# Role of Surface Chemistry in Photovoltaics

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## Outline

I. Moore's Law for Photovoltaics

II. Energy Bands in Heterojunctions

III. Surface Recombination in Silicon Solar Cells

# Sustainability of Electricity

- Increasing sustainability requires significant PhotoVoltaic generation capacity within a decade
- While PV has realized compound growth rates > 40% for a decade, it presently accounts for <1% of electrical generating capacity
- Can PV reach TeraWatt production capacity in a decade – is there a Moore's Law analog to PV?

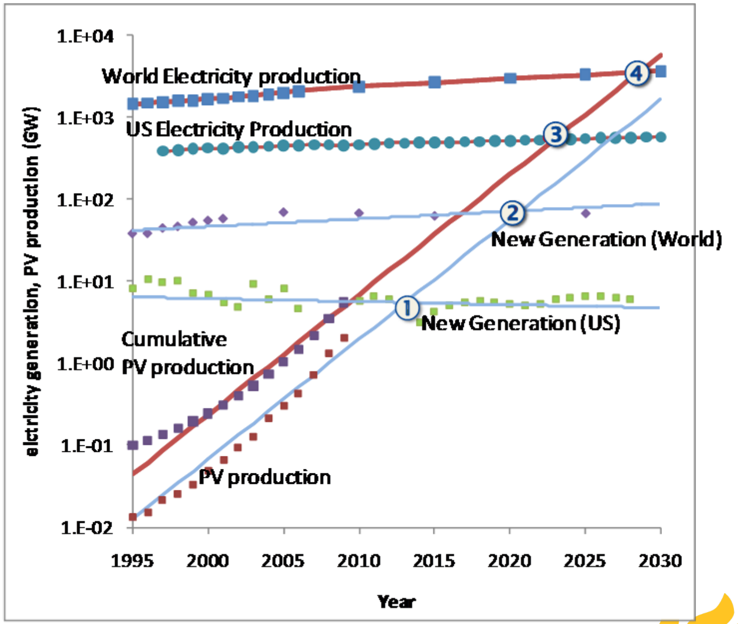
**Example: 40% growth rates**

① All new US electricity needs met by PV – within 5 years

② New world electricity needs met by PV – within about 10 years

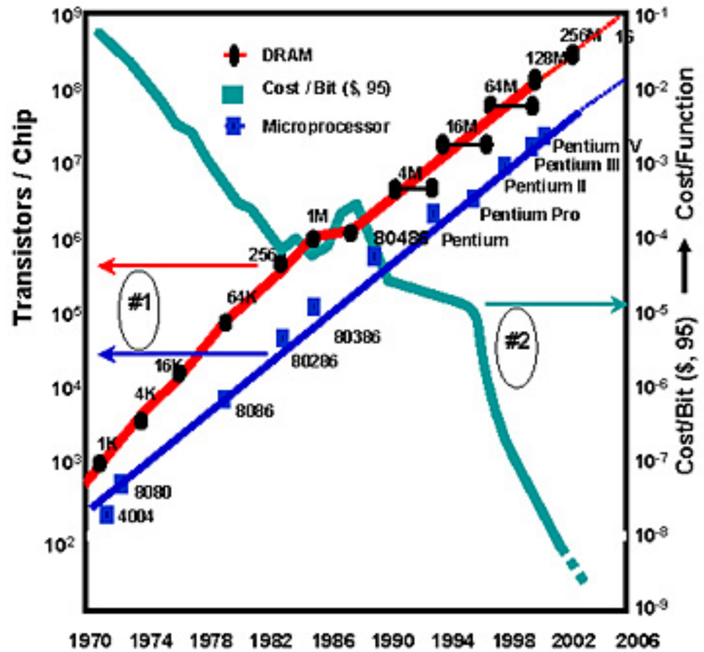
③ US electricity needs met by PV – within 15 years

④ World electricity needs met by PV – within 20 years



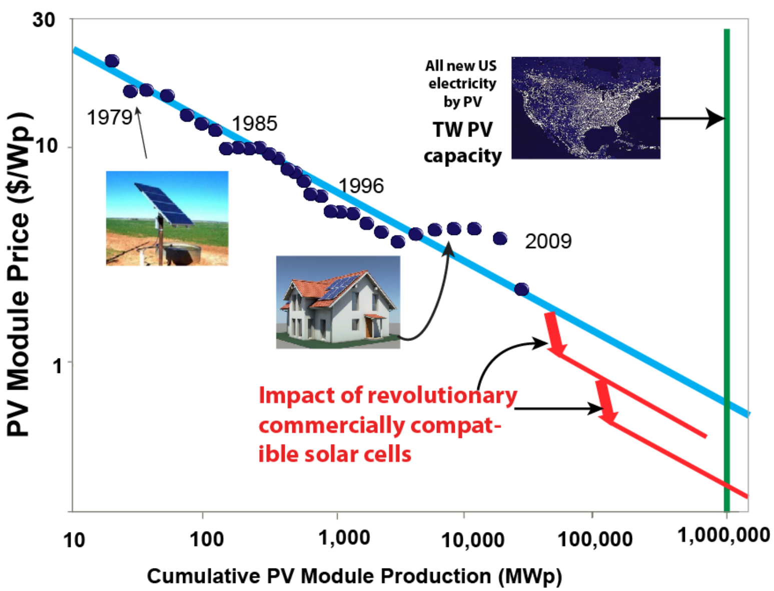
# Moore's Law Analog for PV

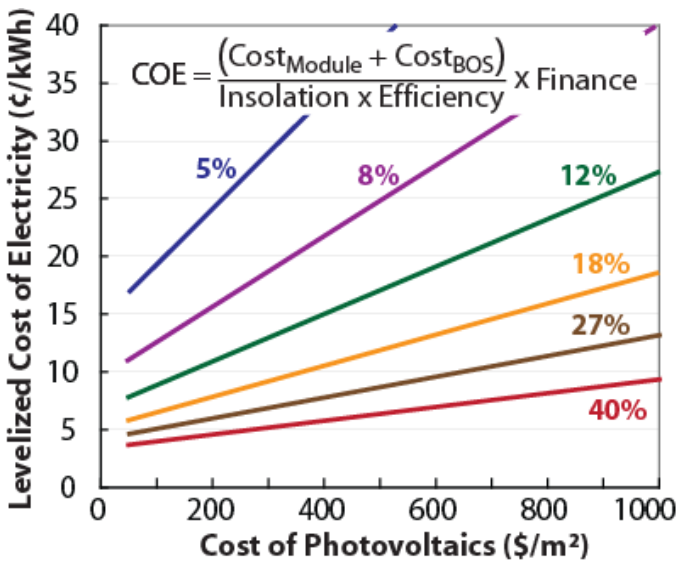
- Integrated circuits have had a transformational impact by increasing performance, reducing costs and integrating electronic circuitry into a wide range of systems, allowing rapid expansion in their use.
- Moore's Law expressed the sustained, rapid growth of transistor.
- Staying on Moore's Law requires focused, integrated projects coupled with scientific and technological innovation driven by a roadmap– e.g., voltage scaling, photolithography, high k-dielectrics, etc.



# QESST Approach

- Improve efficiency, manufacturability and $/kWh for silicon, thin film, and tandem solar cells
  - **Efficiency in a manufacturable process is key metric**
- Develop advanced approaches which increase efficiency and are compatible with existing production
- Integrate with other components to increase functionality, performance and enable new applications.



# II-VI ZnTe/ZnSe Thin Film Solar Cell Structures & Band Alignment

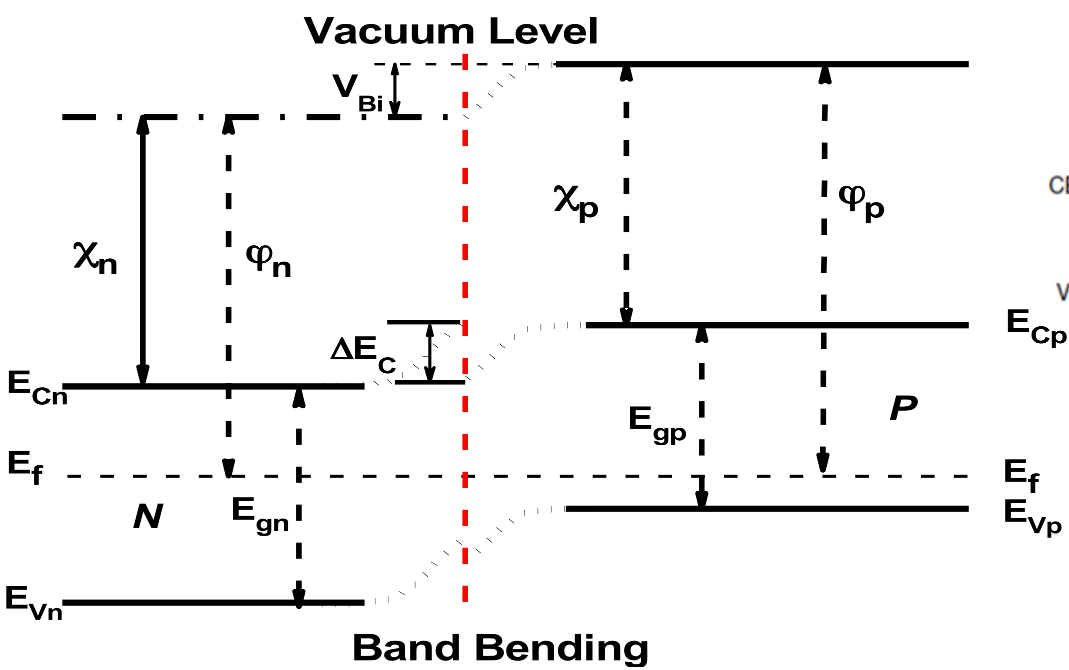
# Heterojunction

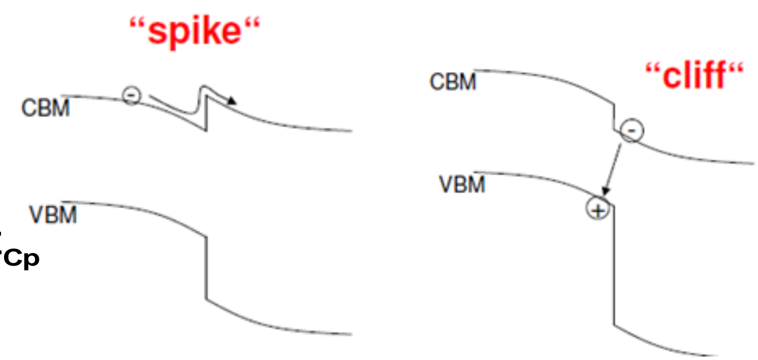
## --- Band alignment at interface

Energy conversion efficiency is the percentage of incident energy of sunlight or heat that actually ends up as electric power

Carrier transport behavior at interface severely affects the device performance

Suitable band offset at interface is critical for carrier transport



# ZnTe-based Solar Cell

A promising II-VI material for TFSC:

- Wide direct band gap ($E_G$>2 eV)
- Tunable bandgap via alloying
- Nontoxic materials
- Various growth techniques

*High diffusion voltage at ZnSe/ZnTe heterojunction, $V_{OC}$ > 1V is feasible*

TABLE II. Collection parameters for II-VI heterojunctions.

| Label | Type | $T$ (°K) | $V_D$ (V) | $\beta$ (V) | $J'_L$ (mA/cm$^2$) | $g(0)$ |
|---|---|---|---|---|---|---|
| C-11 | $n$-CdSe/$p$-ZnTe (110) | 300 | 1.11 | 0.99 | 15.9 | 0.41 |
| C-16 | $n$-CdSe/$p$-ZnTe (111) | 155 | 1.27 | 0.59 | 12.9 | 0.63 |
| | | 300 | 1.18 | 0.48 | 2.83 | 0.67 |
| N-2 | $n$-CdSe/$p$-CdTe | 300 | 0.95 | 1.29 | 2.90 | 0.26 |
| N-3 | $n$-CdSe/$p$-CdTe | 163 | 1.14 | 1.15 | 1.77 | 0.36 |
| | | 222 | 1.02 | 0.82 | 1.78 | 0.45 |
| | | 274 | 0.93 | 0.60 | 1.83 | 0.52 |
| U-2 | $n$-CdTe/$p$-ZnTe (111) | 300 | 1.22 | 1.91 | 3.50 | 0.21 |
| U-4 | $n$-CdTe/$p$-ZnTe (111) | 105 | 1.34 | 0.61 | 0.80 | 0.63 |
| | | 146 | 1.34 | 1.21 | 0.21 | 0.41 |
| M-21 | $n$-ZnSe/$p$-CdTe | 300 | 1.68 | 2.76 | 2.50 | 0.19 |
| P-3 | $p$-ZnTe/$n$-ZnSe[a] | 300 | 1.70 | 1.40 | ... | 0.44 |
| P-4 | $p$-ZnTe/$n$-ZnSe[a] | 190 | 1.97 | 1.16 | 0.83 | 0.55 |

[a] Polycrystalline ZnSe.

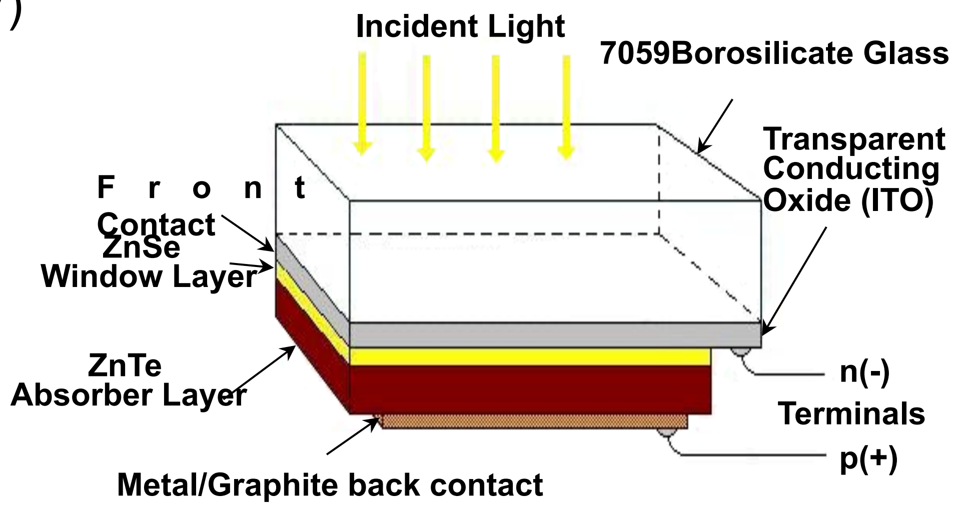
*F. Buch, et al, J. Appl. Phys., 48 (4), 1977*

# ZnTe-based Solar Cell

A promising II-VI material for TFSC:

- Wide direct band gap ($E_G$ 2.24 eV)
- Tunable bandgap via alloying
- Nontoxic materials
- Various growth techniques

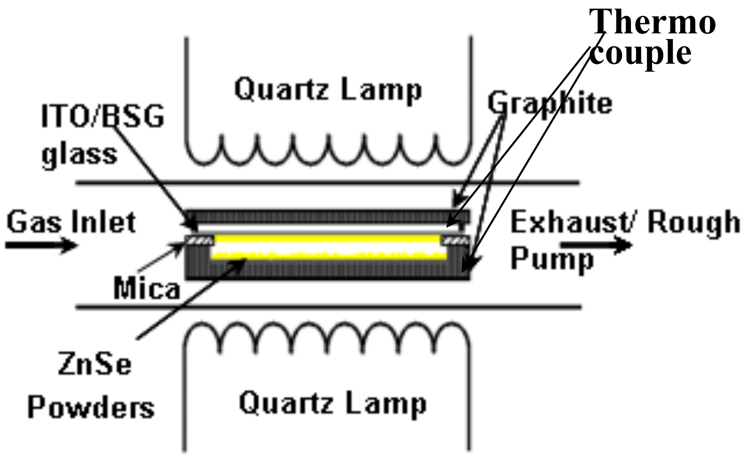
ZnSe/ZnTe thin film device structure




*High diffusion voltage at ZnSe/ZnTe heterojunction, $V_{OC}$ > 1V is feasible*

# Film growth

## --- *Close Space Sublimation/ Vapor transport*




Device diagram of a CSS system

***Low cost --- No HV required***

***Reliability & Reproducibility***

***Scalable (compatible to roll-roll processing)***

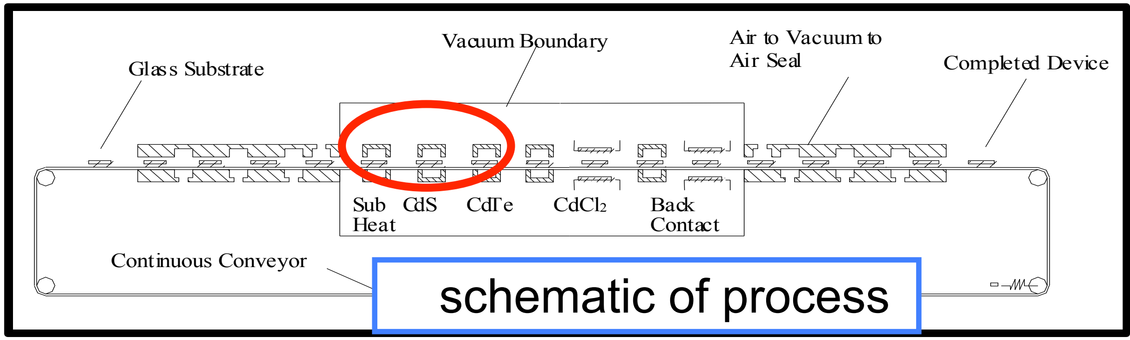
**Abound Solar (formerly known as AVA Solar)**

**Production Prototype**

***(National CdTe Team Meeting April 5 and 6, 2005 )***

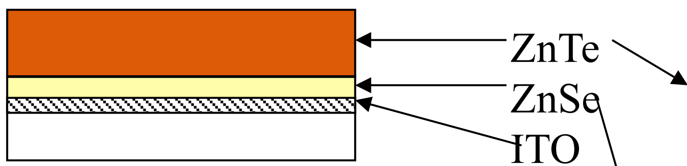
**CSS growth**

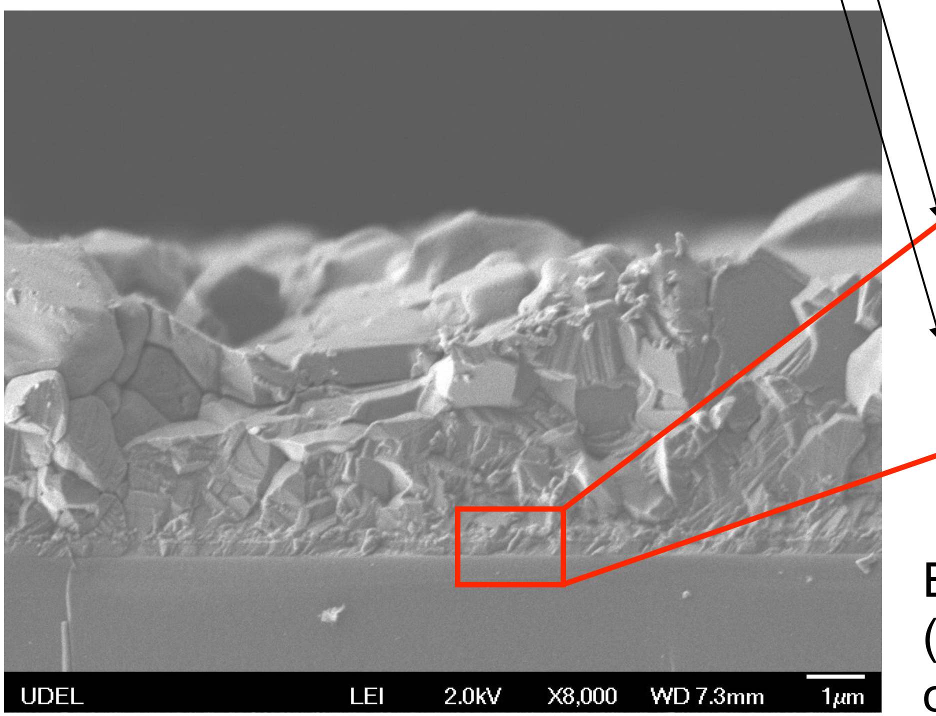
| Thin Film | Source T (°C) | Sub T (°C) | Growth Rate (nm/s) |
|---|---|---|---|
| ZnSe | 730 | 575 | 0.1 |
| ZnTe | 670 | 575 | 2.5 |

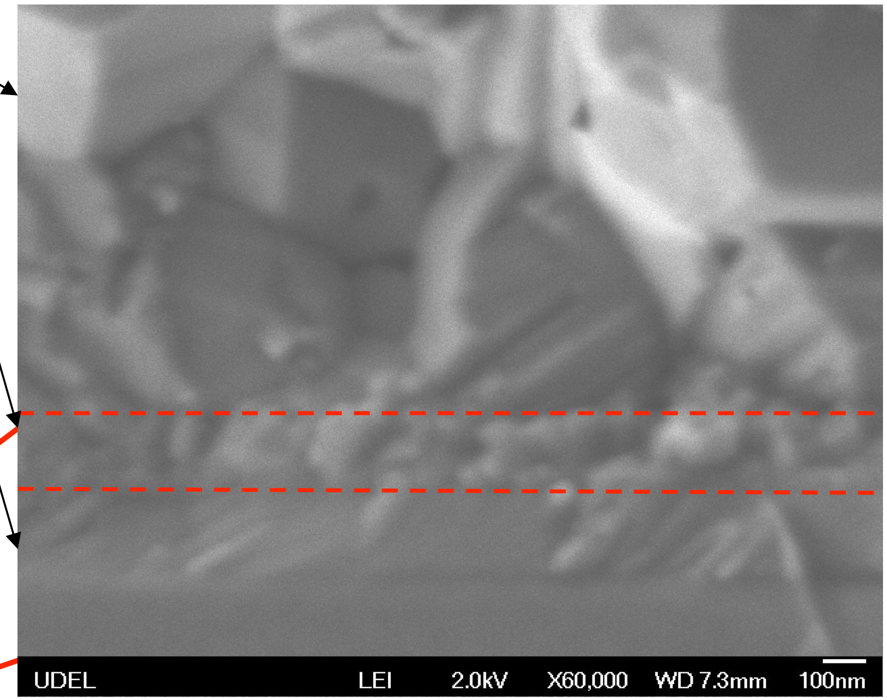


# *SEM cross-section image*

4 um ZnTe on ZnSe/ ITO/BSG glass



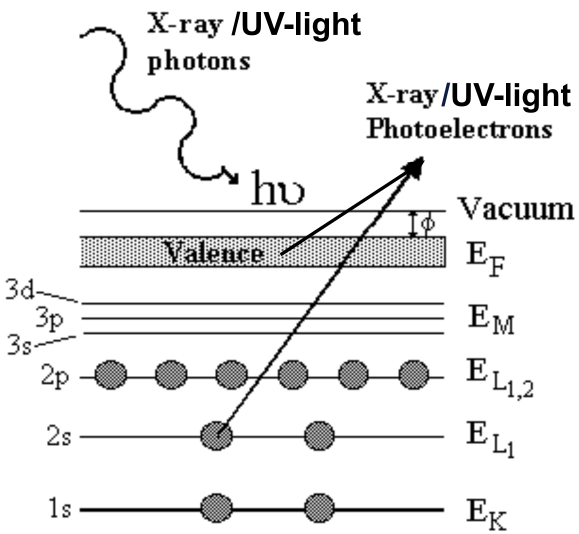



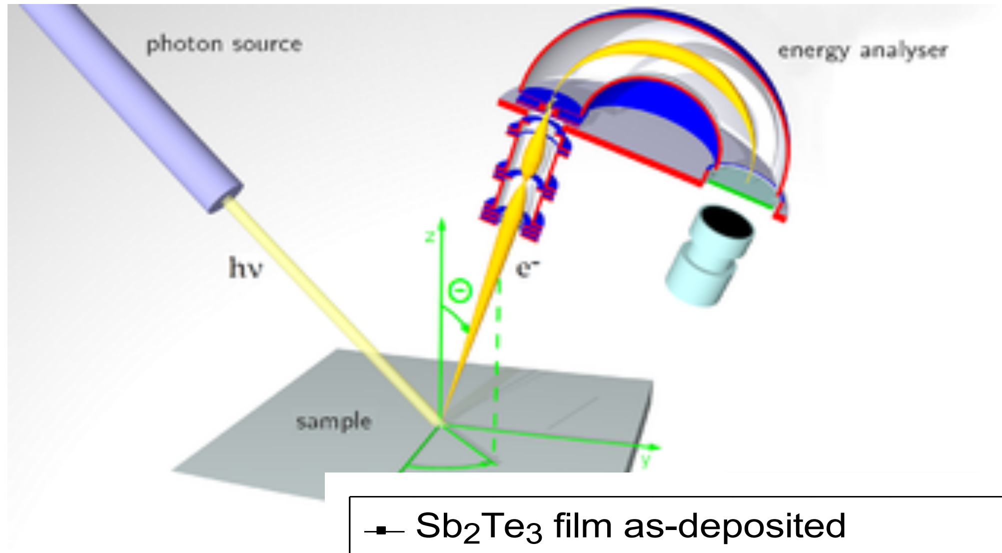




Energy-dispersive X-ray spectroscopy (EDS) confirmed the chemical composition of distinctive films.

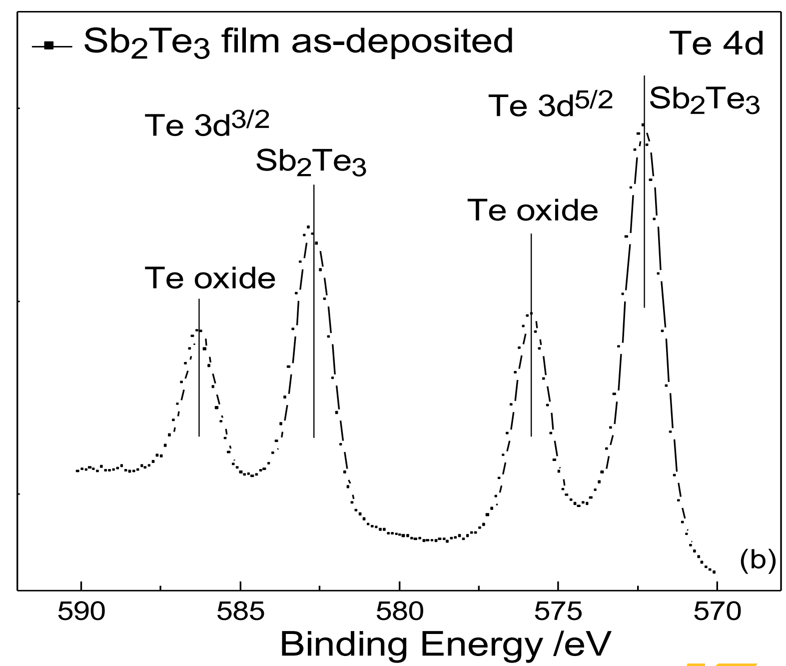
# Photoemission Spectroscopy

$$E_B = h\nu - E_K - \Phi$$




*http://en.wikip*



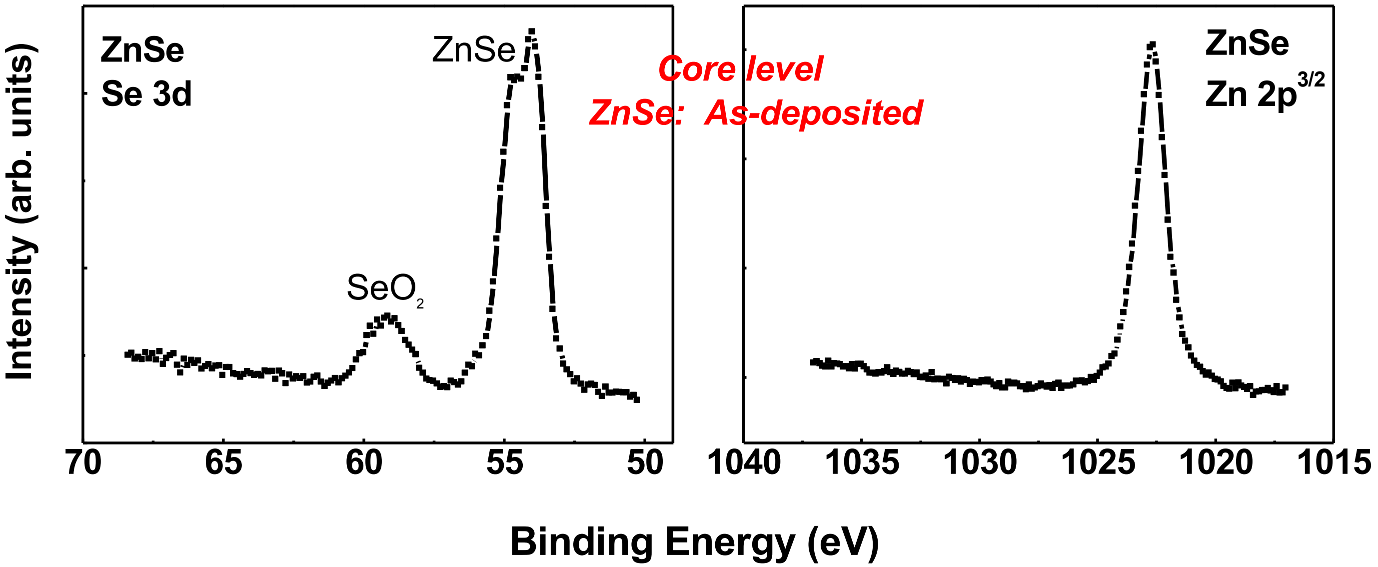

Surface sensitive technique:
Quantitative analysis of small chemical shifts depending on the chemical environment of the atom which is ionized, allowing chemical structure and chemical identification to be determined.

# XPS Measurements on ZnSe Surface

**X-Ray photoelectron spectroscopy using Al-K$\alpha$ source measured core level for ZnSe film surface, confirmed chemical compositions of the film surfaces.**

***High-resolution surface science system PHI 5600***

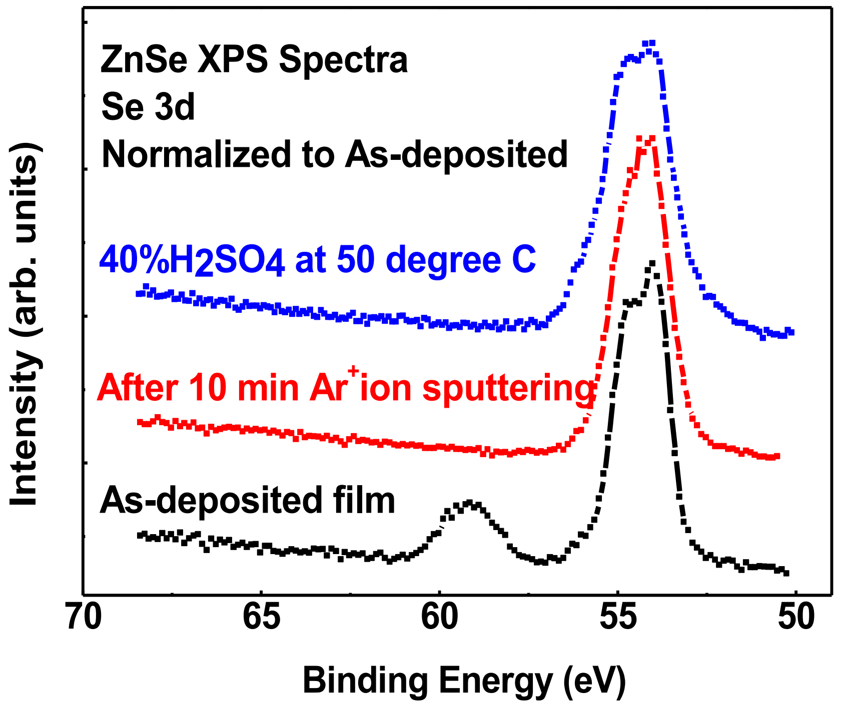
**Probed oxide on ZnSe surface Binding energy of Se 3d core level for $Se^{2-}$ in ZnSe is 54.1eV as for $Se^{4+}$ in $SeO_2$ at 59eV**



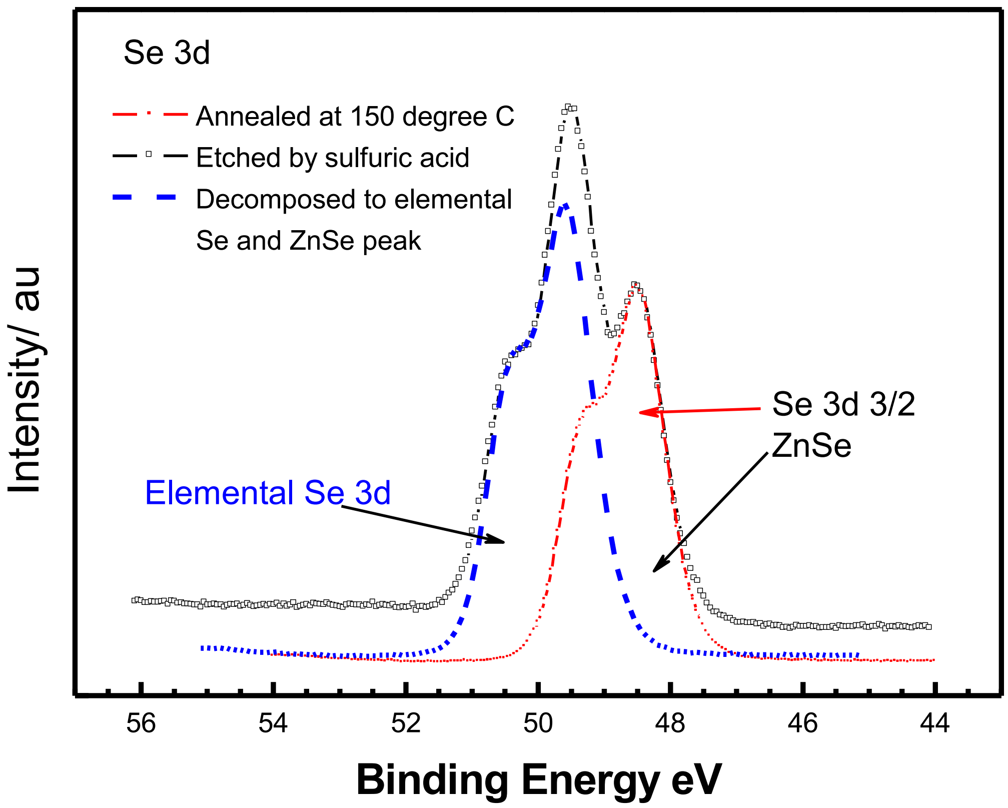
# Surface oxide removed by sputtering or chemical etch

Prior Treatment of XPS measurement
- $Ar^+$ ion Sputtering
- Wet chemical etching
  - 40 % $H_2SO_4$ at 50 ºC
  - 1 % HCl RT

could successfully remove the oxide.



# Elemental Se residual observed after etching--- *Post annealing*

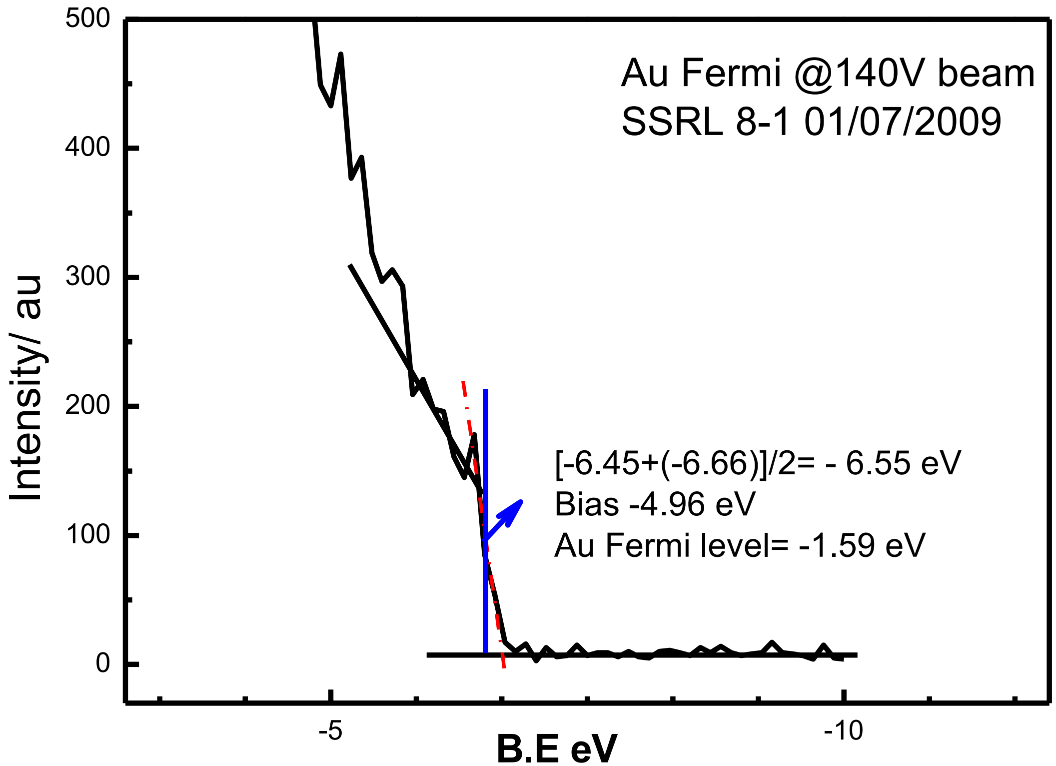



*Elemental Se is observed after etching;*

*Same mild anneal in-situ: inside the UHV photoemission chamber desorb it.*

# Fermi Level Alignment

- UPS measurement of Valence Band Maximum (VBM) at Au film surface
  → Fermi Level
- Aligned with all the other VBM measurements
- Assume all Fermi levels are aligned



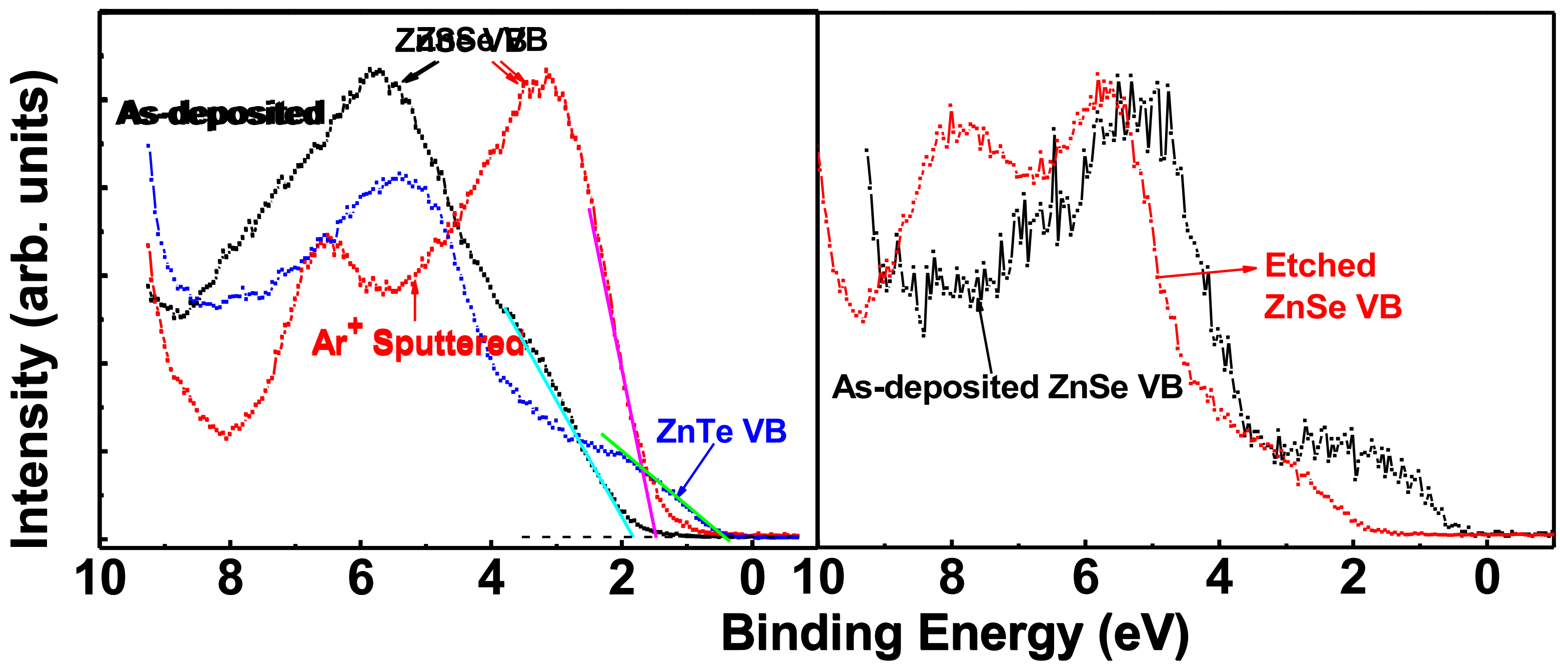
# UPS Measurements

Synchrotron radiation at Brookhaven National Laboratory and SSRL

Valence band (VB) structures for ZnSe and ZnTe films

Surface oxide altered valence band of ZnSe

Extrapolation of the rising edges give the valence-band maximum:



# Energy Band Diagram
# & Device $V_{OC}$ and $J_{SC}$

**As-deposited ZnSe** **Sputtered ZnSe**

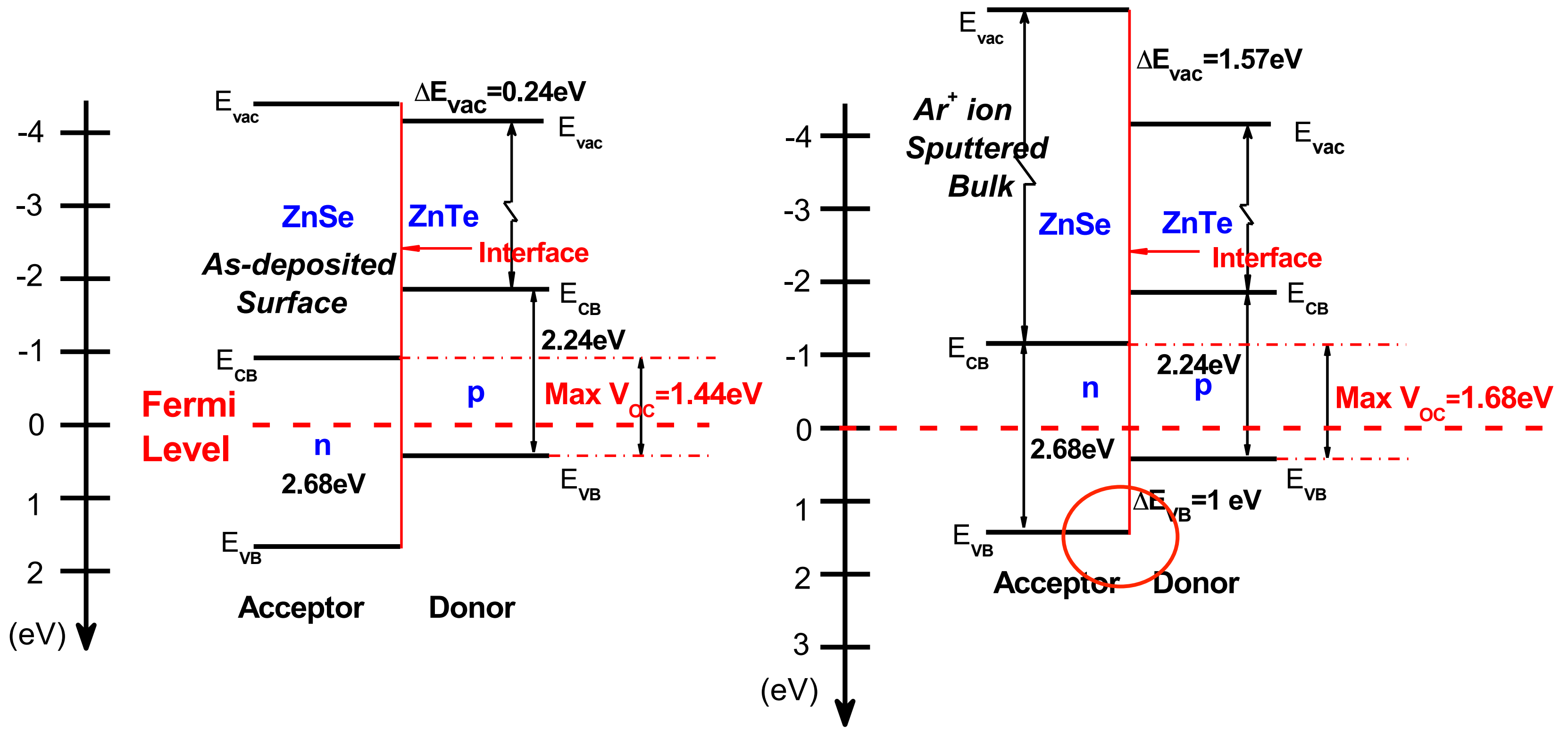
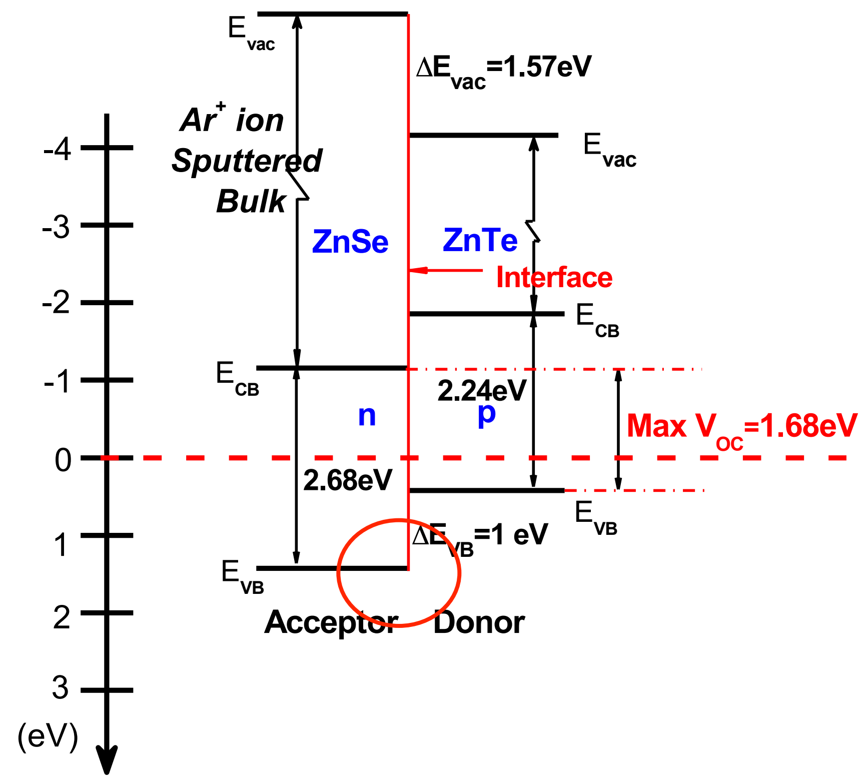



**Diagram based on VB, $E_f$ (UPS) and $E_G$ (optical absorption)**

# Energy Band Diagram & Device $V_{OC}$ and $J_{SC}$

**Solar cell parameters**
**AM1.5 Illumination at 25°C**

| ZnSe Preparation | $V_{oc}$ (mV) | $J_{SC}$(mA/cm²) |
|---|---|---|
| None | 450 | <5 |
| Rapid transfer (<1 min) | 600 | ~5 |
| Chemical Etched | 750 | >5 |



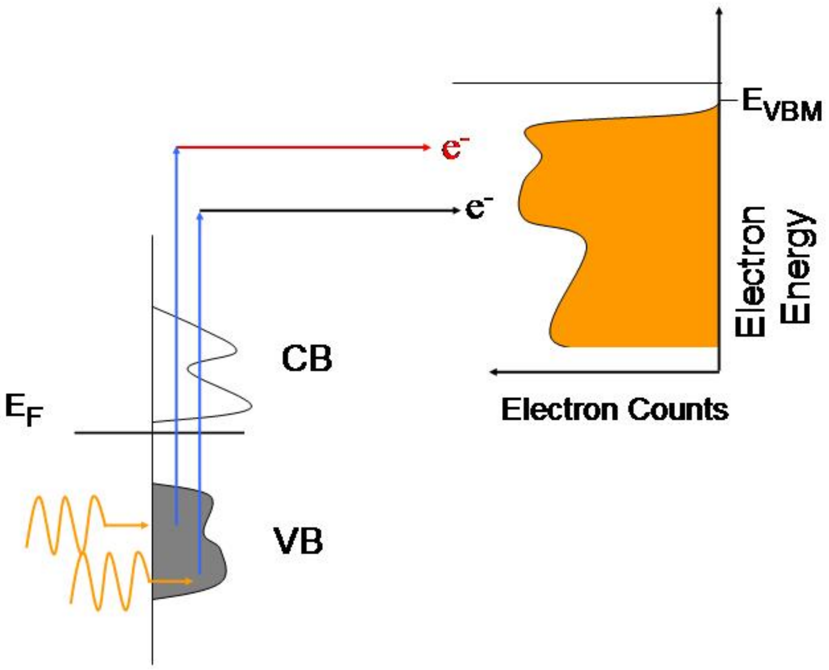
# Direct measurement of CBM

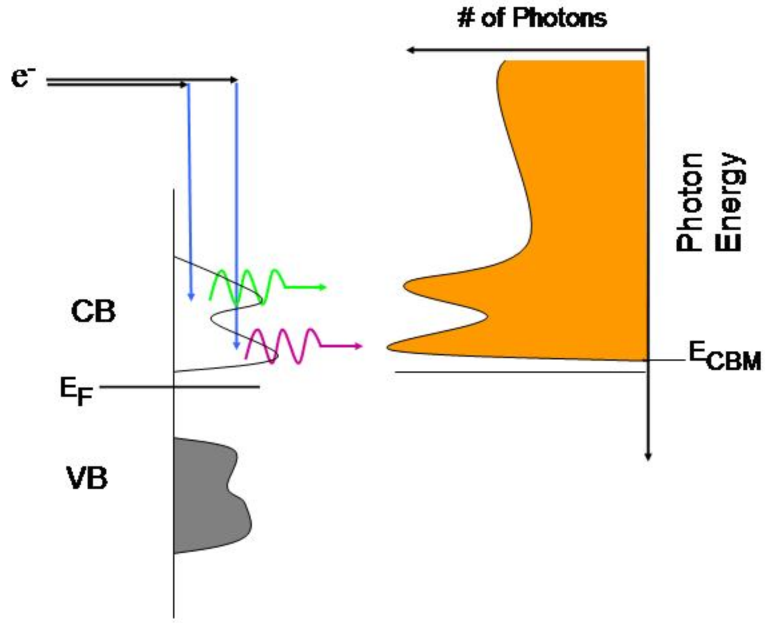
## --- *Inverse photoemission*

Inverse photoemission is the time-reversed process of photoemission, complementary technique to measure the conduction band edge directly.

*PE* $E_B = h\nu - E_K$

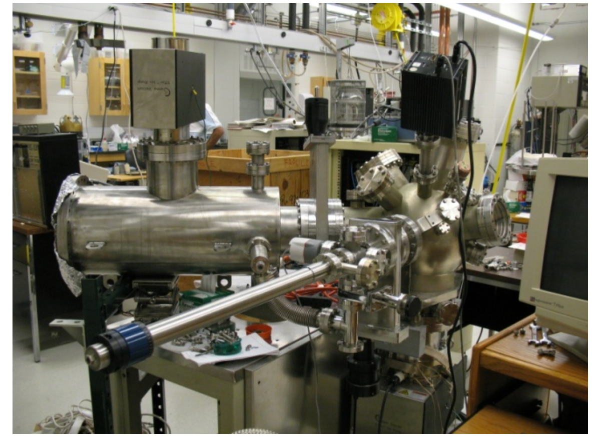
*IPE* $E_{(above\ EF)} = h\nu - E_K$



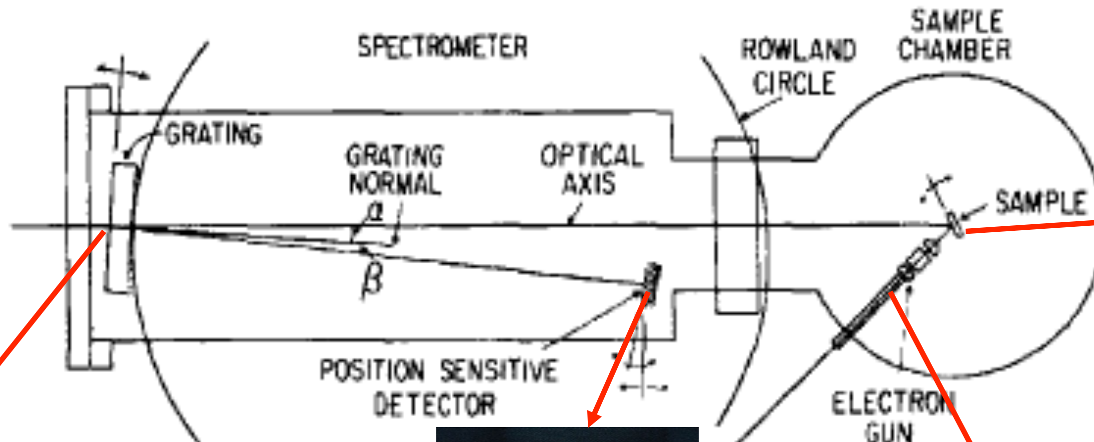

*http://www.physics.rutgers.edu/%7Ebart/grouphome/PE_IPE_RAB.htm*

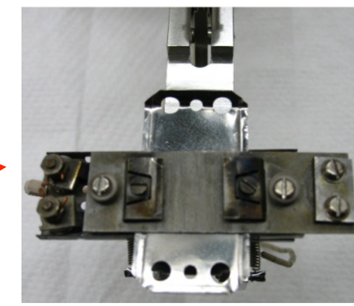
# IPES Schematic Diagram



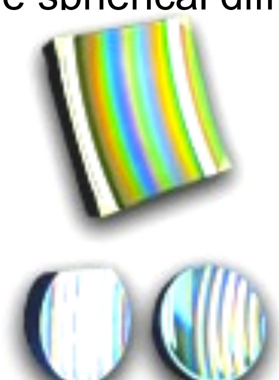
***Main blocks:*** **UHV system / <$10^{-7}$ Torr)**

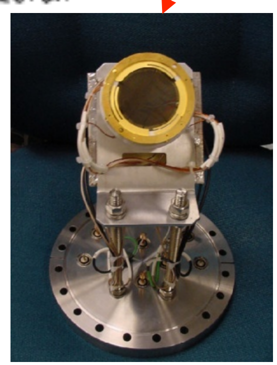
- **Source: electron gun**
- **Diffraction grating**
- **Position sensitive detector**
- **Analysis programming**



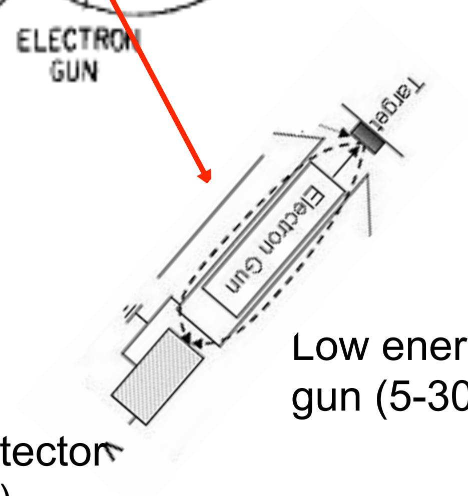



Concave spherical diffraction grating





Position sensitive MCP detector
(Micro-channel plate detector )




Low energy electron gun (5-30 eV)

# *Thin Film Solar Cell Summary*

- CSS & evaporation of sequential ZnSe/ZnTe growth demonstrated:

- Significant chemical oxidation and sensitivity to storage of ZnSe
  - *Oxidation state observed by PES*
  - *UPS using synchrotron radiation detected band structure offsets changed by oxidation*
  - *Robust device baseline → minimize exposure of films to oxygen*

- *Film structure characterization:*

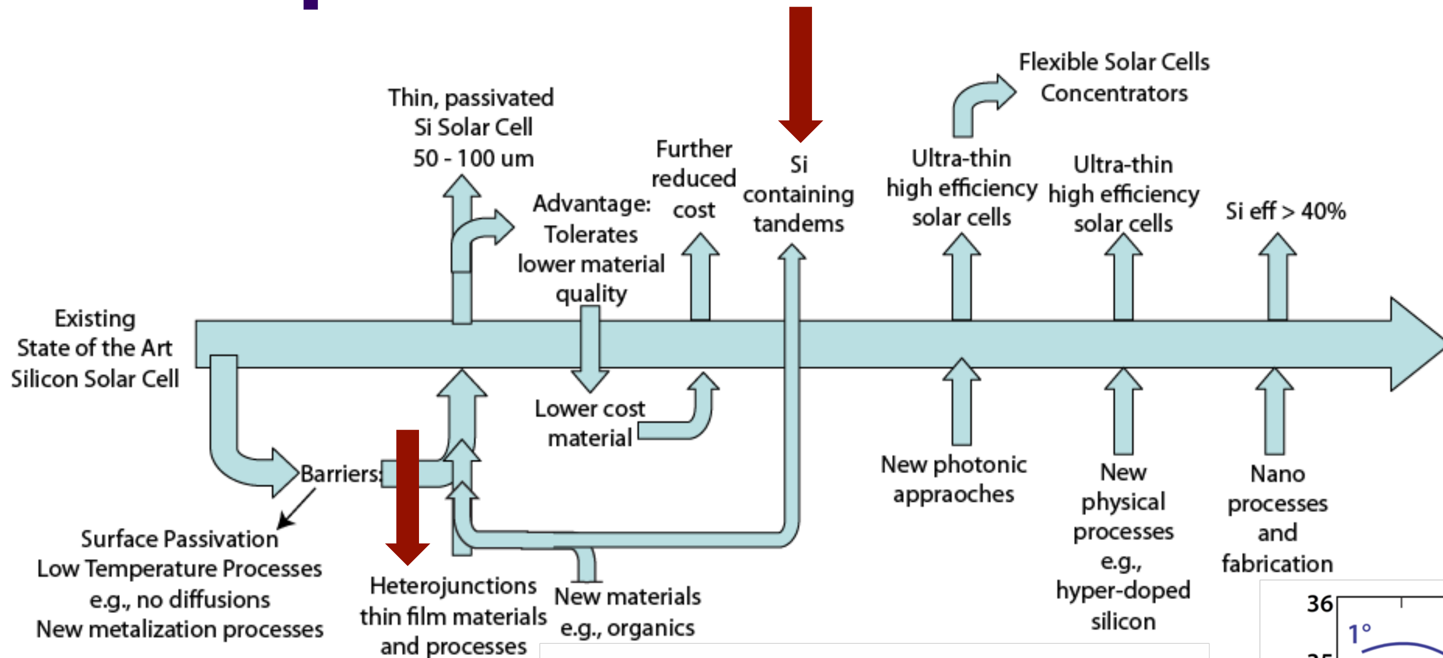
  *Optimize CSS grown ZnSe film → diminish lateral facets*

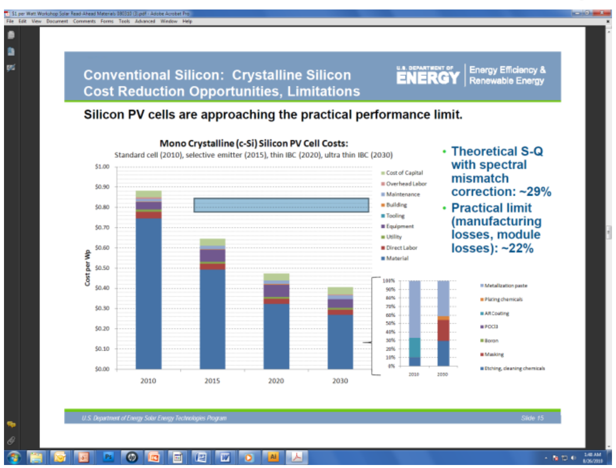
  *Refine the CSS equipment and enable better control of the ZnTe growth*

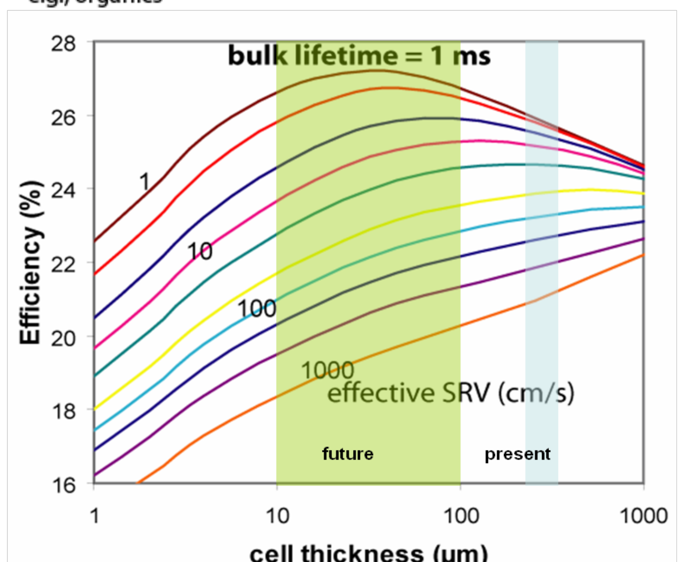
  *Increase grain size of ZnSe and ZnTe in evaporation growth;*

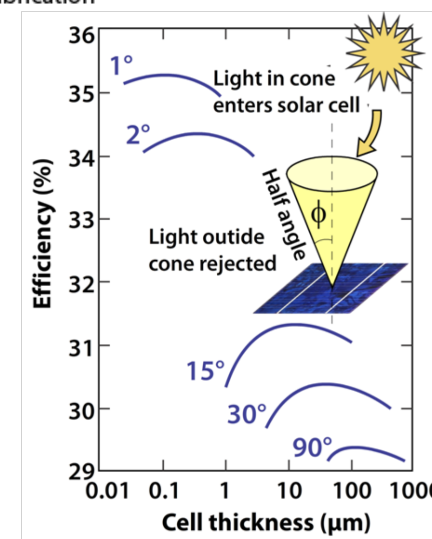
  *Recrystallization →post annealling*

# Roadmap for silicon devices



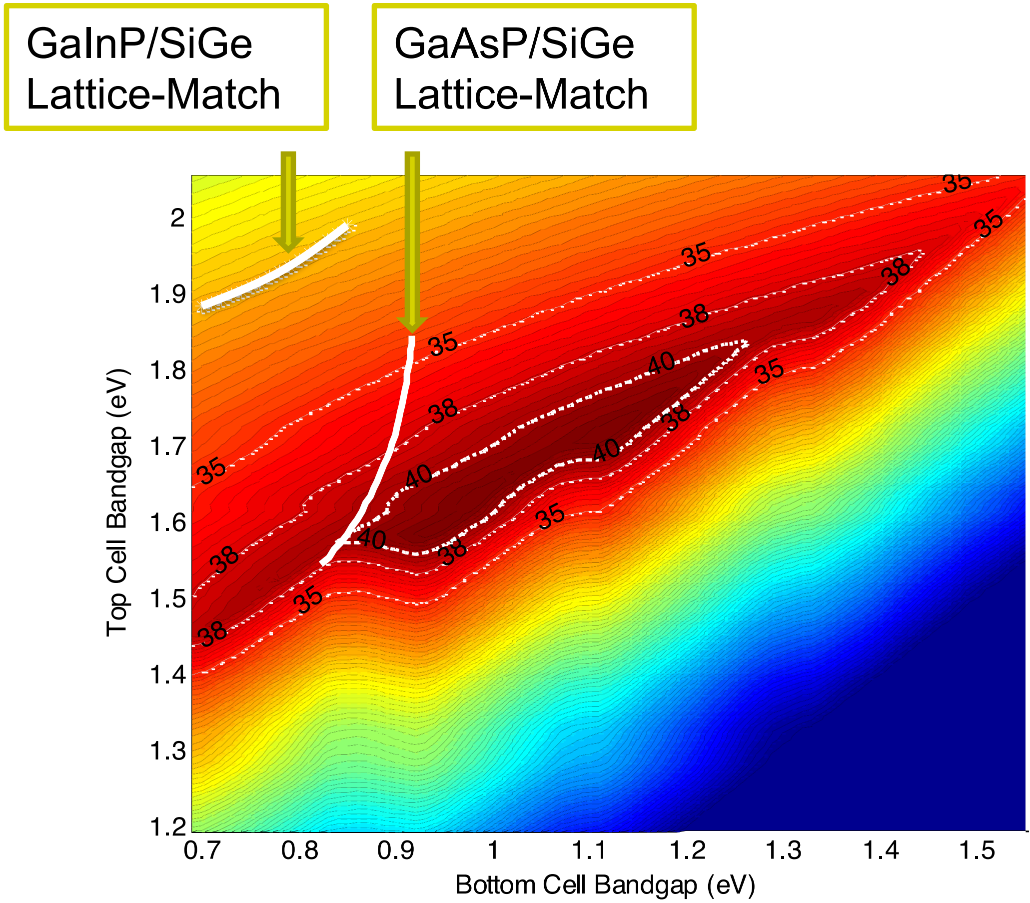



# Dual-Junction "Limit" Results

- III-V/Si Device
  - Unconstrained
    - 1.72eV/1.12eV
    - 42% Efficiency
- III-V/SiGe Device
  - Lattice-matched
    - 1.58eV/0.84eV GaAsP/SiGe
    - 40% Efficiency

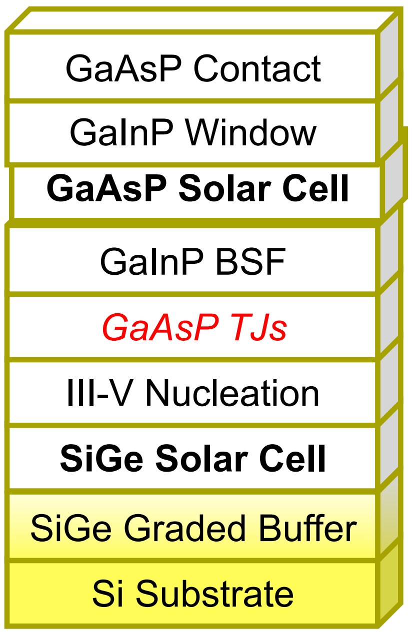


# GaAsP/SiGe Tandem Device

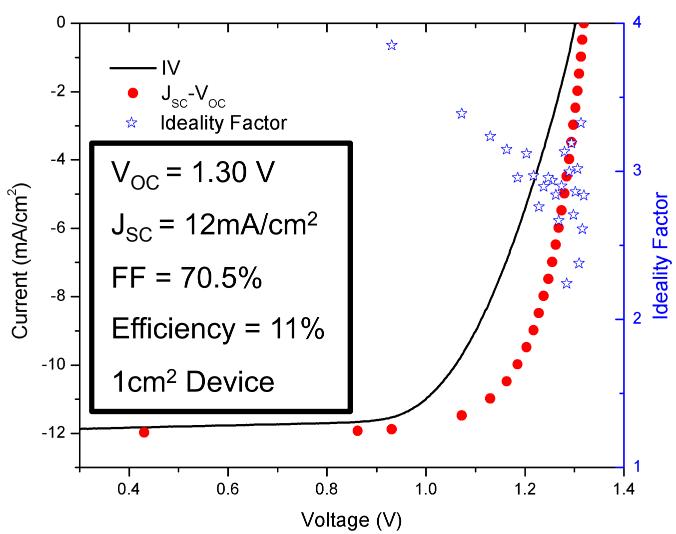
**Schmeider, Diaz, Barnett, Veeco, Amber Wave**

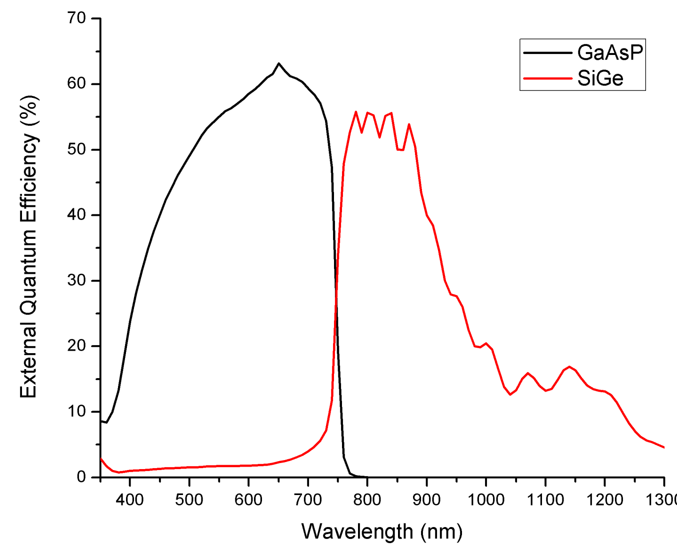
Generation 3

Solar Cell

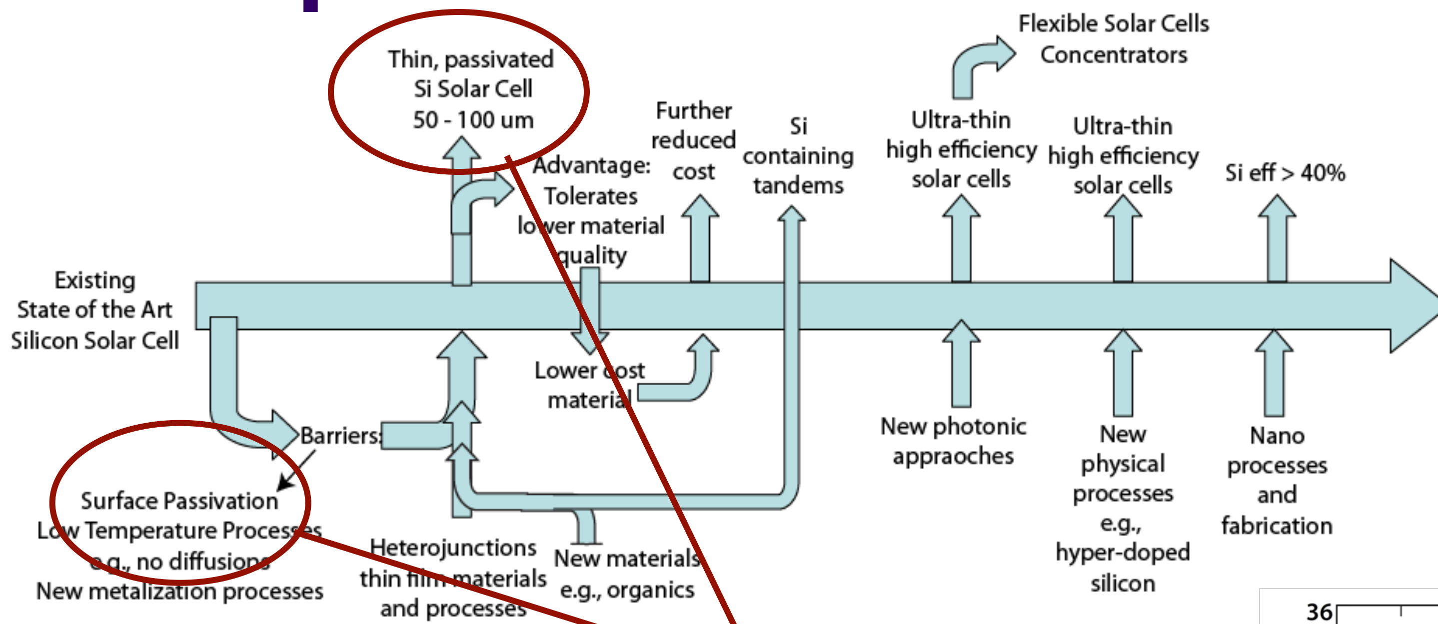


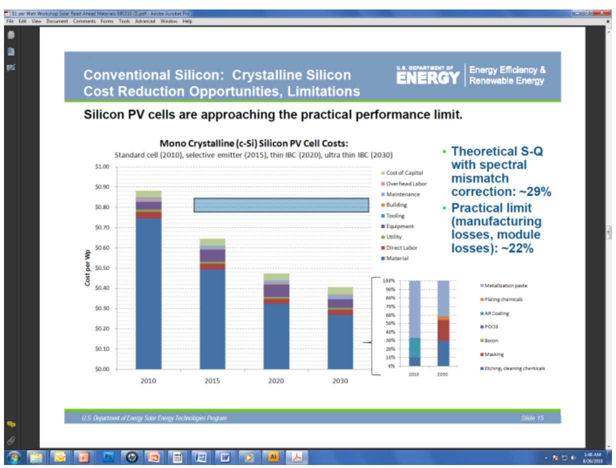

- Improved TJs, Window layers, Integration (Martin, Brianna, ….)
  - Voc as high as 1.32 V
  - Efficiency as high as 15.2% (AR corrected)
  - $J_{SC}$-$V_{OC}$ FF = 78%
  - Top cell ideality factor = 1.84 (Assumes n=1 in SiGe)
- Bottom cell not optimized (Xin, Dun, Anastasia, ….)
  - Low bottom cell current—Ge:Si not optimized

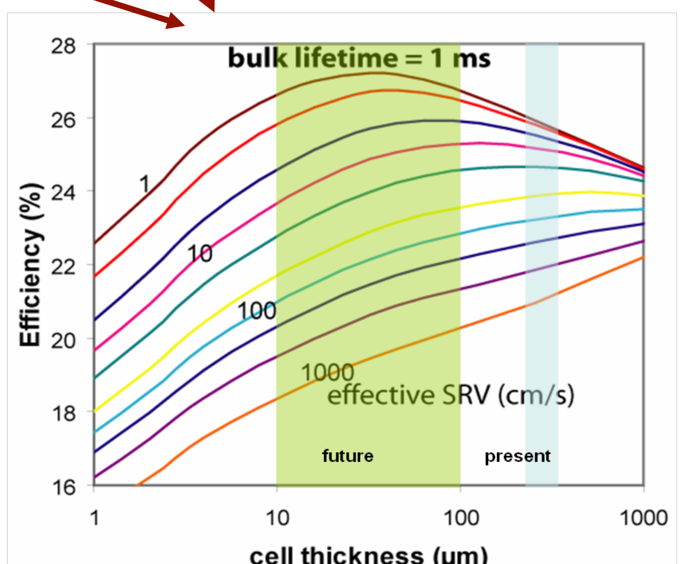


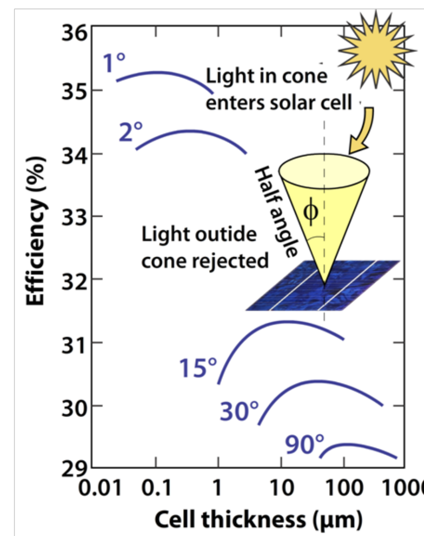



# Roadmap for silicon devices



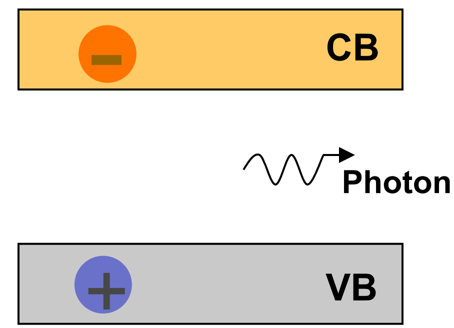



# Recombination Processes

- Process where an electron & a hole annihilate
- Both Carriers disappear - no collection!!
- Recombination types
  - Radiative
  - Trap-Assisted
  - Auger
  - Surface
  - Emitter

**BULK**

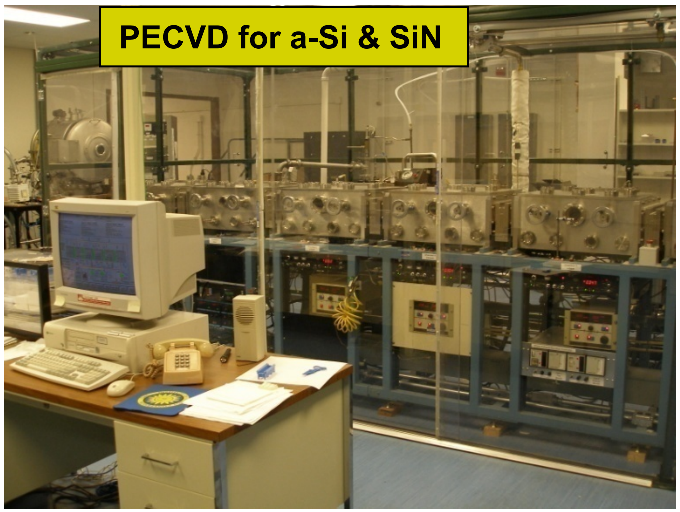


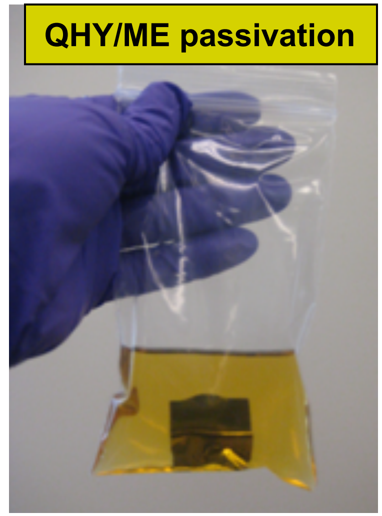

- How good are the surfaces?
  - Minority carrier lifetime (μs or ms)
  - Surface recombination velocity (S in cm/sec)

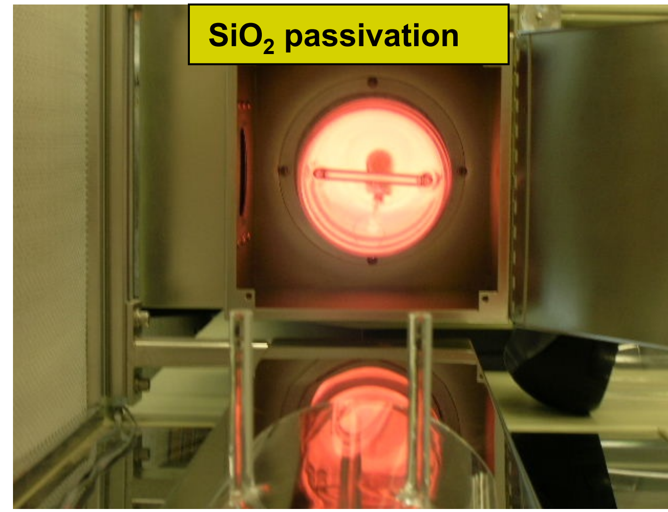
$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S}{W}$$

# Si Passivation Schemes

**Surface recombination is controlled by growing a passivation**



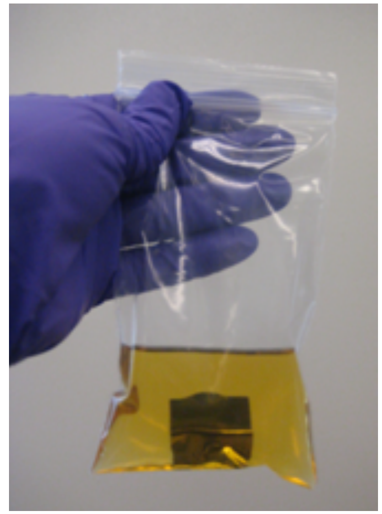




| Moderate-to-high Temp. Techs. | ROOM Temp Techs. |
| --- | --- |
| ❖ a-Si (PECVD at 200°C) | ❖ Hydrogen Fluoride (HF) |
| ❖ SiN (PECVD at 200-350°C) | ❖ **Quinhydrone-Methanol (QHY/ME)** |
| ❖ $SiO_2$ (Diff. Furnaces at 800-900°C) | ❖ Iodine-Methanol ($I_2$/ME) |

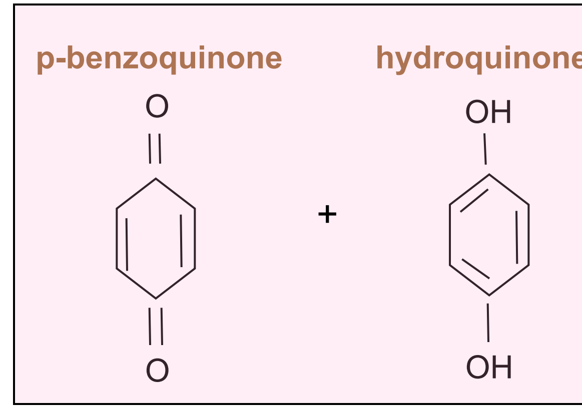
# QuinHYdrone/MEthanol Passivation

## Why QHY-ME?

- Easy to use
- Low cost
- Important characterization tool
- Room temperature operation
- Reversible
- Ideal passivation if stable



Quinhydrone Structure




## Procedure

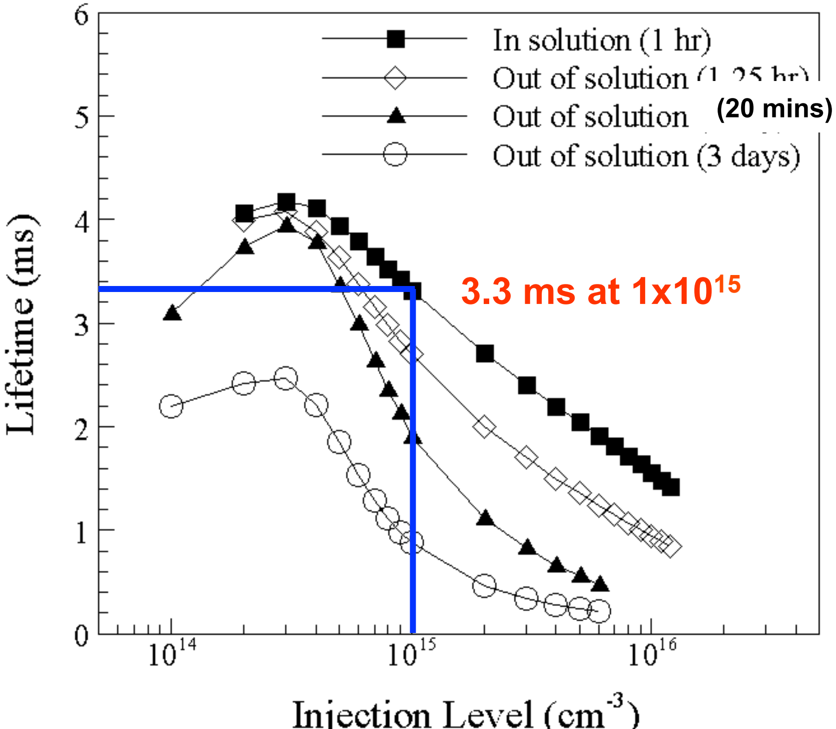
- QHY-ME = 0.01 mol/L
- Wafer cleaning: Piranha & HF
- Wafers in solution in acid resistant plastic bag
- Passivation time - 1 hour at room temp
- Measure lifetime/ Implied-Voc/ S

## Limitations

Lifetime not stable if sample exposed to air

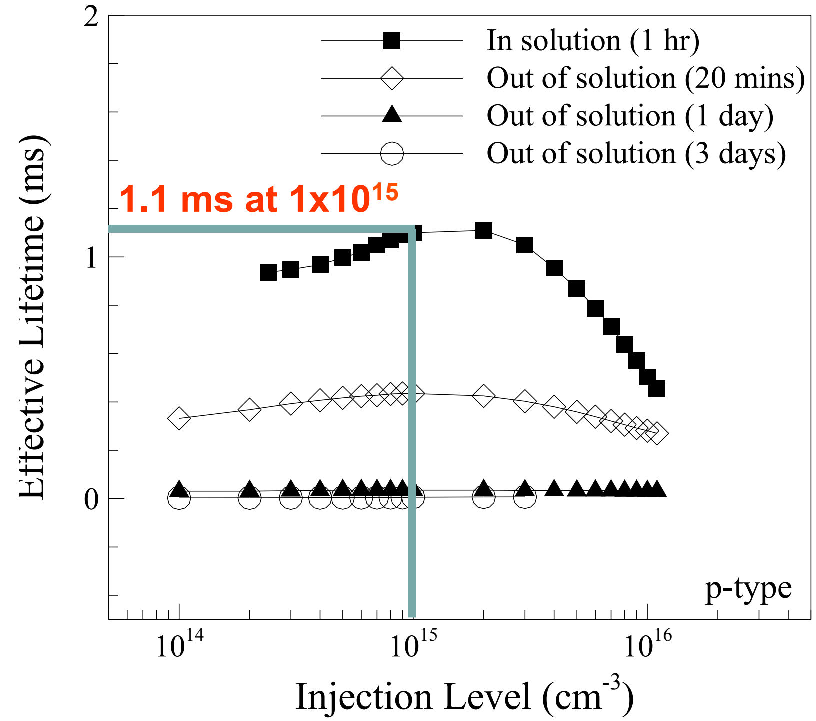
# Lifetime Results (QHY/ME)

**n-type Si <100>, 100 ohm-cm, 460 μm**




| Lifetime (IN solution) | Lifetime (20 mins OUT of solution) |
|---|---|
| 3.3 ms; 7 cm/s | 2.7 ms; 8.7 cm/s |

**p-type Si <100>, 3 ohm-cm, 170 μm**




| Lifetime (IN solution) | Lifetime (20 mins OUT of solution) |
|---|---|
| 1.1 ms; 21 cm/s | 0.436 ms; 53 cm/s |

Chhabra *et al*, **Appl. Phys. Lett.**, 96 (2010) 063502

# Hydrogen Passivation of Silicon

- hydrocarbons
- metallic impurities
- silicon oxide layer
- ionic contamination
- particles

**Premium RCA clean:**

SC-1: $NH_4OH$, $H_2O_2$ , and $H_2O$ at typically 80 C for 10 min

Removal of hydrocarbons and may cause oxidation and metal contamination.

Immersion in HF in $H_2O$ at 25 C

Removal of oxide and the ions dissolved in the oxide.

SC-2: HCl, $H_2O_2$ , and $H_2O$ at 80 C.

Removes the remaining metallic contamination.

Final HF rinse to remove oxide.

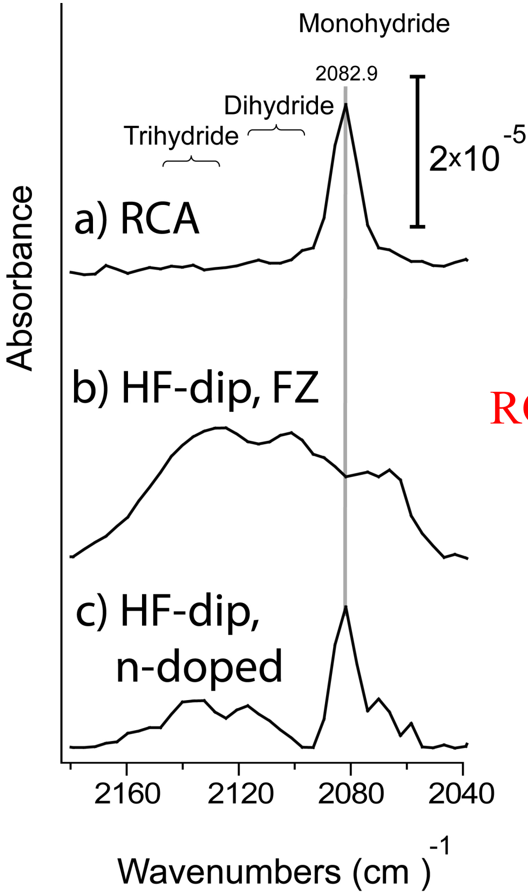
**Alternative wet cleaning method:**

Hot $H_2O_2$ –$H_2SO_4$ solution (Piranha clean)

Cleans heavily contaminated Si wafers.

Dilute HF/water solution.

# Infrared spectra of the Si-H stretching region of H-terminated Si(111) surfaces




a) RCA method;
b) HF-dip method with a float zone crystal
c) HF-dip method with n-doped crystal.

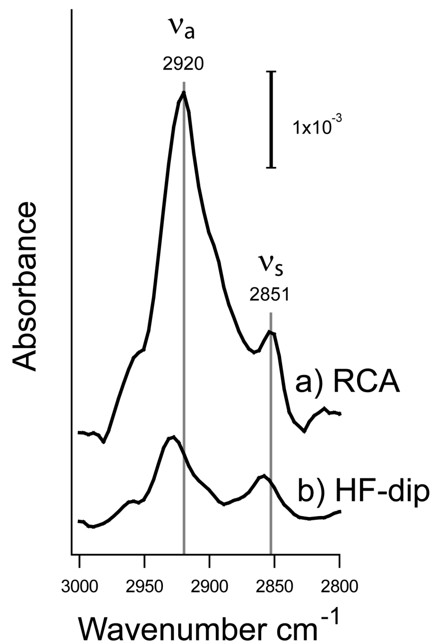
RCA clean has better surface chemistry and morphology (AFM)

| Surface Preparation | Charge-carrier Lifetime, τ (μs) | Surface Recombination Velocity, S (cm $s^{-1}$) |
|---|---|---|
| RCA | 60.7±28.9 | 1002.7±577.3 |
| HF-dip | 169.9±14.0 | 295.3±24.4 |

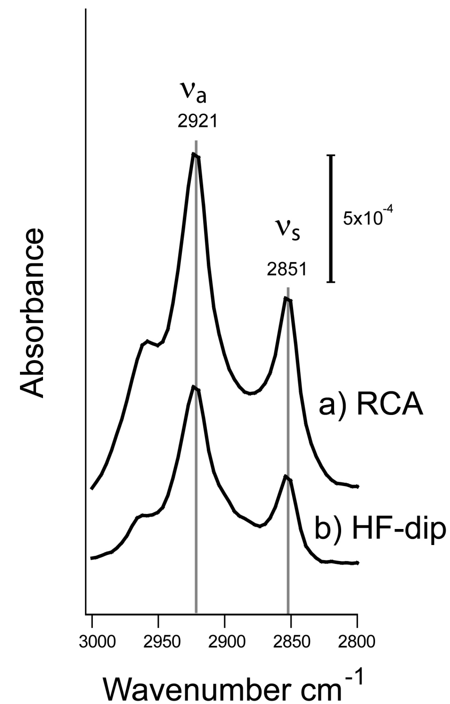
But *worse* lifetimes!!

F. Tian, D. Yang, R. Opila and A. Teplyakov, *Appl. Surf. Sci.*, **258,** 3019-3026 *(2012).*

# Chemical and electrical passivation of Si(111) surfaces



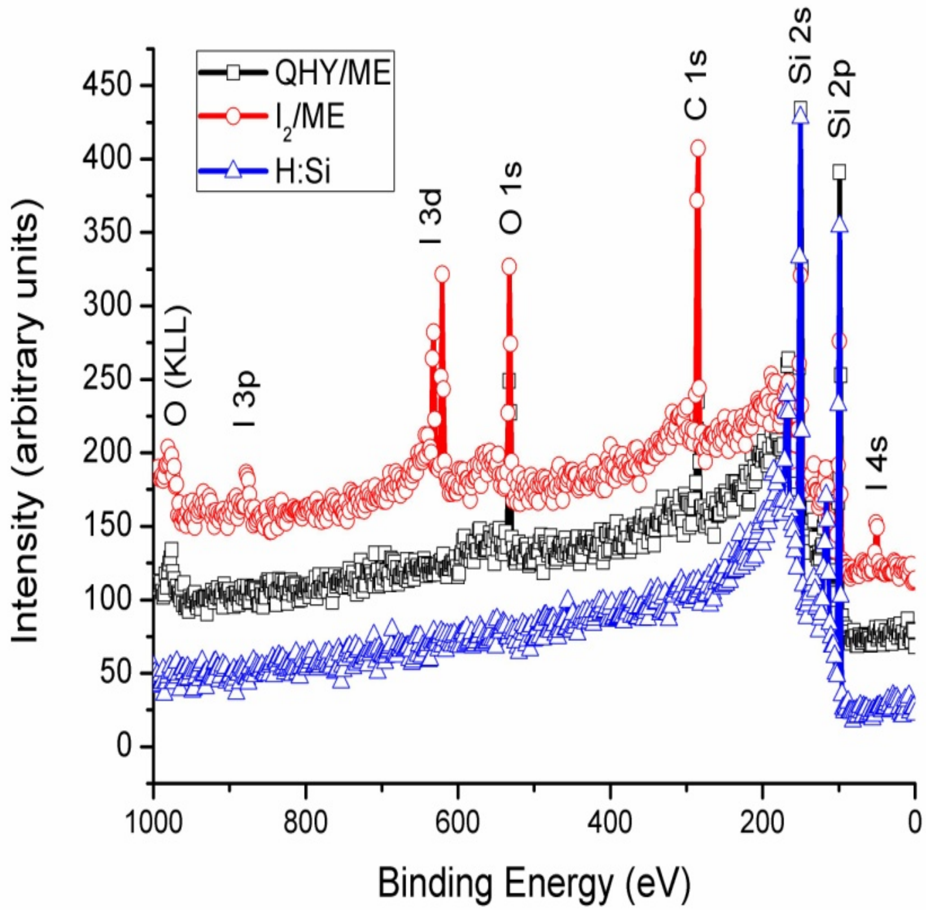

IR investigation of the C-H stretching spectral region of the 1-decene modified Si (111) surface produced by a) RCA method and b) HF-dip procedure.




IR investigation of the C-H stretching spectral region of the 1-octadecene modified Si (111) surface produced by a) RCA method and b) HF-dip procedure.

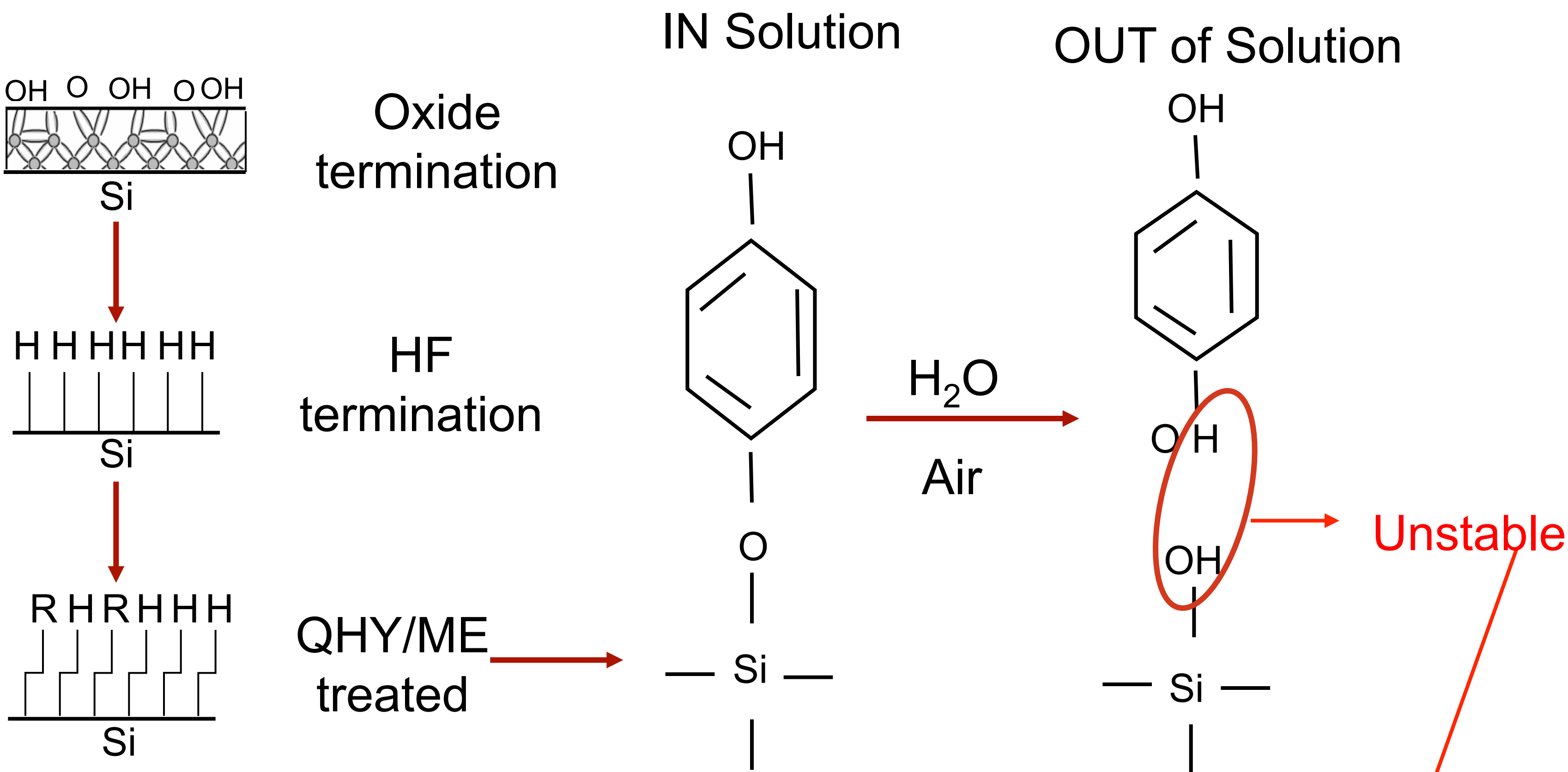

F. Tian, D. Yang, R. Opila and A. Teplyakov, *Appl. Surf. Sci.*, **258,** 3019-3026 *(2012).*

# XPS Studies Si substrates after QYH/Me



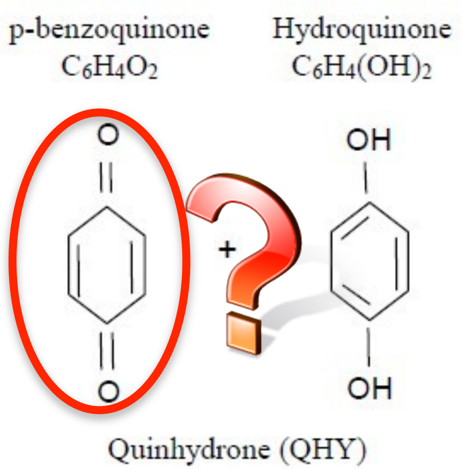

Chhabra *et al*, Phys. Status Solidi A, DOI: 10.1002/pssa.201026101

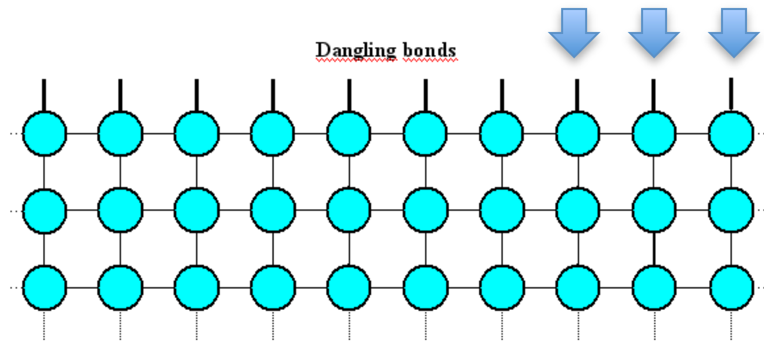
# First Proposed Surface Bonding from XPS

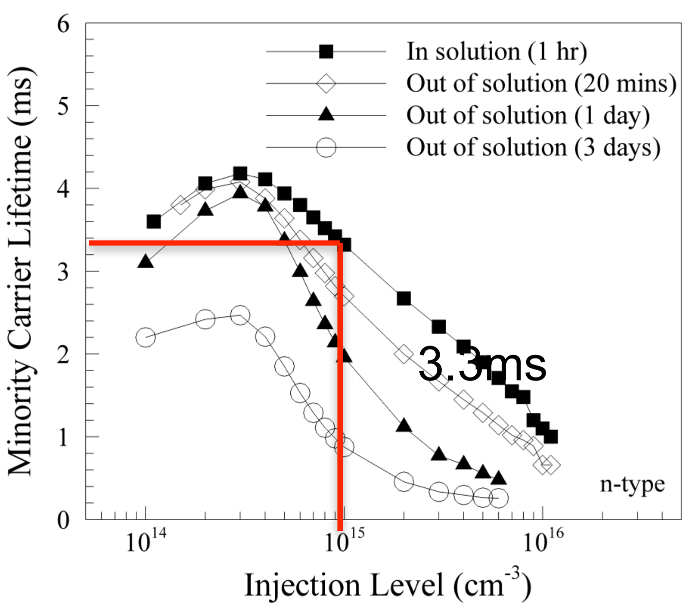



| Lifetime (IN solution) | Lifetime (24 hrs OUT of solution) |
|---|---|
| 3.3 ms | 1.9 ms |

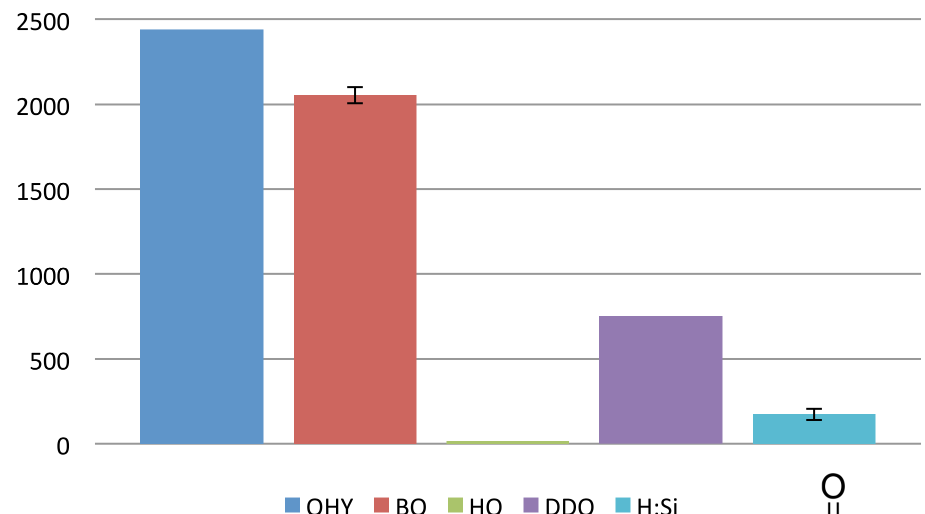
# Recombination center



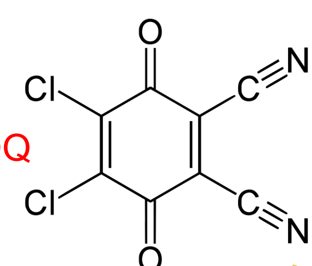



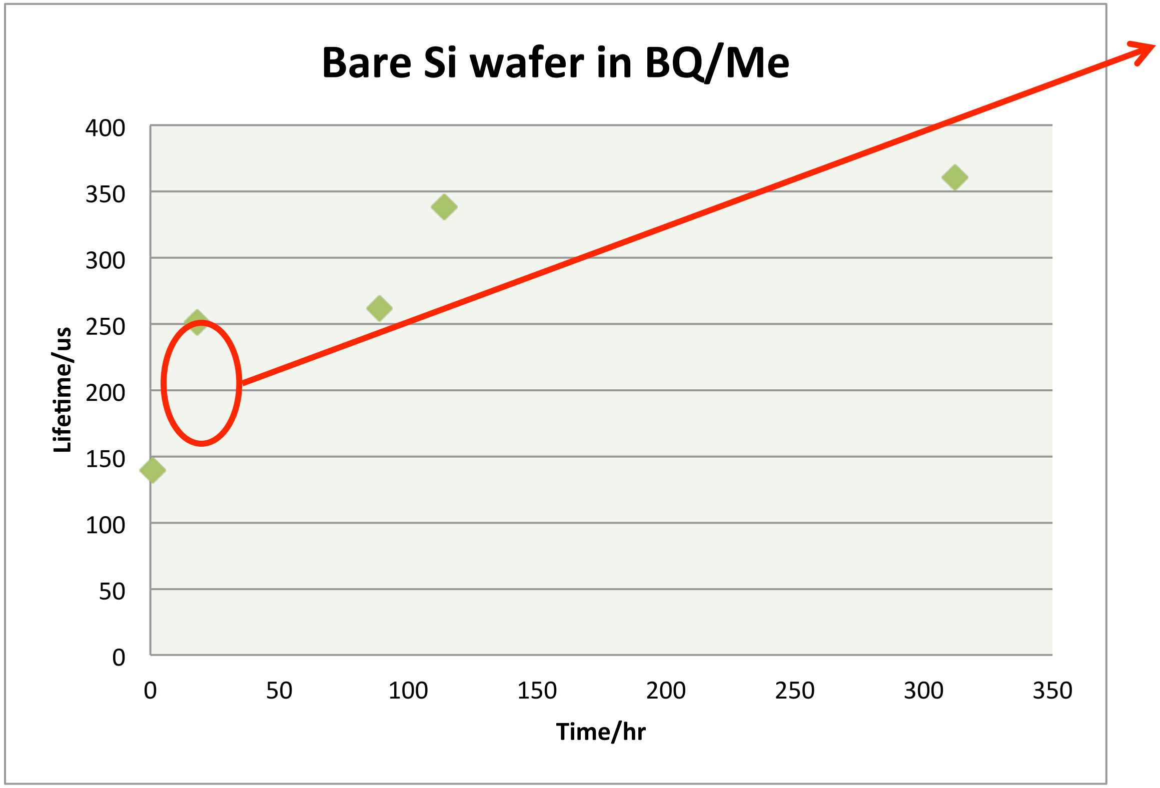



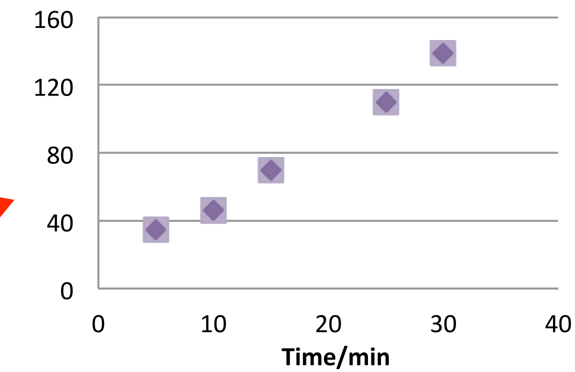

## Lifetime in solution at 1hr

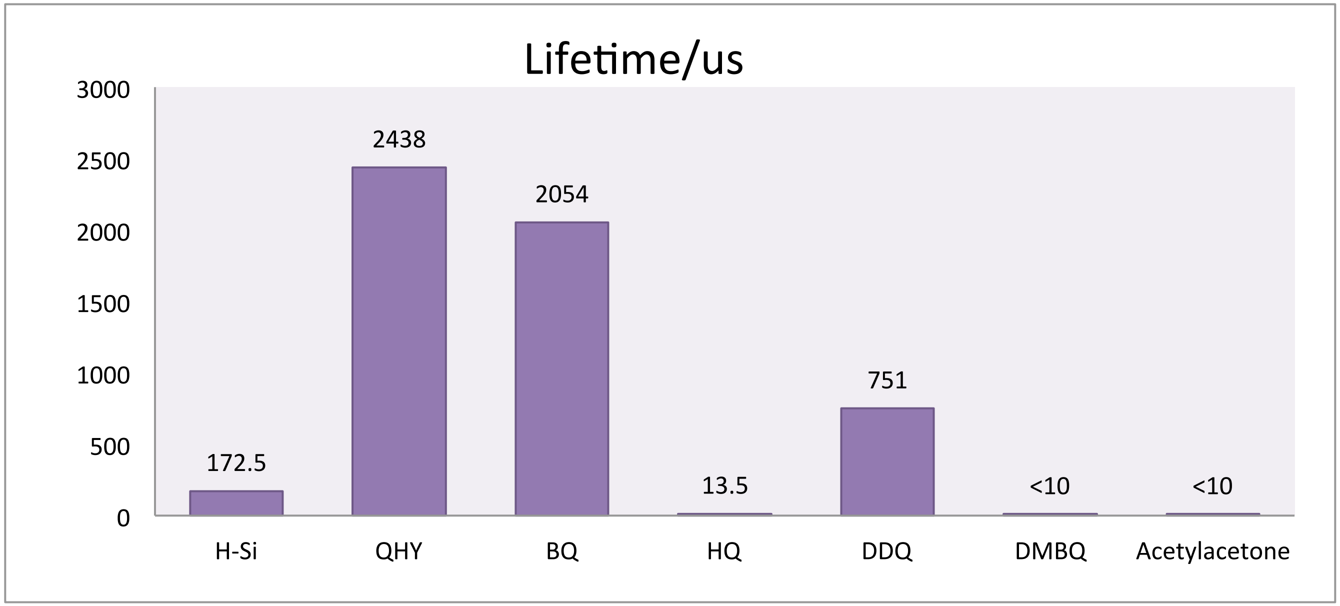


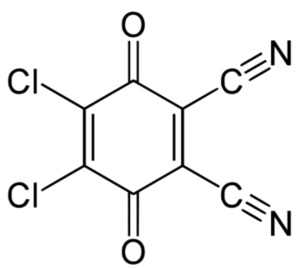

DDQ



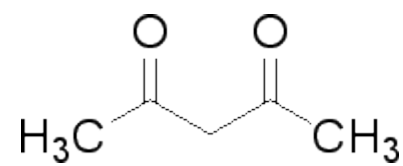

Bare Si wafer in BQ/Me
Lifetime/us
400
350
300
250
200
150
100
50
0
0
50
100
150
200
250
300
350
Time/hr


160
120
80
40
0
0
10
20
30
40
Time/min

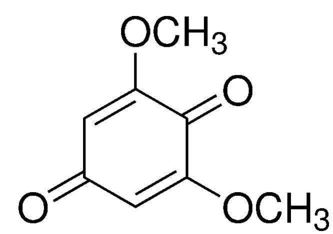


2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)

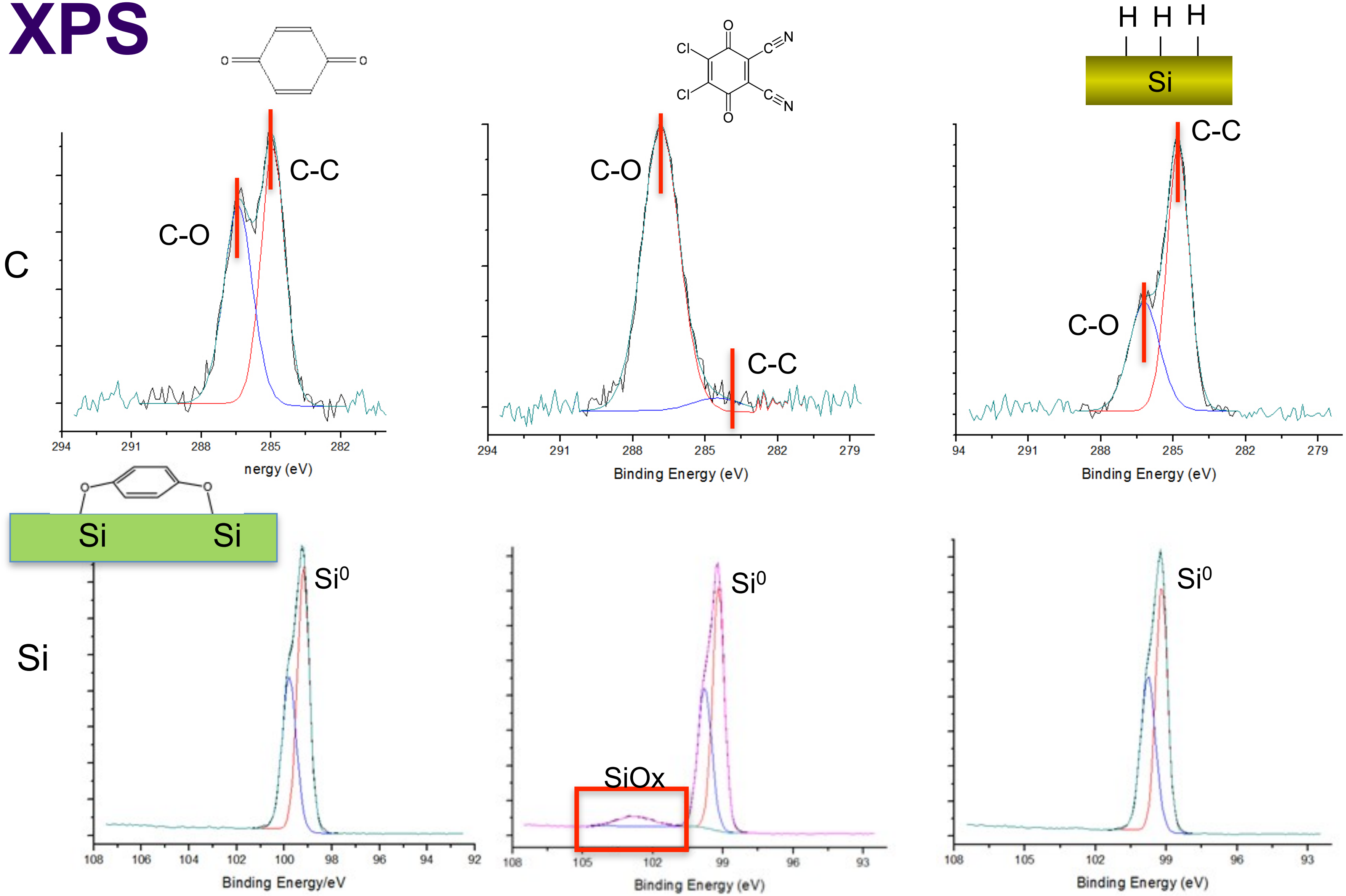


Acetylacetone



2,6-dimethoxy-(1,4)-benzoquinone(DMBQ)

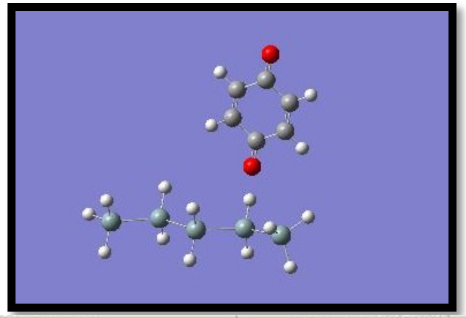
# XPS



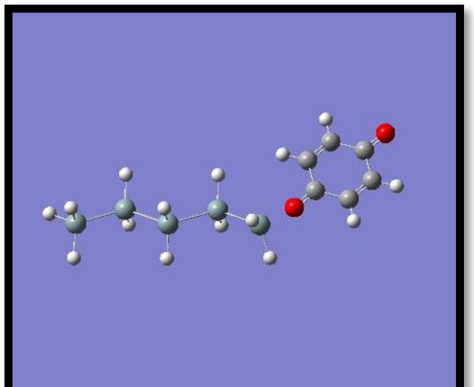
C
Si
C-O
C-C
nergy (eV)
Binding Energy (eV)
Si
Si
H H H
Cl
O
C≡N
$Si^0$
SiOx
Binding Energy/eV

# Surface passivation of Si with hydroquinone

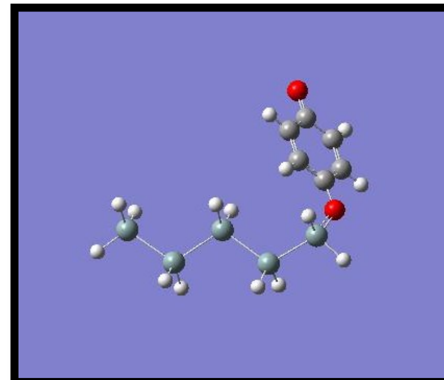
- Increases carrier lifetime dramatically.
- Slows oxidation rate compared to Hydrogen passivation
- How
  - What reaction?
    - Density functional theory says BQ will not react with H-terminated Si, but will react with Si(111)7x7. What defects are important? (D. Okeeva)
    - BQ is photoactive—is light from Sinton test important in observed passivity? (L. Costello, M. Chen)
    - Are protons in MeOH important in passivity (L. Costello)?
  - Is passivating site a charge center?
  - Can we generalize it?
    - How do we make organic/Si induced junctions (N. Kotulak, ASU)
    - Can organic passivation of Si nanowires be improved (Cal Tech)



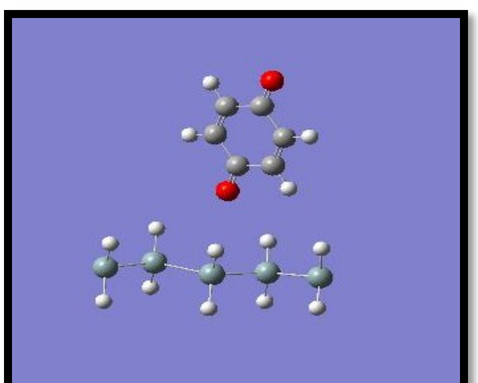
E(RB3LYP) -1836.13906522 a.u.



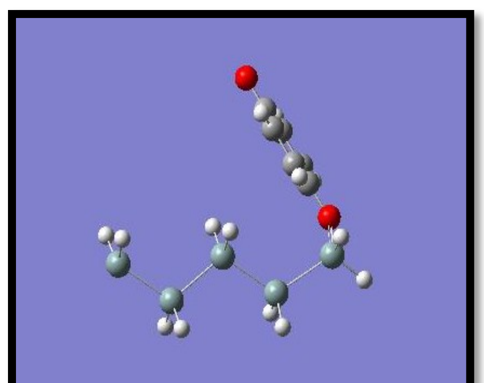
E(UB3LYP) -1835.49367944 a.u.



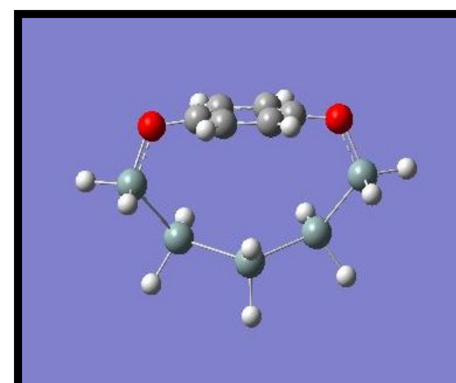
E(UB3LYP) -1835.57636854 a.u.



E(RB3LYP) -1834.83111993 a.u.



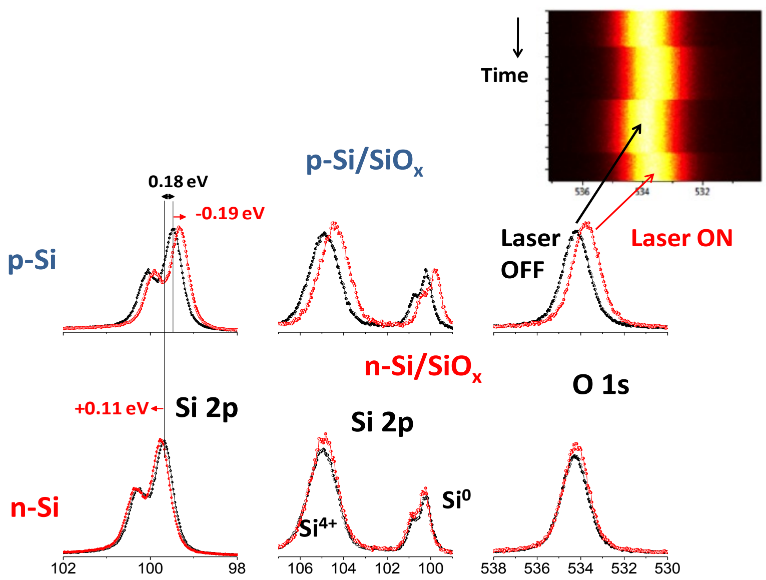
E(RB3LYP) -1834.89637738 a.u.

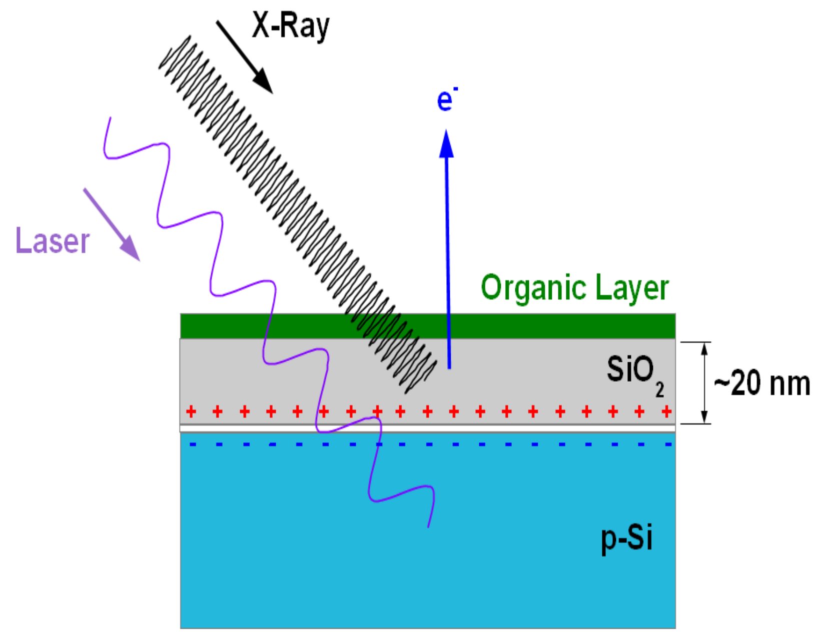


E(RB3LYP) -1835.04268090 a.u.

# Surface Photovoltage

with Prof. Sefik Suzer, Bilkent University



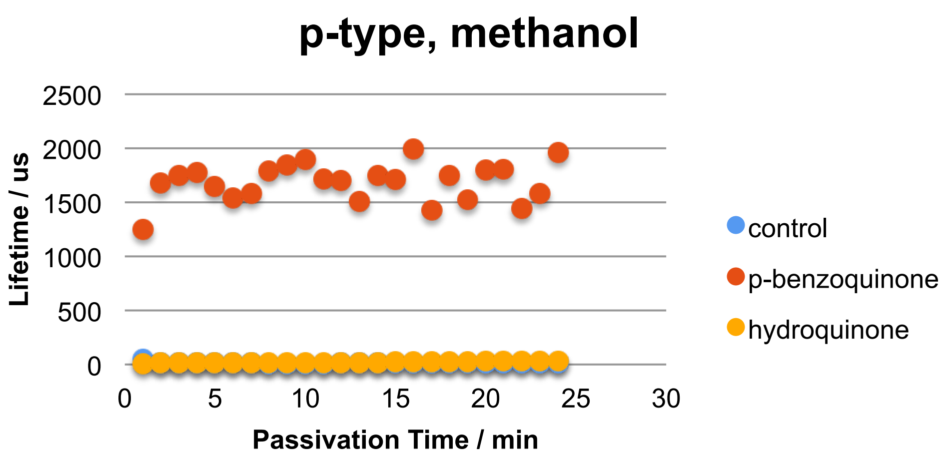



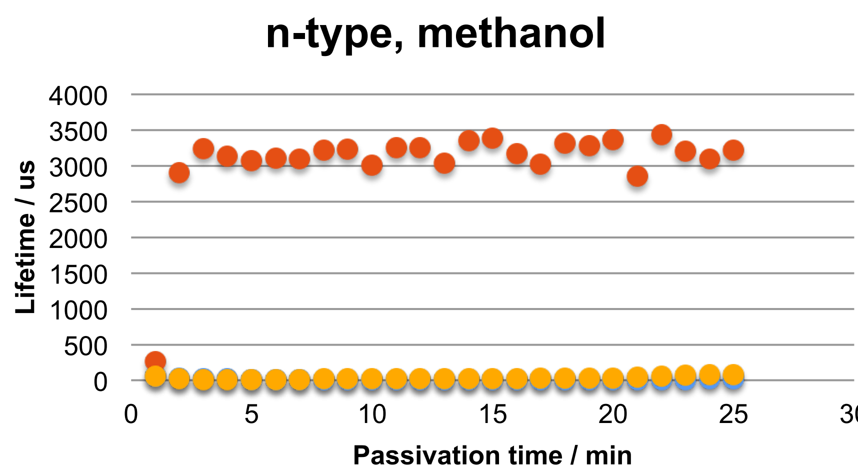

Can induce shifts in surface potential (binding energy) by up to 0.5 eV with laser

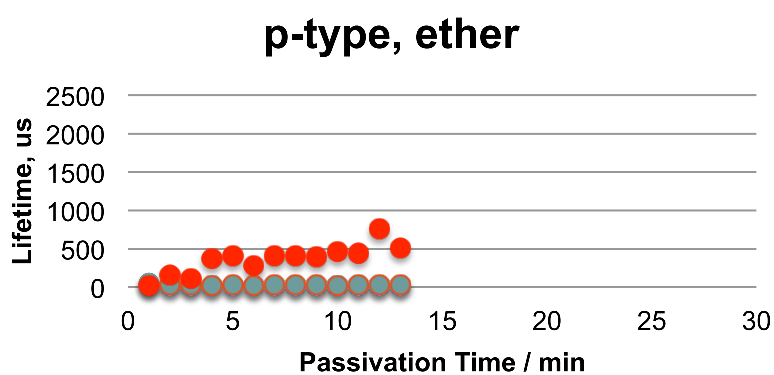
- Can this induce changes in contact angle?
- Different surface chemistry (redox chemistry)?

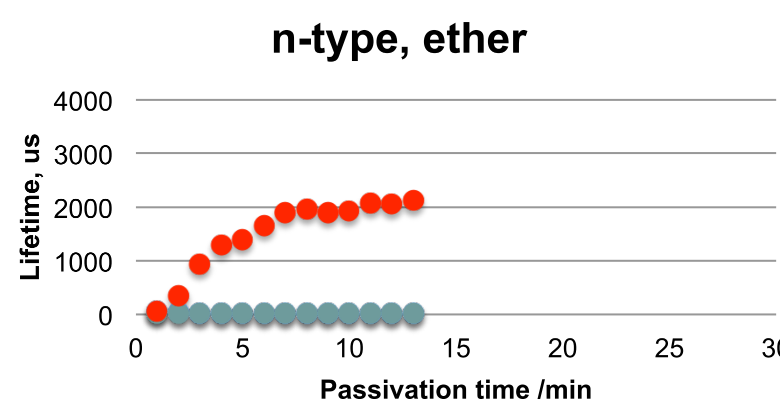
# Lifetime tester, data

**Kotulak, Costello, Chen**




Not simple redox

Protons are important

# Surface chemistry is crucial in next generation solar cells!!!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Darika Okeeva, Bilkent University
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