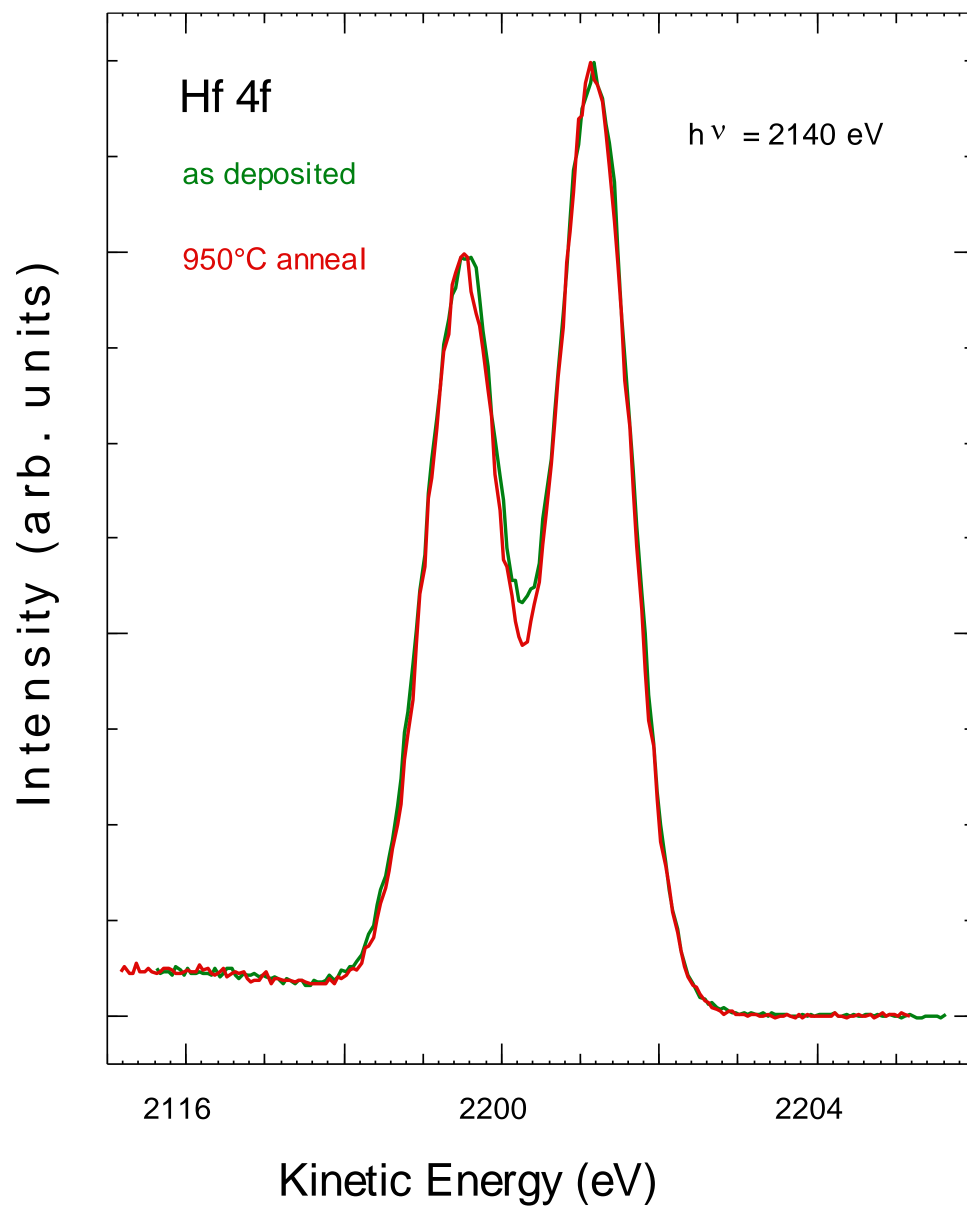


# $HfO_2$/SiGe/Si

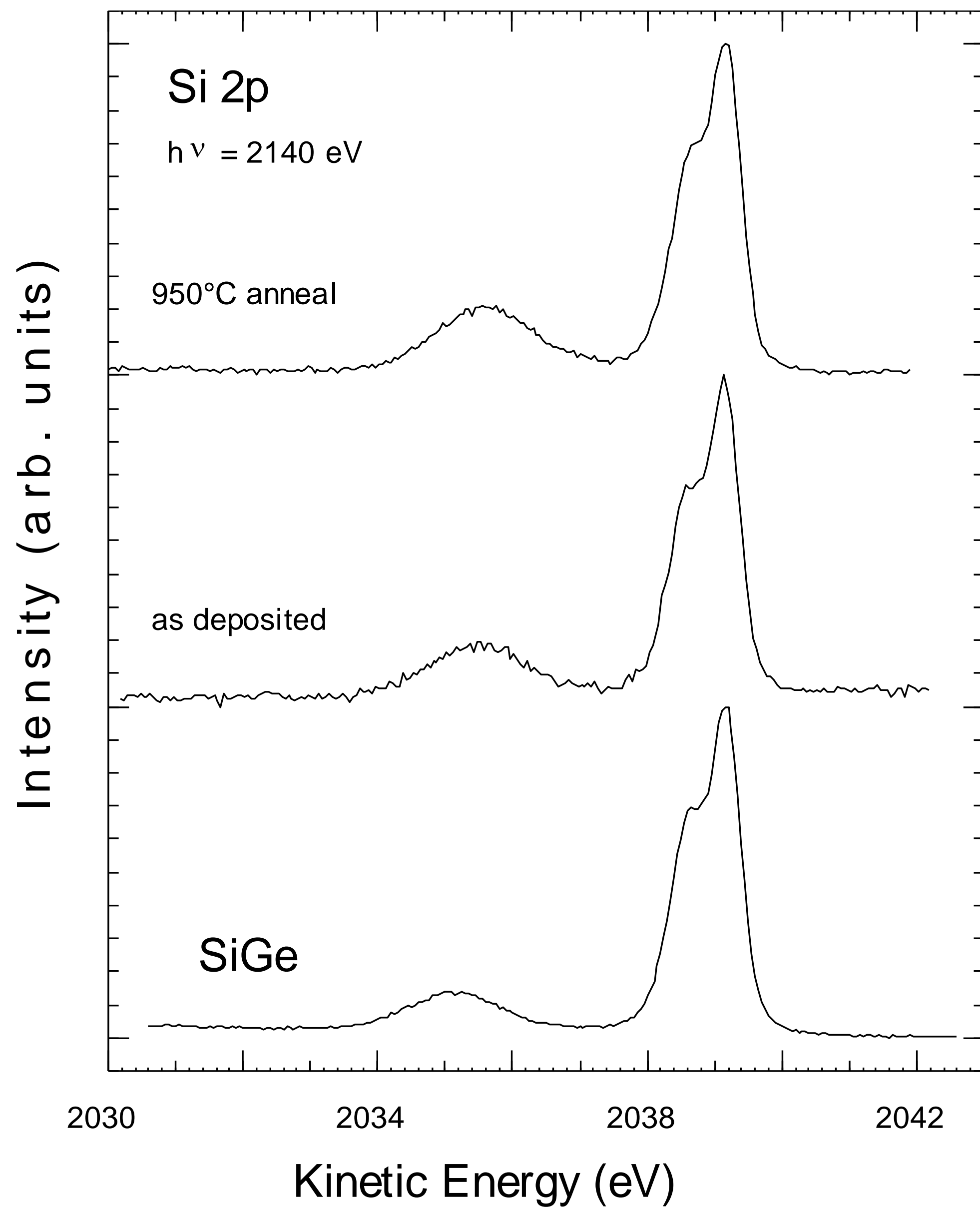



SiGe
hν = 2140 eV
Si 2p
Ge 3d
Intensity (arb. units)
-8
-6
-4
-2
0
2
4
Kinetic Energy (E - E c)

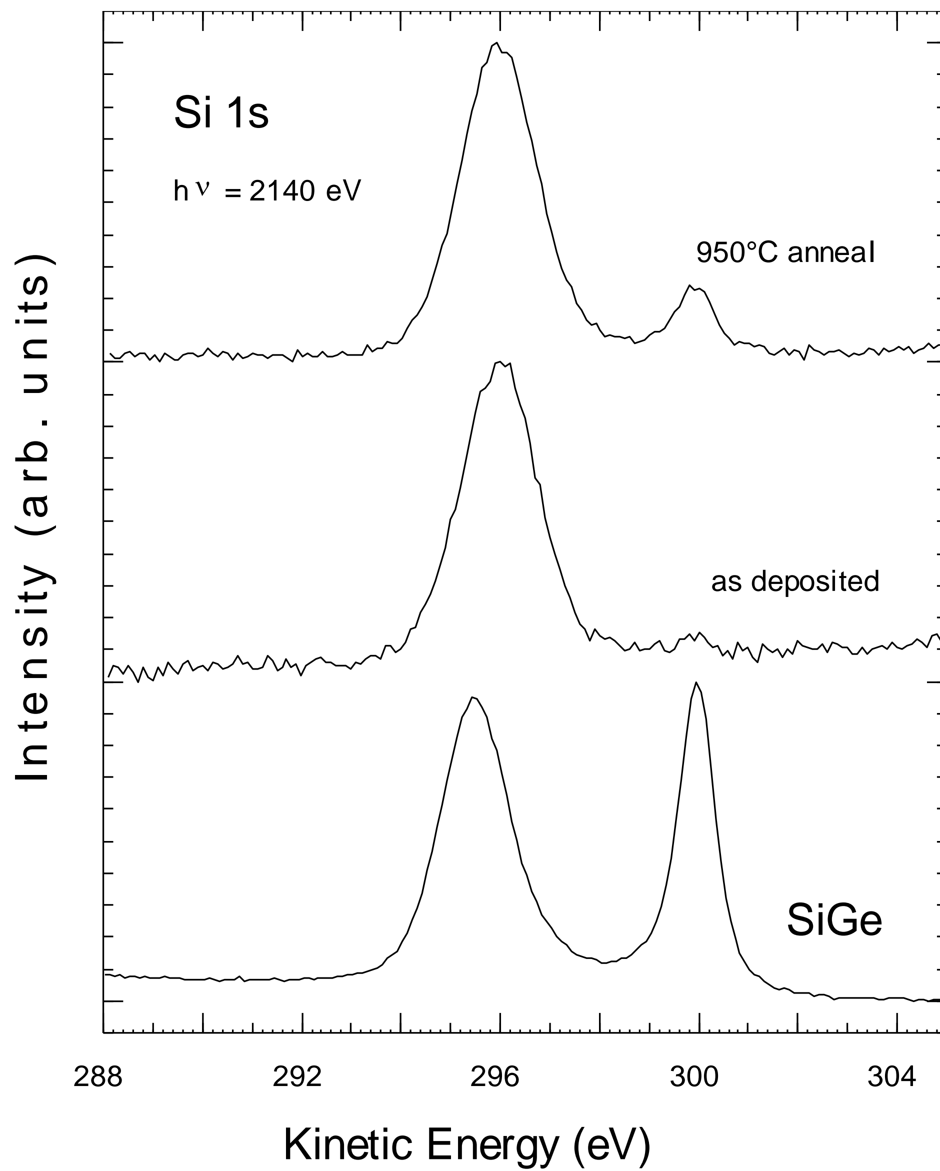

SiGe
hν = 2140 eV
Si 1s
Ge 2p
Intensity (arb. units)
-12
-8
-4
0
4
Kinetic Energy (E - E c)



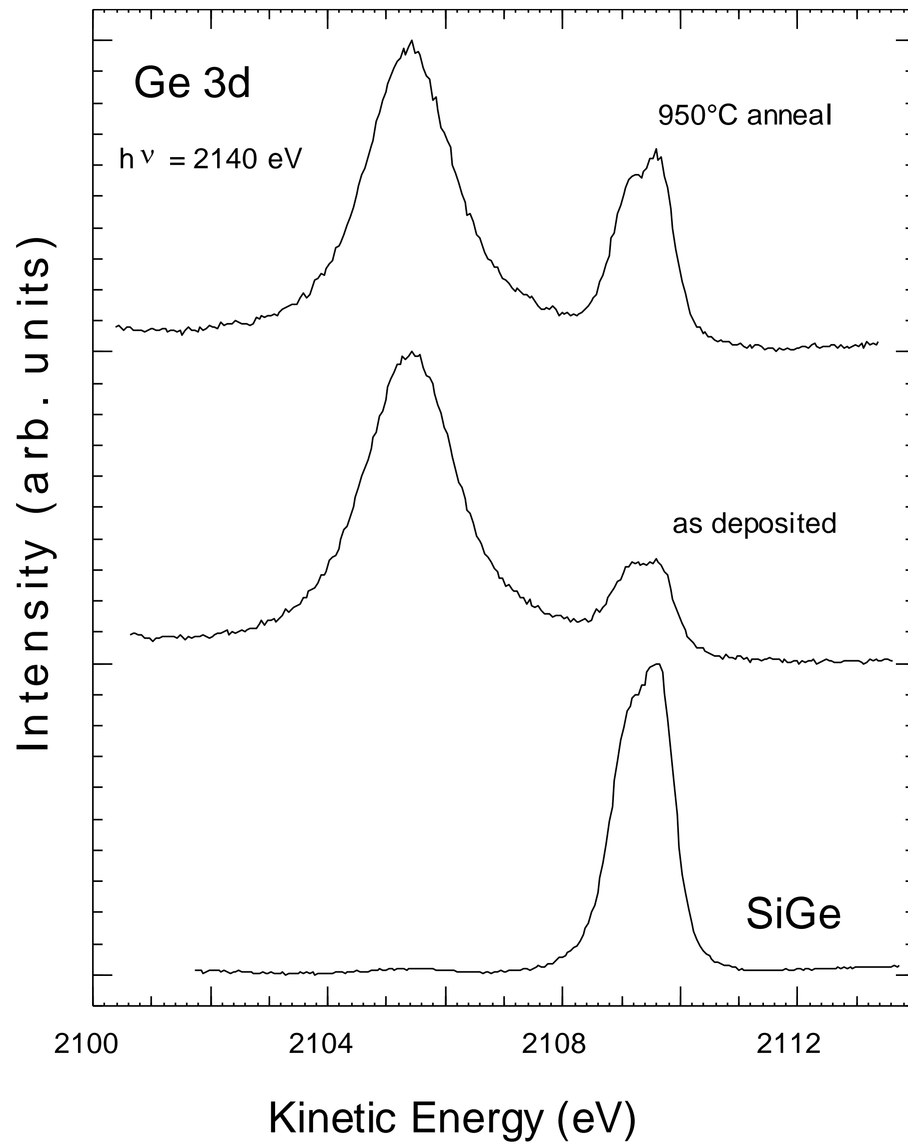
Hf 4f
as deposited
950°C anneal
hν = 2140 eV
Intensity (arb. units)
2116
2200
2204
Kinetic Energy (eV)



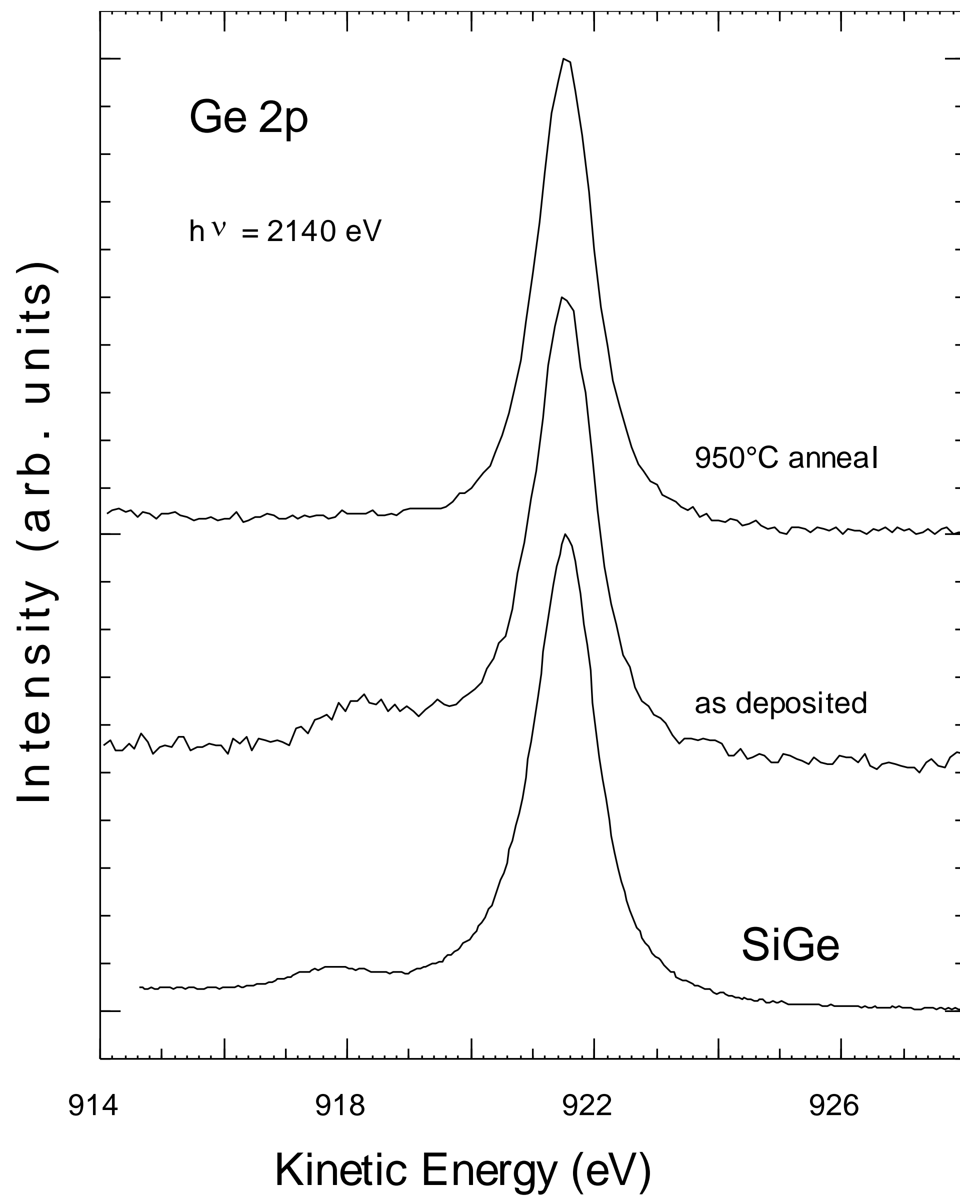
Si 2p
h ν = 2140 eV
950°C anneal
as deposited
SiGe
Intensity (arb. units)
2030
2034
2038
2042
Kinetic Energy (eV)



Si 1s
h ν = 2140 eV
950°C anneal
as deposited
SiGe
Intensity (arb. units)
288
292
296
300
304
Kinetic Energy (eV)



Ge 3d
hν = 2140 eV
950°C anneal
as deposited
SiGe
Intensity (arb. units)
2100
2104
2108
2112
Kinetic Energy (eV)


Ge 2p
hν = 2140 eV
950°C anneal
as deposited
SiGe
Intensity (arb. units)
914
918
922
926
Kinetic Energy (eV)

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- *Tune λ for experimental system*
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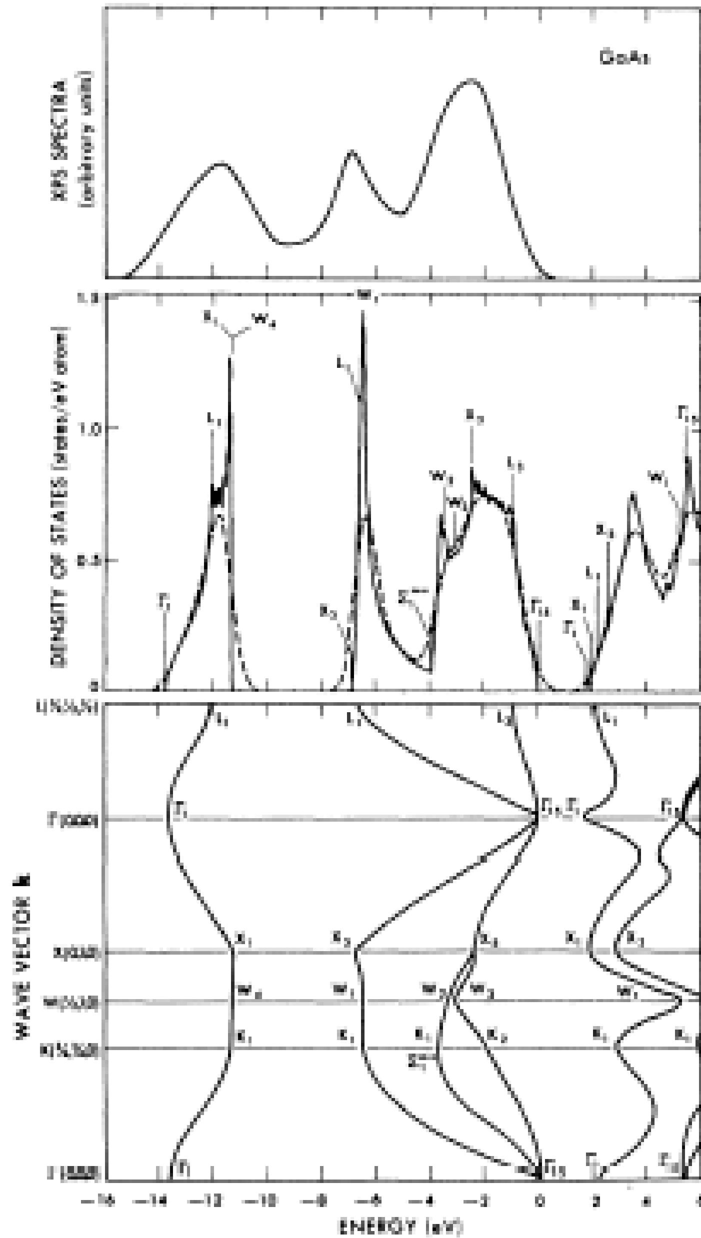
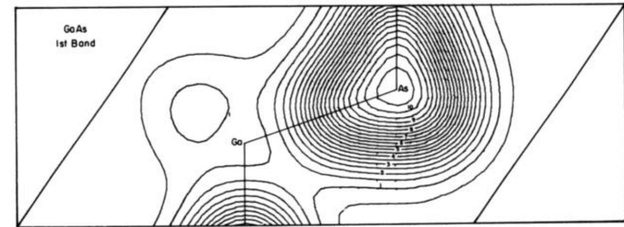
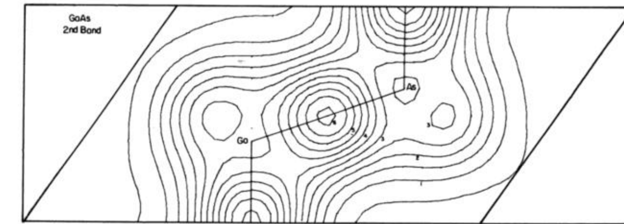
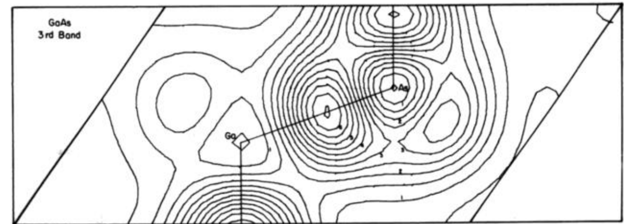
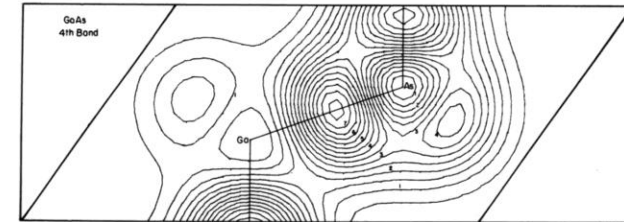
# *Electronic Structure of GaAs*



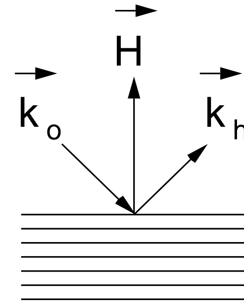




J. Chelikowsky, D.J. Chadi, and M.L. Cohen

# X-ray Standing Waves

## Bragg's Law:

$$\vec{H} = \vec{k}_h - \vec{k}_o$$




## Electric Field:

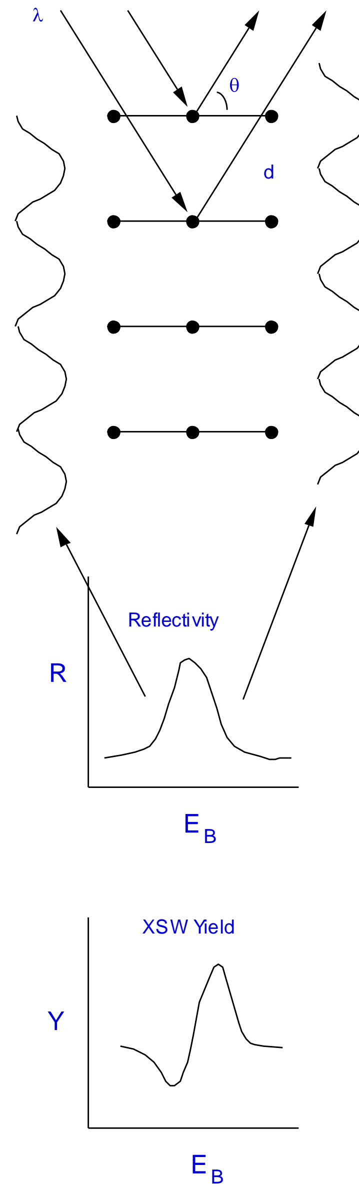
$$\vec{E}(\vec{r},t) = [\hat{\varepsilon} E_o e^{i\vec{k}_o \cdot \vec{r}} + \hat{\varepsilon} E_h e^{i\vec{k}_h \cdot \vec{r}}] e^{-i\omega t}$$

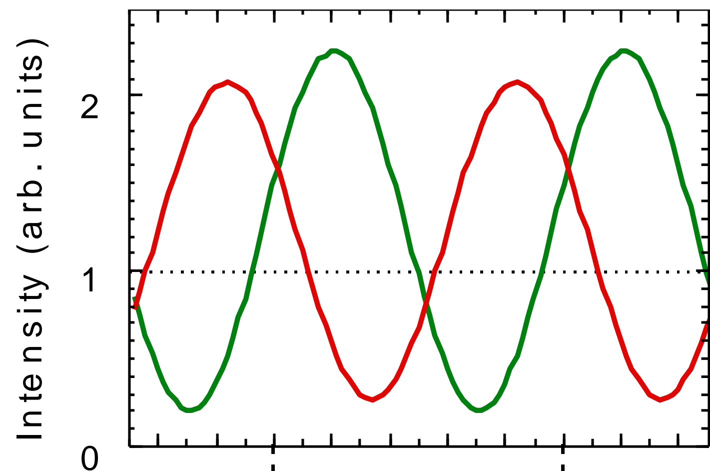
## Electric Field Intensity:

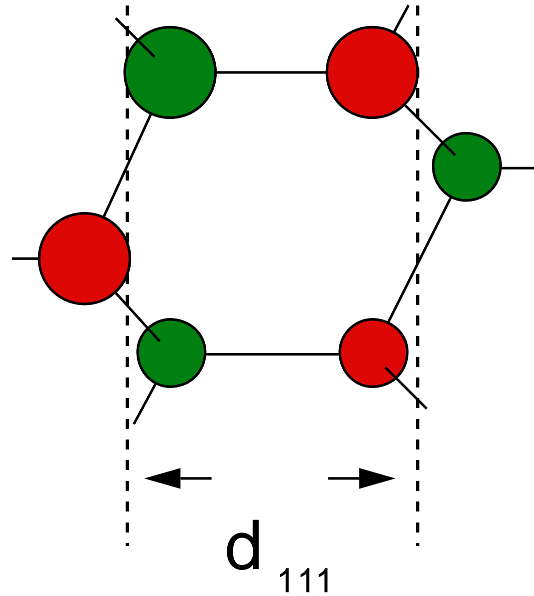
$$I(\vec{r}) = \vec{E}\vec{E}^* = |E_o|^2 [1 + R + 2\sqrt{R}\cos(\nu + \vec{H} \cdot \vec{r})]$$

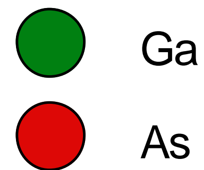
where $E_h / E_o = \sqrt{R}\, e^{i\nu}$ and $0 < \nu < \pi$

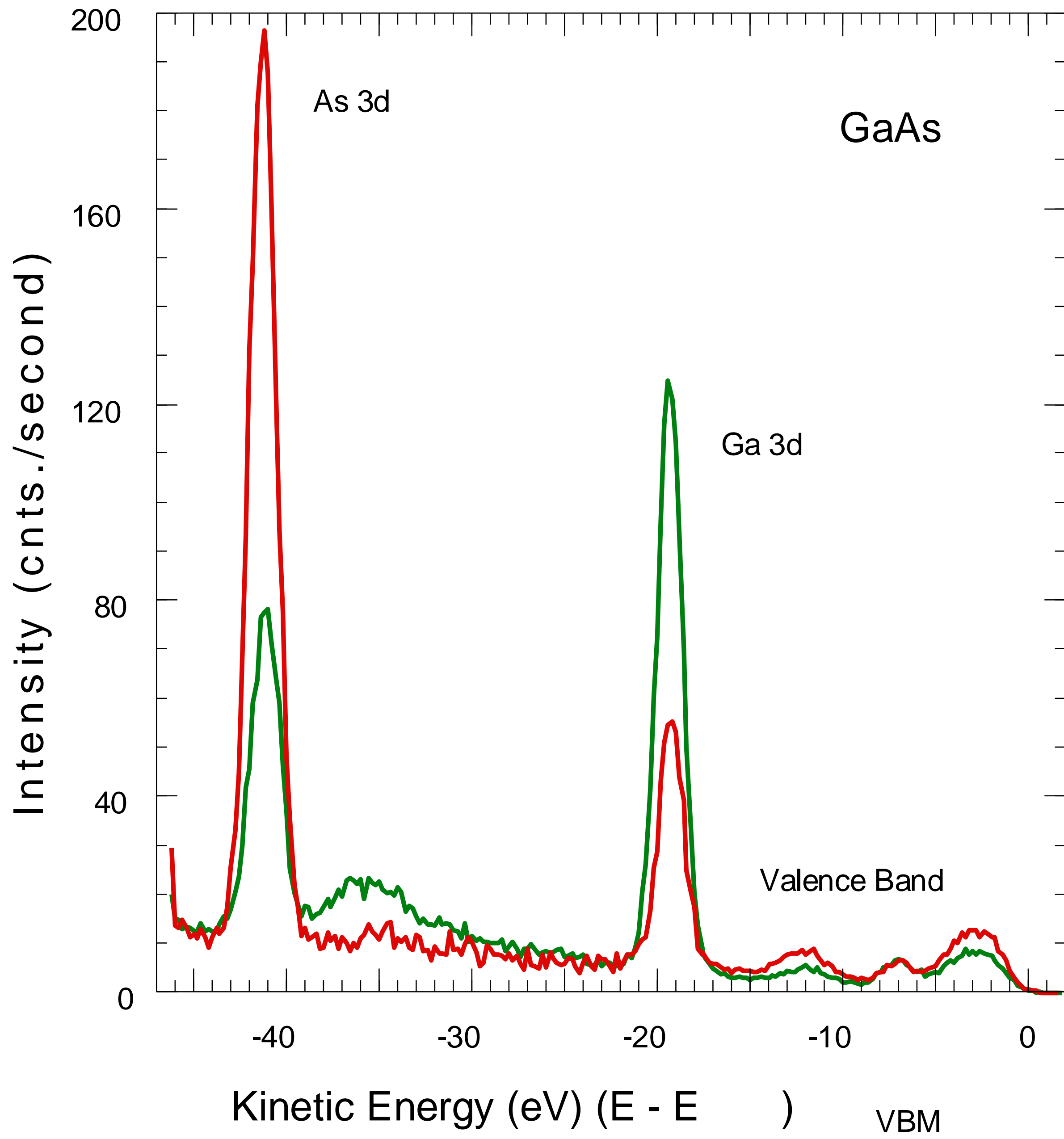
Bragg Diffraction: $\lambda = 2d \sin(\theta)$



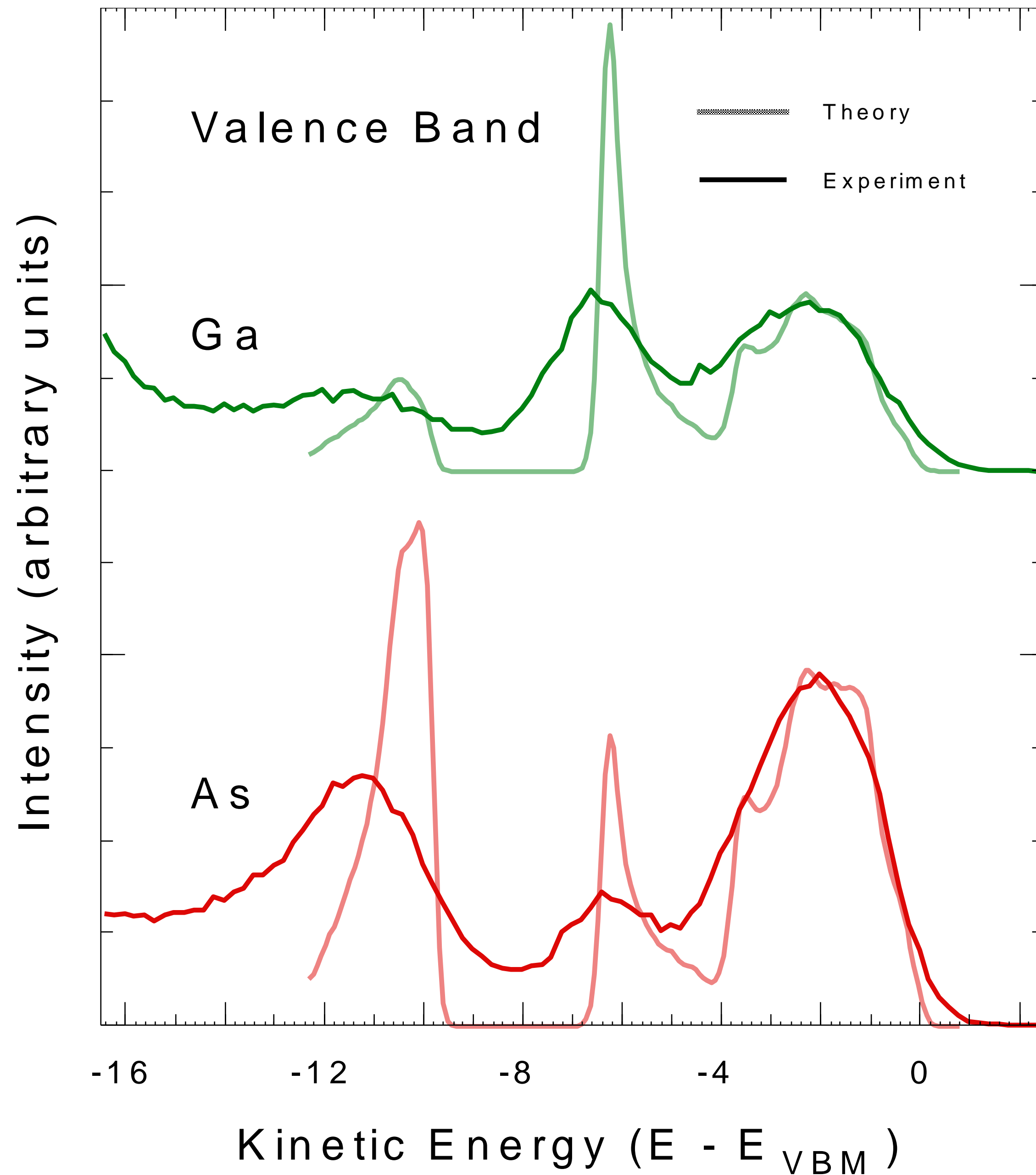

Intensity (arb. units)
0
1
2


d 111

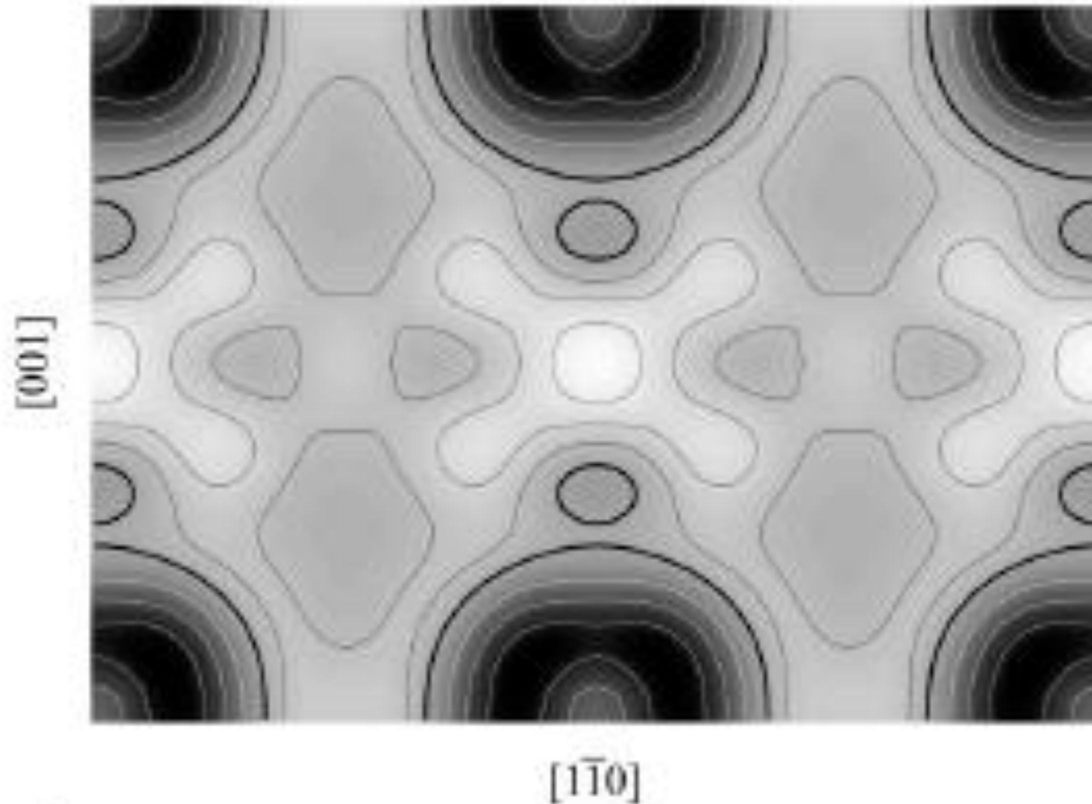

Ga
As



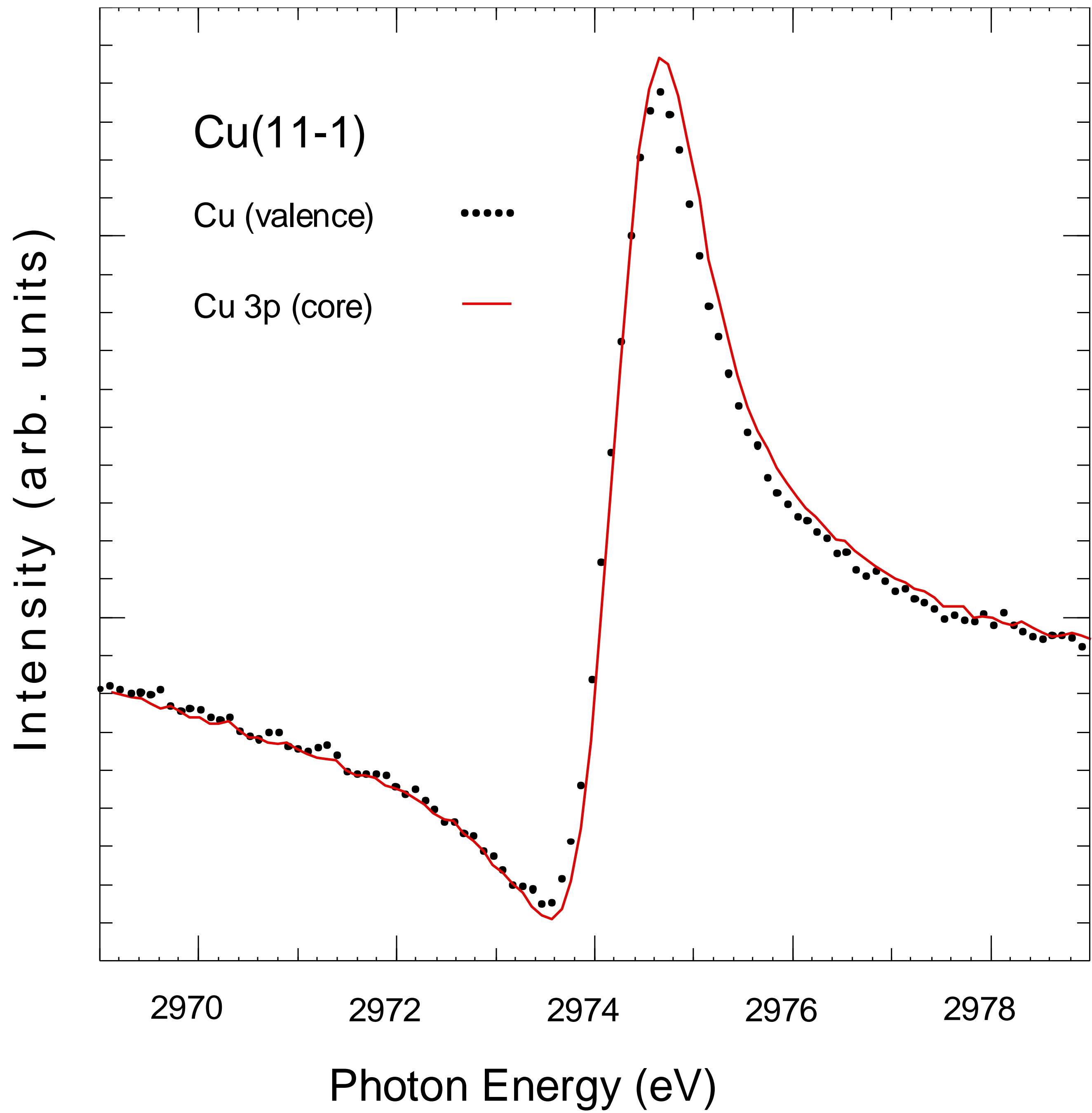
200
160
120
80
40
0
Intensity (cnts./second)
As 3d
GaAs
Ga 3d
Valence Band
-40
-30
-20
-10
0
Kinetic Energy (eV) (E - E
)
VBM


Valence Band
Theory
Experiment
Ga
As
Intensity (arbitrary units)
-16
-12
-8
-4
0
Kinetic Energy (E - E VBM )

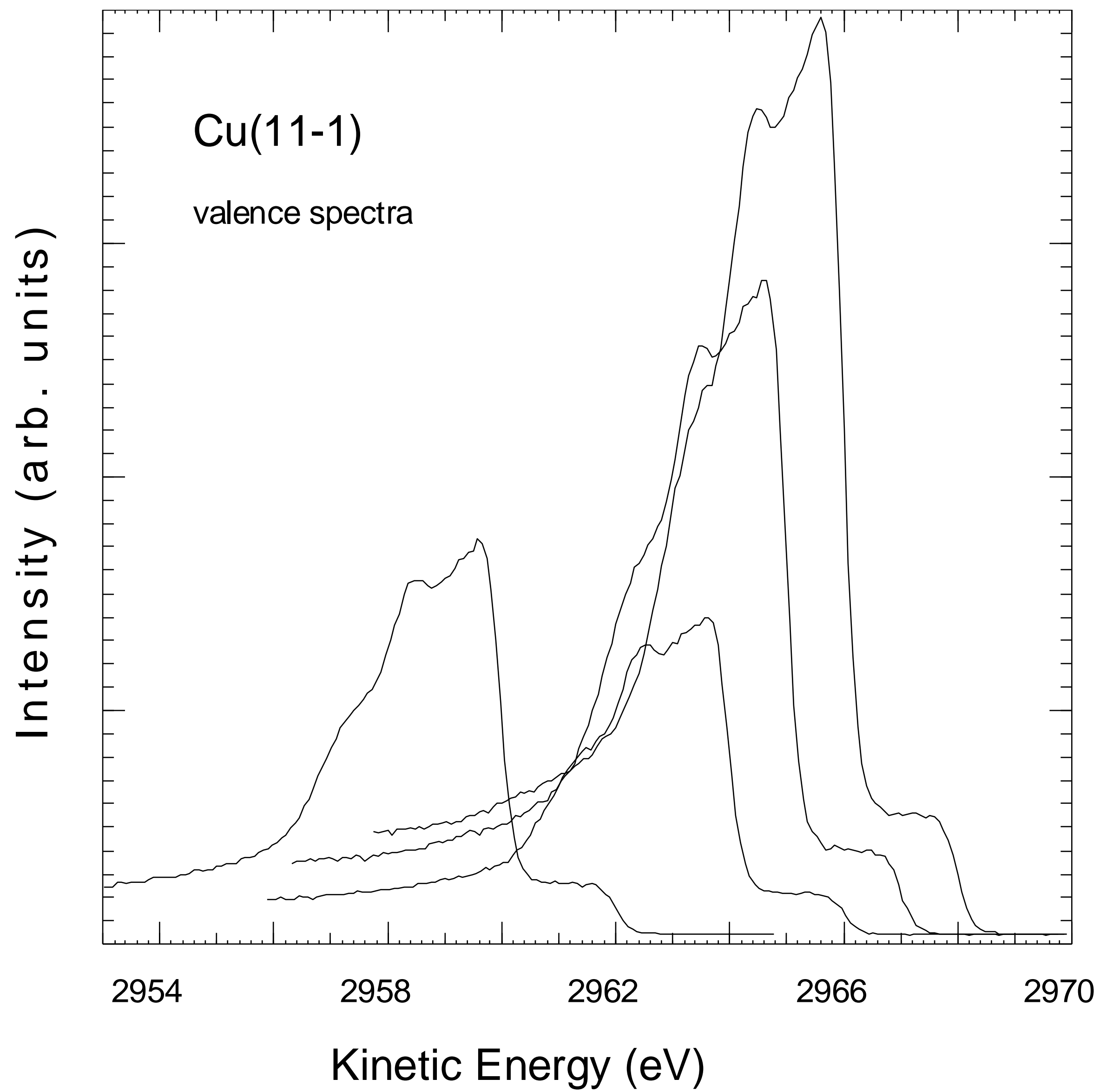
# Electronic Structure of Cu



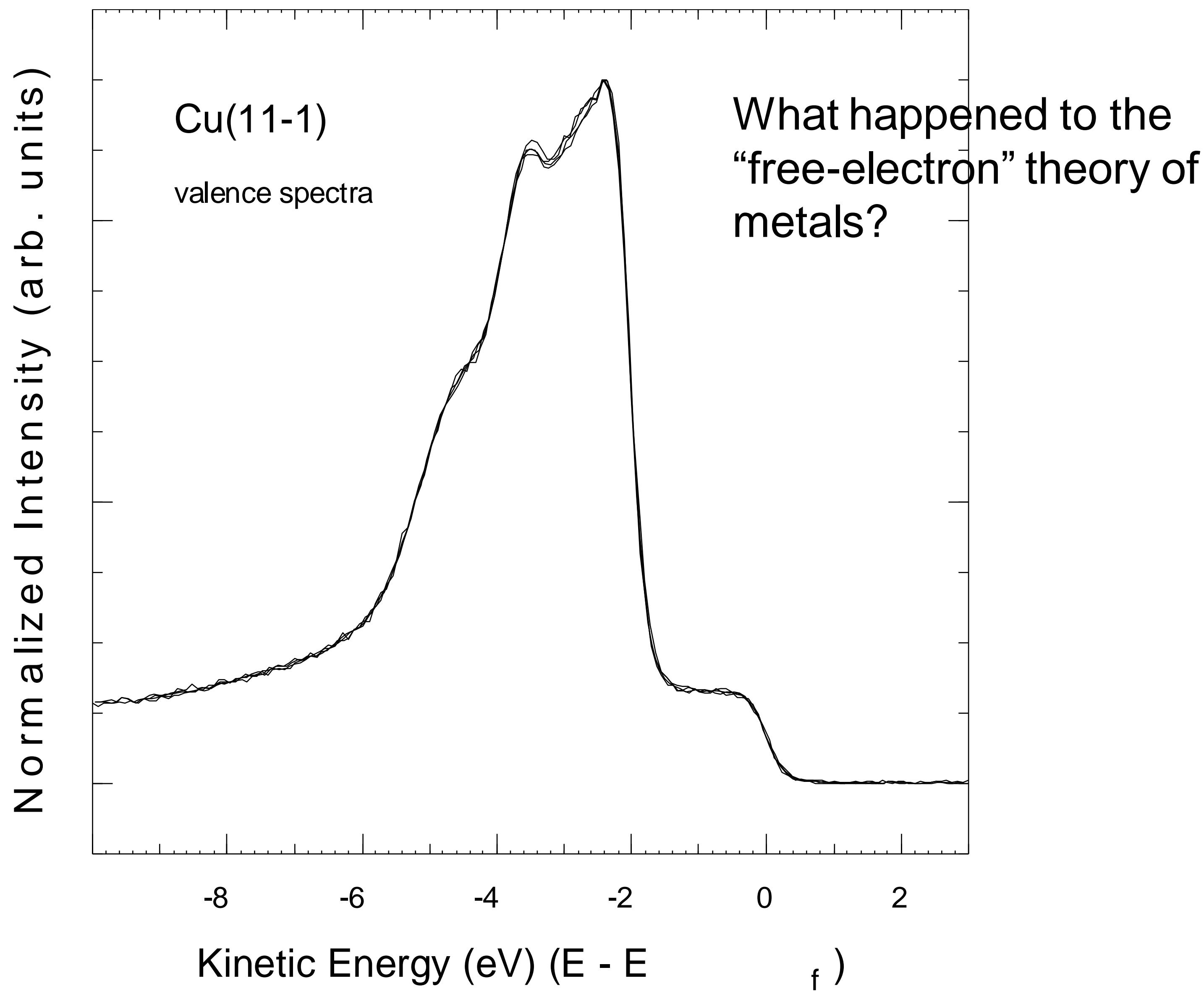

J. Friis, B. Jiang, K. Marthinsen, and R. Holmestad



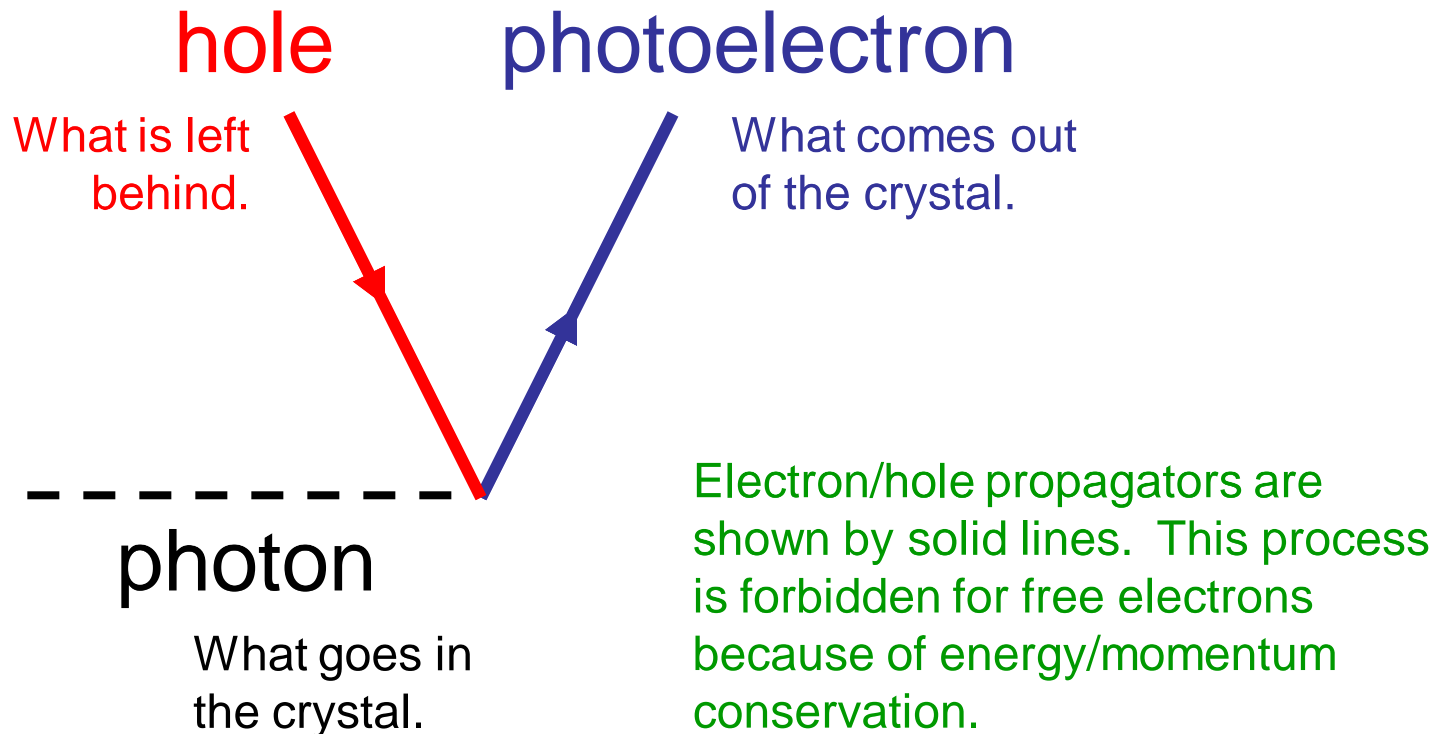
Cu(11-1)
Cu (valence)
Cu 3p (core)
Intensity (arb. units)
2970
2972
2974
2976
2978
Photon Energy (eV)



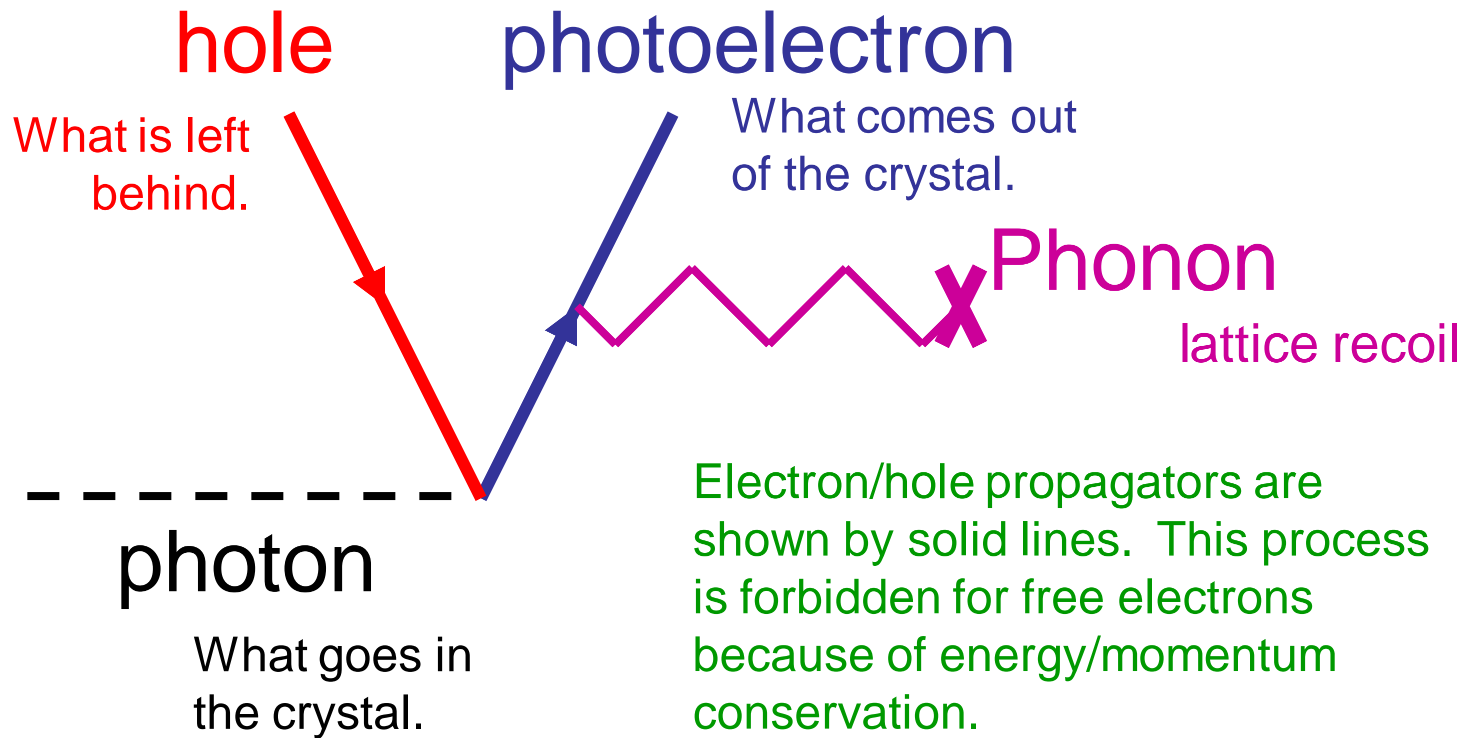
Cu(11-1)
valence spectra
Intensity (arb. units)
2954
2958
2962
2966
2970
Kinetic Energy (eV)


Cu(11-1)
valence spectra
What happened to the "free-electron" theory of metals?
Normalized Intensity (arb. units)
-8
-6
-4
-2
0
2
Kinetic Energy (eV) (E - E f )

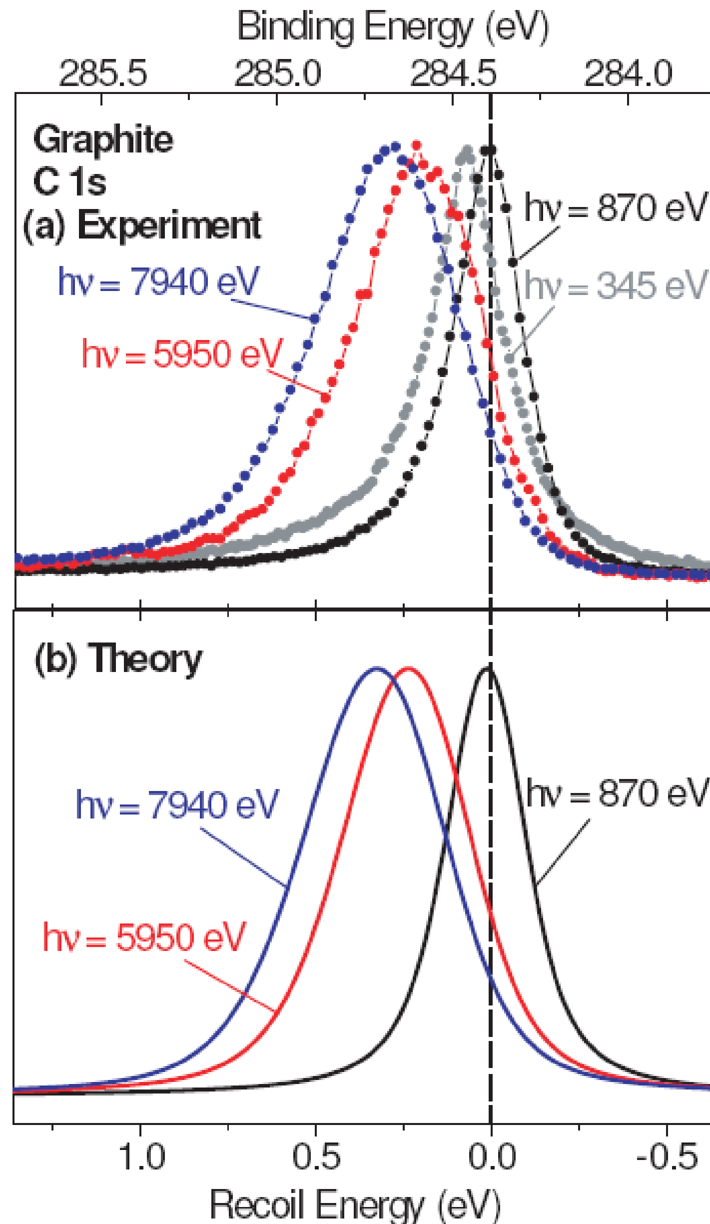
# Photoemission process Feynman diagram:



# Photoemission process Feynman diagram:

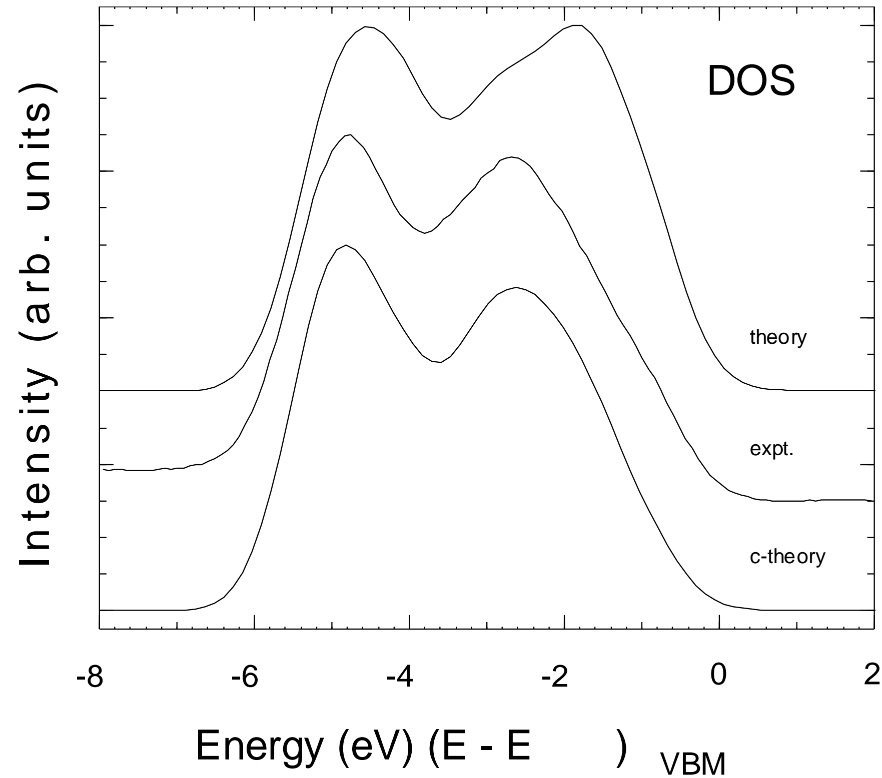


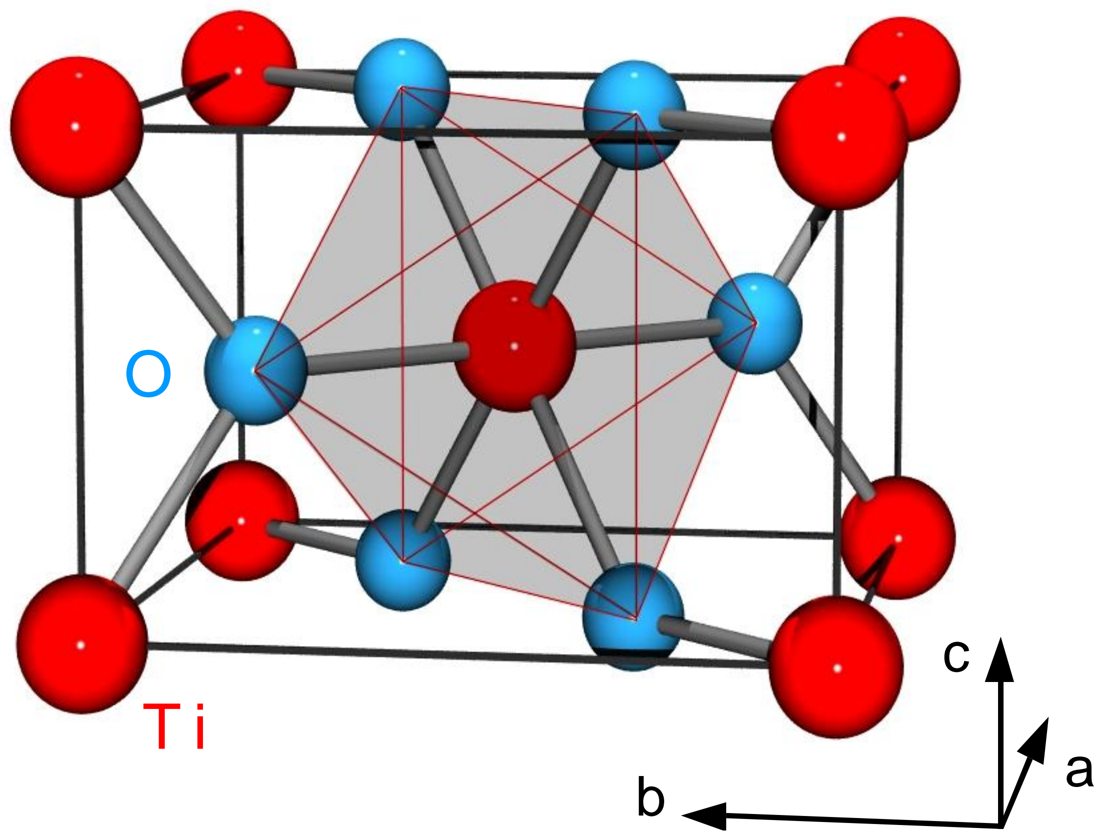
# *Recoil Effects of Photoelectrons in a Solid*

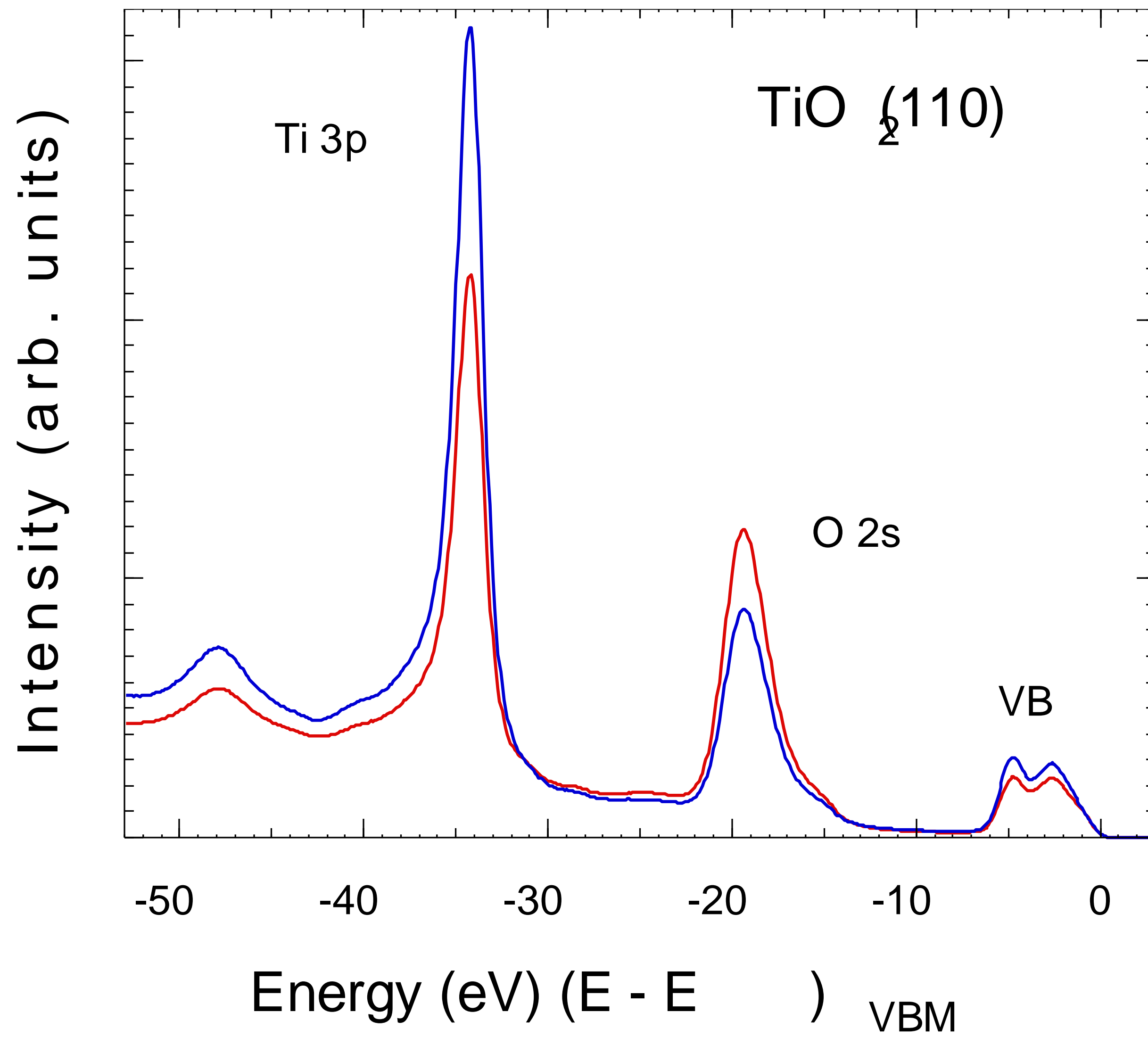



Y. Takata, Y. Kayanuma, M. Yabashi, K. Tamasaku, Y. Nishino, D. Miwa, Y. Harada, K. Horiba, S. Shin, S. Tanaka, E. Ikenaga, K. Kobayashi, Y. Senba, H. Ohashi, and T. Ishikawa

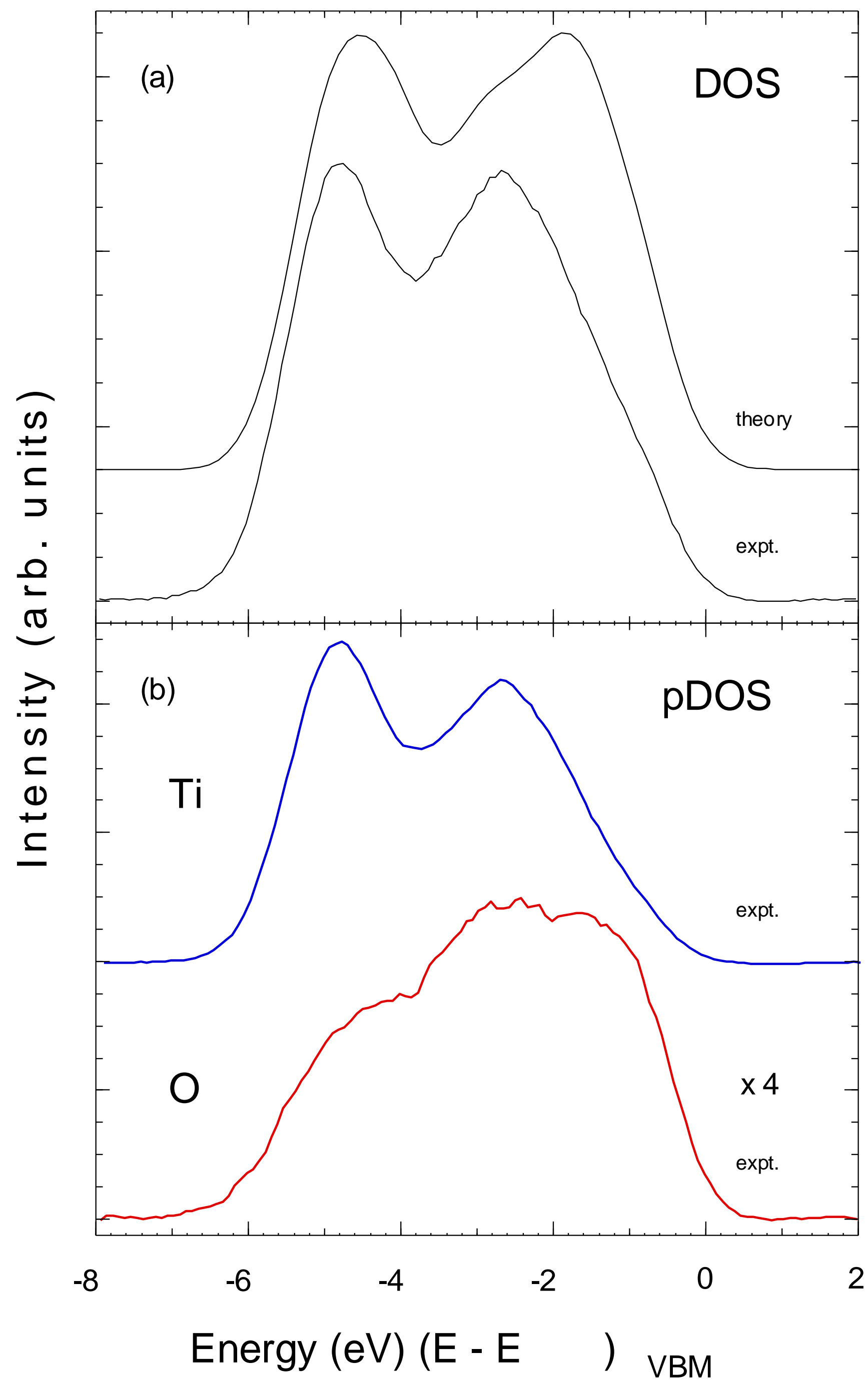
# *Electronic Structure of Rutile $TiO_2$*




O
Ti
c
a
b



TiO 2 (110)
Ti 3p
O 2s
VB
Intensity (arb. units)
-50
-40
-30
-20
-10
0
Energy (eV) (E - E VBM)


(a)
DOS
theory
expt.
(b)
pDOS
Ti
expt.
O
x 4
expt.
Intensity (arb. units)
-8
-6
-4
-2
0
2
Energy (eV) (E - E ) VBM

# *Chemical Hybridization*

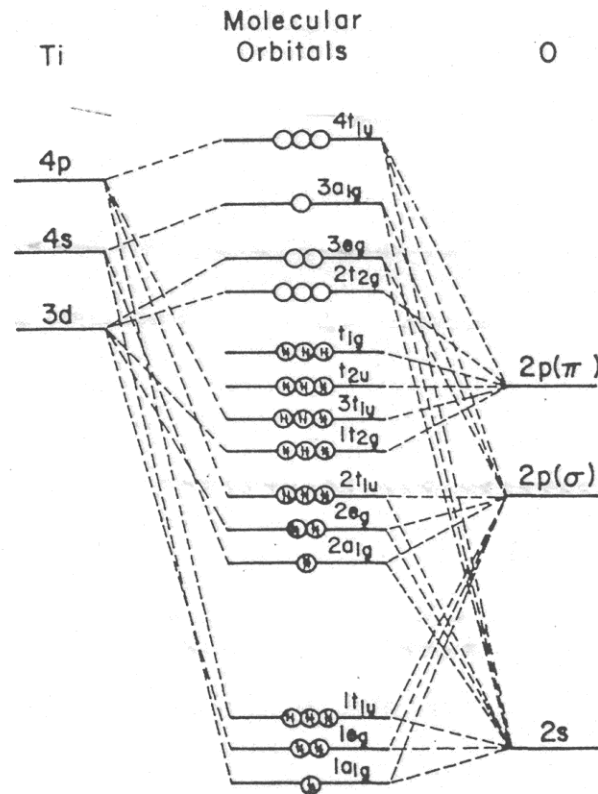
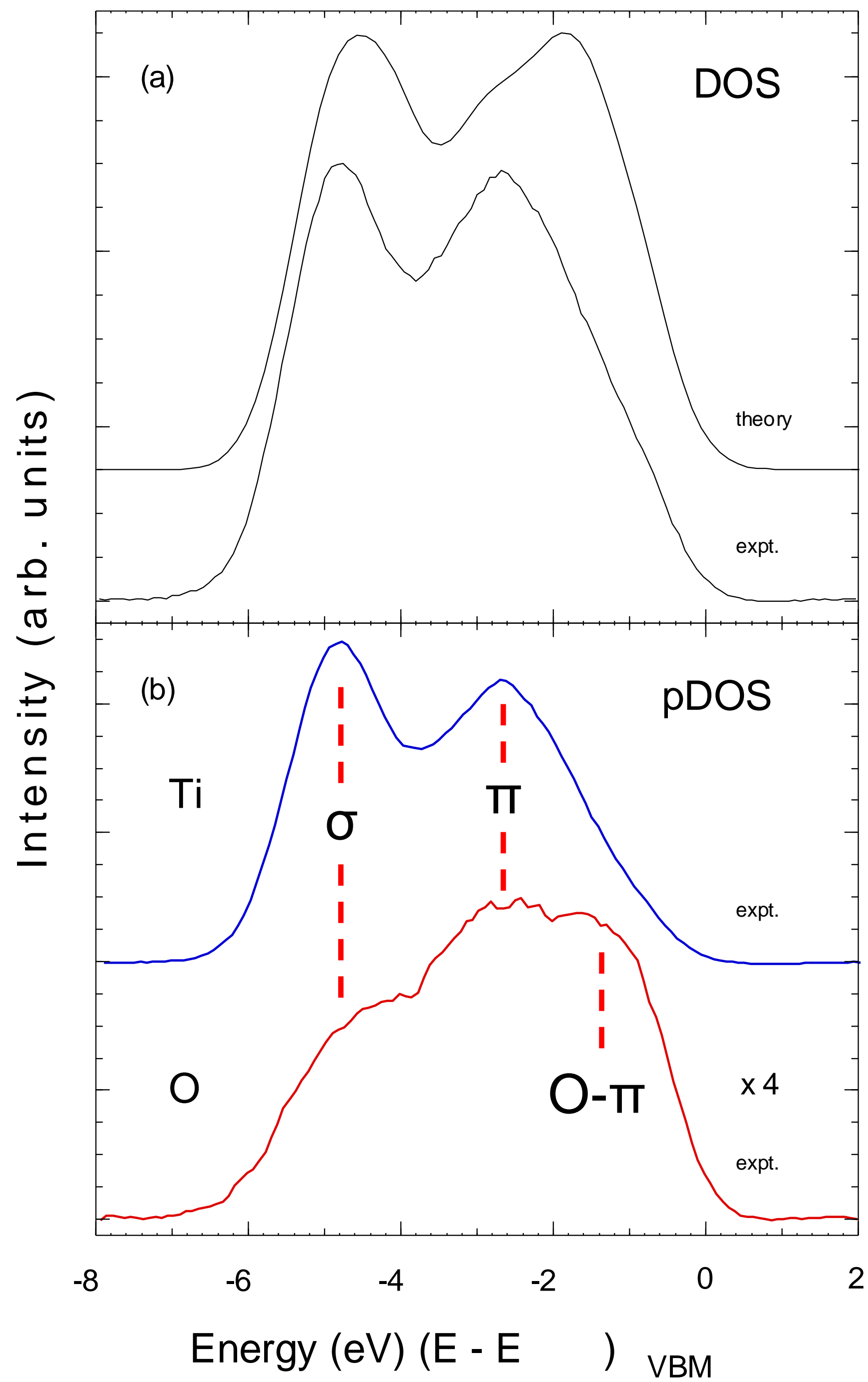
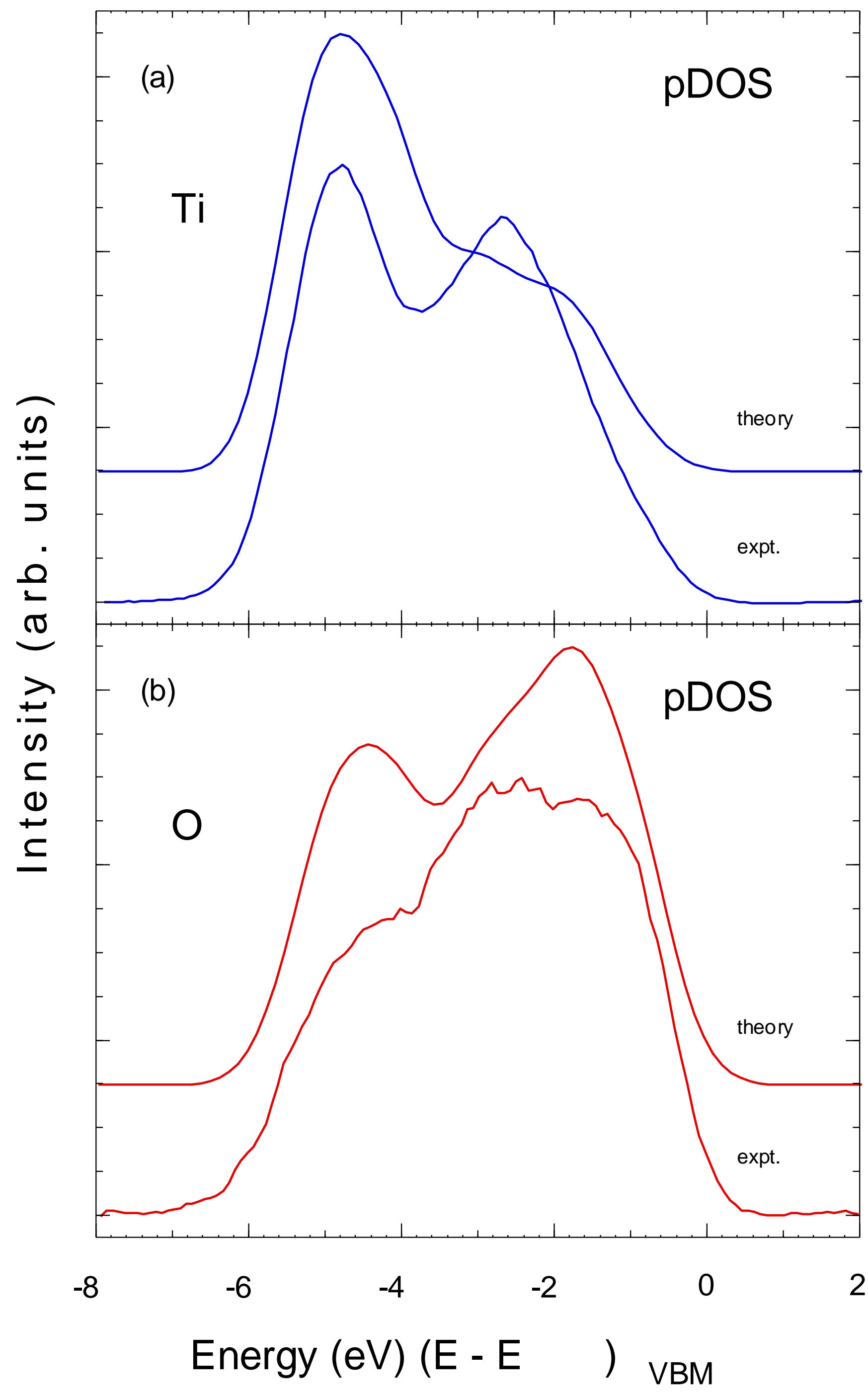
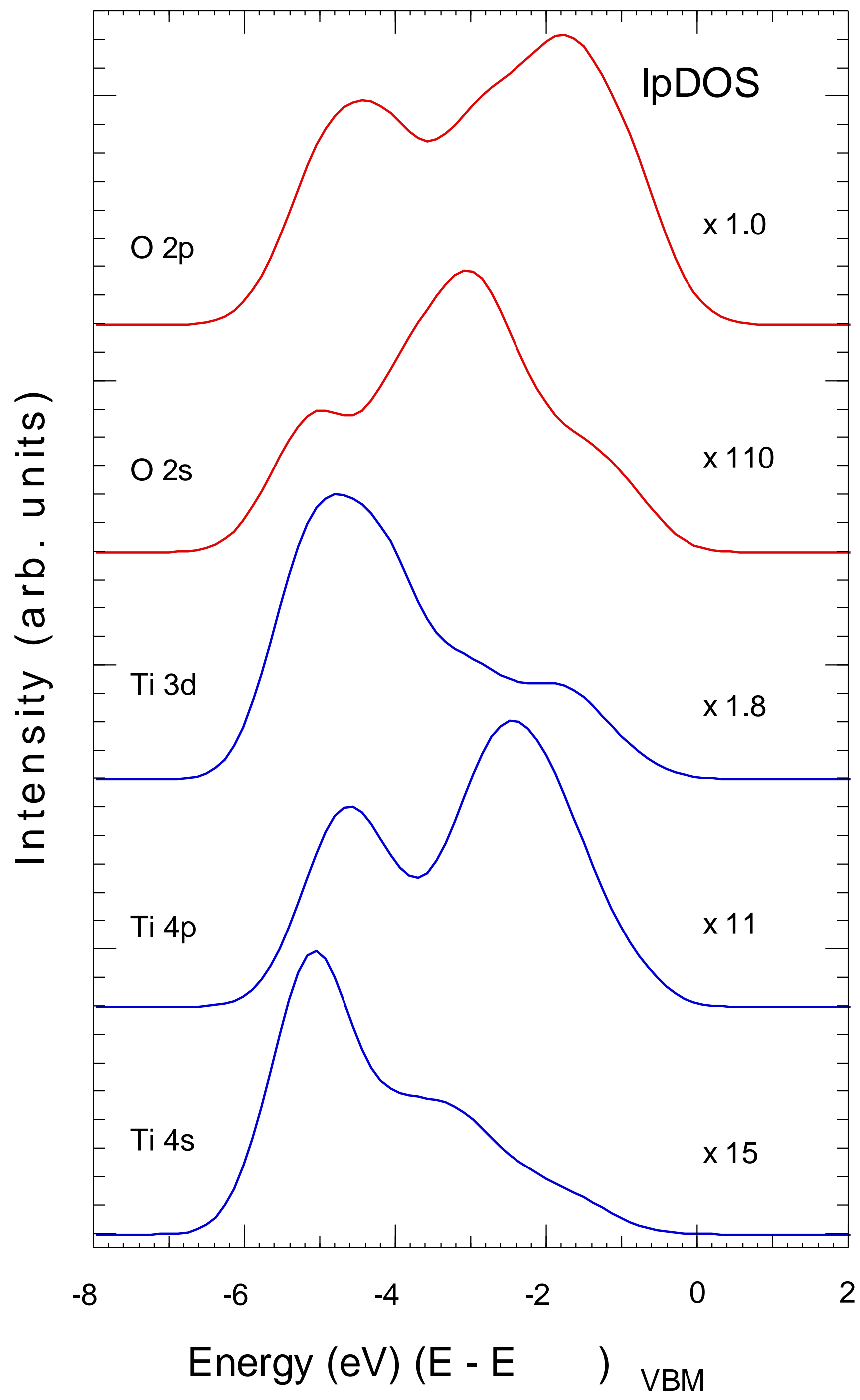



FIG. 2. MO energy-level diagram for $(TiO_6)^{8-}$, representing the environment around Ti in $TiO_2$ (Ref. 30).


(a)
DOS
theory
expt.
(b)
pDOS
Ti
σ
π
expt.
O
O-π
x 4
expt.
Intensity (arb. units)
-8
-6
-4
-2
0
2
Energy (eV) (E - E ) VBM



(a)
pDOS
Ti
theory
expt.
(b)
pDOS
O
theory
expt.
Intensity (arb. units)
-8
-6
-4
-2
0
2
Energy (eV) (E - E ) VBM



lpDOS
O 2p
x 1.0
O 2s
x 110
Ti 3d
x 1.8
Ti 4p
x 11
Ti 4s
x 15
Intensity (arb. units)
-8
-6
-4
-2
0
2
Energy (eV) (E - E ) VBM

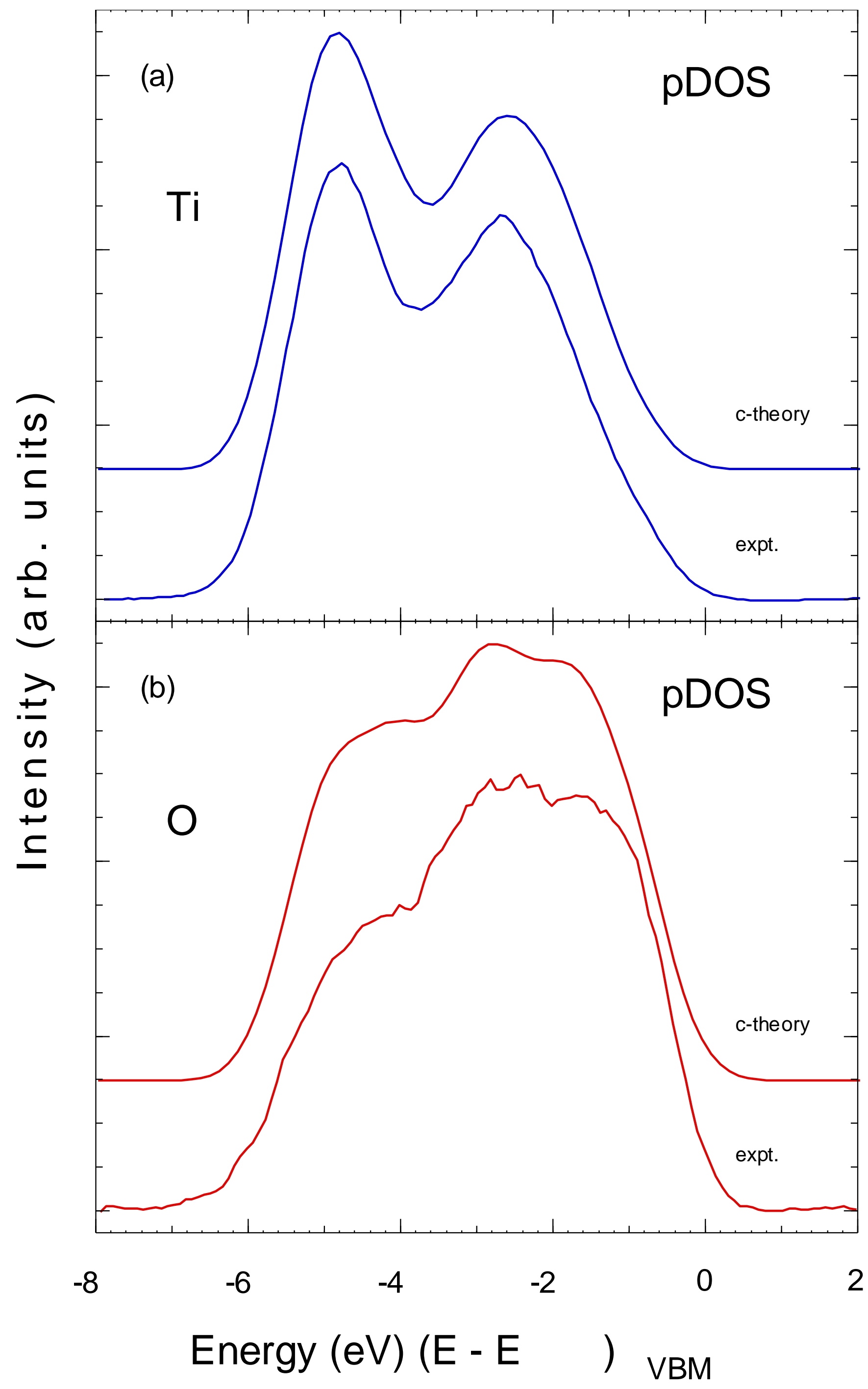
# *Theoretical Atomic Cross Sections*

$$\frac{\sigma_{Ti_{4s}}}{\sigma_{Ti_{3d}}} \approx 30\ !$$

$$\frac{\sigma_{O_{2s}}}{\sigma_{O_{2p}}} \approx 10\ !$$

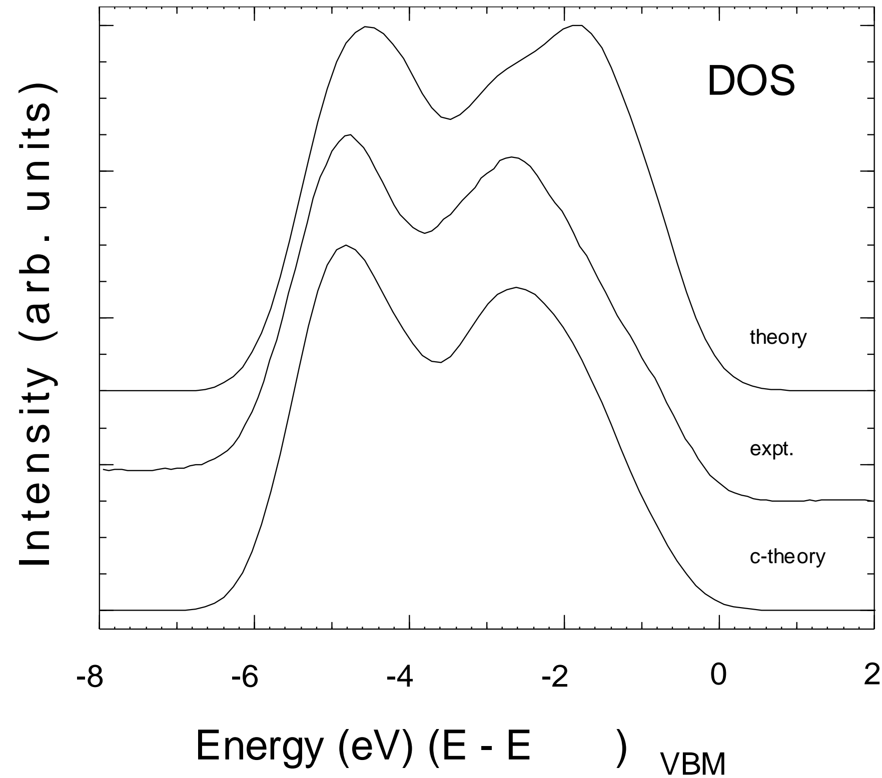
*XPS favors states with smaller values of angular momentum!*

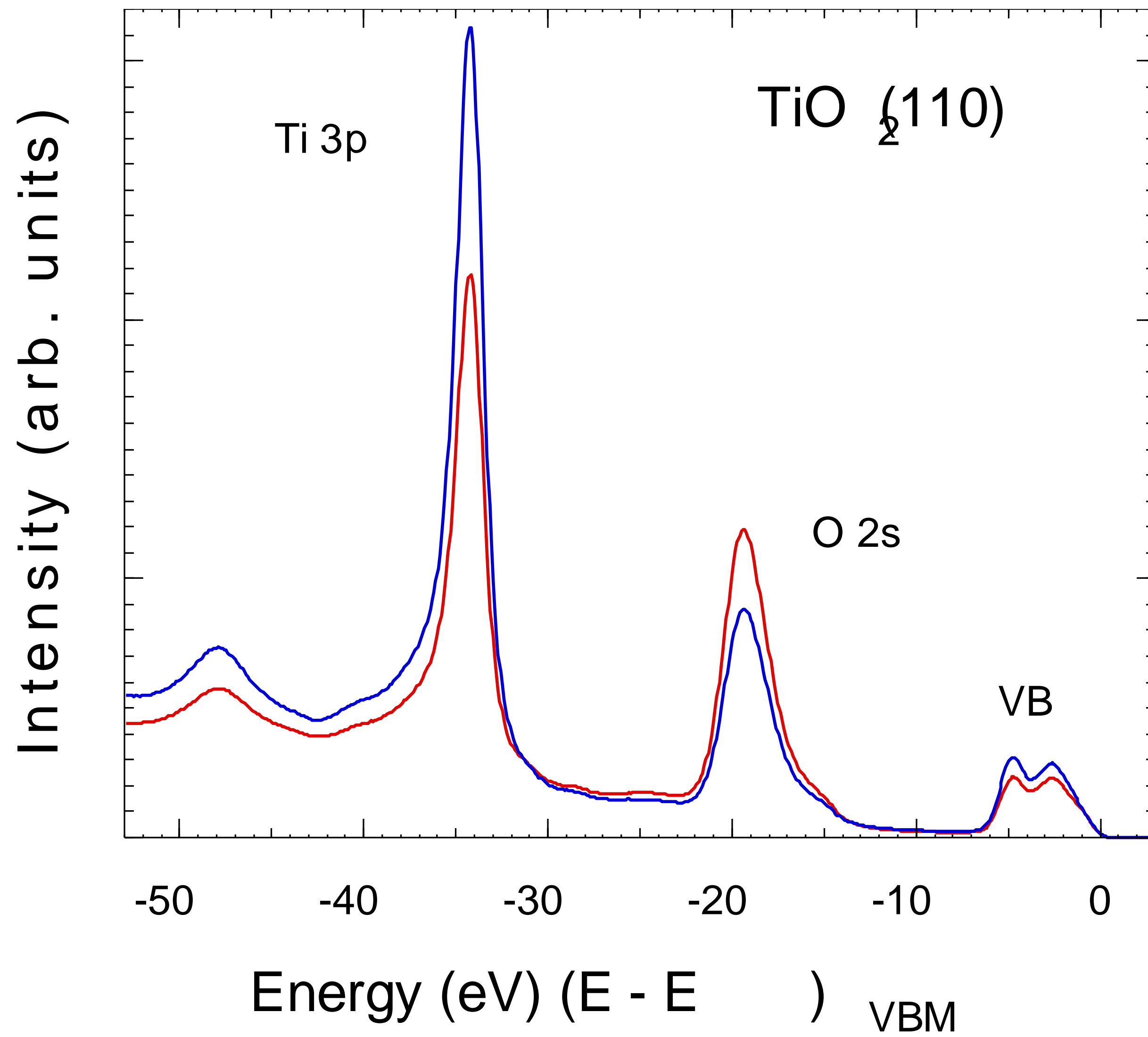
$$I(E,\hbar\omega)\ \alpha\ \sum_{i,l} \rho_{i,l}(E)\ \sigma_{i,l}(E,\hbar\omega)$$



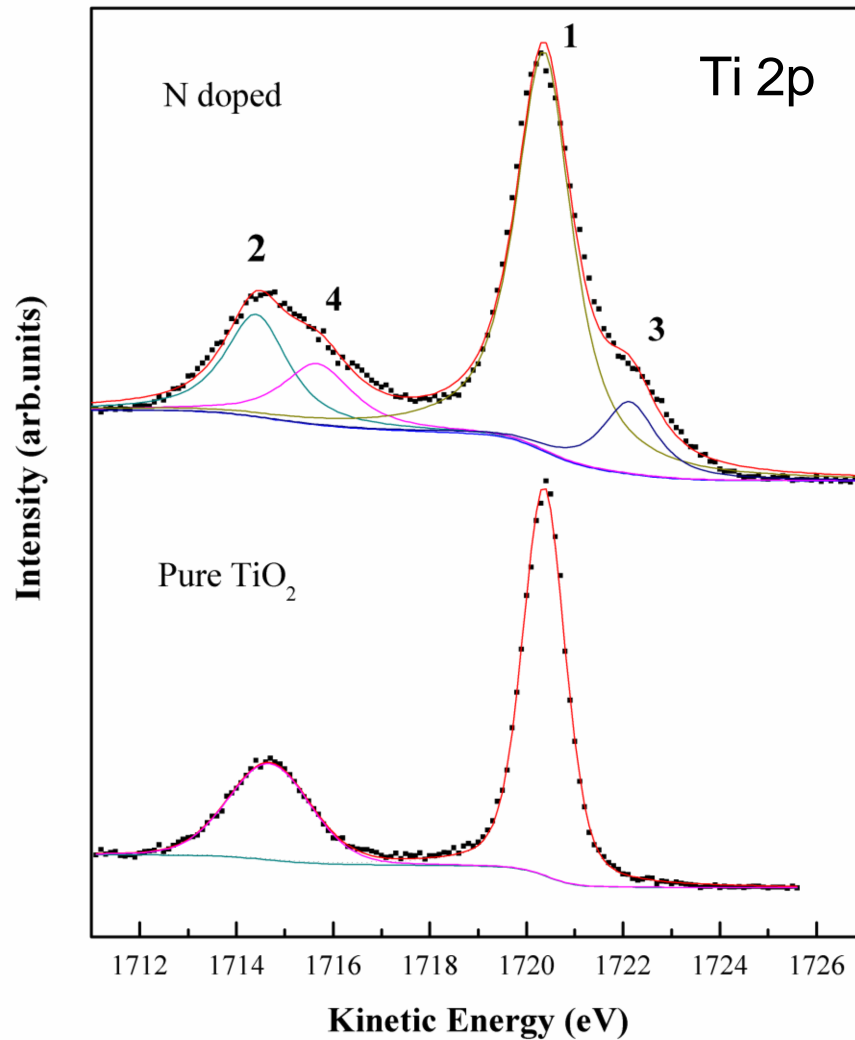
(a)
pDOS
Ti
c-theory
expt.
(b)
pDOS
O
c-theory
expt.
Intensity (arb. units)
-8
-6
-4
-2
0
2
Energy (eV) (E - E
) VBM

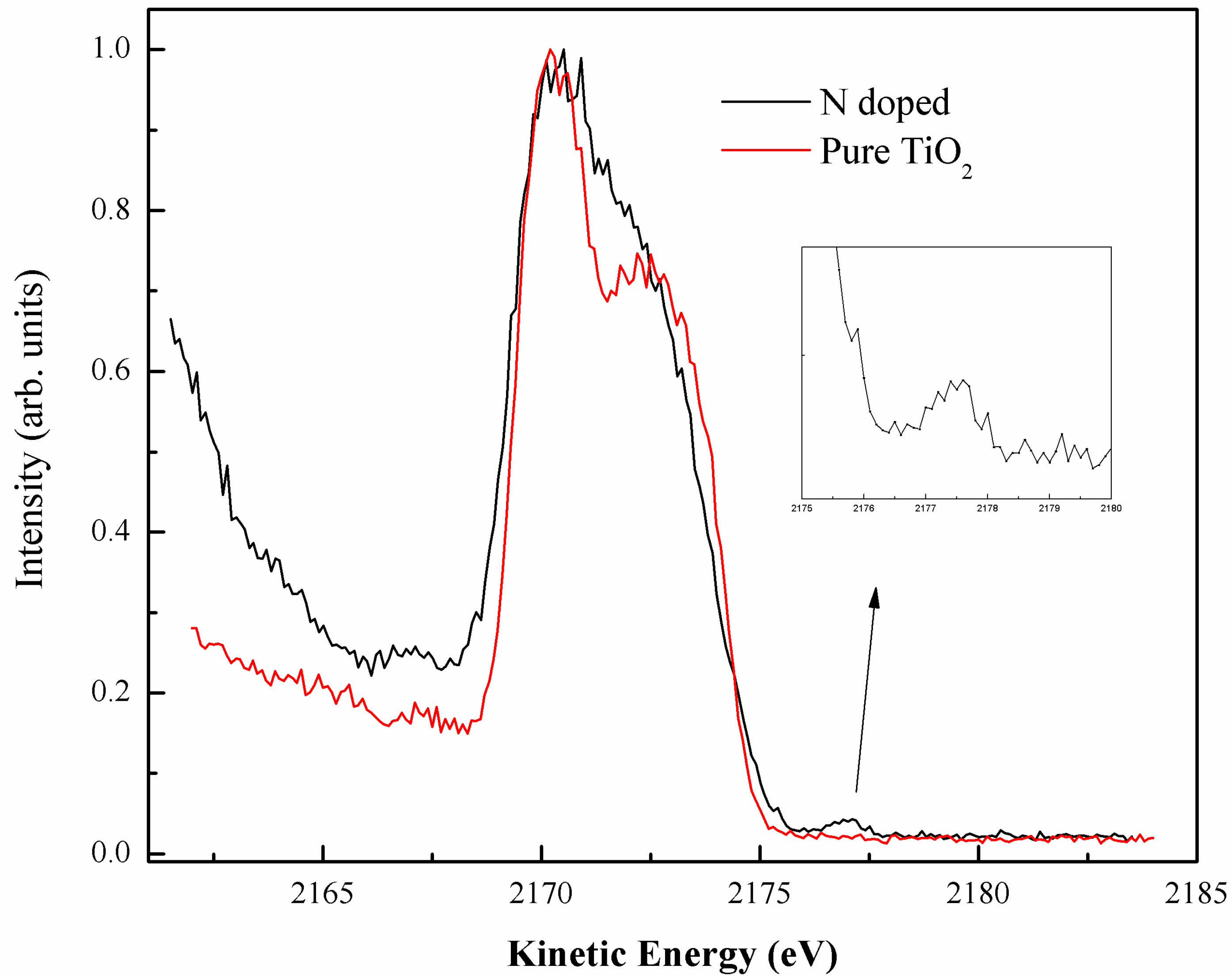
# *Electronic Structure of Rutile $TiO_2$*



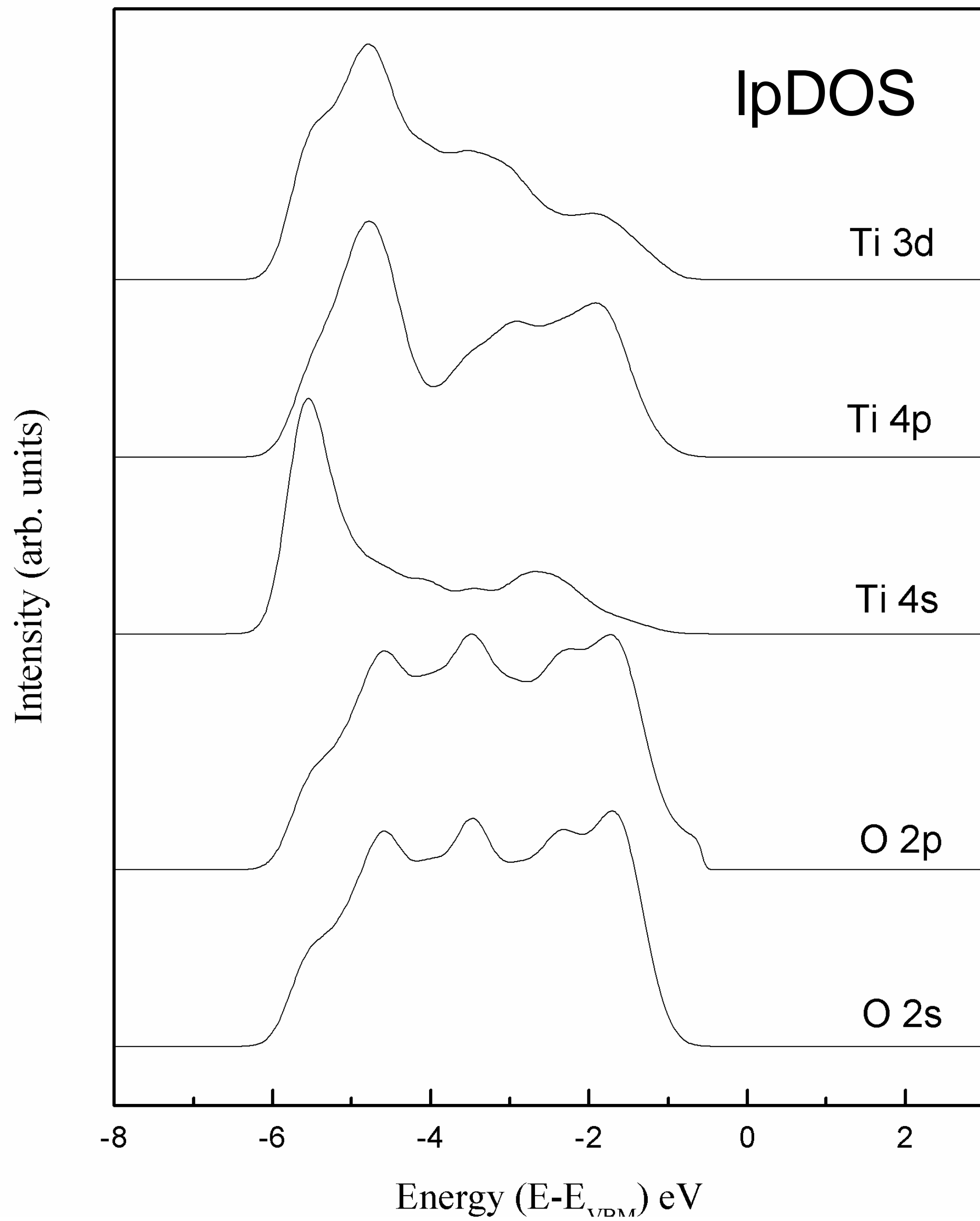

TiO 2 (110)
Ti 3p
O 2s
VB
Intensity (arb. units)
-50
-40
-30
-20
-10
0
Energy (eV) (E - E ) VBM

# *N doped $TiO_2$ (anatase)*

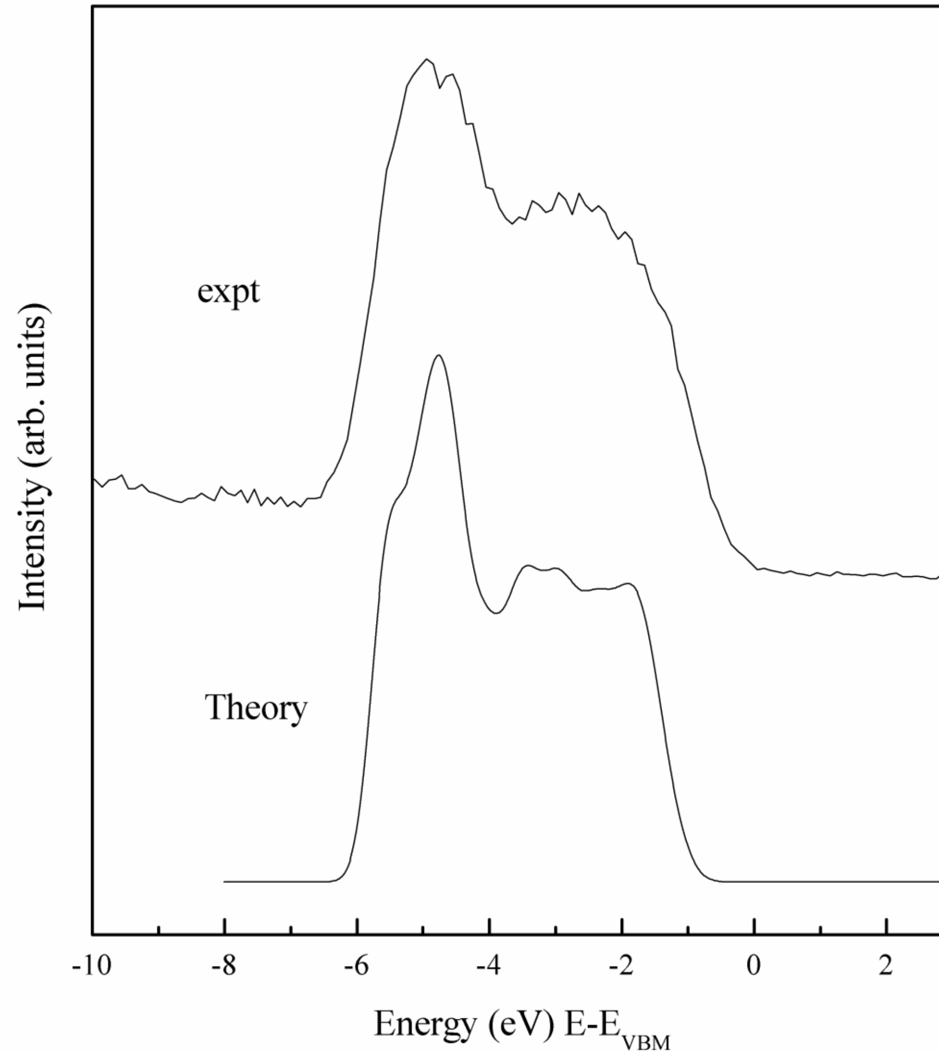


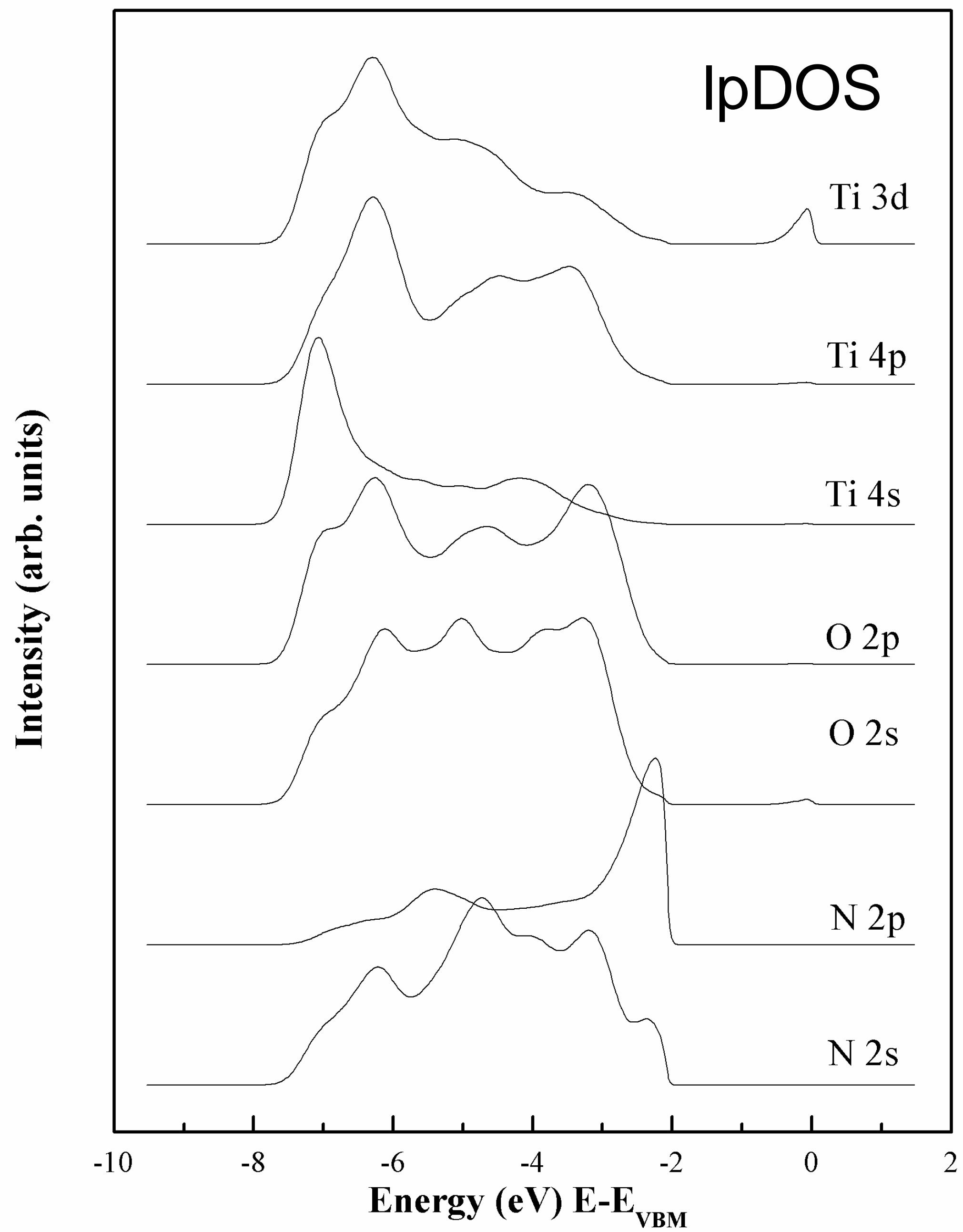


N doped
Pure TiO2
Intensity (arb. units)
Kinetic Energy (eV)
0.0
0.2
0.4
0.6
0.8
1.0
2165
2170
2175
2180
2185
2175
2176
2177
2178
2179
2180

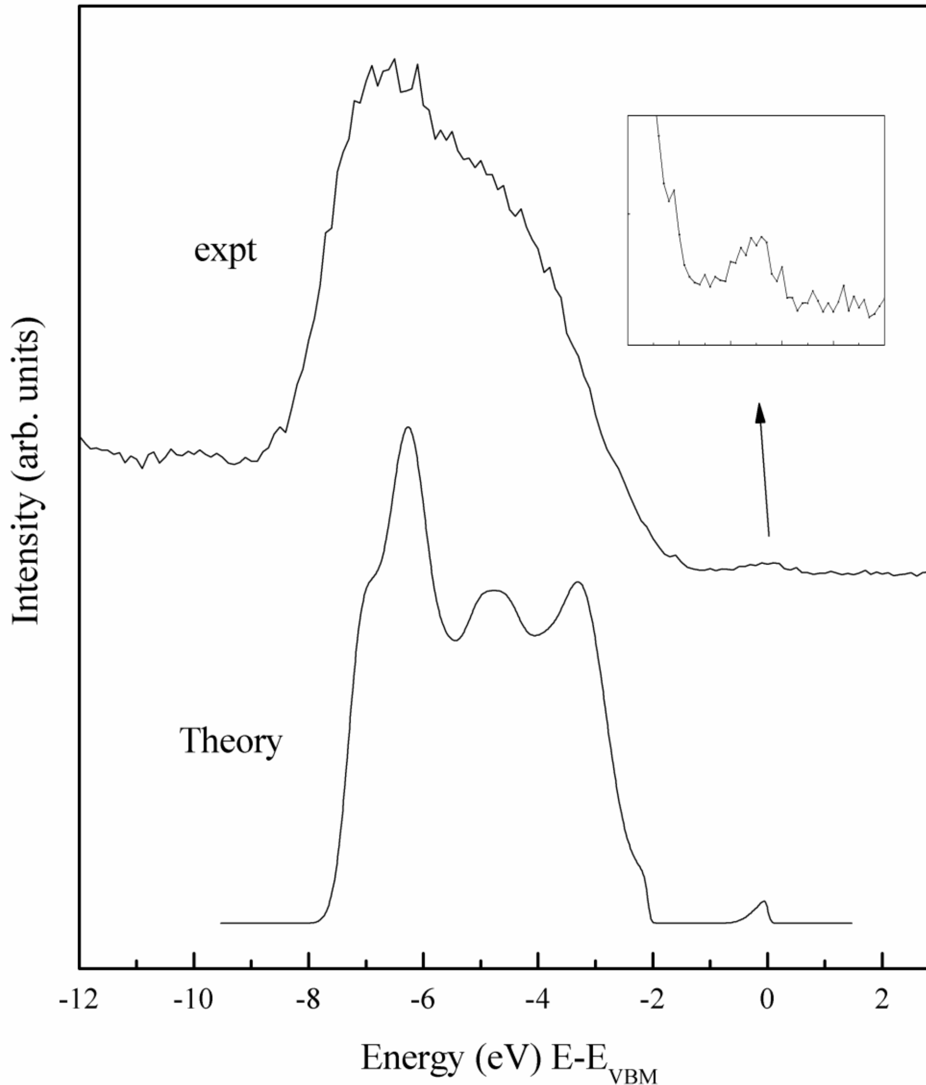

IpDOS
Ti 3d
Ti 4p
Ti 4s
O 2p
O 2s
Intensity (arb. units)
-8
-6
-4
-2
0
2
Energy (E-E$_{VBM}$) eV

# Electronic Structure of $TiO_2$ (anatase)




IpDOS
Ti 3d
Ti 4p
Ti 4s
O 2p
O 2s
N 2p
N 2s
Intensity (arb. units)
-10
-8
-6
-4
-2
0
2
Energy (eV) E-E$_{VBM}$

# *Electronic Structure of N doped $TiO_2$ (anatase)*



# *Many Thanks……*

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- *Hao Li (Motorola Labs)*
- *Erik Nelson (SSRL), David Heskett (URI), and Lonny Berman (NSLS)*
- *Leeor Kronik (Weizmann) and Jim Chelikowsky (Austin)*
- *Abdul Rumaiz (NSLS) and Eric Cockayne (NIST)*

Photoelectron spectroscopy can uniquely measure the electronic structure of a solid. However, due to the generally limiting electron mean-free path, the technique is extremely surface sensitive, probing only the first few atomic layers of a structure, especially if low energy, ultra-violet photons are used. For this reason, hard x-ray photoelectron spectroscopy (HAXPES), where the photon energy is typically in the 1.5 – 15 keV range, is emerging as a technique with substantial promise for studying the electronic structure of complex systems.

# International Workshop for New Opportunities in Hard X-Ray Photoelectron Spectroscopy

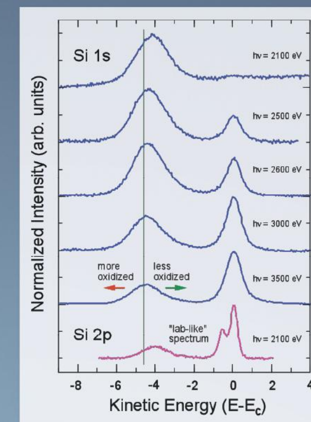
## May 20-22, 2009

Brookhaven National Laboratory, Long Island, NY, USA

This 3-day international conference will cover the fundamental science enabled by HAXPES, while providing a forum for more discussion than previous workshops on the relevance of HAXPES to industrial applications. The primary goal of the conference is to present an overview of the world effort in HAXPES that will include:

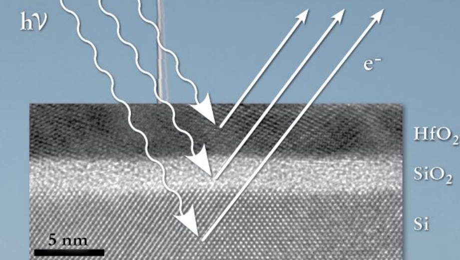
- electronic and atomic structure
- correlated materials
- industrial applications
- the combination of photoemission and other techniques
- high pressure
- theory
- imaging
- instrumentation

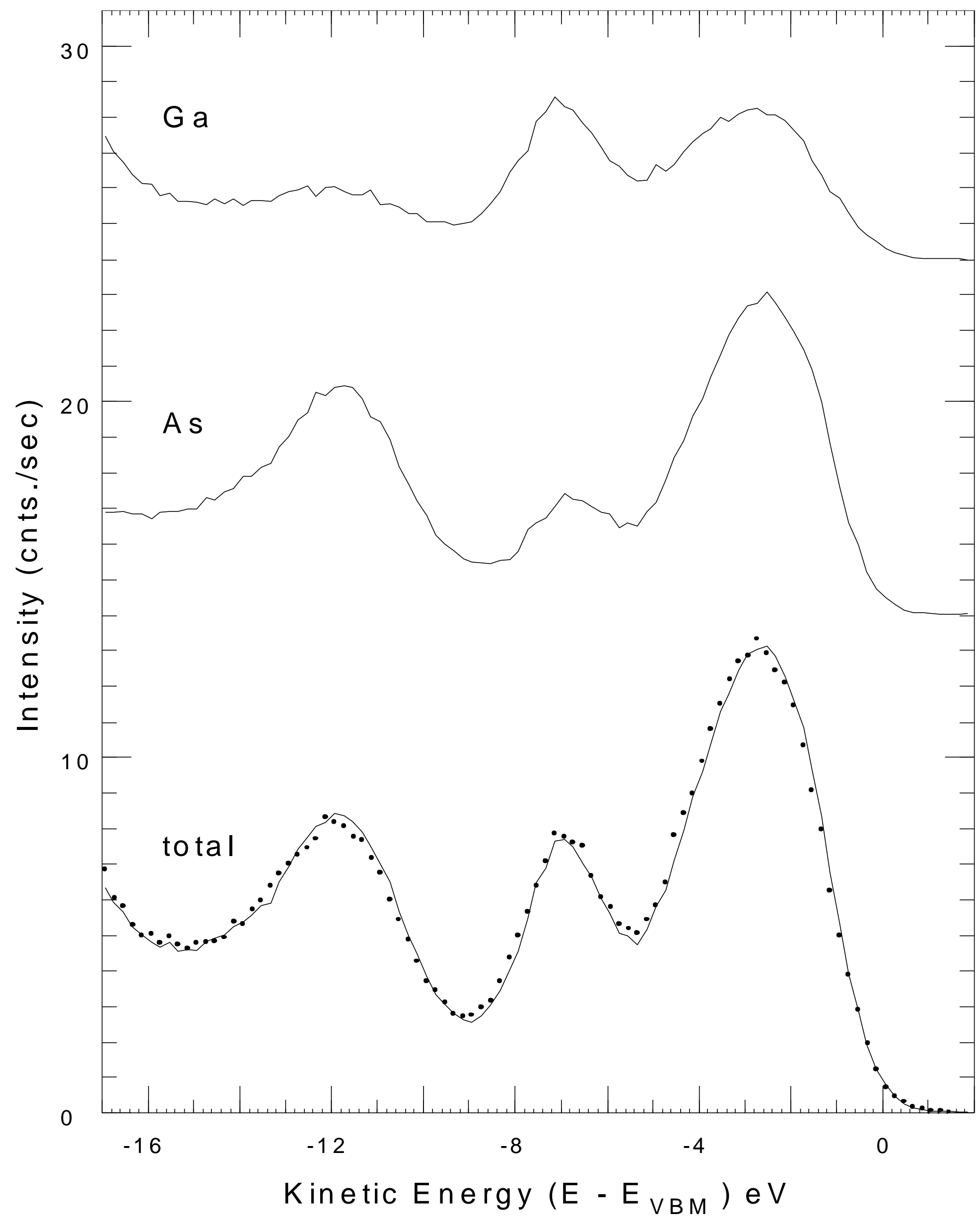
For more information please visit the conference website:
http://www.nsls.bnl.gov/newsroom/events/workshops/2008/haxpes/




hν

e⁻





Intensity (cnts./sec)
30
20
10
0
Ga
As
total
-16
-12
-8
-4
0
Kinetic Energy (E - E VBM ) eV

$$\frac{d\sigma}{d\Omega} \propto |\langle f|e^{i\mathbf{k}_o\cdot\mathbf{r}}(\boldsymbol{\varepsilon}_o\cdot\mathbf{p})|i\rangle|^2$$

$$H_o = \Sigma_i\, p_i^2/2m + V(\mathbf{r})$$

$$H' = \mathbf{A}_o\cdot\mathbf{p}$$

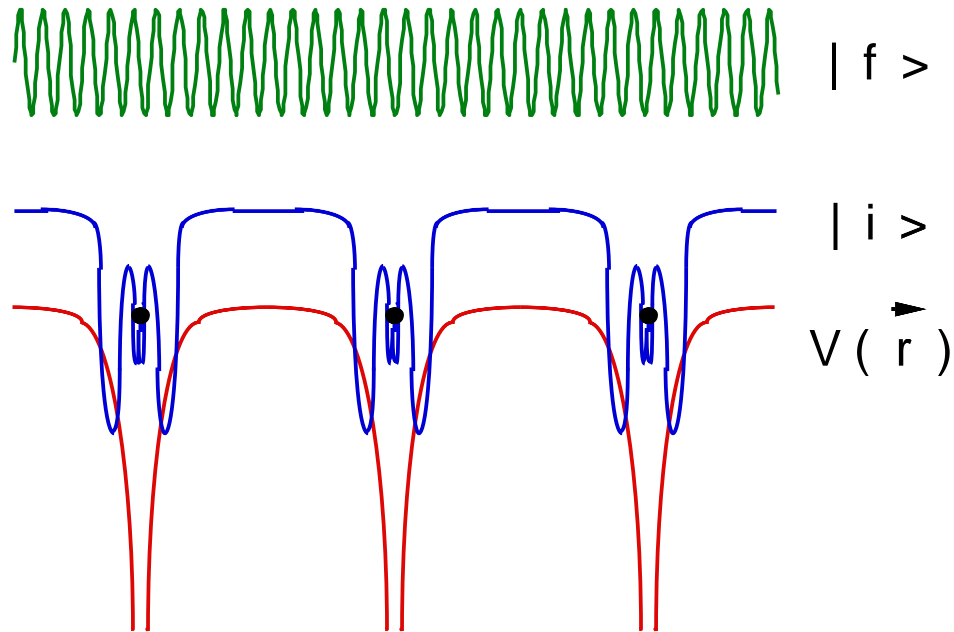
$$E_{kin} = \hbar\omega - E_b \qquad (\hbar\omega >> E_b)$$

$$|f\rangle = e^{i\mathbf{k}_f\cdot\mathbf{r}} \qquad (k_f >> k_o)$$

$$[\mathbf{p},H] = -i\hbar\nabla V(\mathbf{r})$$

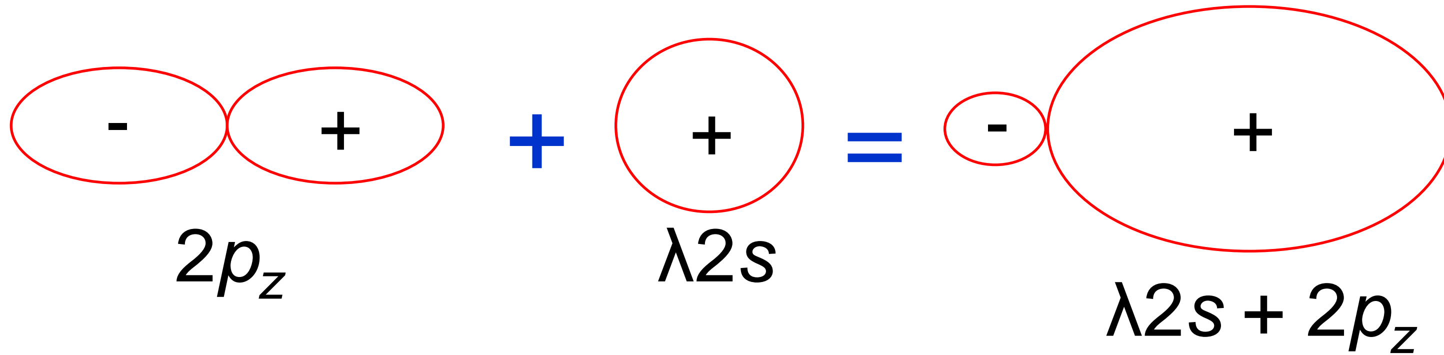
$$\frac{d\sigma}{d\Omega} \propto |\langle f|\boldsymbol{\varepsilon}_o\cdot\nabla V(\mathbf{r})|i\rangle|^2$$

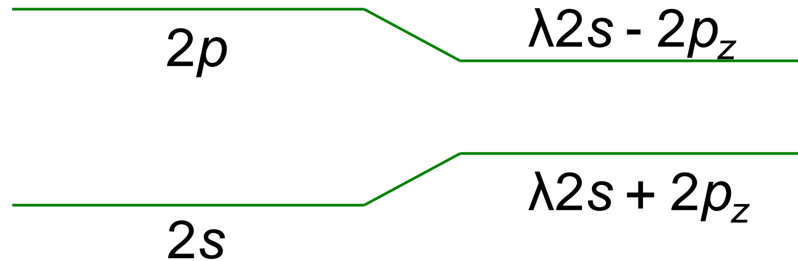
# Valence Photoemission

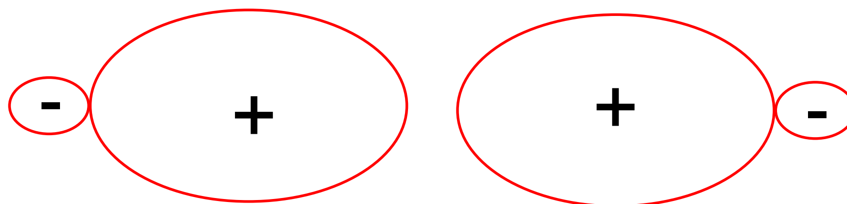



$$\frac{d\sigma}{d\Omega} \;\alpha\; \left| \langle f \,|\, e^{i\vec{k}_o \cdot \vec{r}} (\hat{\varepsilon}_o \cdot \vec{p}) \,|\, i \rangle \right|^2$$

# Chemical Hybridization




"*s-p* hybrid"

$$H_{i,j} = \int \psi_i \, H \, \psi_j \, dV$$

Stronger Chemical Bond!