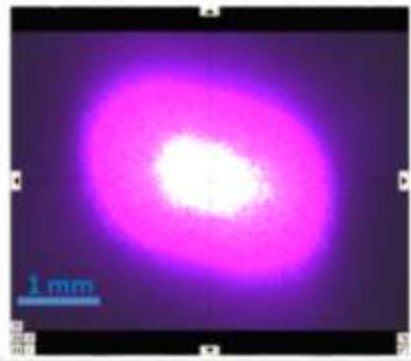
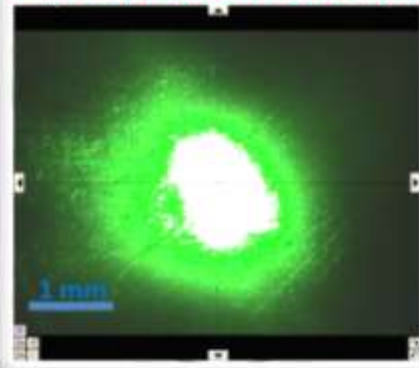


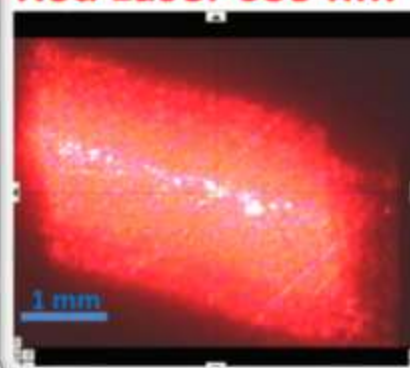
Violet Laser 405 nm



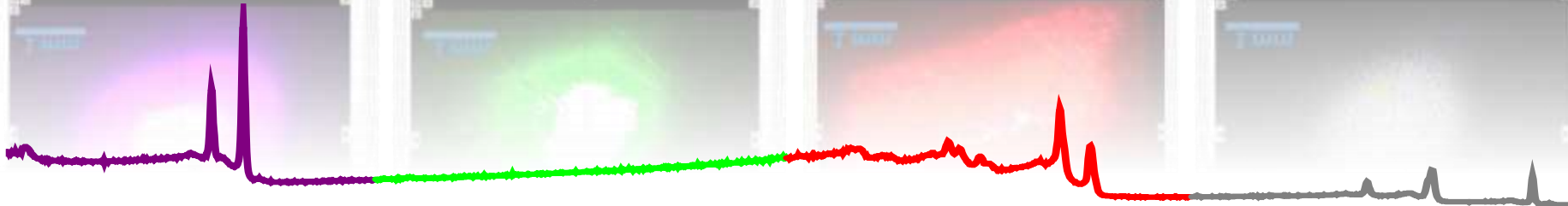
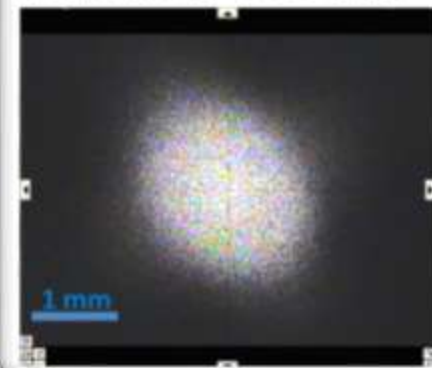
Green Laser 532 nm



Red Laser 635 nm



NIR Laser 980 nm



# Dynamic XPS for Photoinduced Voltage Changes on Semiconducting Materials



Chemistry Department

## Hikmet Sezen

May 15, 2013  
Karlsruhe



Karlsruhe Institute of Technology  
Institute of Functional Interfaces (IFG)

# Outline:

- **Part I(2009-2011):**

- **Introduction**

- **X-ray Photoelectron Spectroscopy (XPS)**

- ❖ Controlled Surface Charging

- *DC, SQW, Model*

- **Photoconductivity**

- **Our Motivation**

- **Results & Discussions**

- **np-Si and np-Si/SiO<sub>x</sub>**

- **CdS**

- **np-GaN**

- **Conclusions**

- **Part II(2012-):**

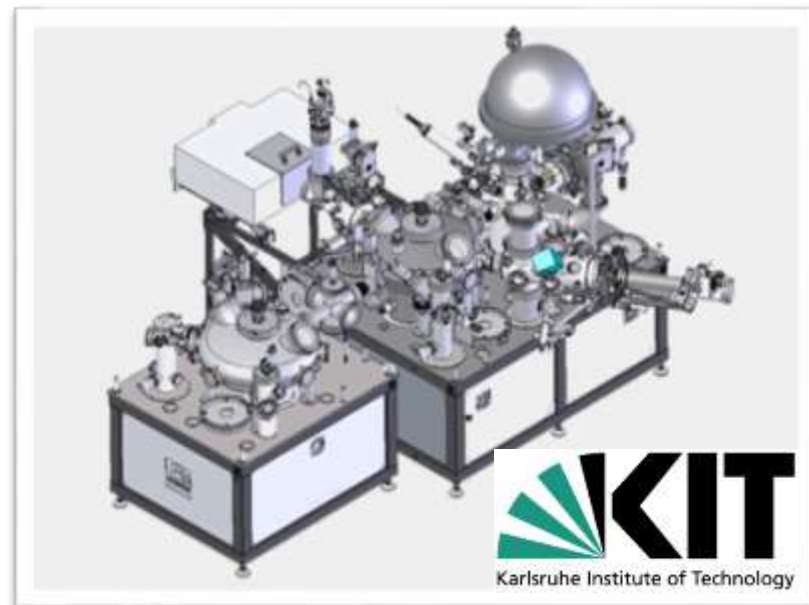
- **Instrument: Theo**

- ❖ **TiO<sub>2</sub>**

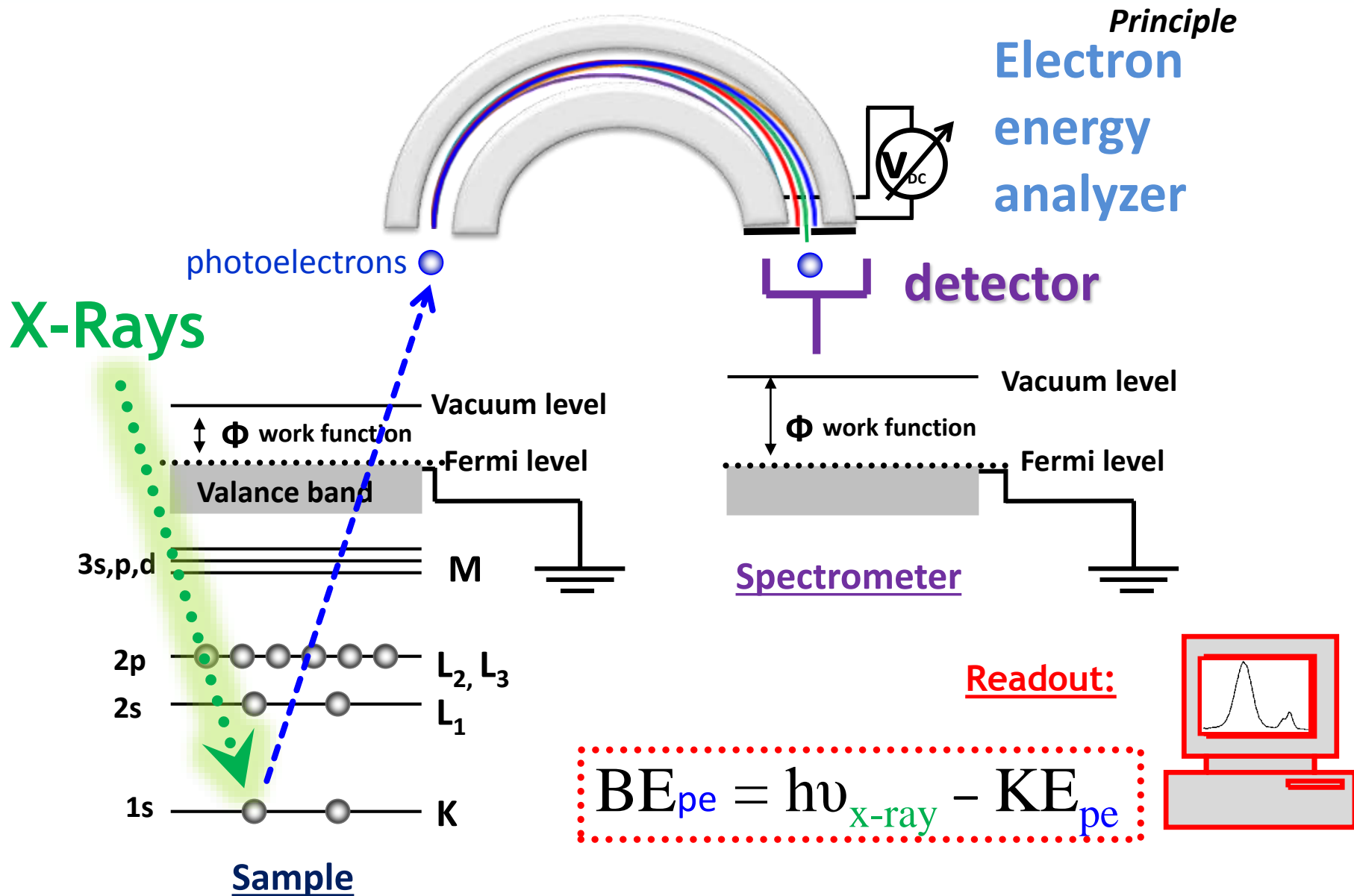
Ankara/Turkey, Prof. Şefik Süzer



Karlsruhe/Germany, Prof. Christof Wöll



# X-ray Photoelectron Spectroscopy:



# X-ray Photoelectron Spectroscopy:

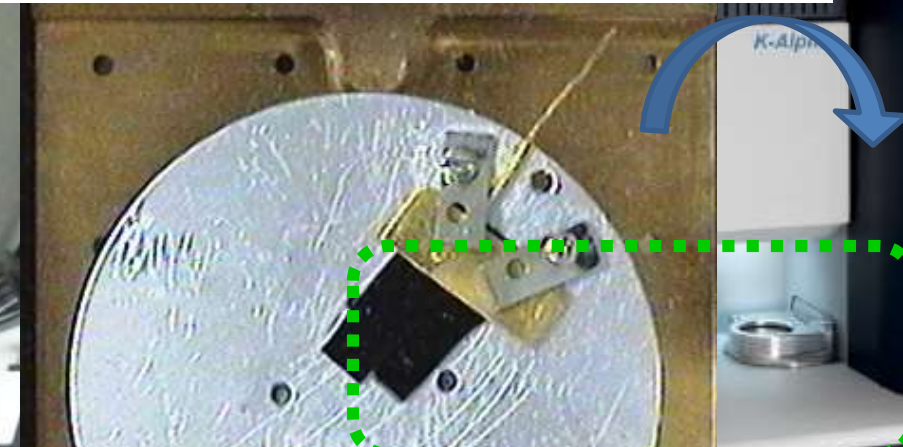
- Provide **Chemical/Elemental** Information
- Capable to Separate **Chemical States** of Elements
- Highly **Surface Sensitive** : 1-20 nm
- **Quantative** Analysis:
  - Stoichiometric, Thickness, and Depth Profile

....

# Instrument (Part I)

## Cracking Hardware

Customized Sample  
**Optics Board**  
Holder



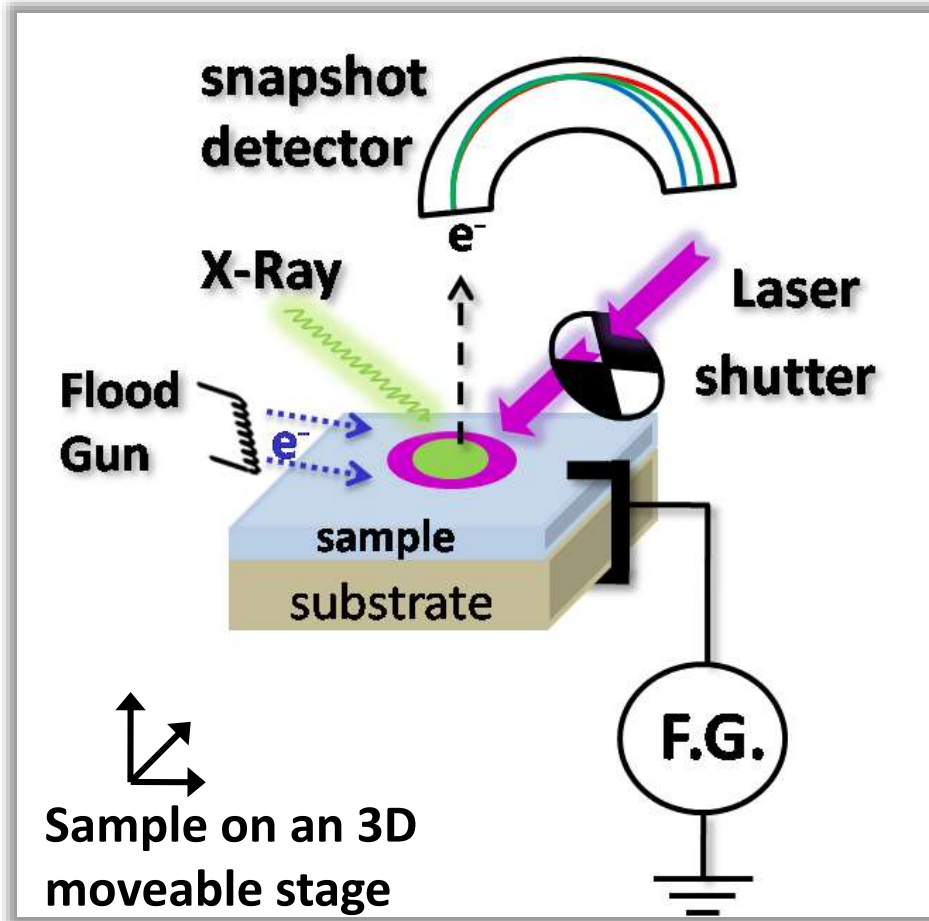
## Cracking Software



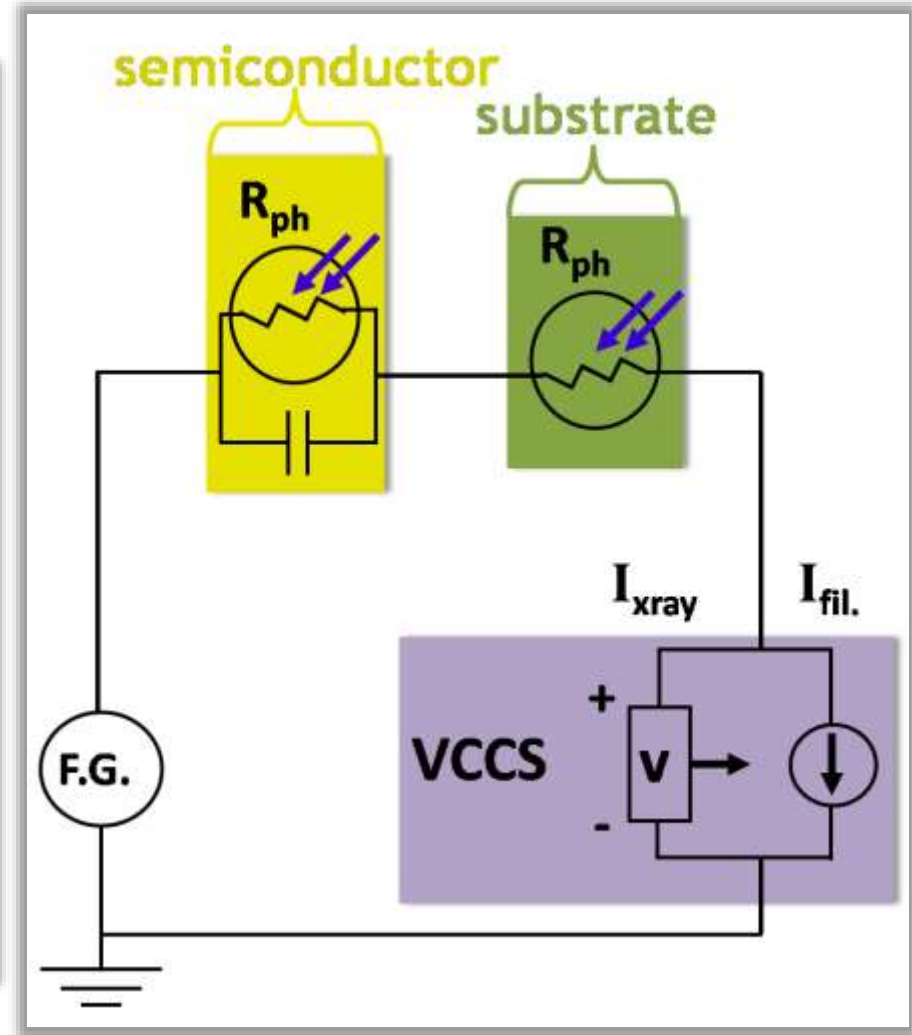
## Specifications:

- Monochromatic Al K- $\alpha$  (1486.68 eV) X-ray source
- X-ray spot 400-30  $\mu\text{m}$
- ~100 msec snapshot with an 128 channel detector

# Method:



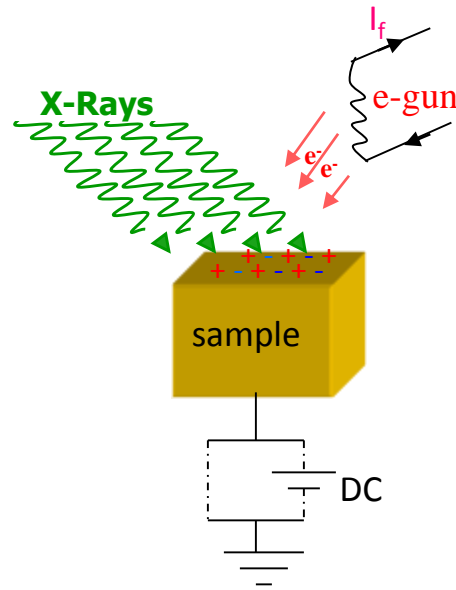
# Model:



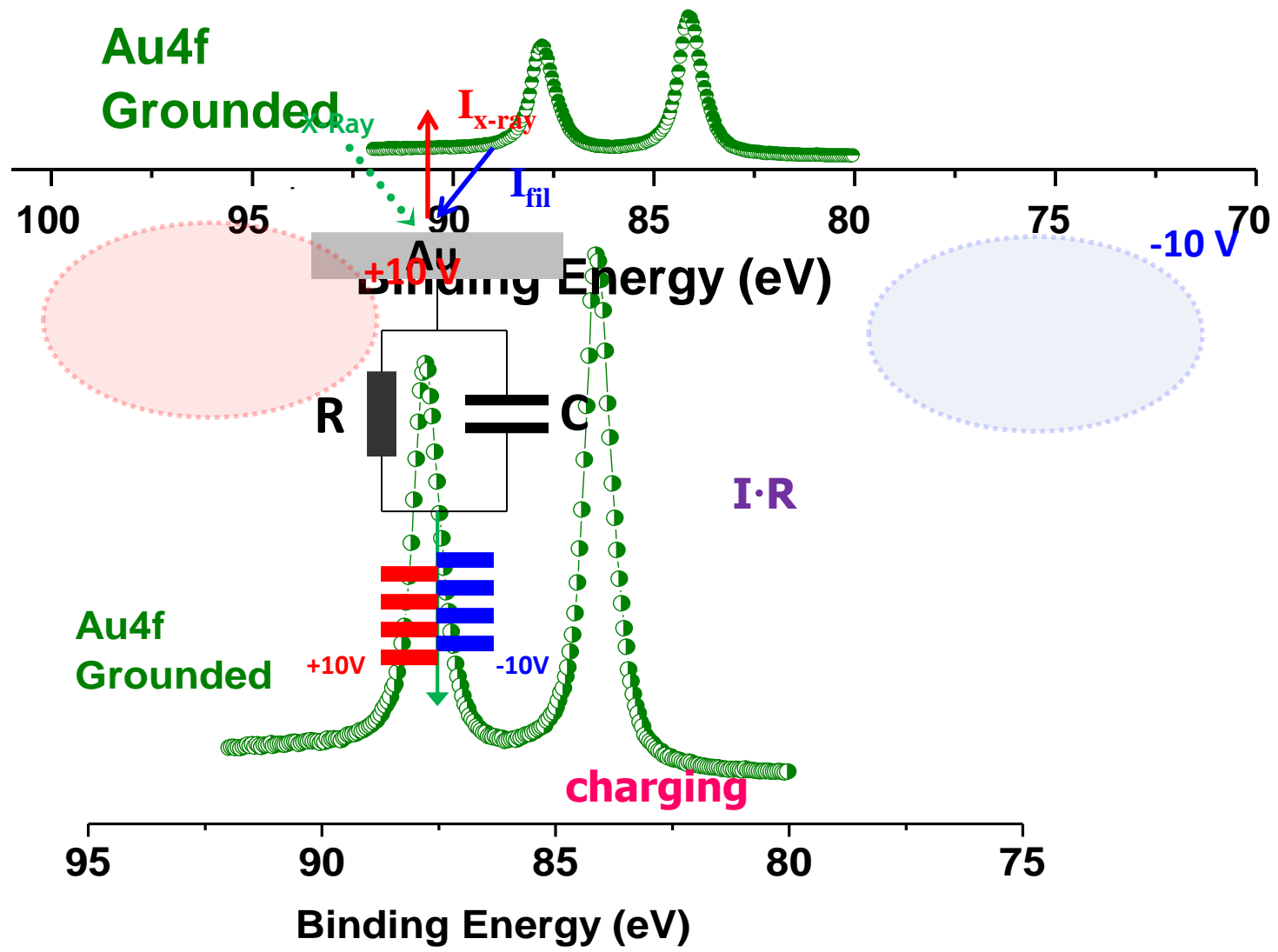
$$BE_{pe} = h\nu_{x-ray} - KE_{pe}$$

# Controlled Surface Charging (DC):

# Surface Charging:



# Controlled Surface Charging (SQW):

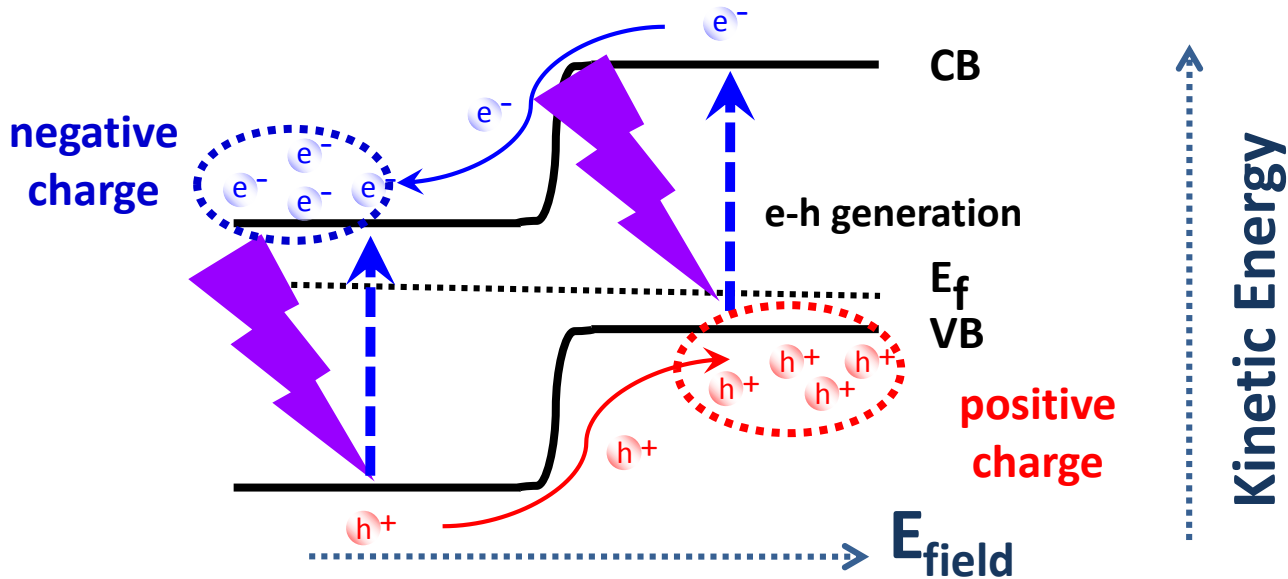
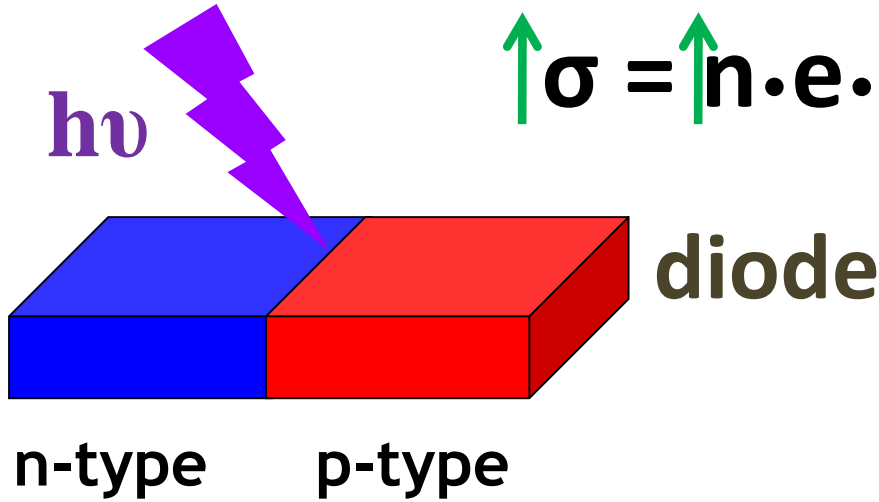


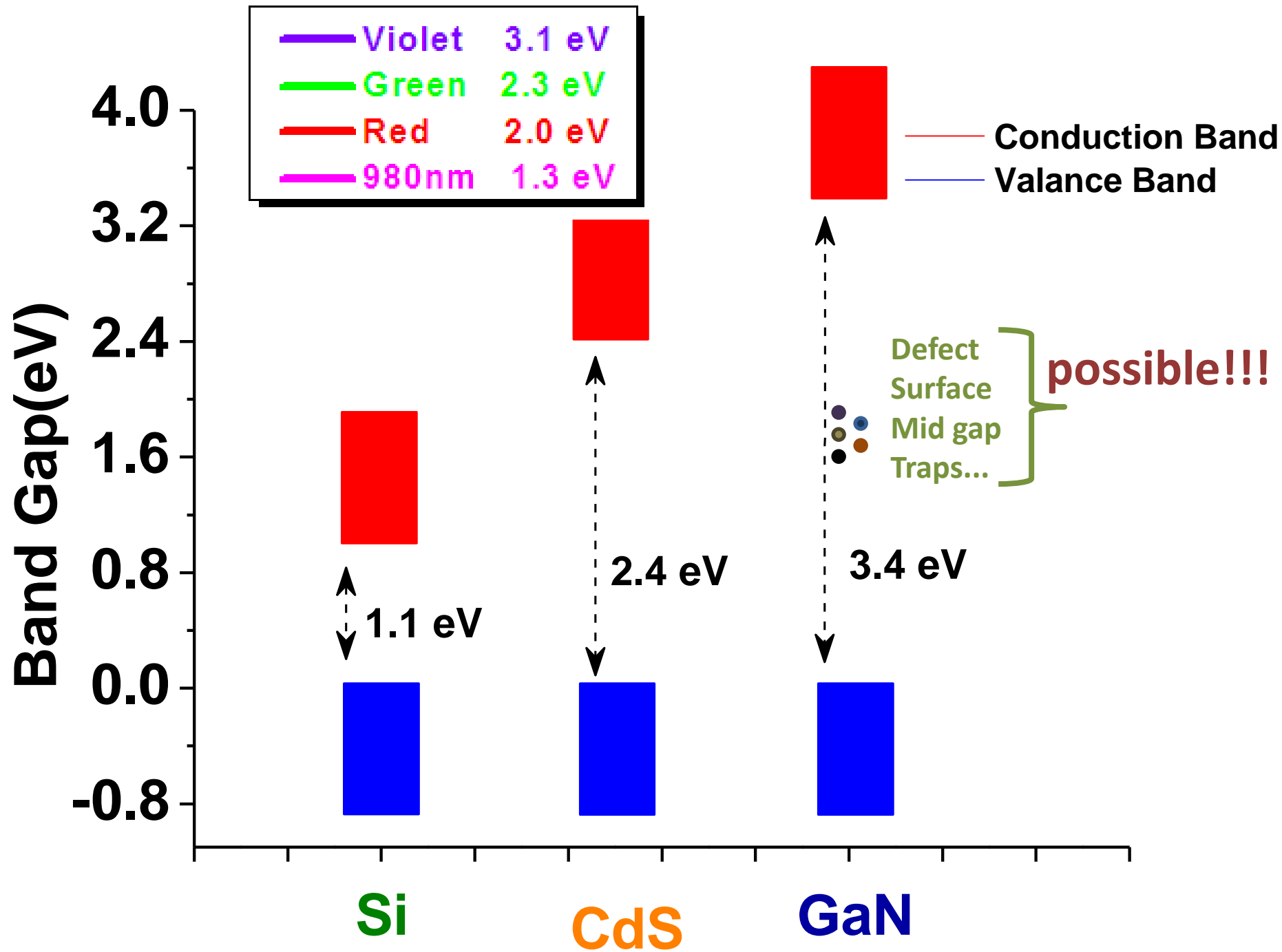


# Photoconductivity:

## Charge Separation

$$\uparrow \sigma = \uparrow n \cdot e \cdot \mu$$



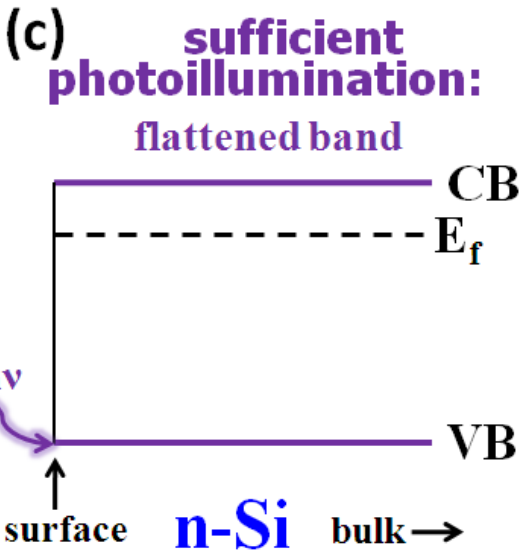
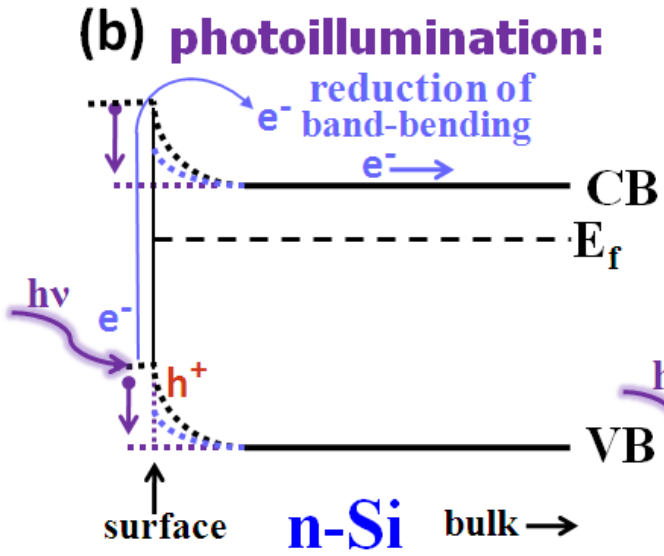
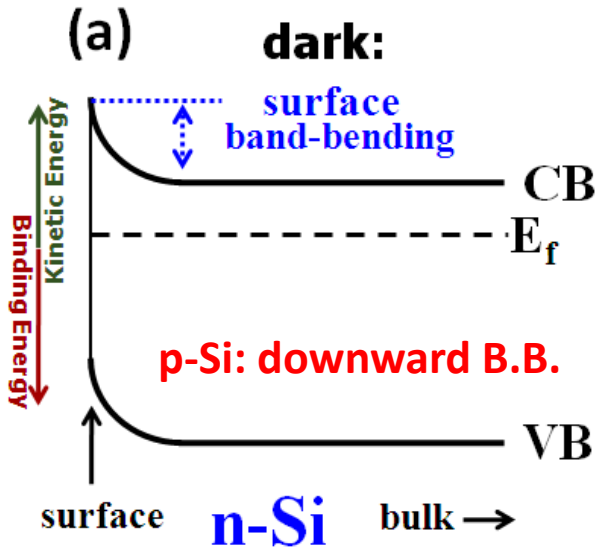
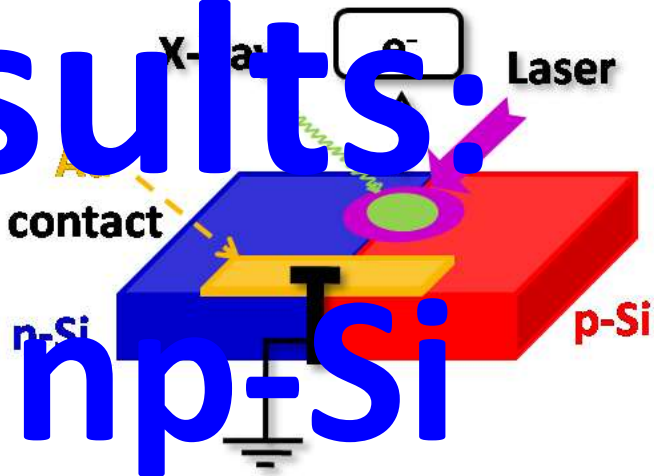


# Band Offset Measurement

## Surface Photo-voltage:

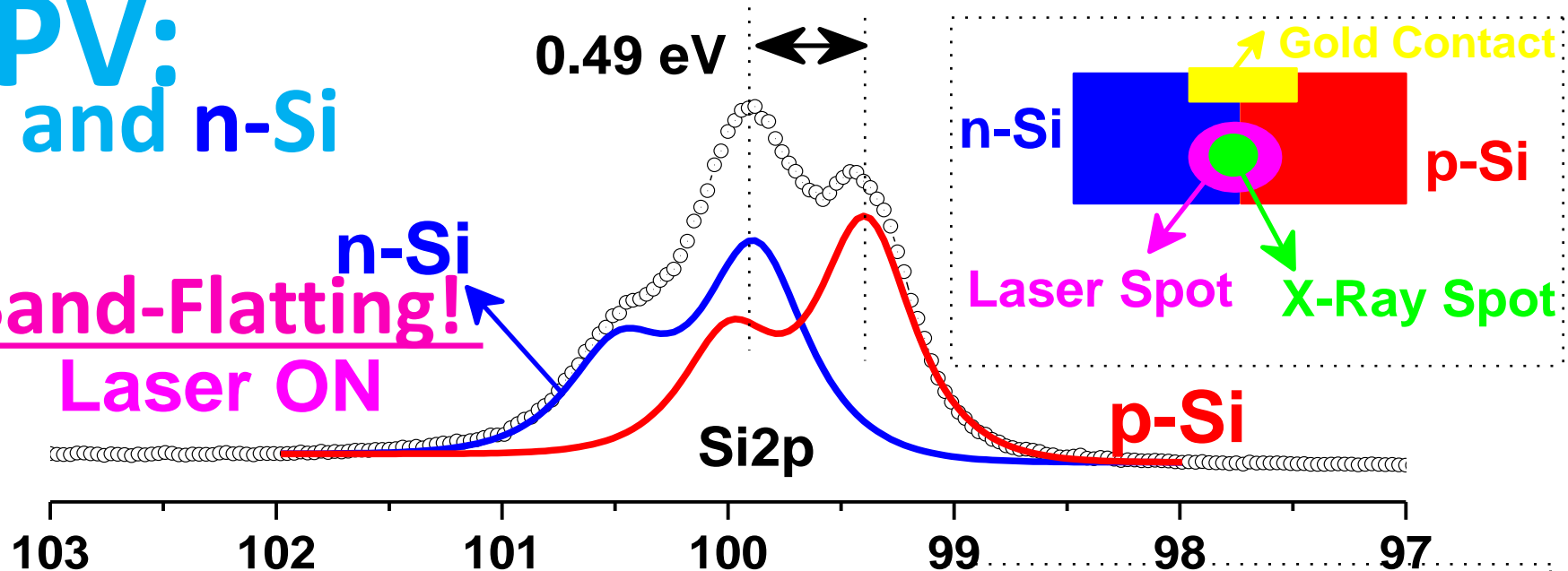
# Results:

# np-Si

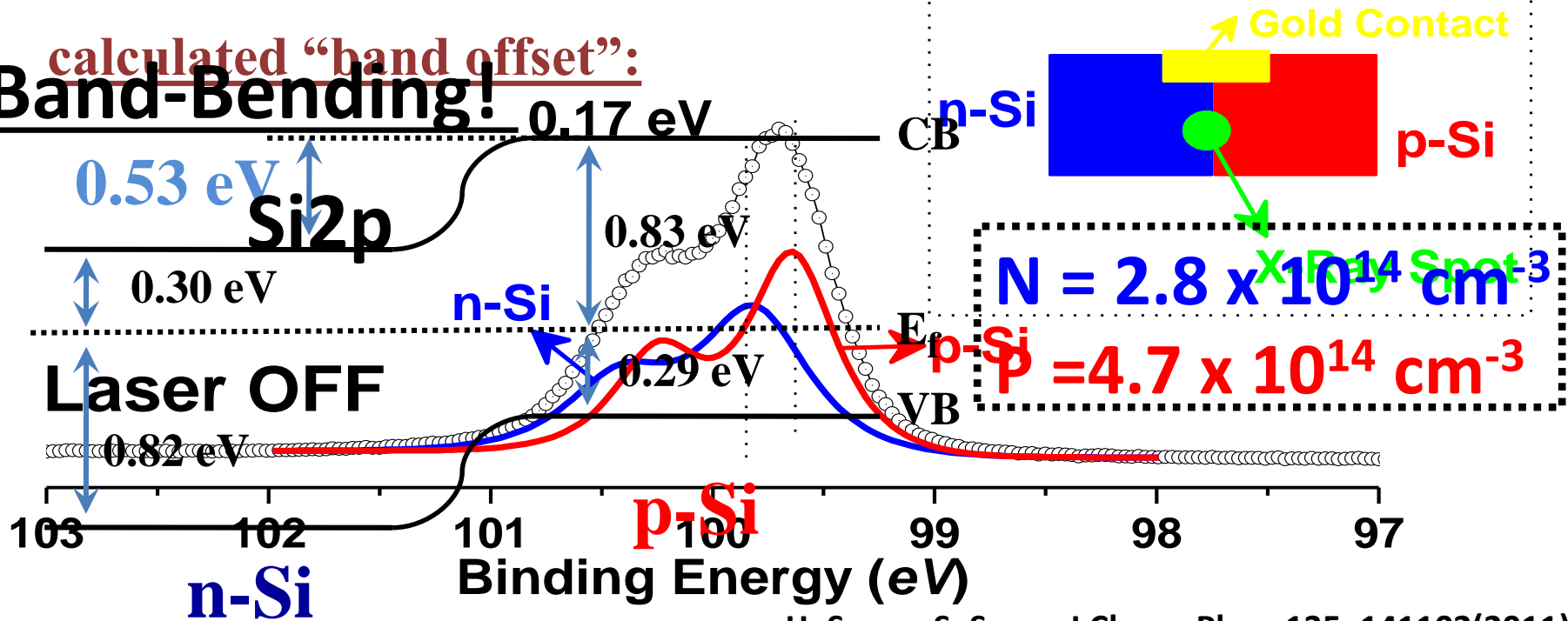


# SPV: p- and n-Si

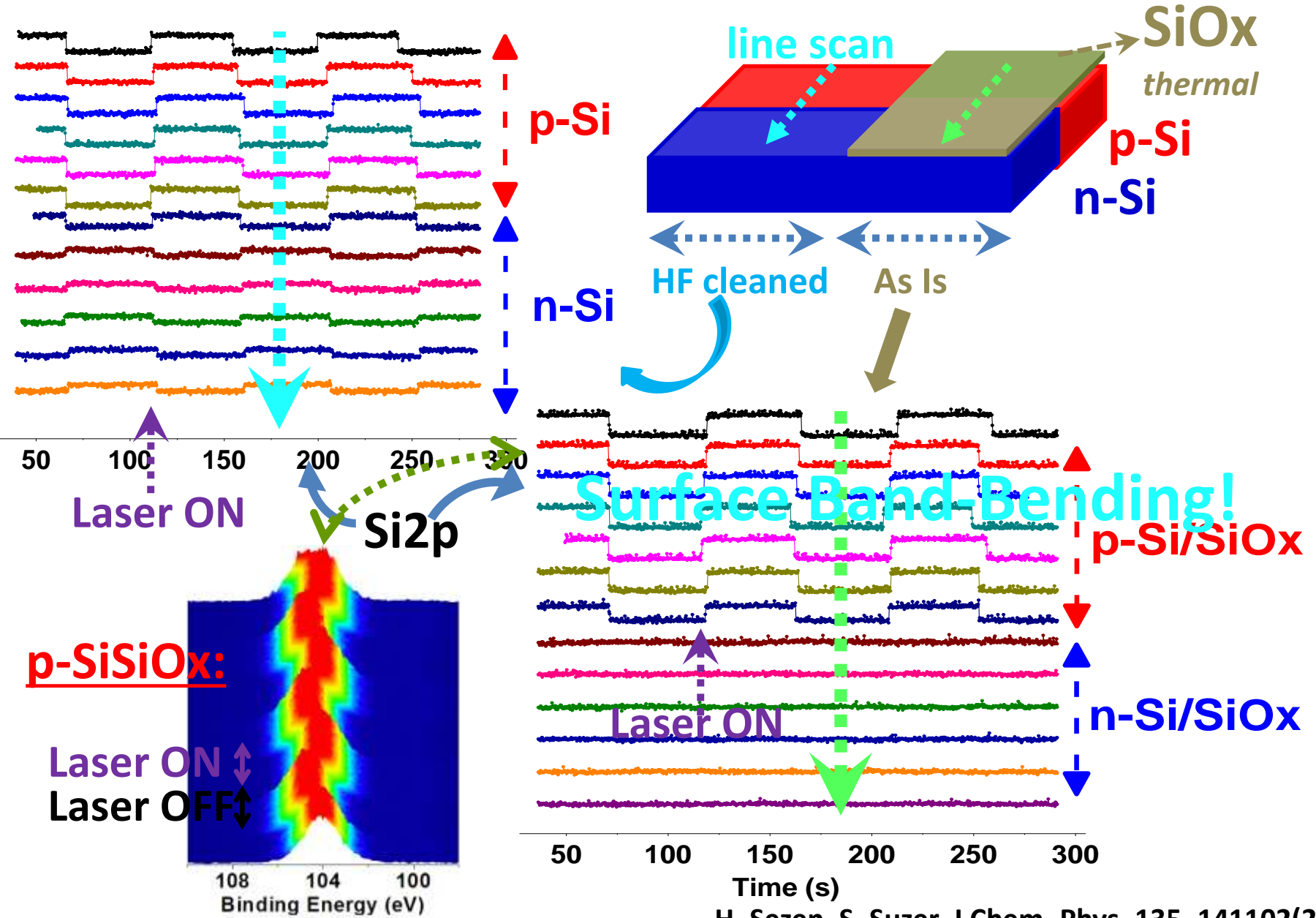
**Band-Flattening!**  
**Laser ON**



**Band-Bending!**  
**Laser OFF**



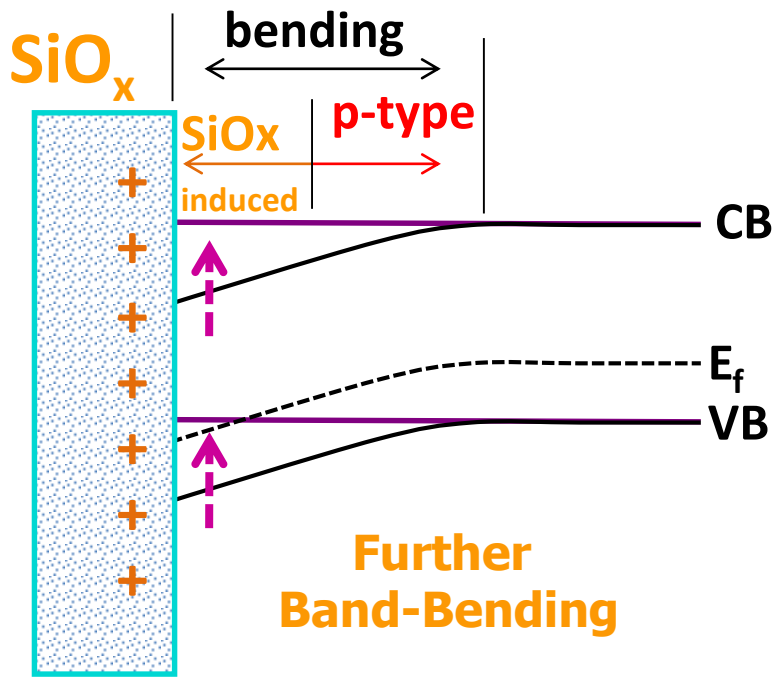
# Band Bending / $p$ - and $n$ -Si of SiO<sub>x</sub> / $p$ - and $n$ -Si



# Band Bending / Inversion of SiOx/p- and n- Si

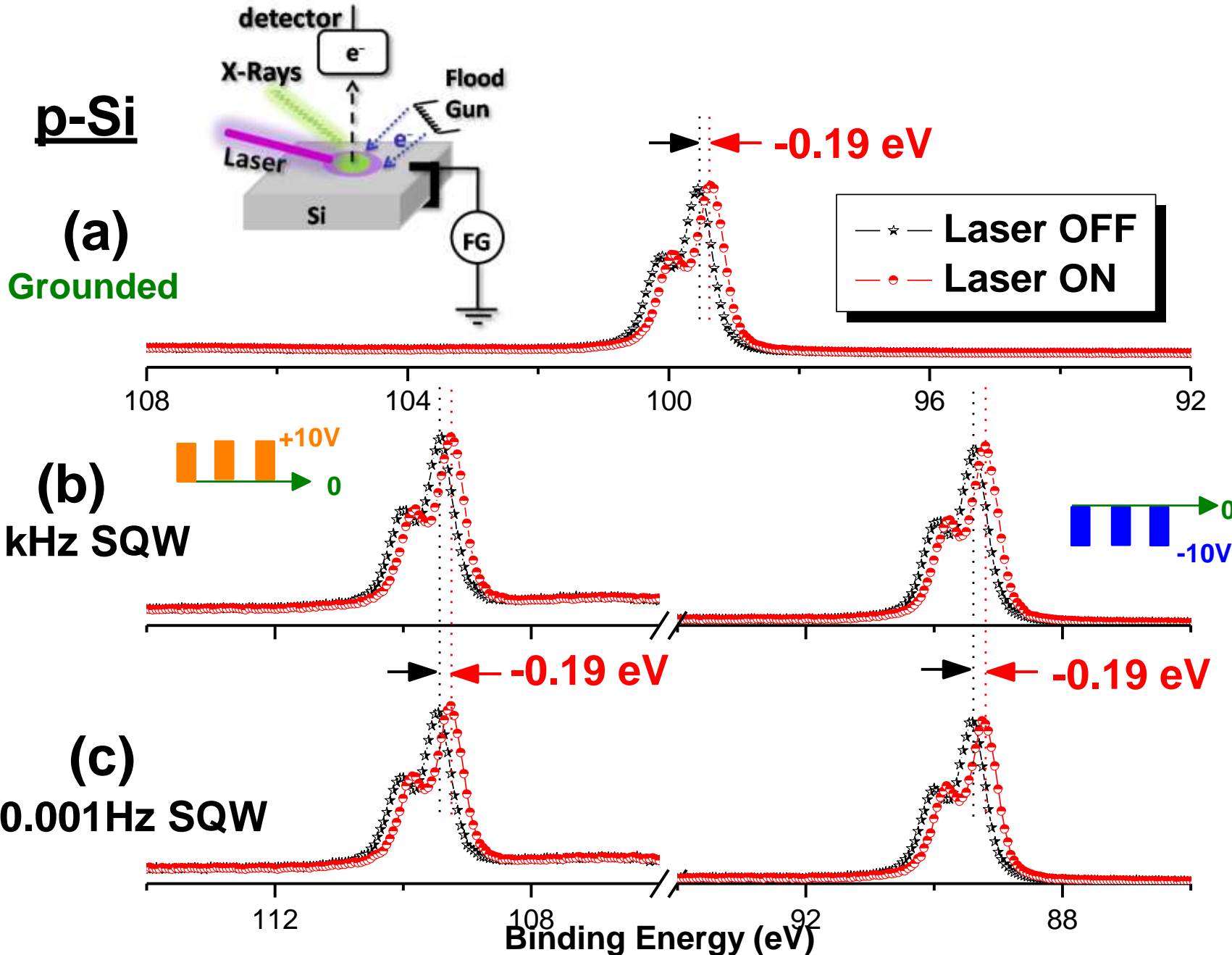
## Possible band diagram:

### SiOx/p-Si

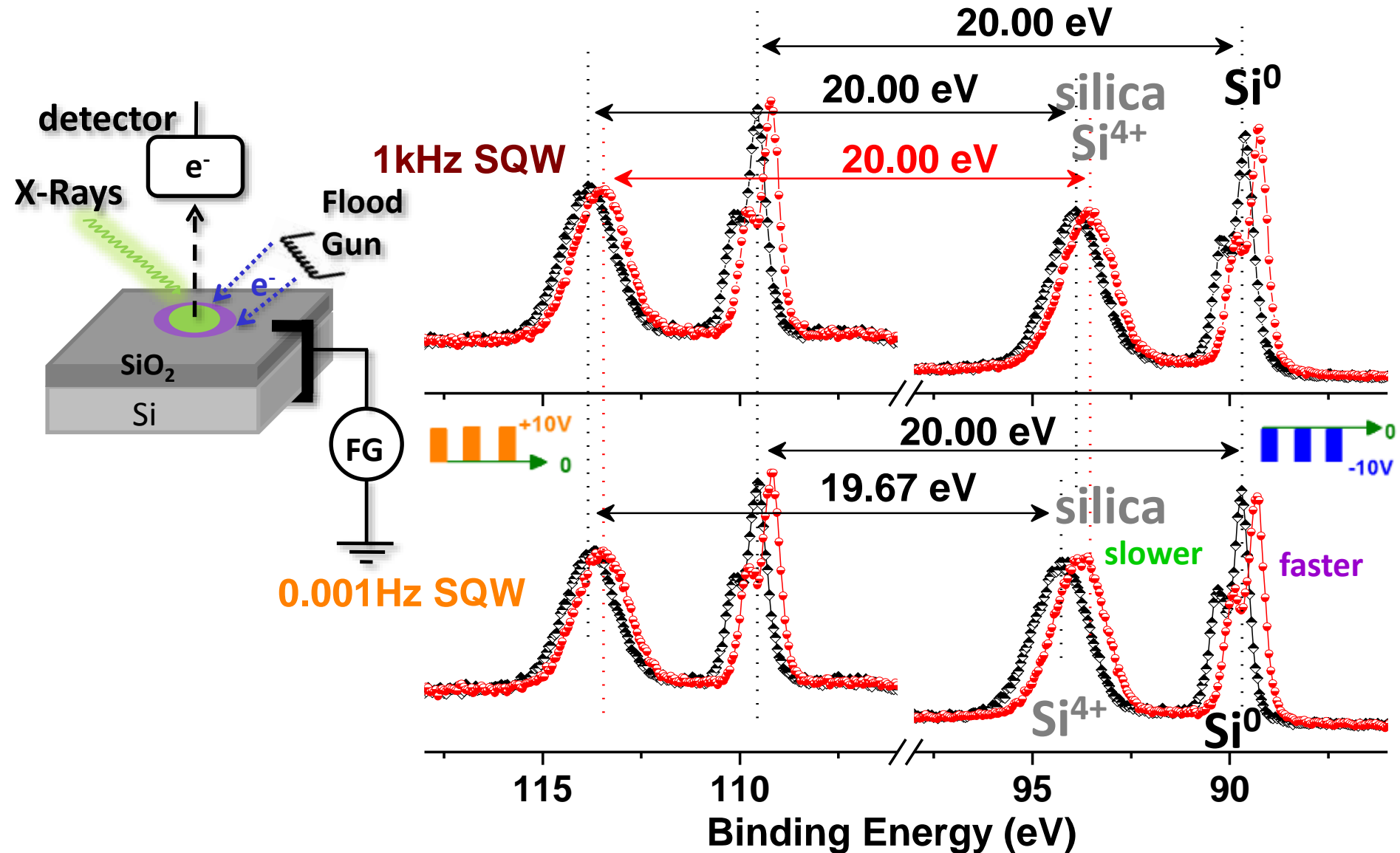


H. Kobayashi et al. Appl. Phys. Lett. 73 933(1998)  
C. Munakata, et al. Jp. Appl. Phys. 23, 1451(1984)  
H. Sezen, S. Suzer, J Chem .Phys. 135, 141102(2011)

# Photo-Dynamic XPS with p-Si:



# Photo-Dynamic XPS with SiO<sub>x</sub>/p-Si:





# SPV:

## CdS

n-type shift

+0.2eV

## SPV or photoconductivity?

|        |        |
|--------|--------|
| Violet | 3.1 eV |
| Green  | 2.3 eV |
| Red    | 2.0 eV |
| 980nm  | 1.3 eV |

# CdS

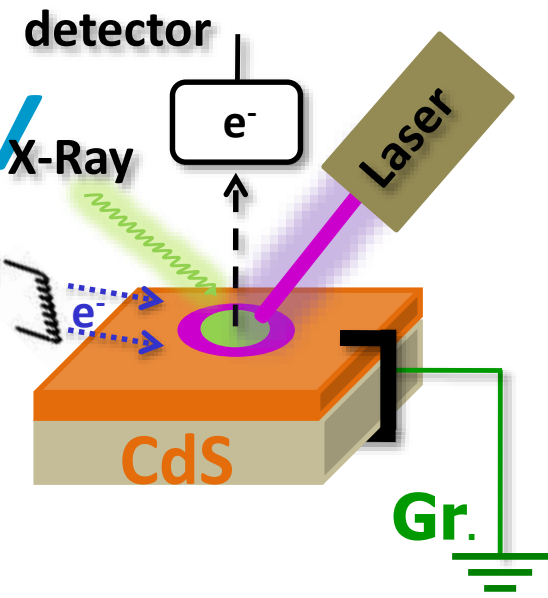
## Band gap 2.4 eV

Laser OFF

Violet Laser ON

Grounded

### Cd3d<sub>5/2</sub>

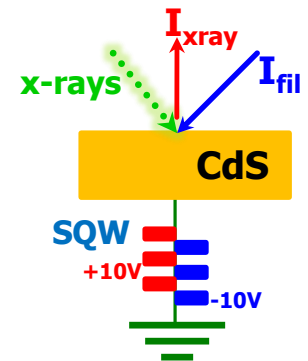
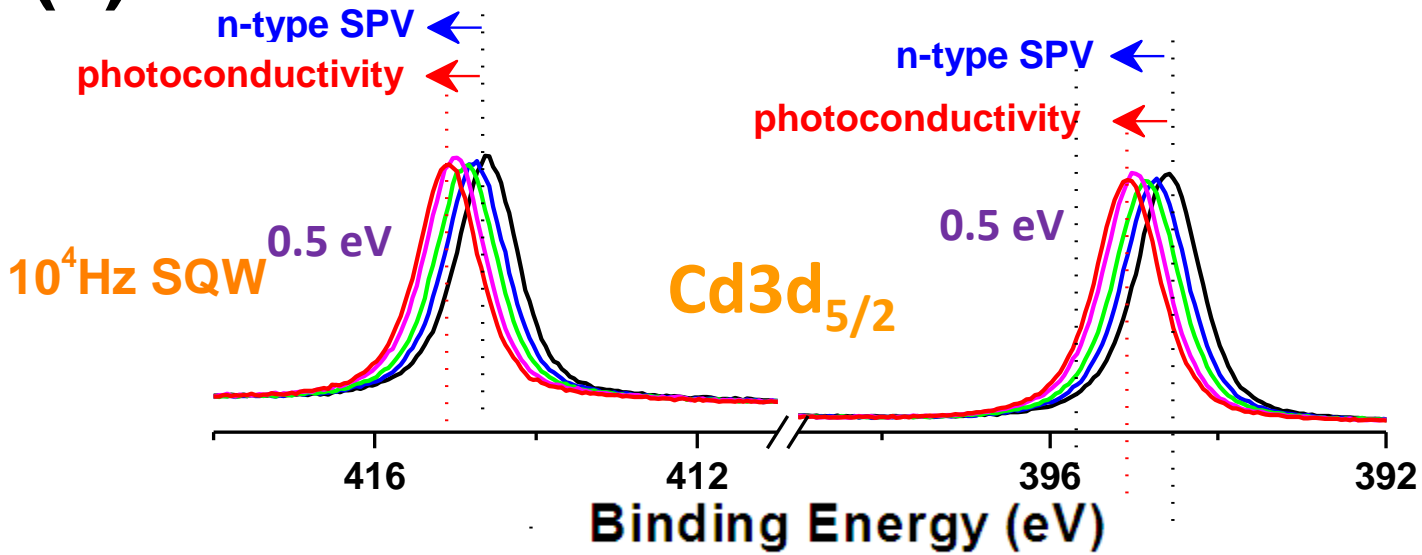


407      406      405      404

Binding Energy (eV)

# Photo-dynamic XPS(SQW):

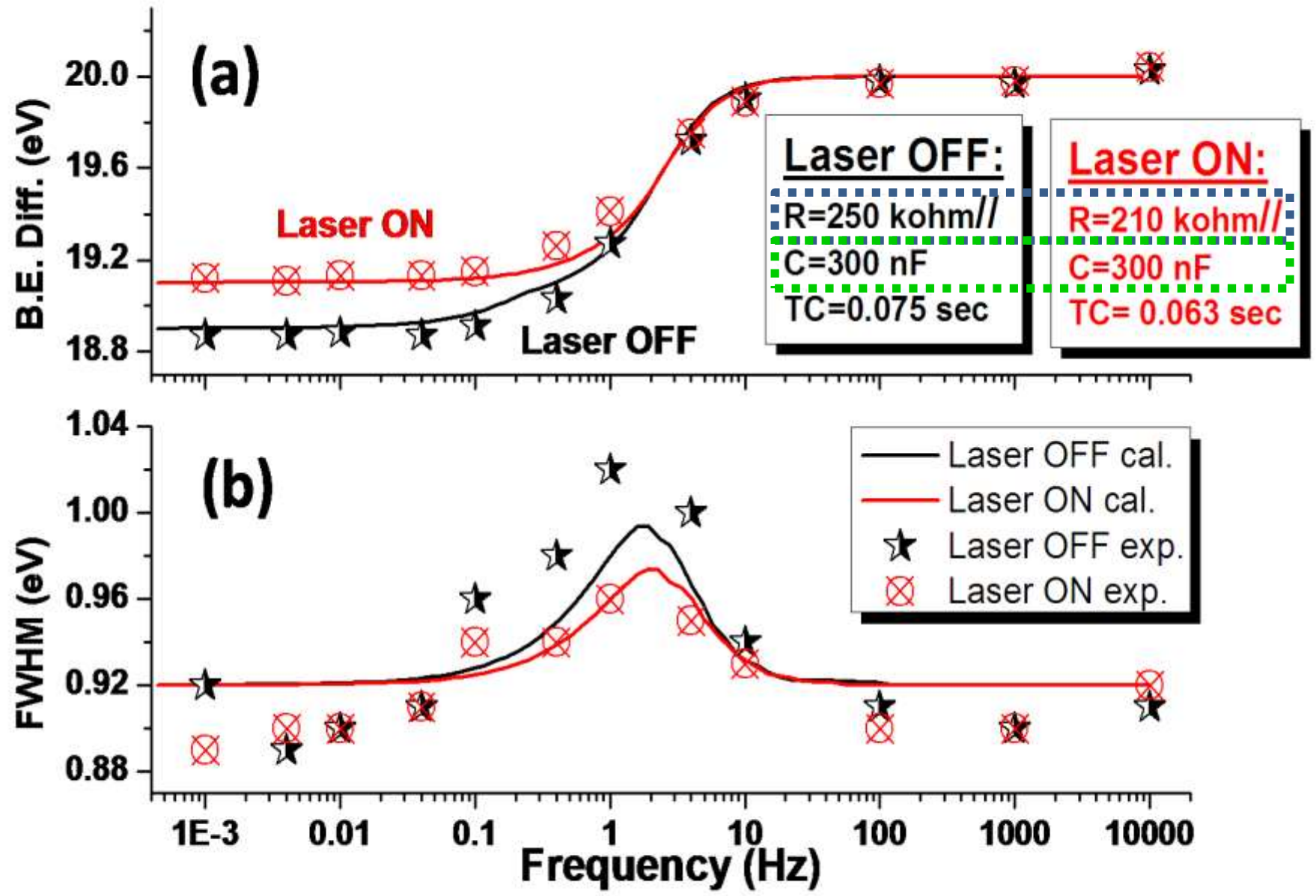
(a)



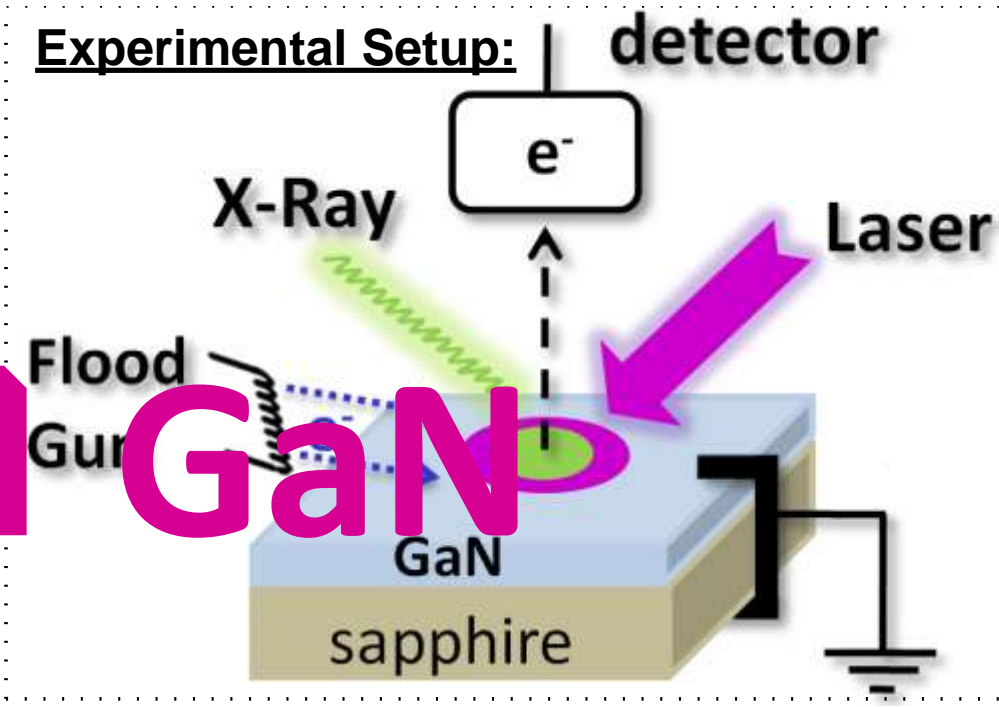
- Laser OFF
- 3.0 OD
- 2.0 OD
- 0.3 OD
- Laser ON

Resolved  
different  
phenomena

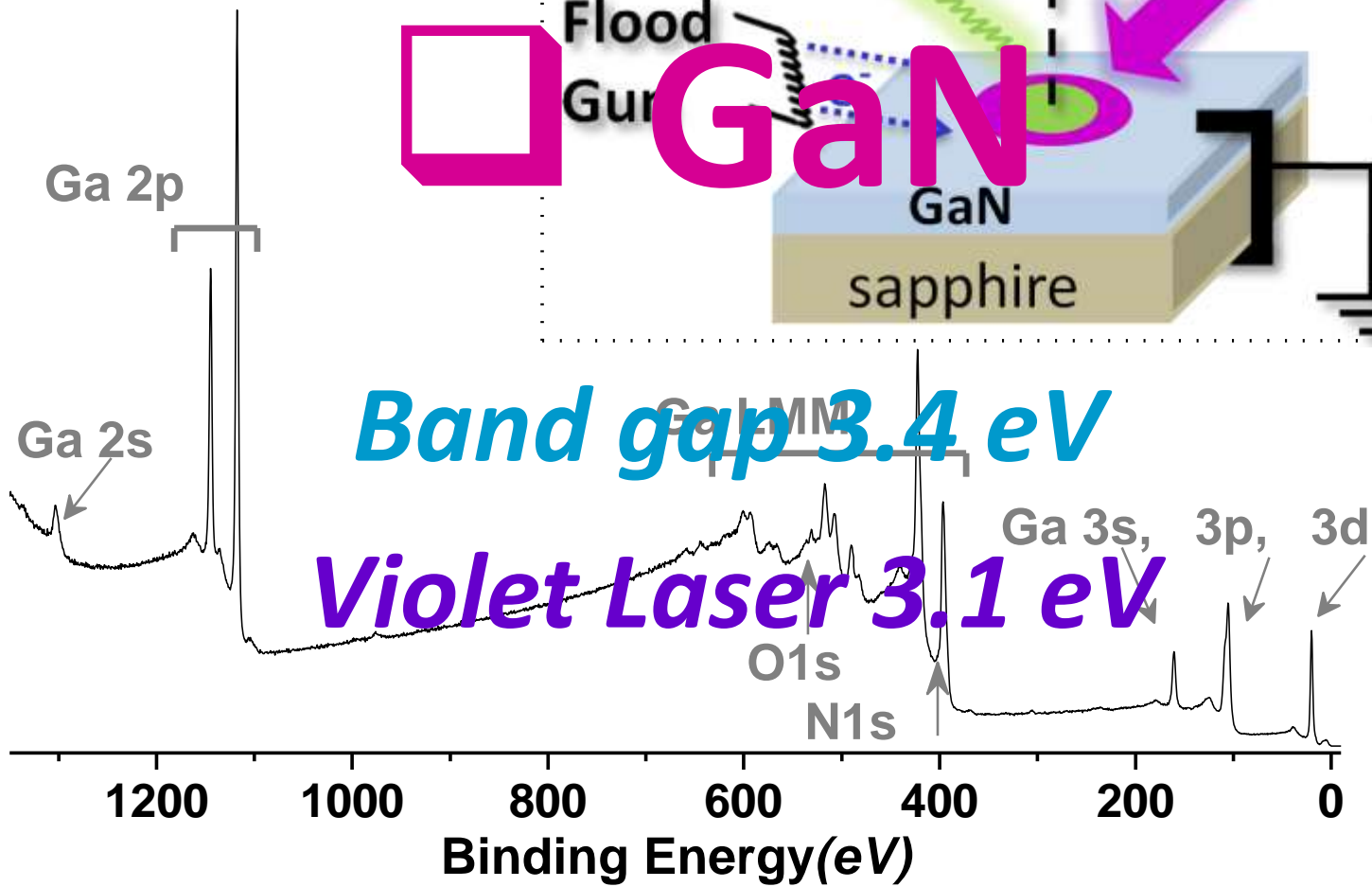
# The electrical parameters of CdS film



**p-GaN**  
Band gap 3.4 eV



**GaN**



# Static SPV :

**GaN**

**n-GaN**

+0.15 eV ←

*Ga2p<sub>3/2</sub>*

**p-GaN**

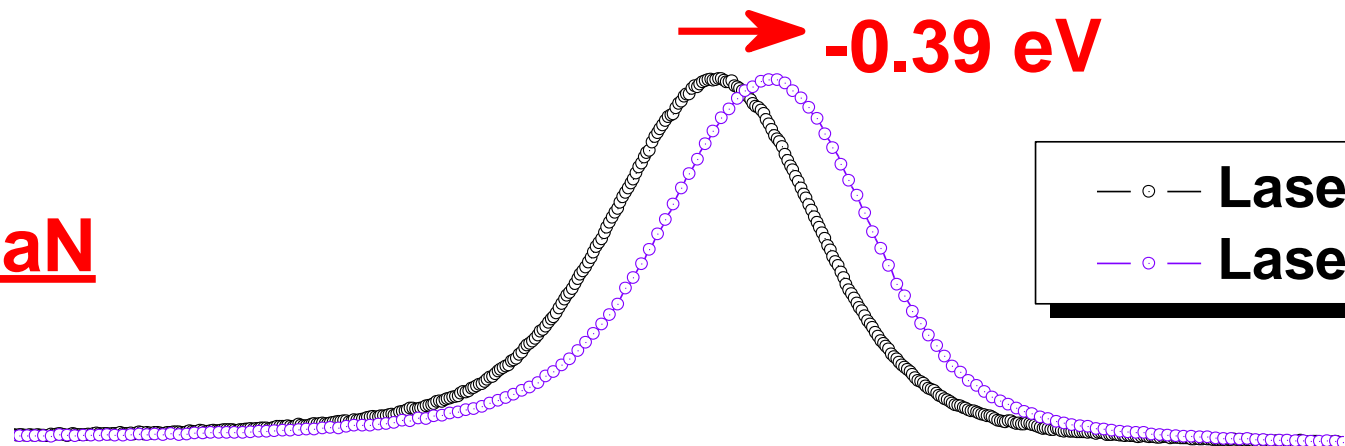
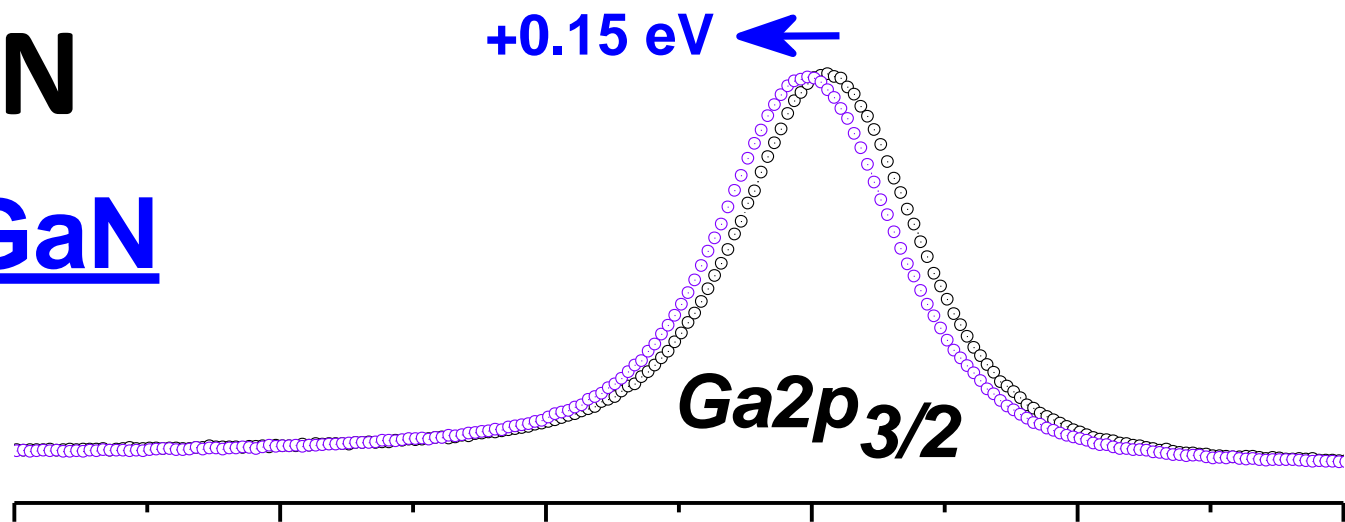
→ -0.39 eV

—○— Laser OFF  
—○— Laser ON

1124      1122      1120      1118      1116      1114

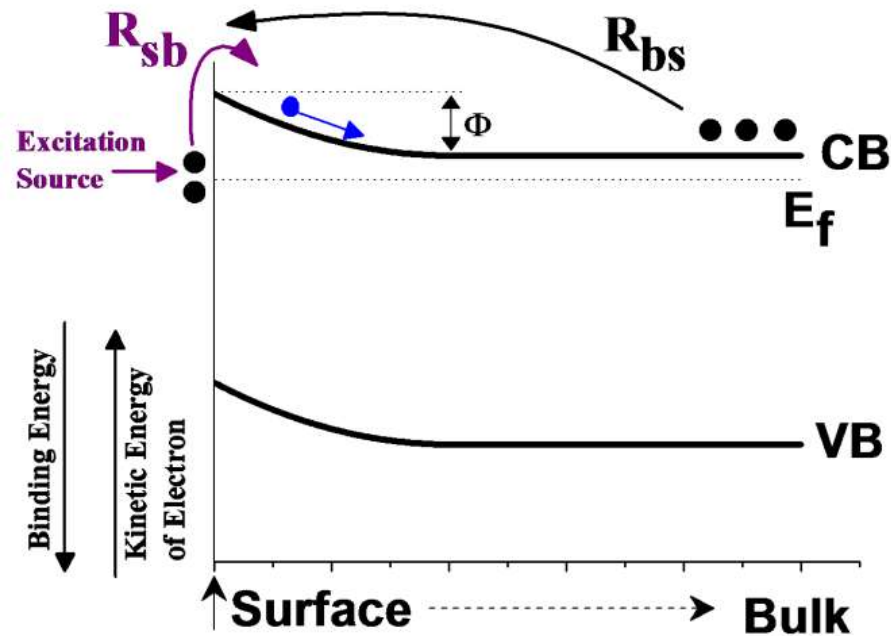
**Binding Energy(eV)**

H. Sezen, E. Ozbay, O. Aktas, S. Suzer Appl. Phys. Lett. 98, 111901(2011)

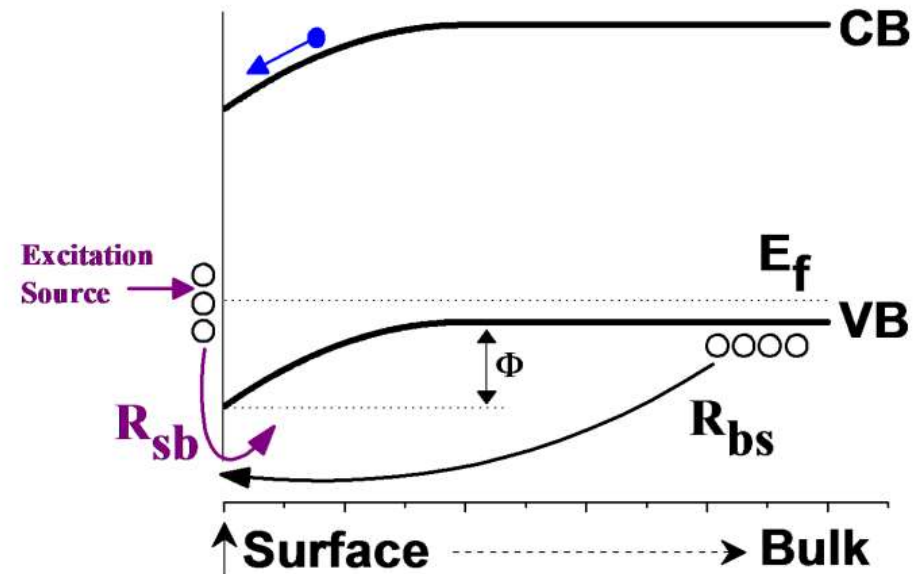


# SPV Mechanisms:

(a) n-GaN



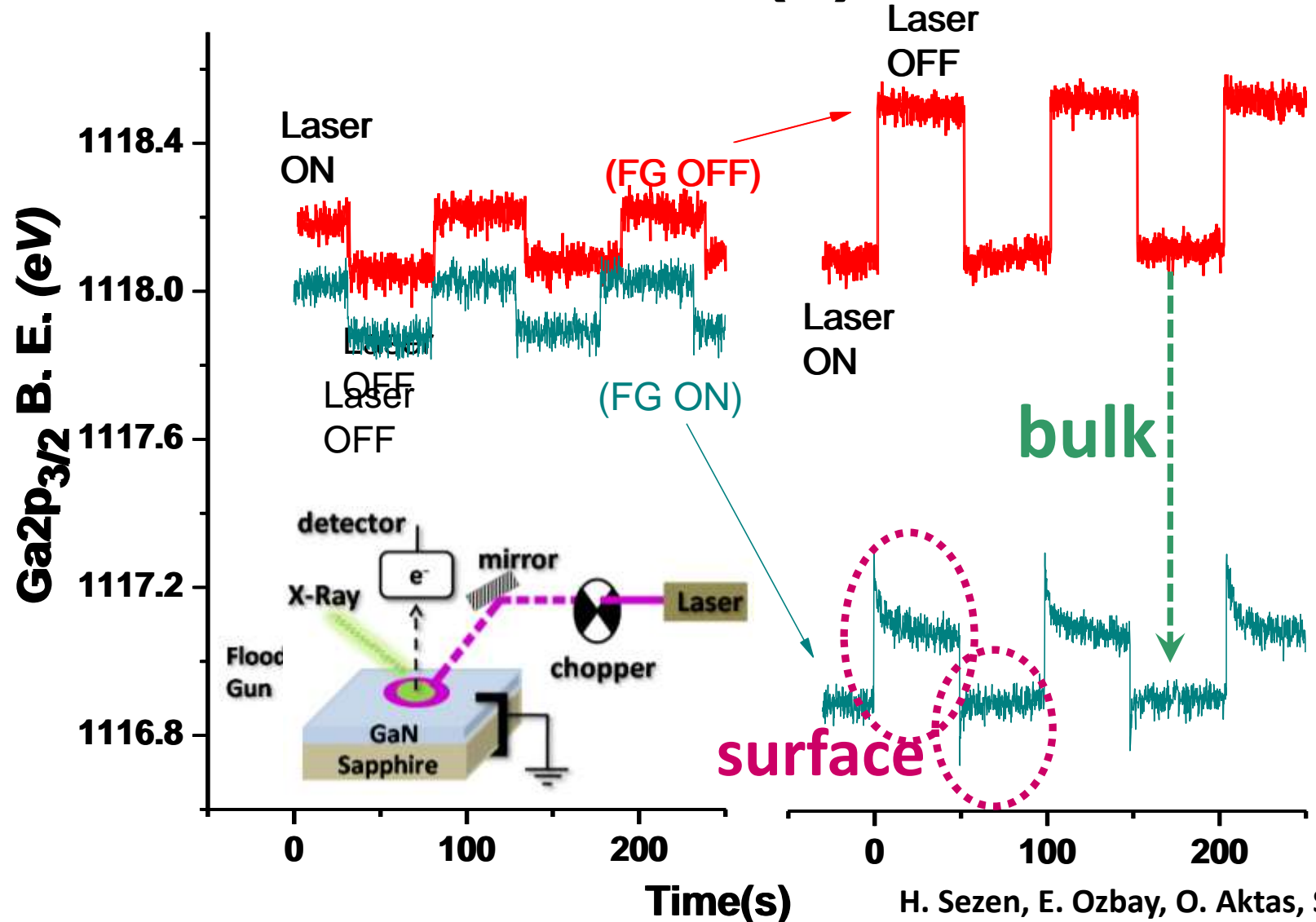
(b) p-GaN

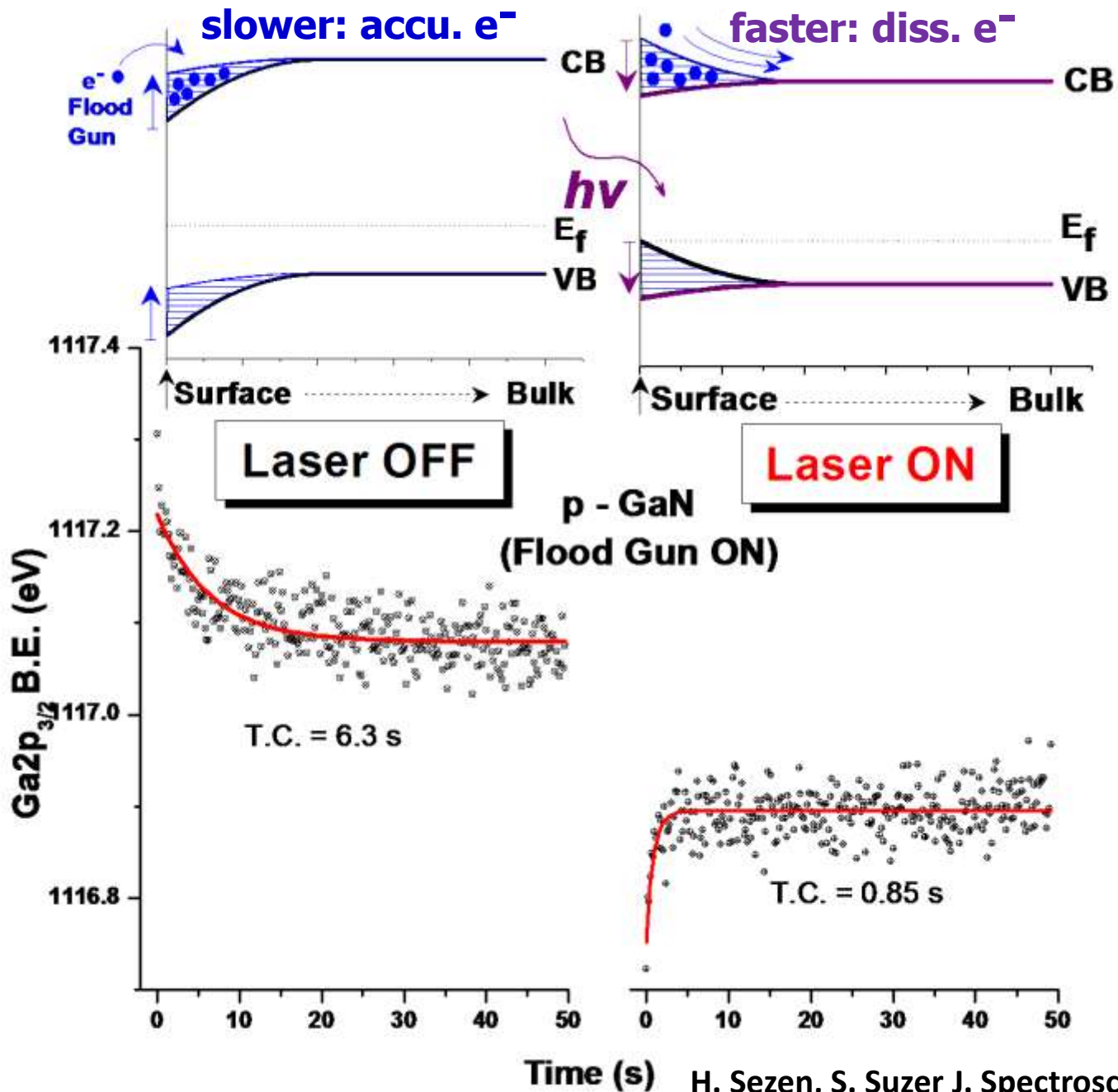


# Dynamic SPV Transients:

**(a) n-GaN**

**(b) p-GaN**





H. Sezen, S. Suzer J. Spectrosc. Dyn. 2, 3(2012)

H. Sezen, E. Ozbay, O. Aktas, S. Suzer Appl. Phys. Lett. 98, 111901(2011)





# Conclusions

## “Photo “Dynamic” XPS”

rest of the world **but we:** **but we:**  
 $BE_{ne} = h\nu - BE_{x\text{-ray}}$   $BE_{ne} = h\nu - K_{\text{photo}}$   $BE_{ne} = h\nu - K_{\text{photo}} - e\phi_{\text{work}}$   $BE_{ne} = h\nu - K_{\text{photo}} - e\phi_{\text{work}} - e\phi_{\text{sc}}$   $BE_{ne} = h\nu - K_{\text{photo}} - e\phi_{\text{work}} - e\phi_{\text{sc}} - e\phi_{\text{spv}}$  ...

Thin Solid Films 534 (2013) 1–11



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Thin Solid Films

journal homepage: [www.elsevier.com/locate/tsf](http://www.elsevier.com/locate/tsf)



Critical review

XPS for chemical- and charge-sensitive analyses

Hikmet Sezen, Sefik Suzer \*

Bilkent University, Chemistry Department, 06800 Ankara, Turkey

**H. Sezen, S. Suzer Thin Solid Films 534, 1(2013)**

**Organic species: E. Yilmaz, H. Sezen, S. Suzer Angew. Chem. Inter. Ed. 51, 5488(2012).**

# Acknowledgement

## Thanks to

**Prof. Şefik Süzer (*advisor*)**

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*Chem., Bilkent U., TR*

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*Phys, Bilkent U., TR*

**Prof. Ekmel Özbay**

*Phys, Bilkent U., TR*

**Prof. Mehmet Erbudak**

*Phys, ETHZ, CH*

**Prof. Oğuz Gülseren**

*Phys, Bilkent U., TR*

**Asst. Prof. Ömer İlday**

*Phys, Bilkent U., TR*

**Asst. Prof. Özgür Aktaş**

*EE Eng., Bilkent U., TR*

**Asst. Prof. Aykutlu Dana**

*Phys, Bilkent U., TR*

**Asst. Prof. Özgür Birer**

*Chem., Koç U., TR*

**Dr. Tim Nunney and crew of the Surface Analysis**

*Department of Thermofisher, UK*

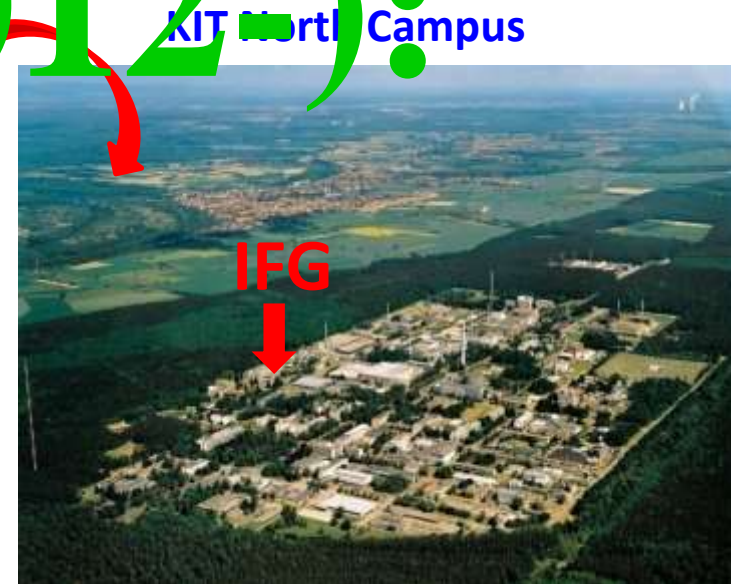
# Probing Shallow trapped electrons of $\text{TiO}_2$ with UHV-IRRAS

Hikmet Sezen, Carsten Natzeck, Alexei Nefedov, Christof Wöll

Institute of Functional Interfaces (IFG)

Chemistry of Oxydic and Organic Interfaces

## Part II (2012-):



# THEO

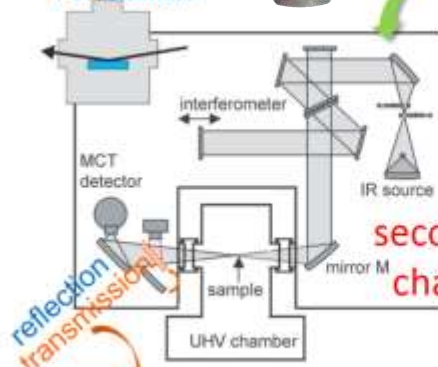
XPS, UPS, AES Analyzer  
**VG Scienta R4000**

UHV-IRRAS and -FTIR  
**Bruker Vertex 80v**

Cryostat for  
LHe cooling

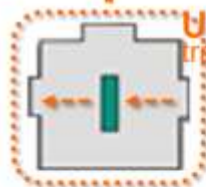
Each sample receiving station has  
LN<sub>2</sub> cooling opportunity and the  
IR chamber has also LHe cooling.

UHV-IRRAS  
reflection



second prep  
chamber

UHV-FTIR  
transmission

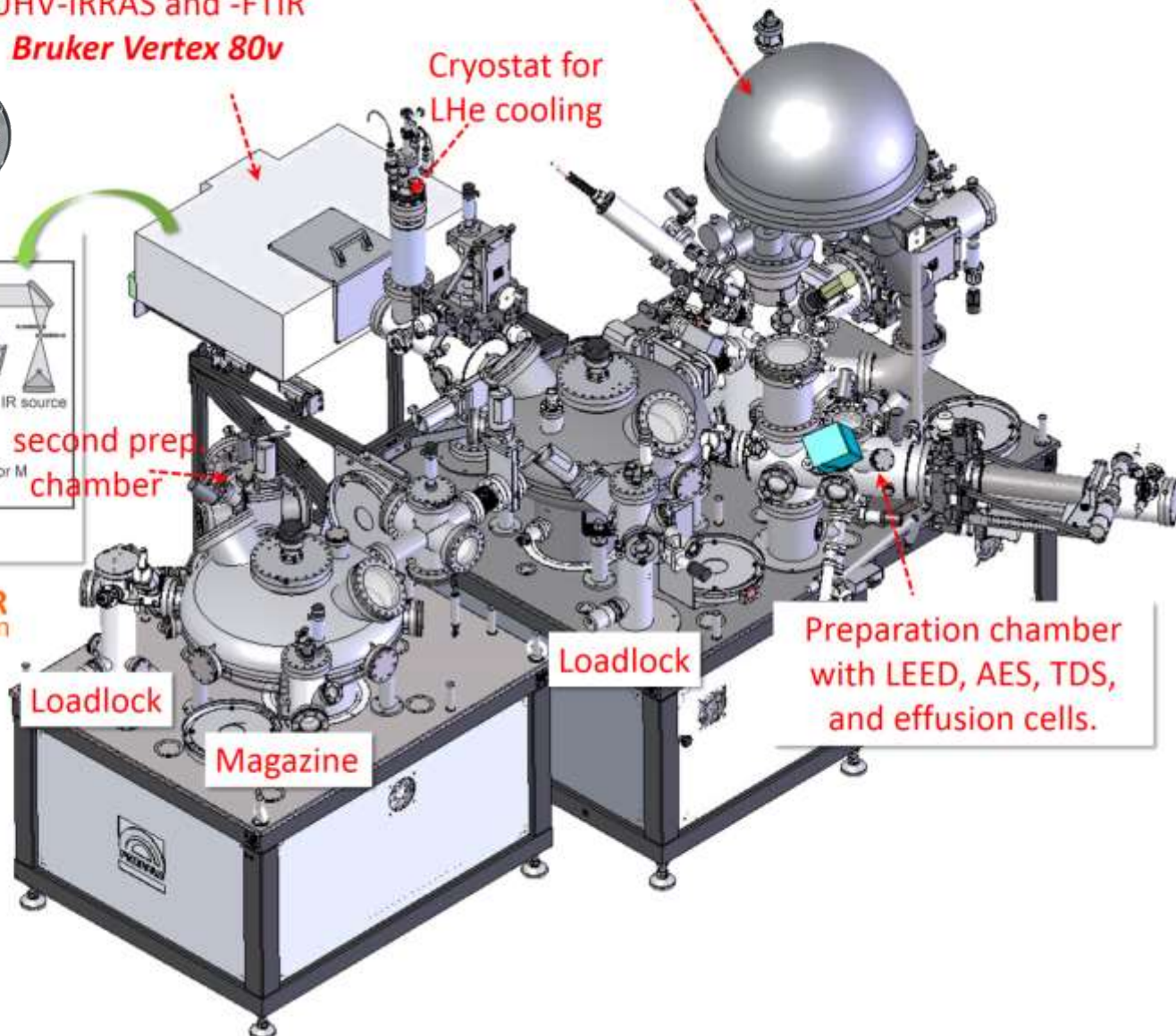


Loadlock

Magazine

Loadlock

Preparation chamber  
with LEED, AES, TDS,  
and effusion cells.

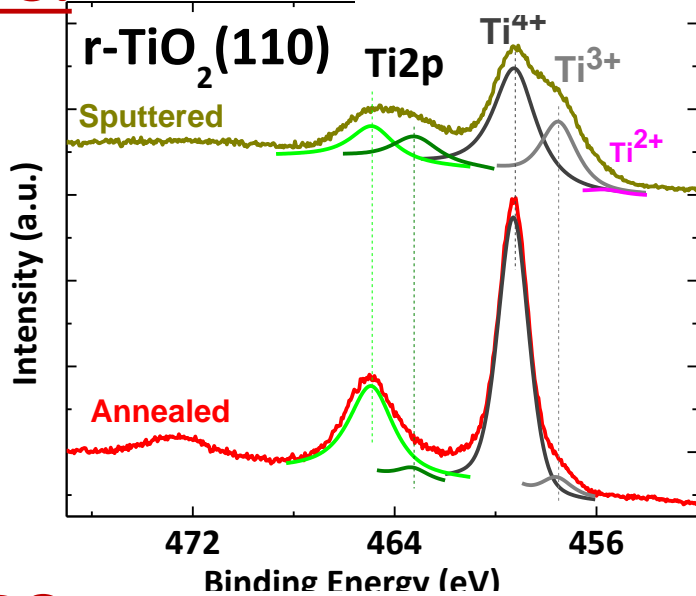


# TiO<sub>2</sub> single crystal:

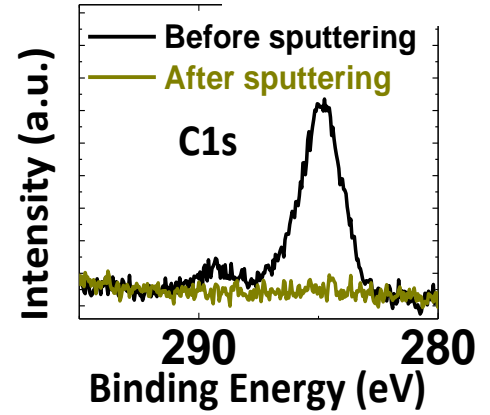
Sample Preparation: >

**XPS:**

oxidation state ✓



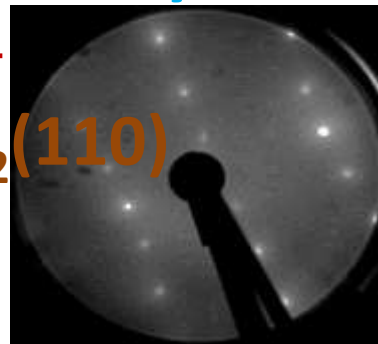
cleanness ✓



surface crystal structure ✓

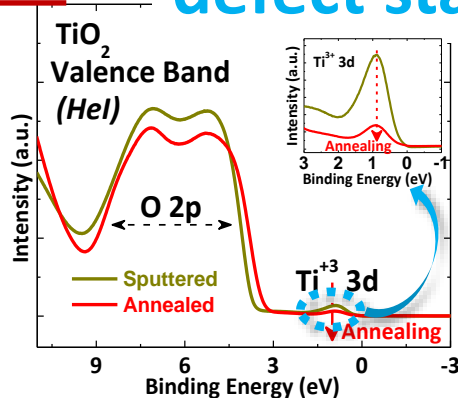
**LEED:**

R-TiO<sub>2</sub>(110)

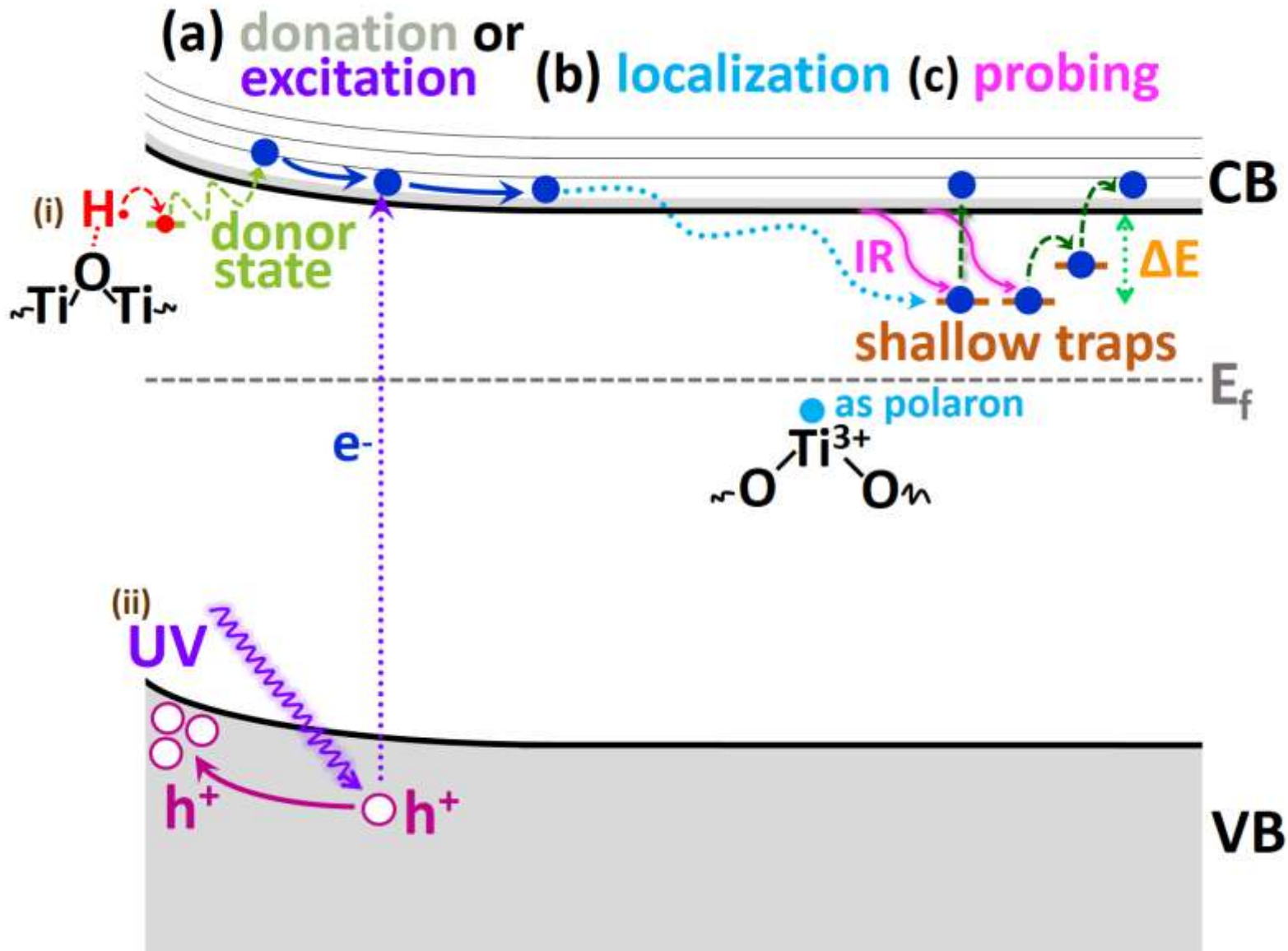


**UPS:**

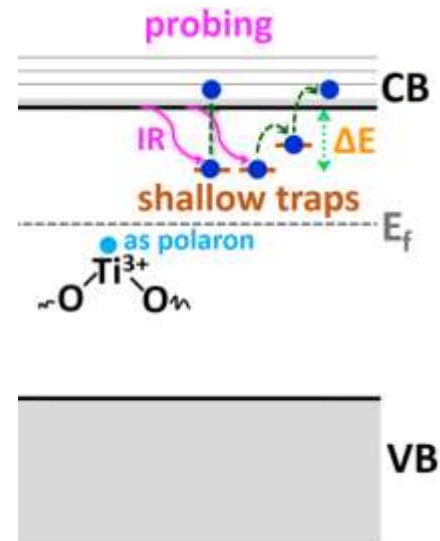
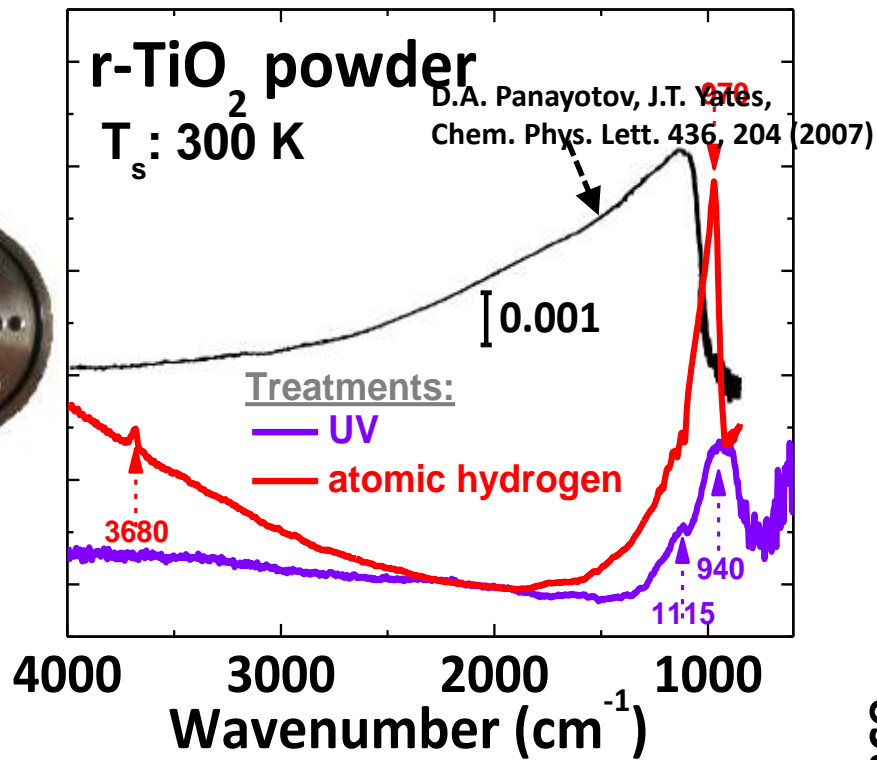
defect state ✓



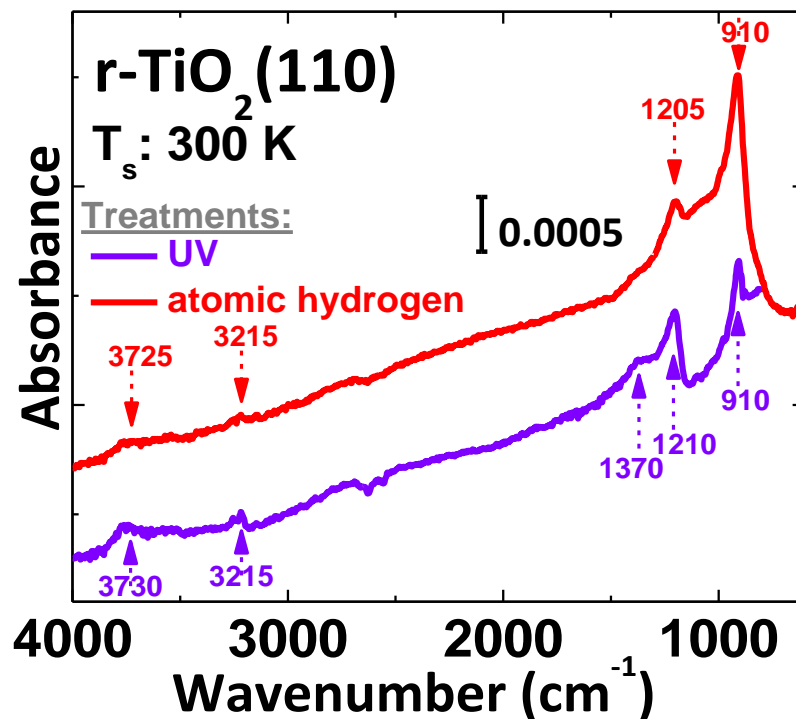
# TiO<sub>2</sub> Band structure: shallow state



# powders:



# single crystal:





***Thank you for your attention!..***