Oxide/(In)GaAs interfacial electronic characteristics by *in-situ* synchrotron radiation photoemission (SRPES)

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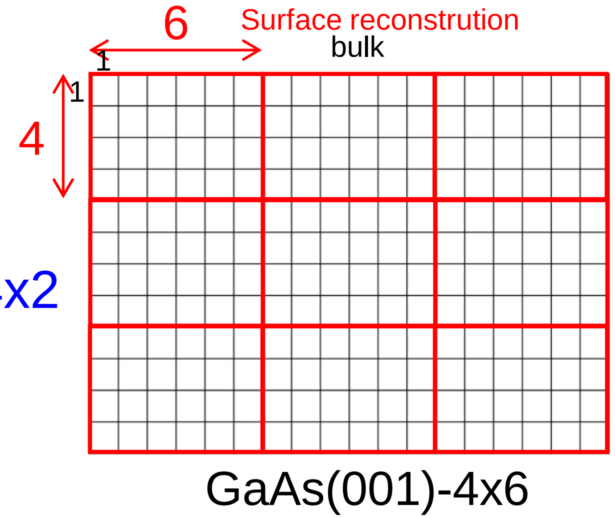
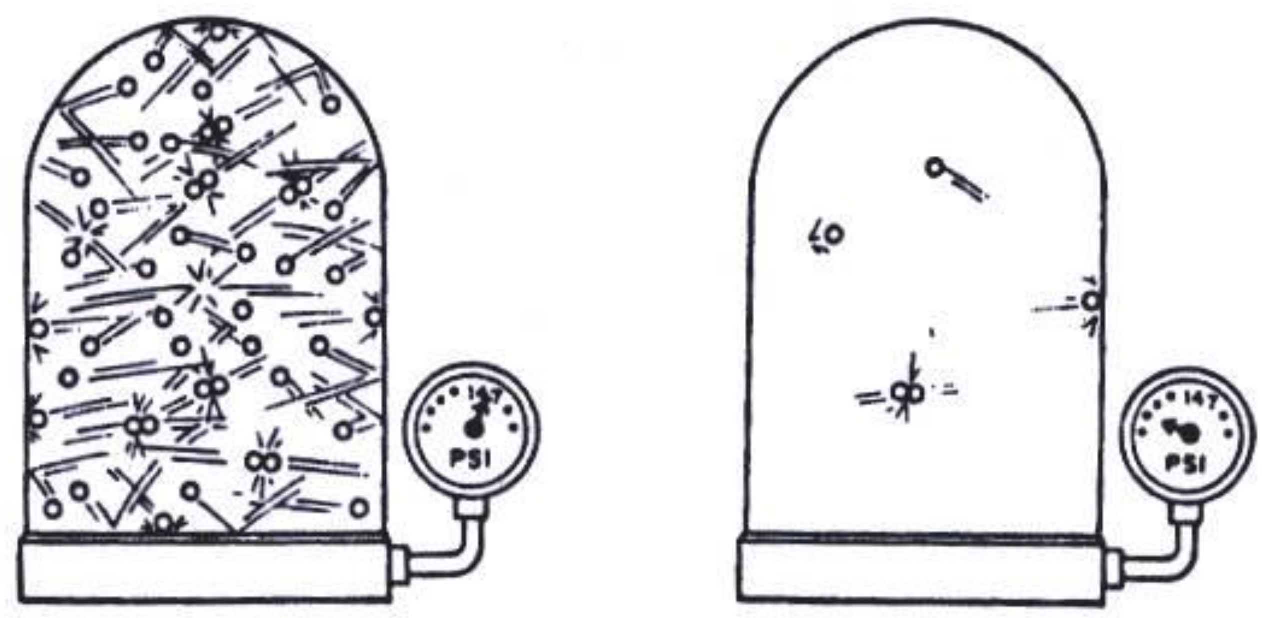
Outline

- Why ultra-high vacuum (UHV)?
  - all UHV process from growth to measurement
- Motivation
  - ALD/MBE high-k/(In)GaAs interfaces with excellent CVs
- Experimental
  - sample growth in an integrated MBE/ALD system
  - *in-situ* synchrotron radiation photoemission (SRPES)
- Initial growth mechanism
  - ALD Y_2O_3/GaAs(001)-4x6
  - MBE Y_2O_3 or HfO_2/GaAs(001)-4x6
  - MBE Y_2O_3 or HfO_2/$In_{0.53}Ga_{0.47}As$(001)-4x2



What is vacuum?



(a)大氣　　(b)真空

壓力<大氣壓力

圖 1.5　大氣與真空狀態下之分子數目

Definition of Vacuum

Atmosphere	1 atom = 760 torr
Rough (low) vacuum	759 - 10^{-3} torr
Medium vacuum	10^{-3} - 10^{-5} torr
High vacuum (HV)	10^{-5} - 10^{-8} torr
Ultra high vacuum (UHV)	< 10^{-8} torr

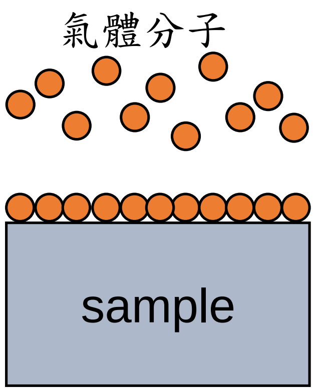
壓力大小與殘留氣體負荷

壓力 (torr)	主要氣體負荷
760	N_2 (約為78%)
10^{-3}	H_2O (約為75%)
10^{-6}	H_2O, CO
10^{-9}	H_2, CO
10^{-10}	H_2, CO
10^{-11}	H_2

Why ultra-high vacuum (UHV)?

壓力與單層膜形成時間之關係

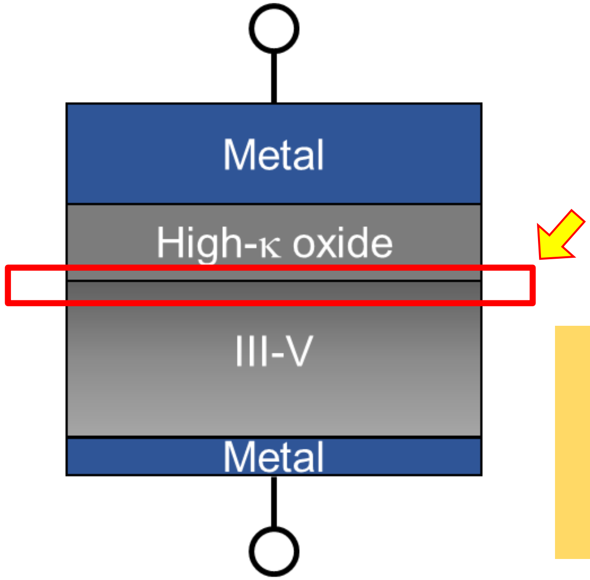
壓力 (torr)	單層膜形成時間 (sec)
10^{-6}	1
10^{-7}	10
10^{-8}	100
10^{-9}	1000



The characterization of a solid surface on an atomic level implies unambiguously that the surface composition remains essentially unchanged over the duration of an experiment.

MBE-oxide/III-V interface

✓ ***Excellent CV characteristics***
✓ ***High thermal stability to 900 ºC***
✓ ***Low D_{it} ~(2-5)x10^{11} eV^{-1}cm^{-2} without peak in the mid-gap***



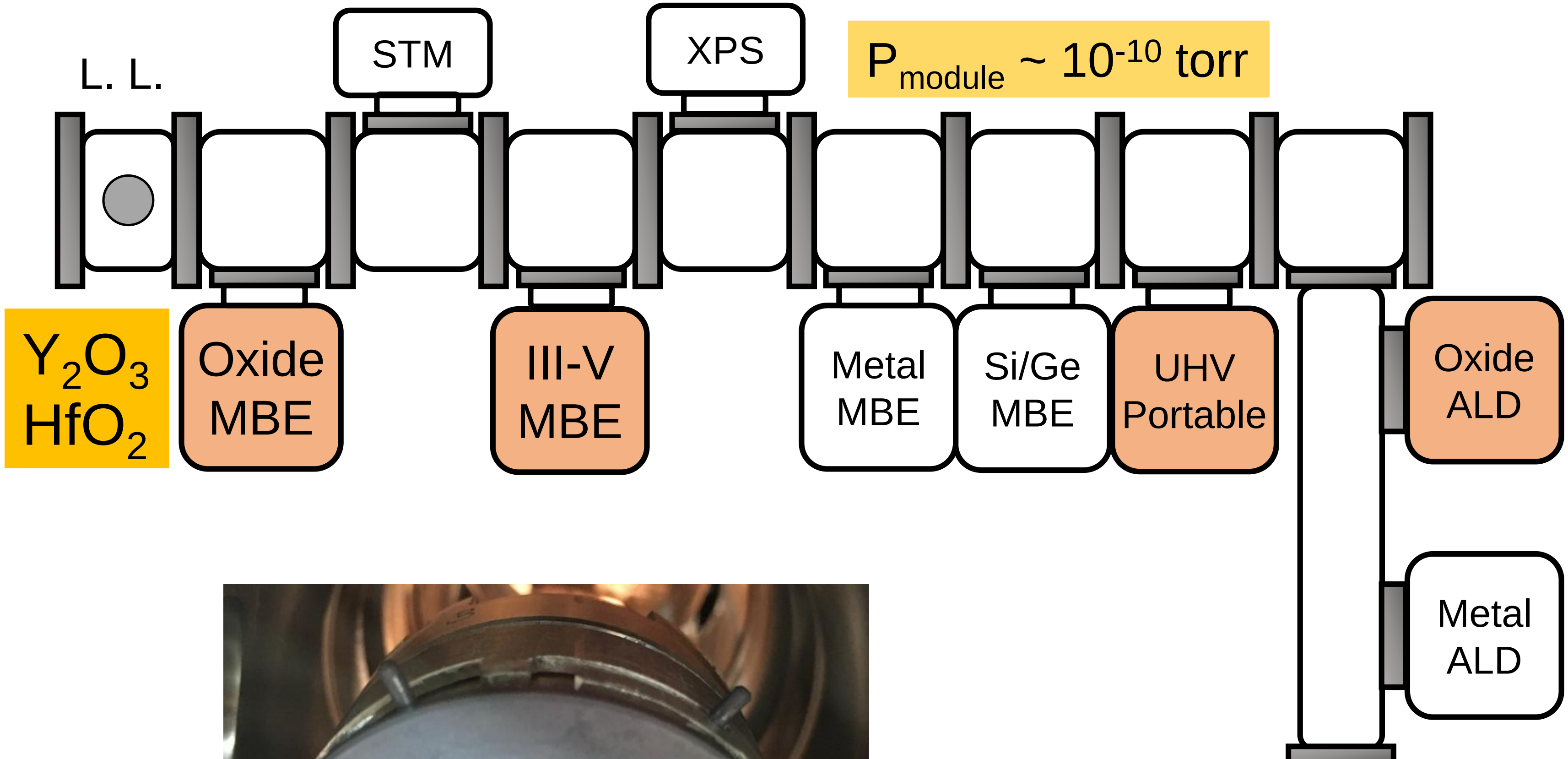
MOSCAP

In-situ
synchrotron radiation photoemission (SRPES)

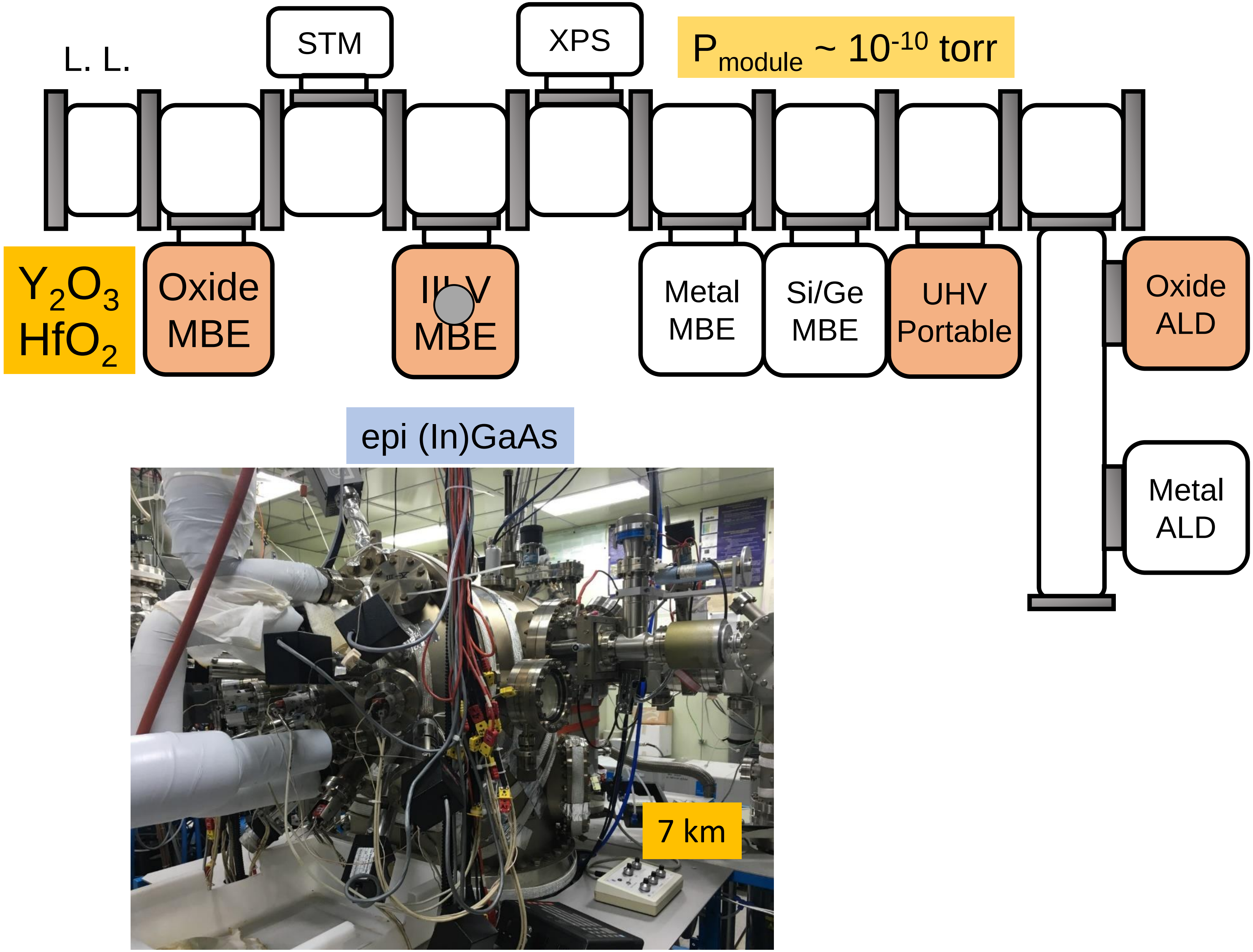
SRPES
- **high surface sensitivity (λ = 4 Å)**
- **high energy resolution (< 40 meV)**

➢ **SRPES**: direct observation of interfacial electronic structure

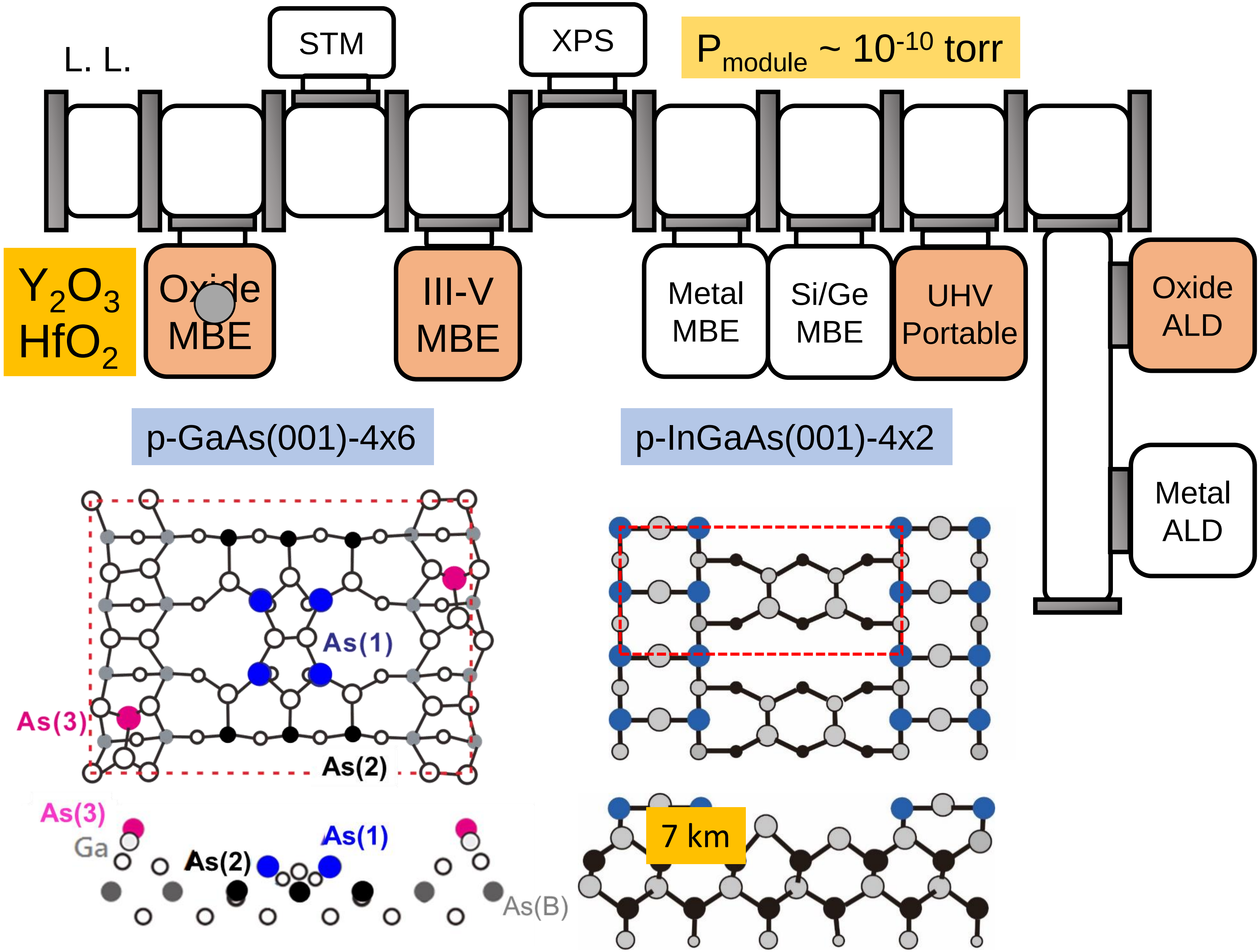
sample growth and transfer



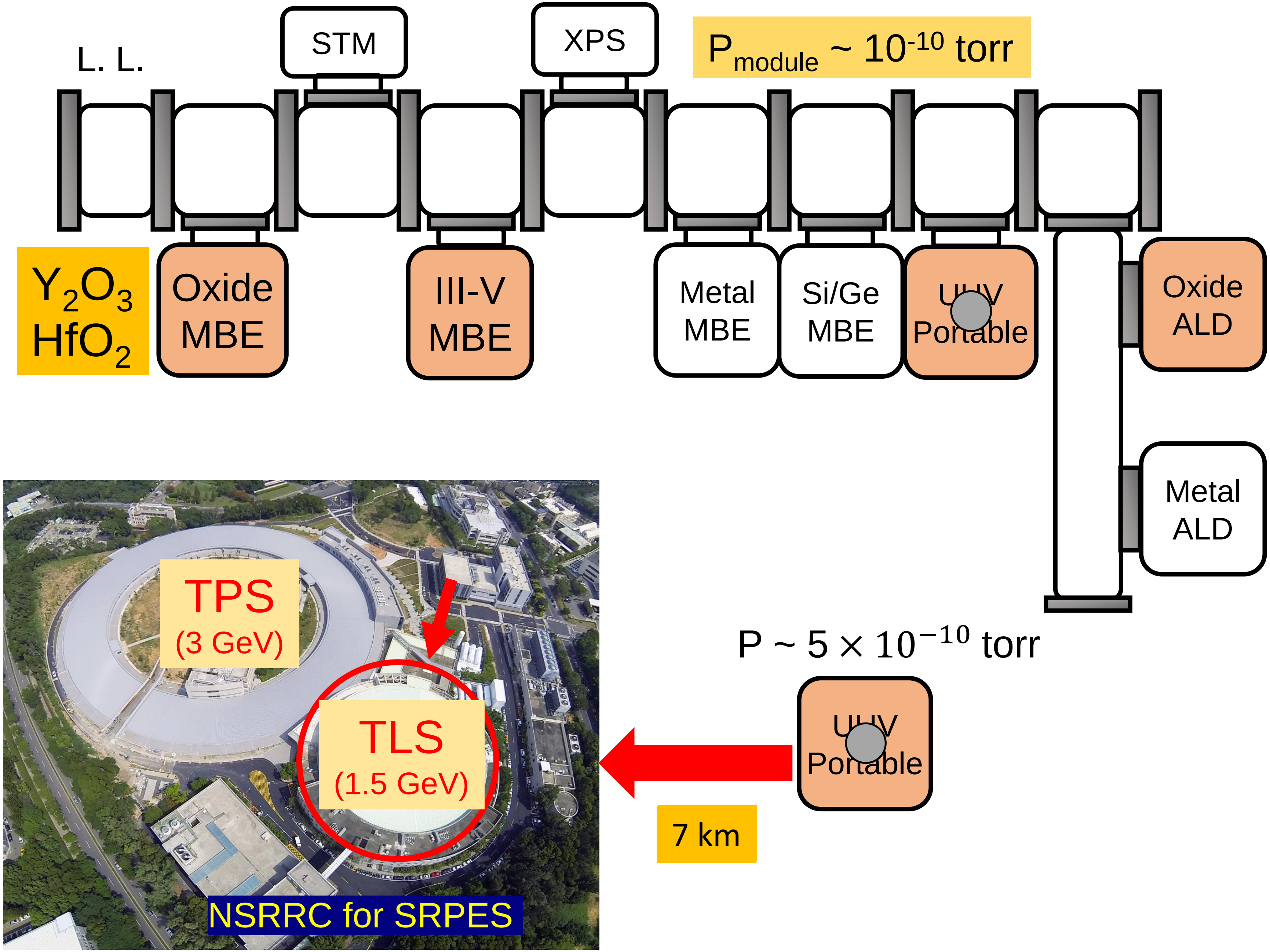
sample growth and transfer



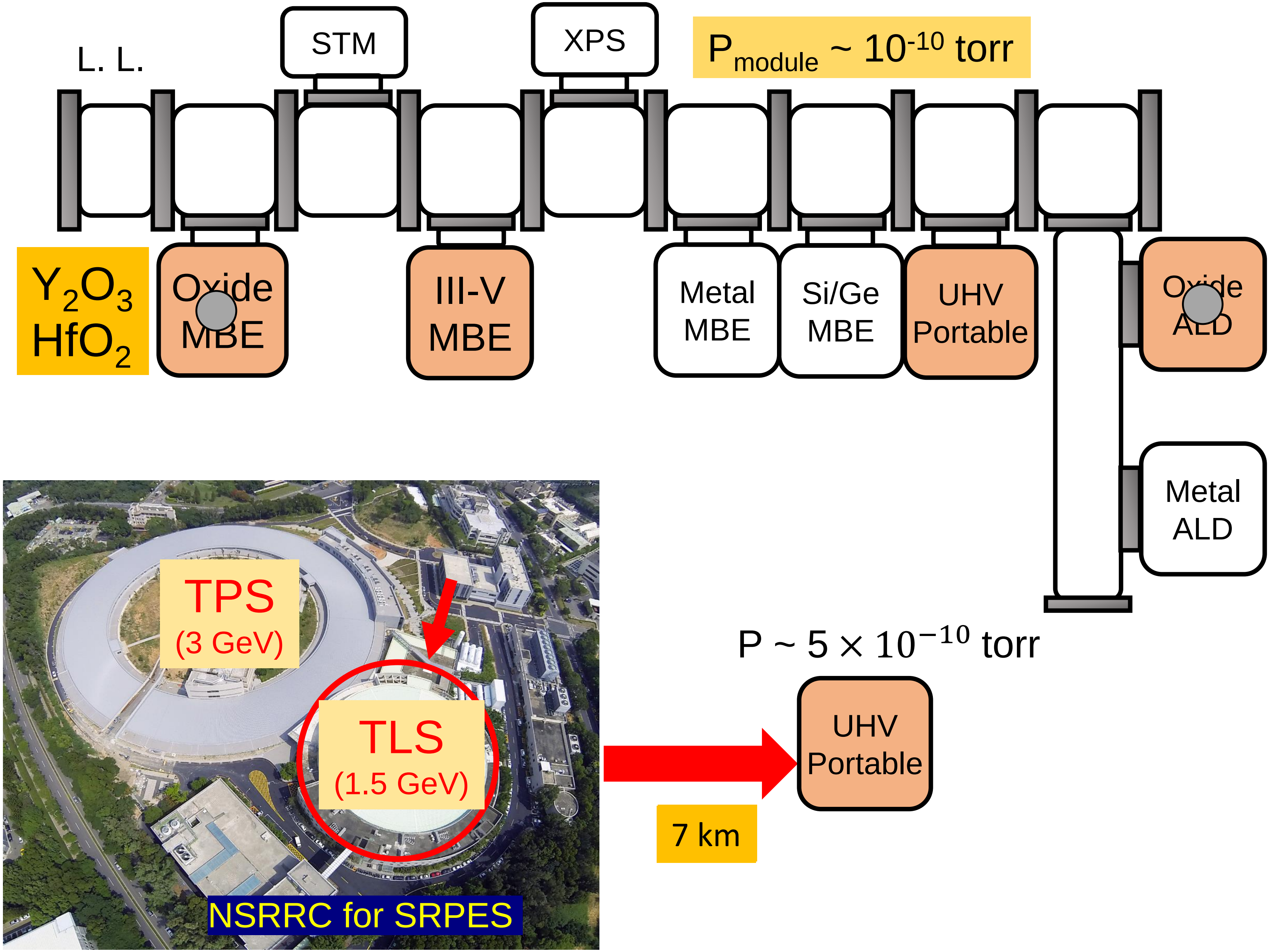
sample growth and transfer



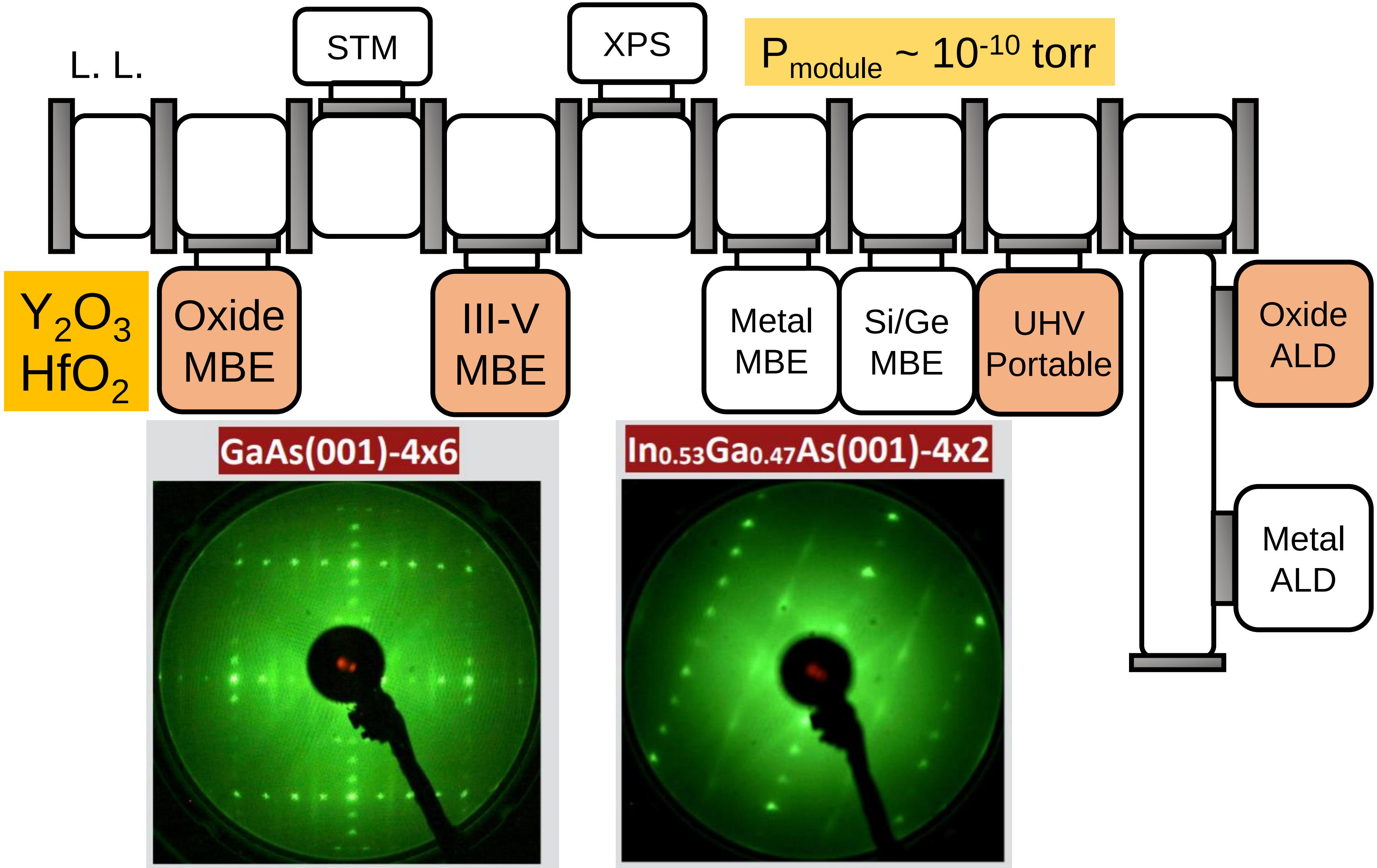
sample growth and transfer



sample growth and transfer



sample growth and transfer



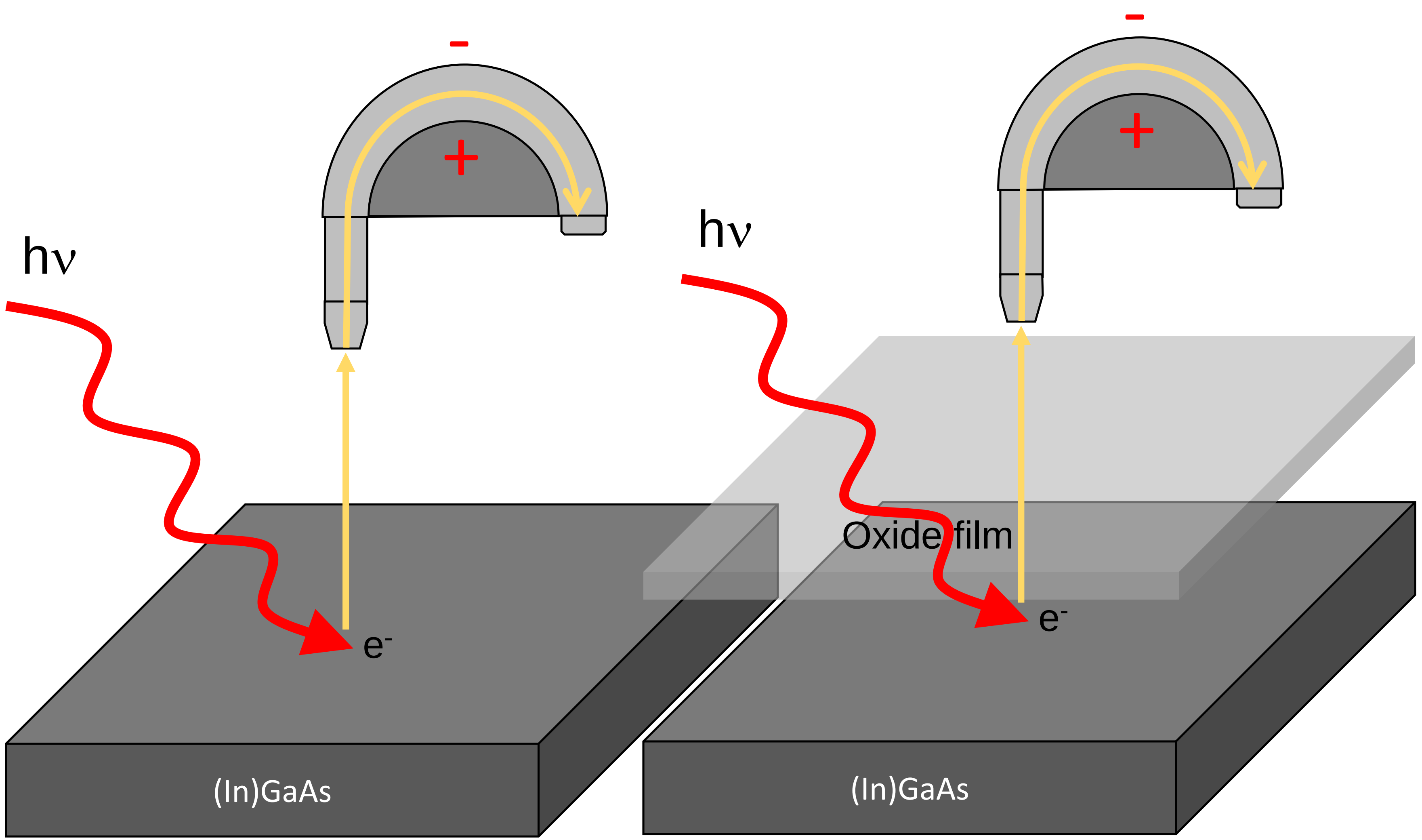
Clear observation of the interfacial evolution for Y_2O_3 / HfO_2 deposited on (In)GaAs.

量測方法

1. Clean (In)GaAs

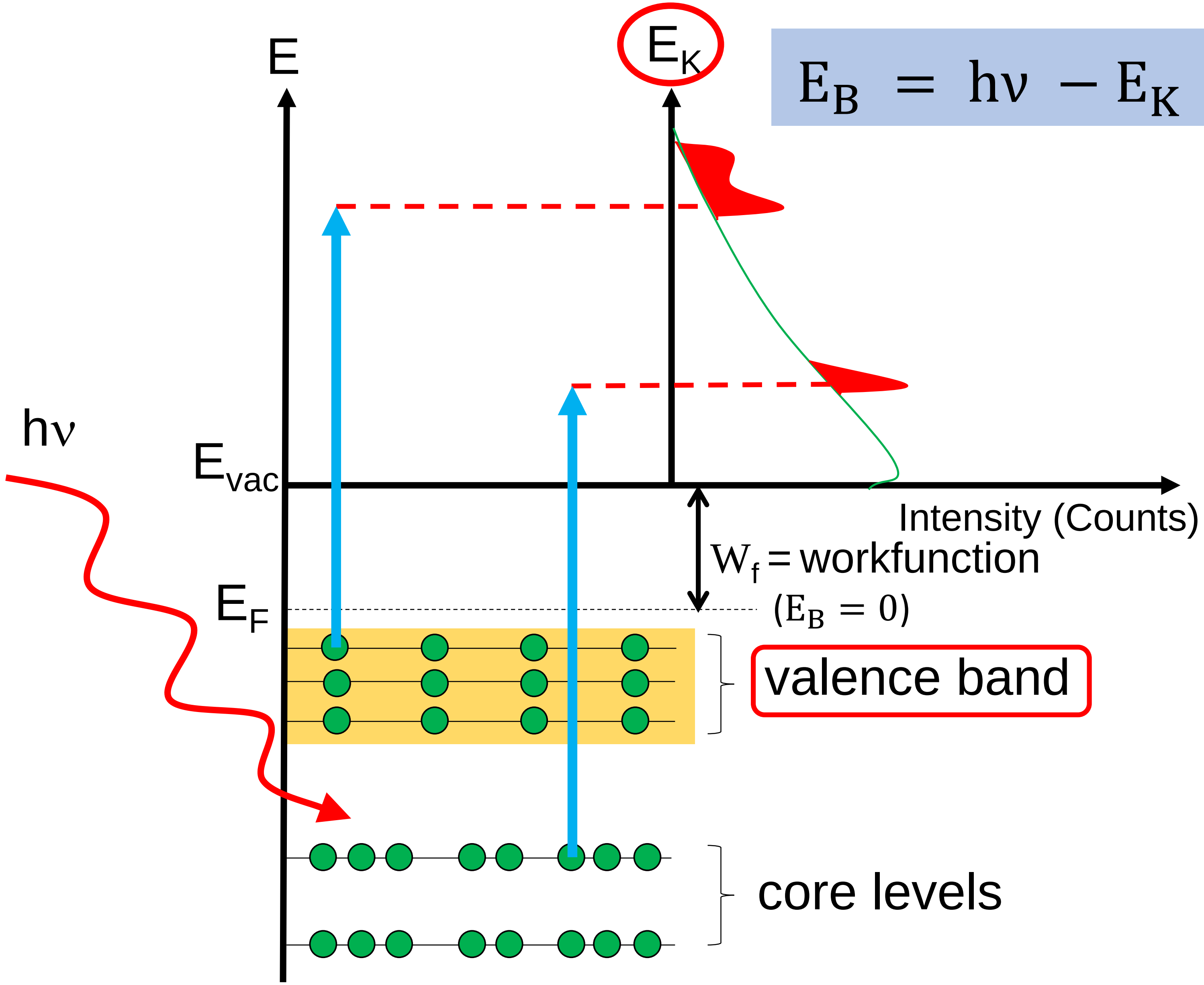
P_{base} = 1 x 10^{-10} torr

2. oxide/(In)GaAs



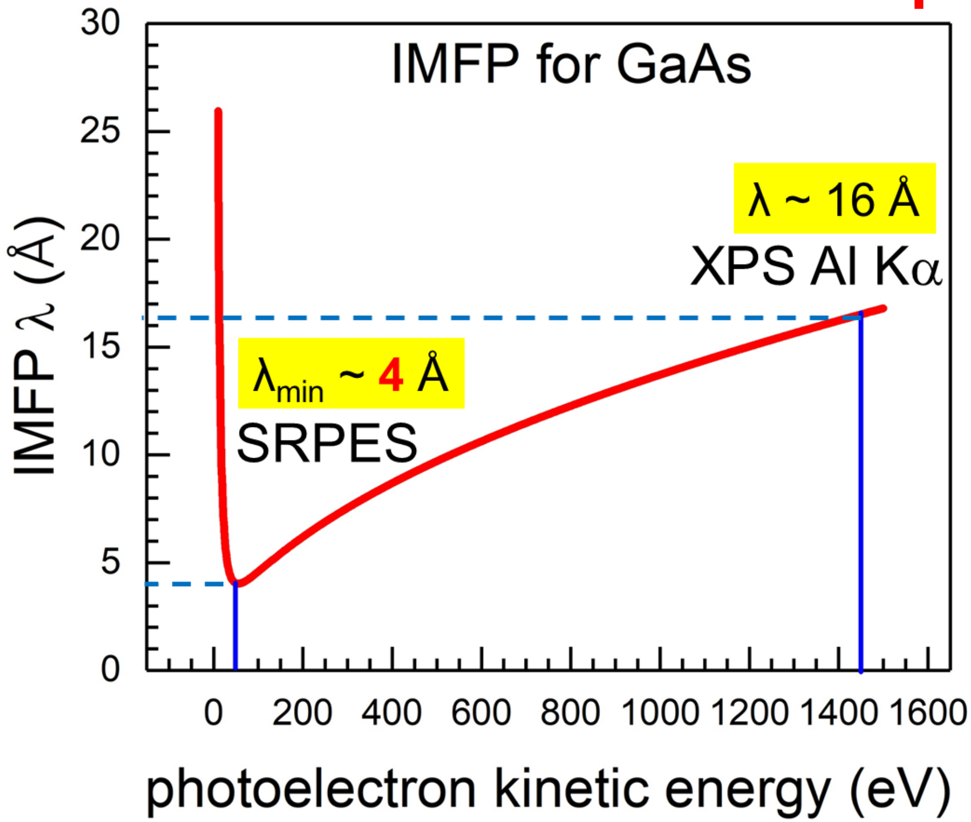
Photoemission

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



Advantage of synchrotron radiation photoemission

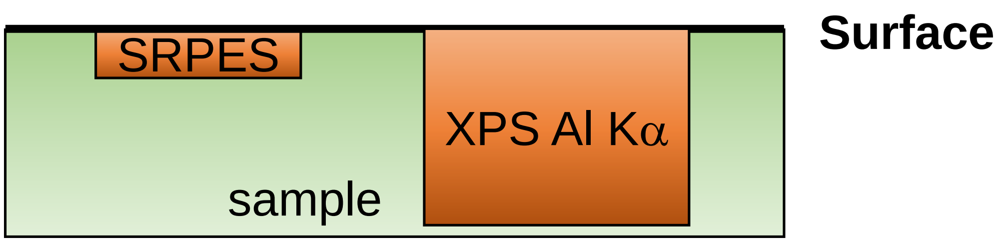
IMFP = inelastic mean free path



[Surf. Interface Anal. **1,** 2 (1979)]

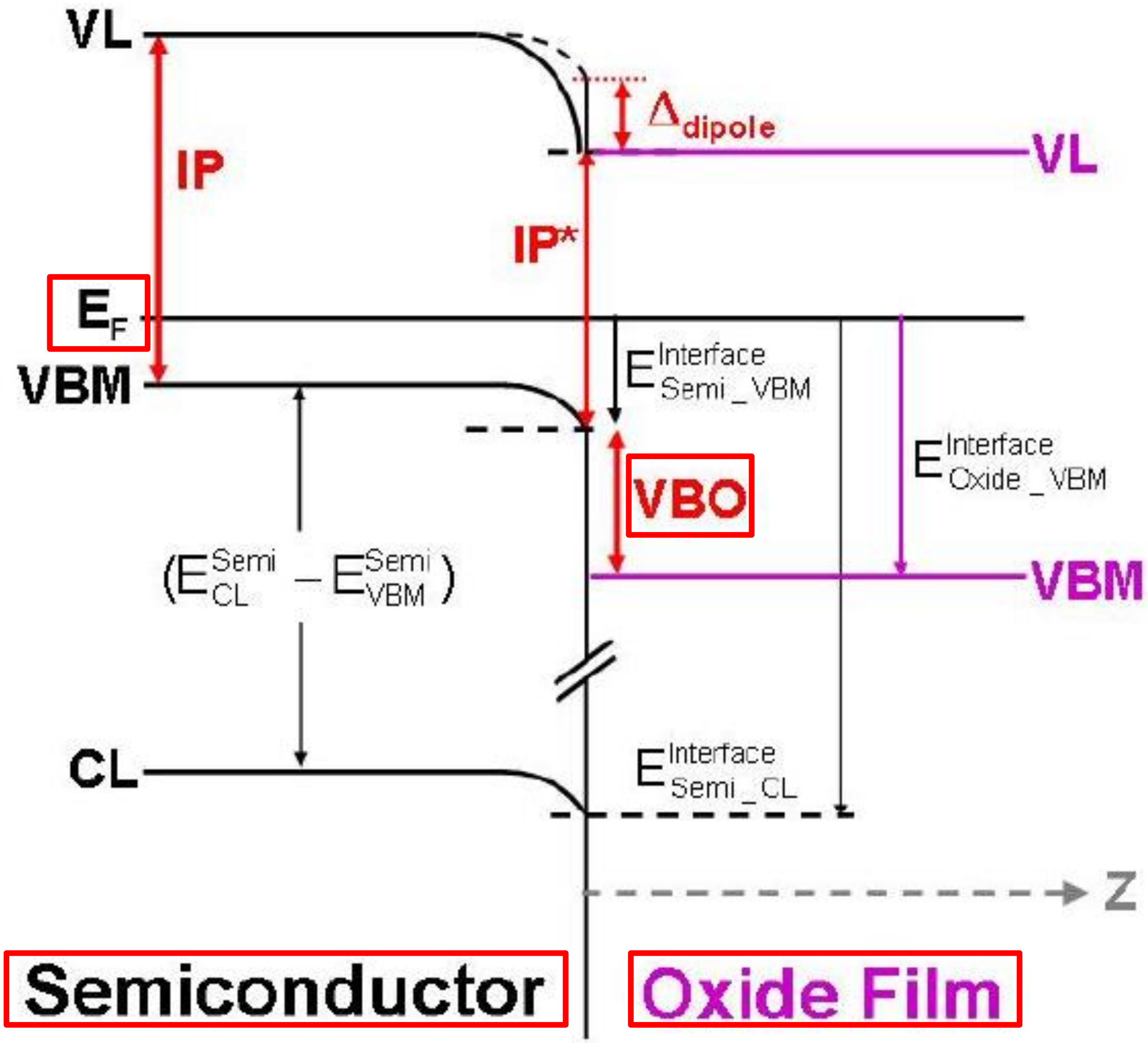
Tunable photon energy

- ✓ high surface sensitivity ($\lambda = 4$ Å)
- ✓ high energy resolution (< 40 meV)

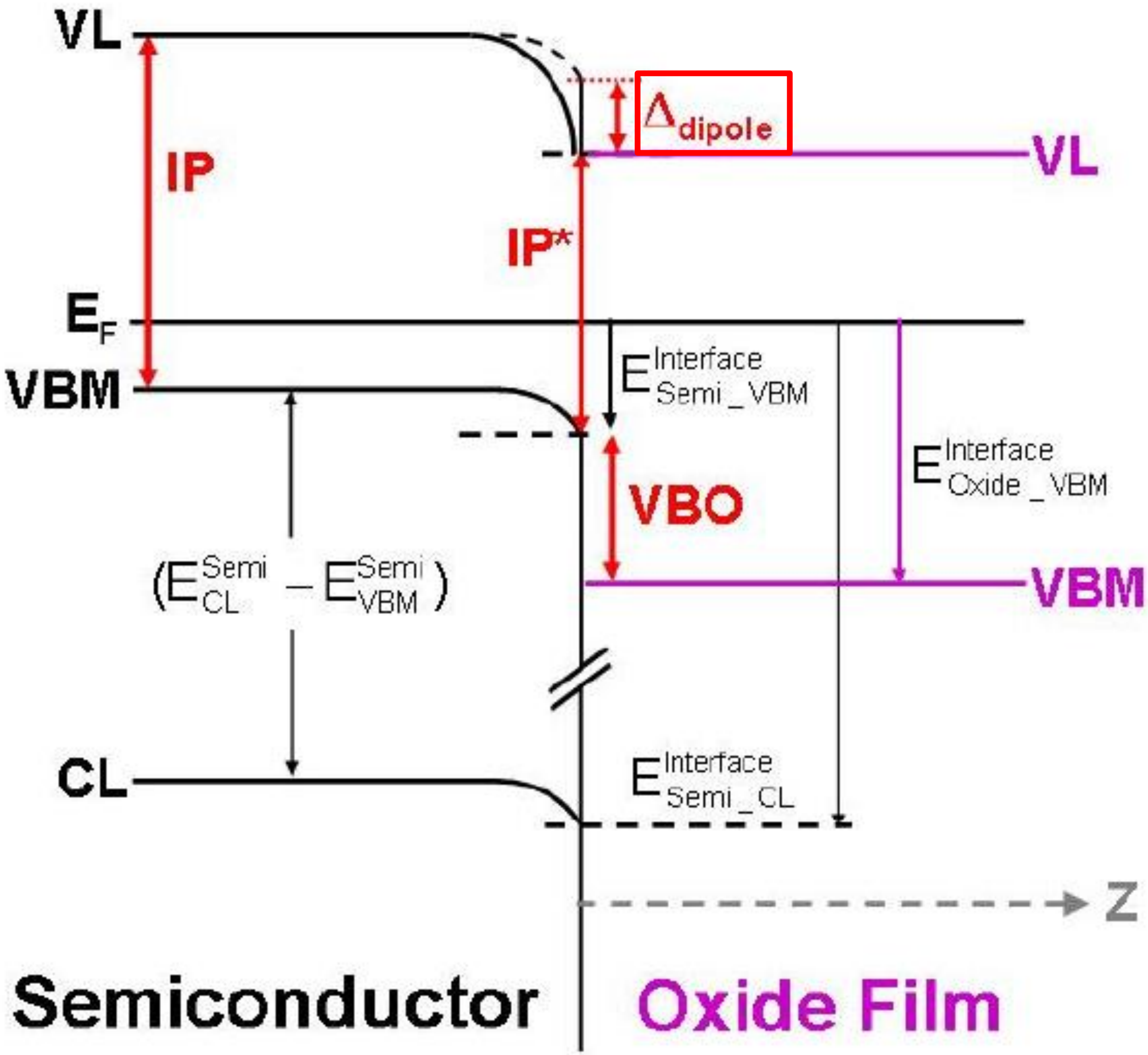


Probing depth from surface

Band diagram

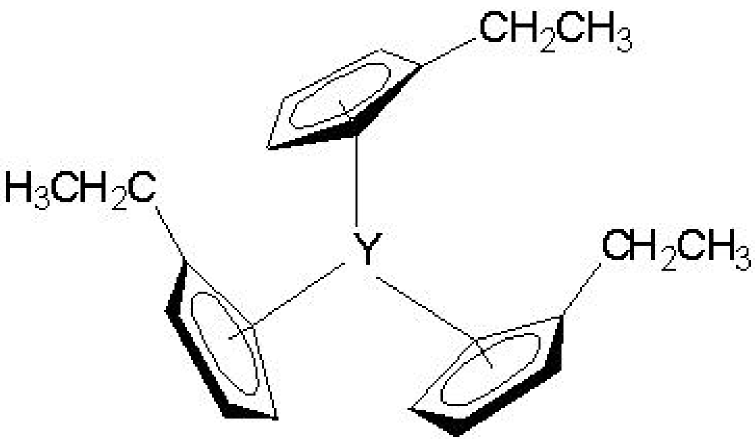


Band diagram

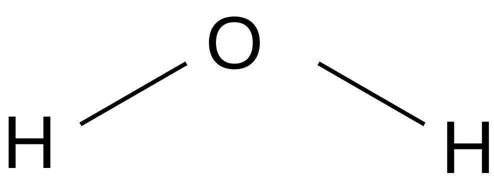


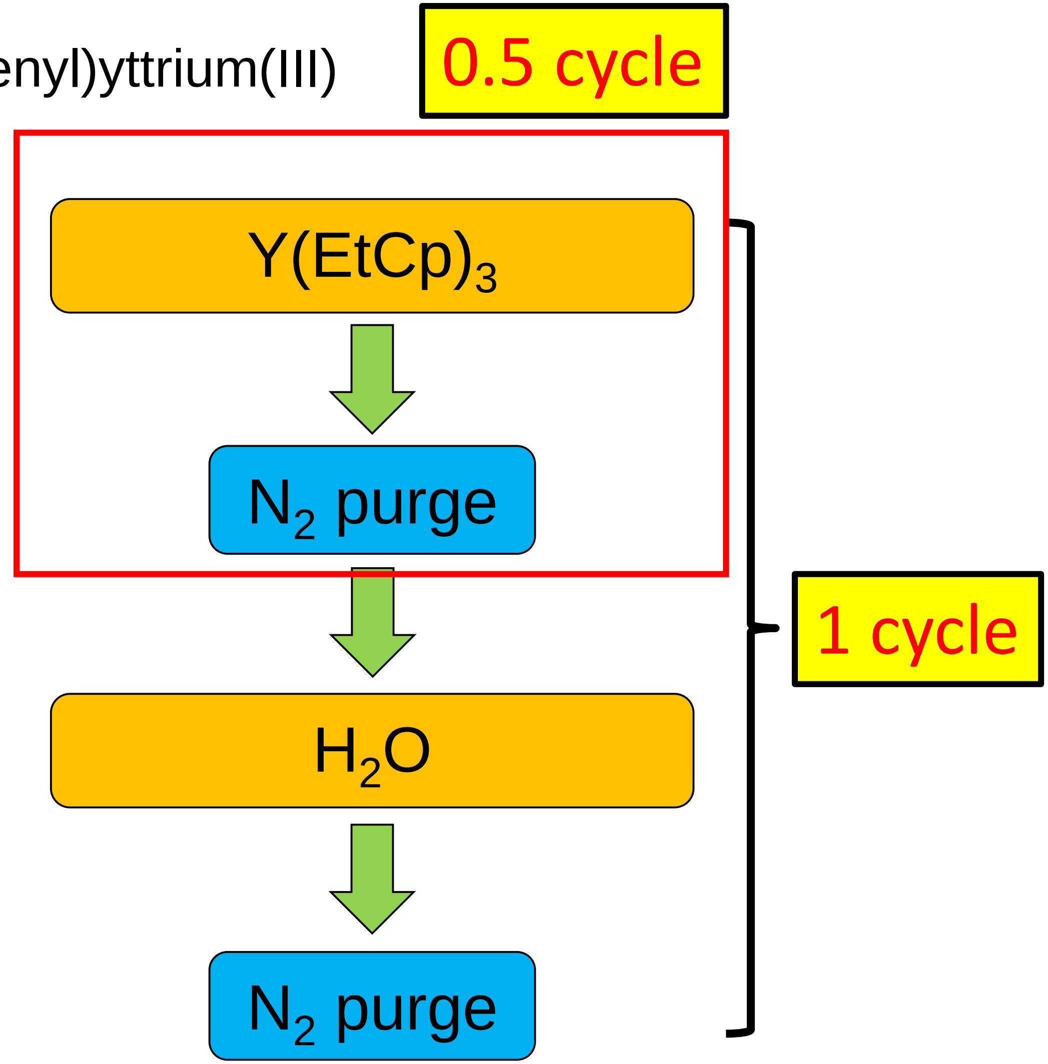
ALD-Y_2O_3 growth

$Y(EtCp)_3$ → Tris(ethylcyclopentadienyl)yttrium(III)



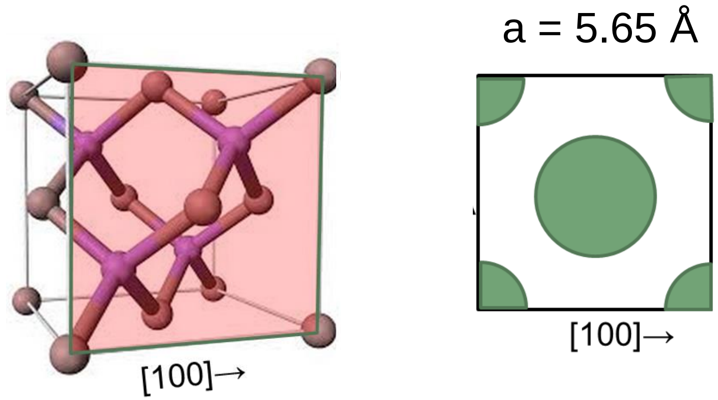
Water (H_2O)



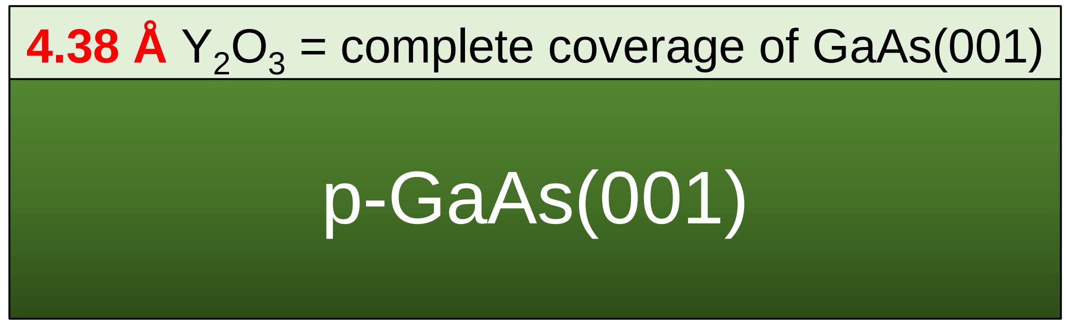


Complete coverage of Y_2O_3 on GaAs(001)

$\theta_{Y_2O_3}$(Å) with respect to GaAs lattice



(a) (b)



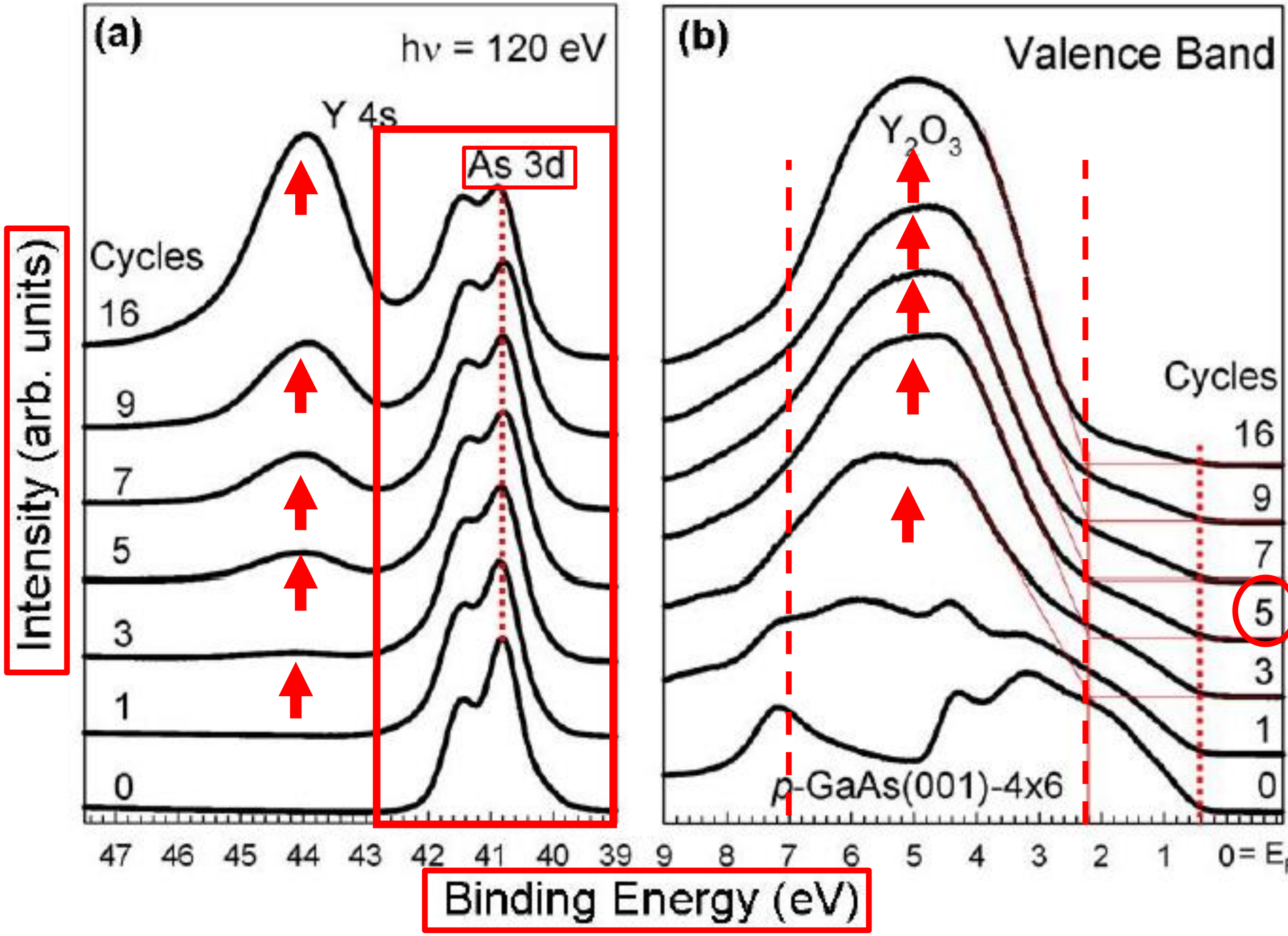
$$\mathrm{D_A} = surface\ atomic\ density\ of\ GaAs(001) = 6.27 \times 10^{14} atoms/cm^2$$

$$D_V = Volume\ density\ of\ Y_2O_3 = 1.43 \times 10^{22}\ atoms/cm^3$$

Complete coverage $= \dfrac{D_A}{D_V} = \dfrac{6.27 \times 10^{14}\ atoms/cm^2}{1.43 \times 10^{22}\ atoms/cm^3} = \mathbf{4.38\ Å}$

SRPES results

No band bending



Complete Y_2O_3 coverage = 4.38 Å

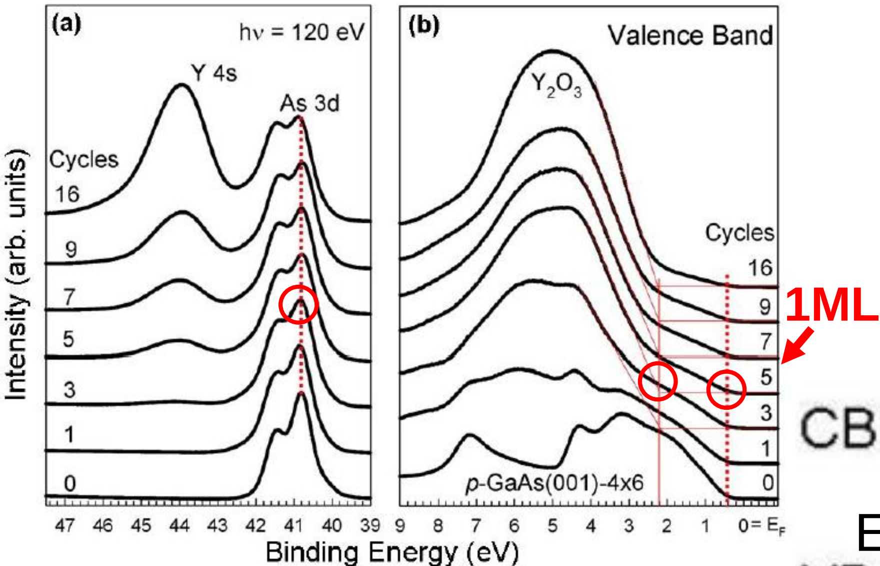
5 cycles ~ 4.59 Å

Complete coverage

$VBM_{Y_2O_3}$ = 2.2 eV

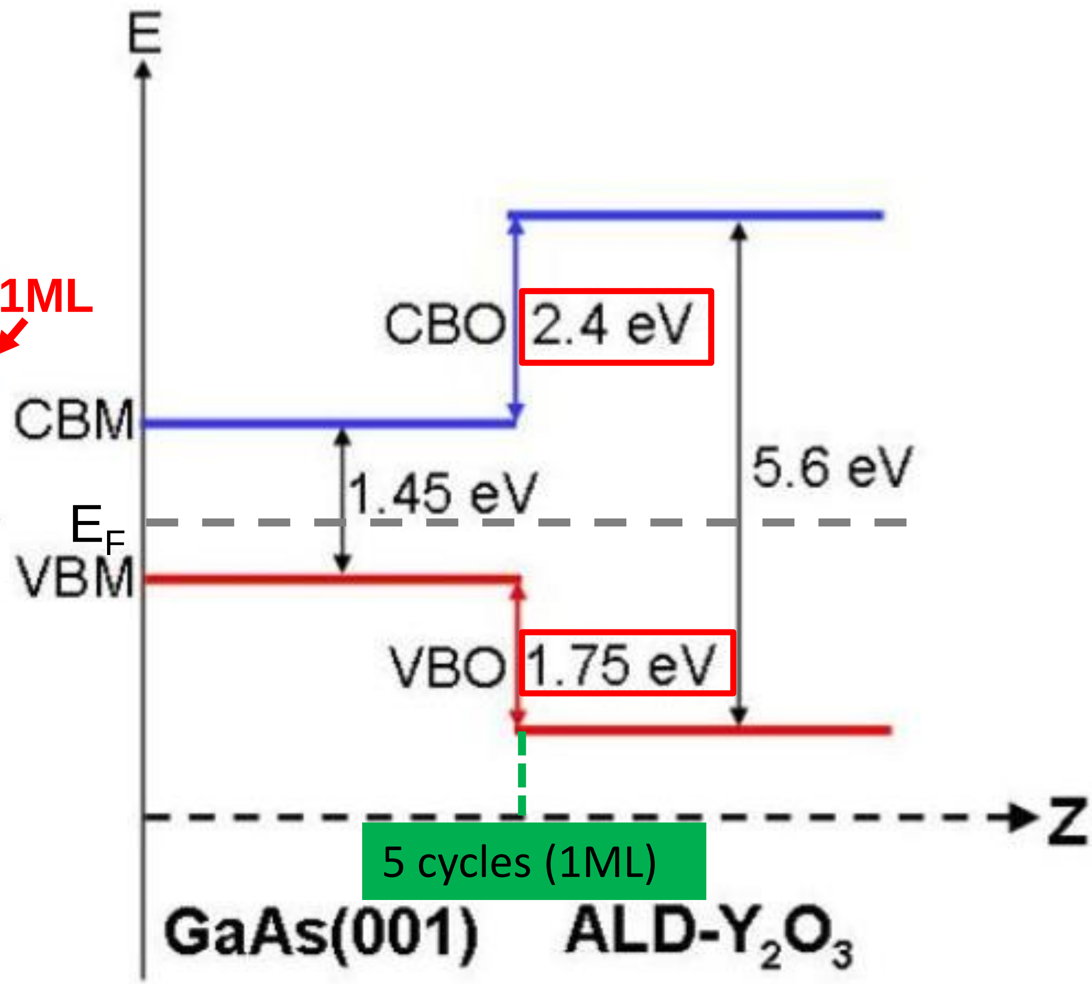
VBM_{GaAs} = 0.45 eV

Band diagram



VBM$_{GaAs}$ = 0.45 eV

VBM$_{Y_2O_3}$ = 2.2 eV



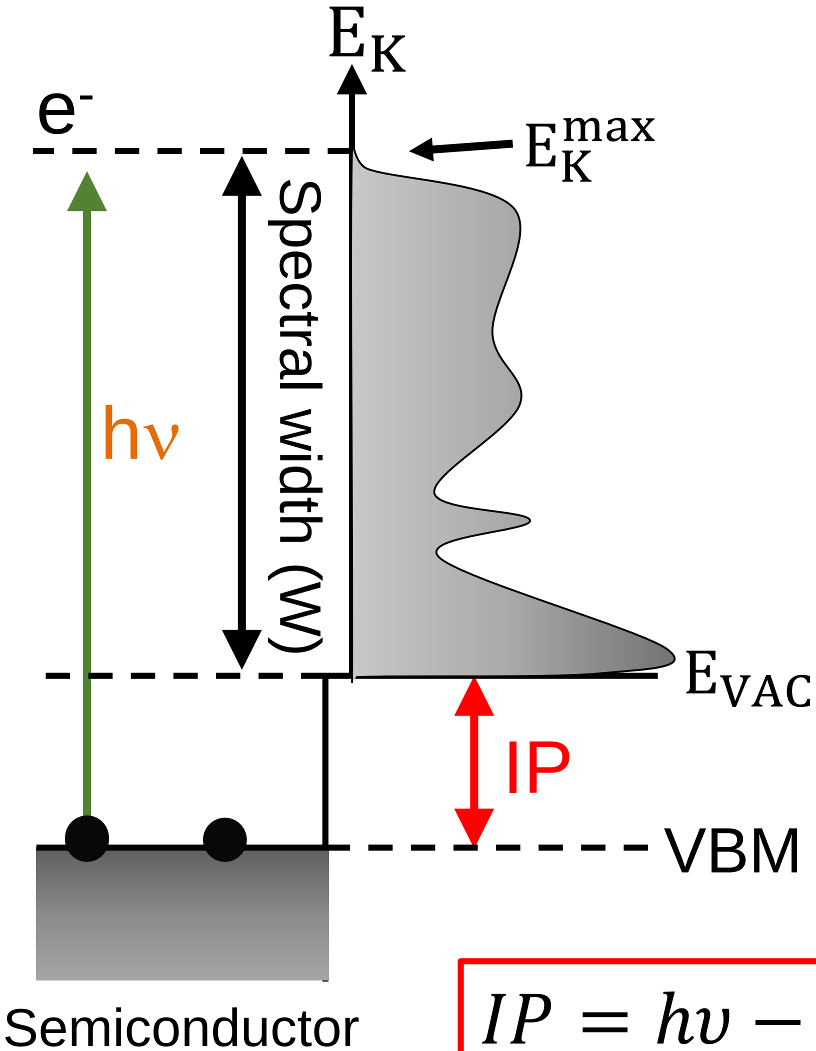
We can obtain the band offset of 1 ML oxide film on semiconductor

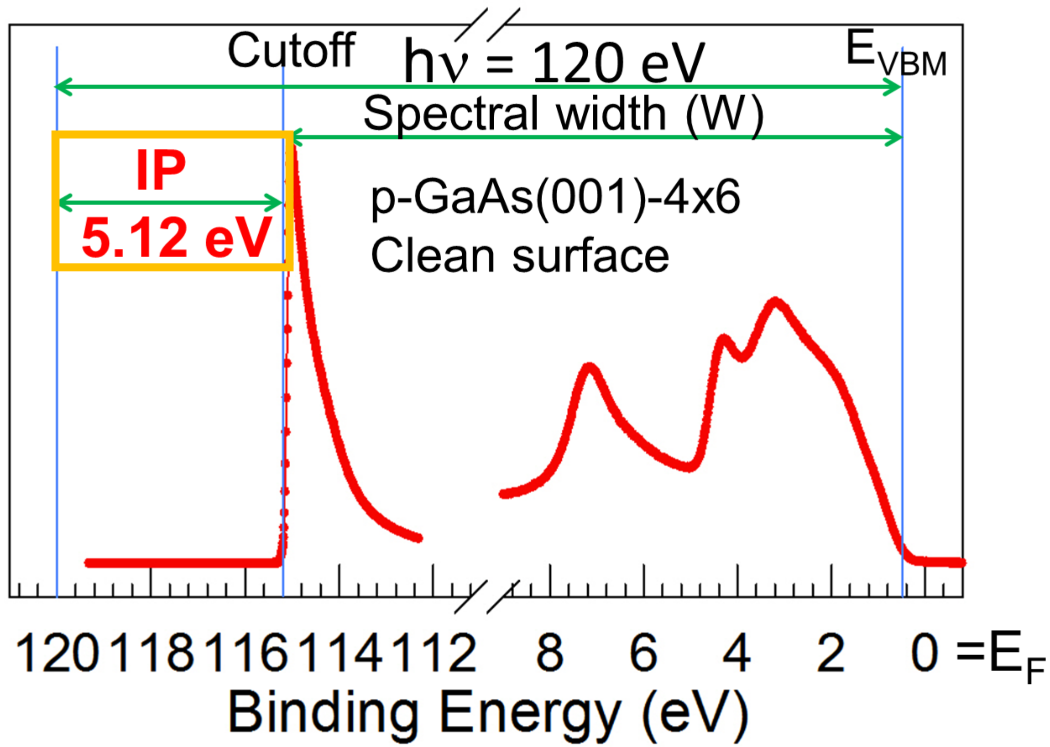
Interfacial dipole potential energy

Interfacial dipole potential energy

$\equiv \; IP_{clean} - IP_{adsorbate}$ 

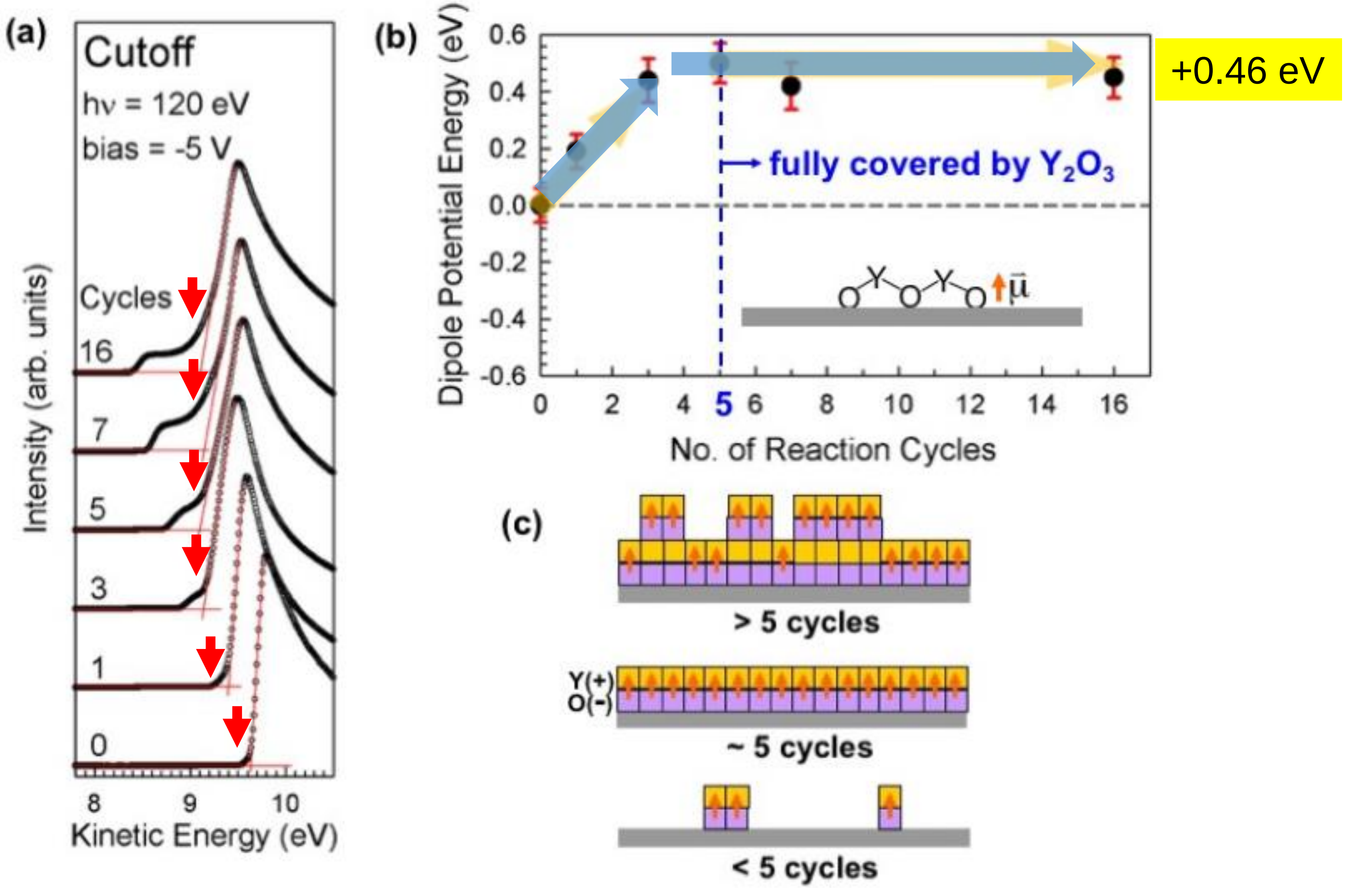
Determination of ionization potential energy

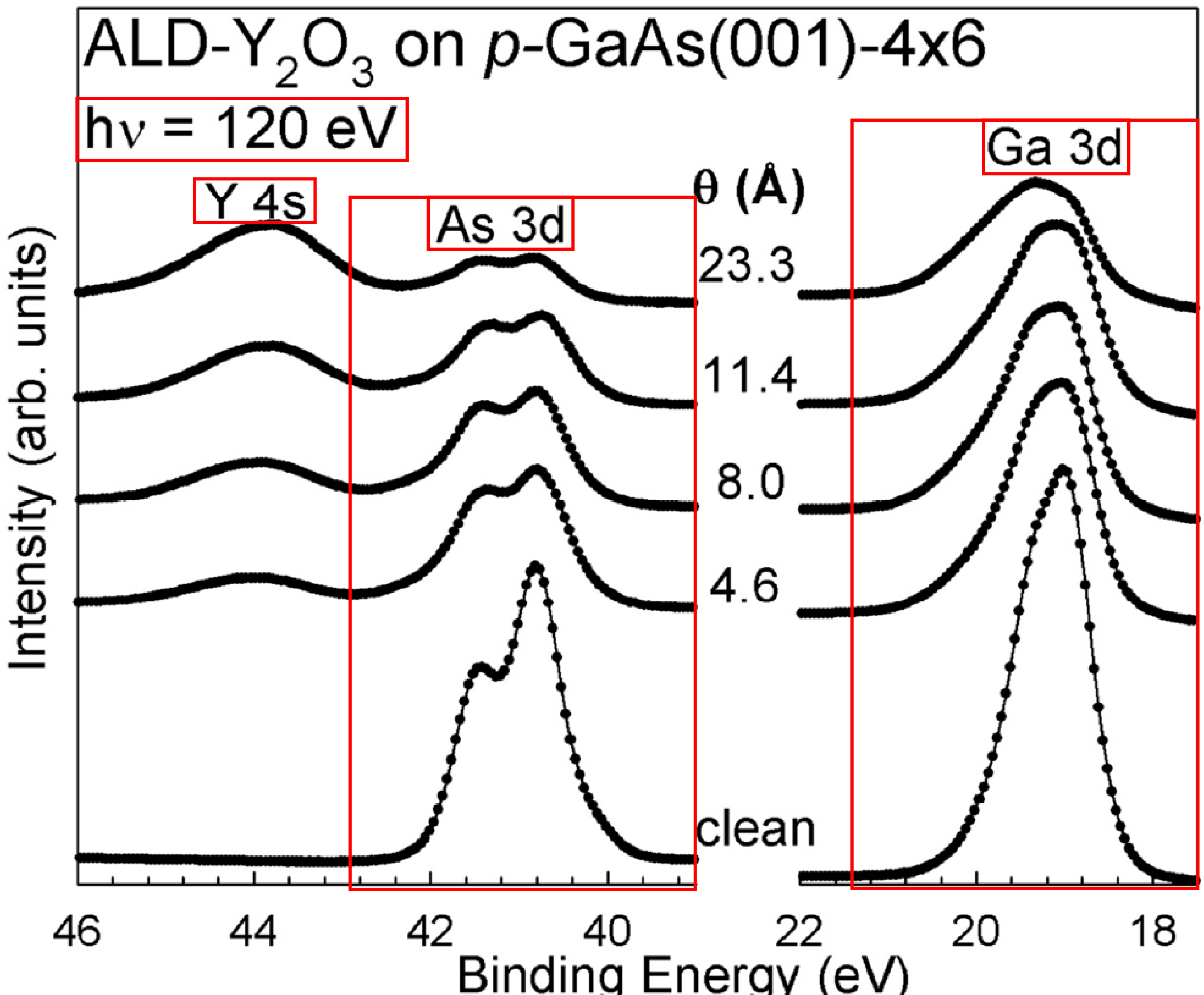




$$IP = h\upsilon - W$$
$$= h\upsilon - (\text{cutoff} - \text{VBM})$$

Interfacial dipole potential energy



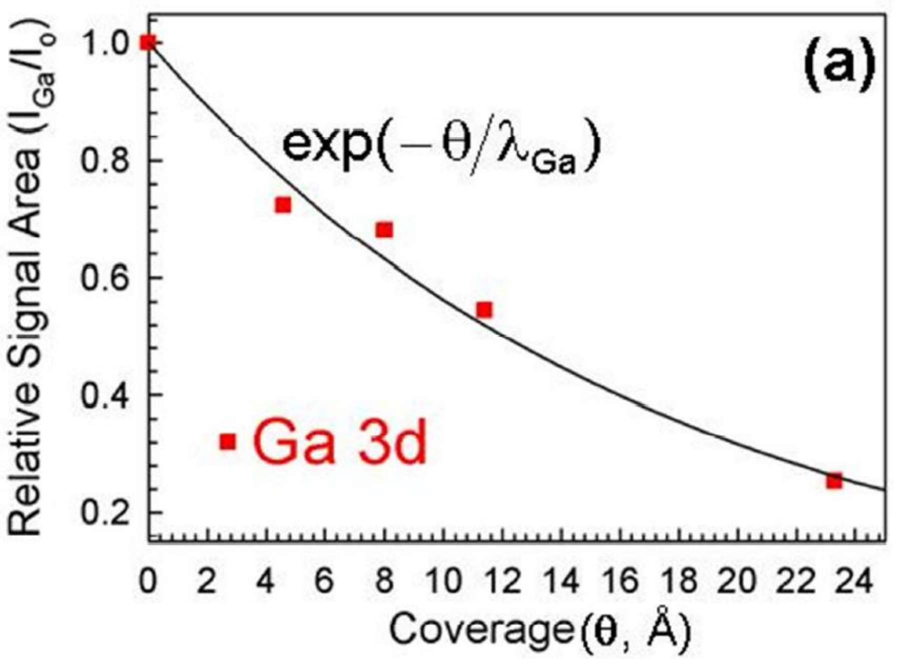


ALD-Y2O3 on p-GaAs(001)-4x6
hν = 120 eV
Y 4s
As 3d
Ga 3d
θ (Å)
23.3
11.4
8.0
4.6
clean
Intensity (arb. units)
46
44
42
40
22
20
18
Binding Energy (eV)

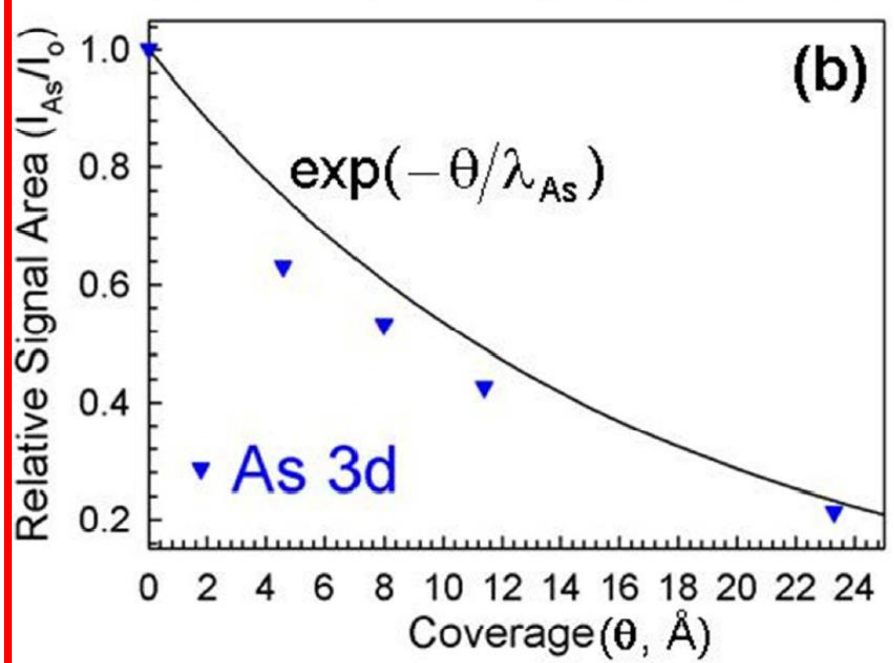
Growth mode

Ideal curve : $\frac{I_\theta}{I_0} = e^{-\theta/\lambda}$

Ga 3d



As 3d



Growth mode

$$I = I_0 e^{-\theta/\lambda}$$

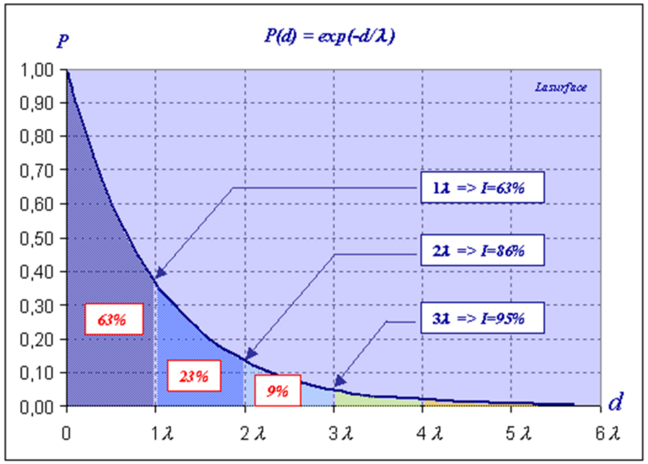
Ideal curve

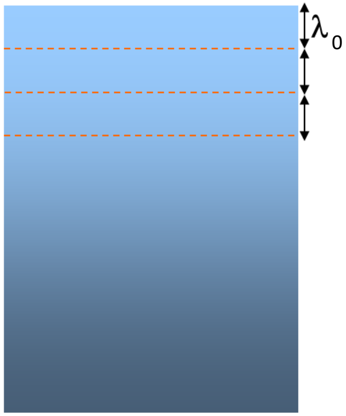
d_0=2.83 Å
λ_0=10.41 Å

$$I_0 = I_s \frac{1}{\left(1 - e^{-d_0/\lambda_0}\right)}$$

Total intensity of clean GaAs

$$\left(I_0 = I_s + I_s e^{-d_0/\lambda_0} + I_s e^{-2\,d_0/\lambda_0} + \cdot\ \cdot\ \cdot\right)$$





⇒ ~ 95% photoelectrons emission from within 3λ below the surface

Growth mode

$$I = I_0 e^{-\theta/\lambda}$$

Ideal curve

$$I_0 = I_s \frac{1}{\left(1 - e^{-d_0/\lambda_0}\right)}$$

Total intensity of clean GaAs

$$I = (I_0 - x * Is)e^{-\theta/\lambda}$$

Assume that x percentage of the surface atoms is removed

$$\frac{I_{As}}{I_{Ga}} = \frac{(I_{0,As} - x * I_{s,As})e^{-\theta/\lambda_{As}}}{I_{0,Ga} e^{-\theta/\lambda_{Ga}}}$$

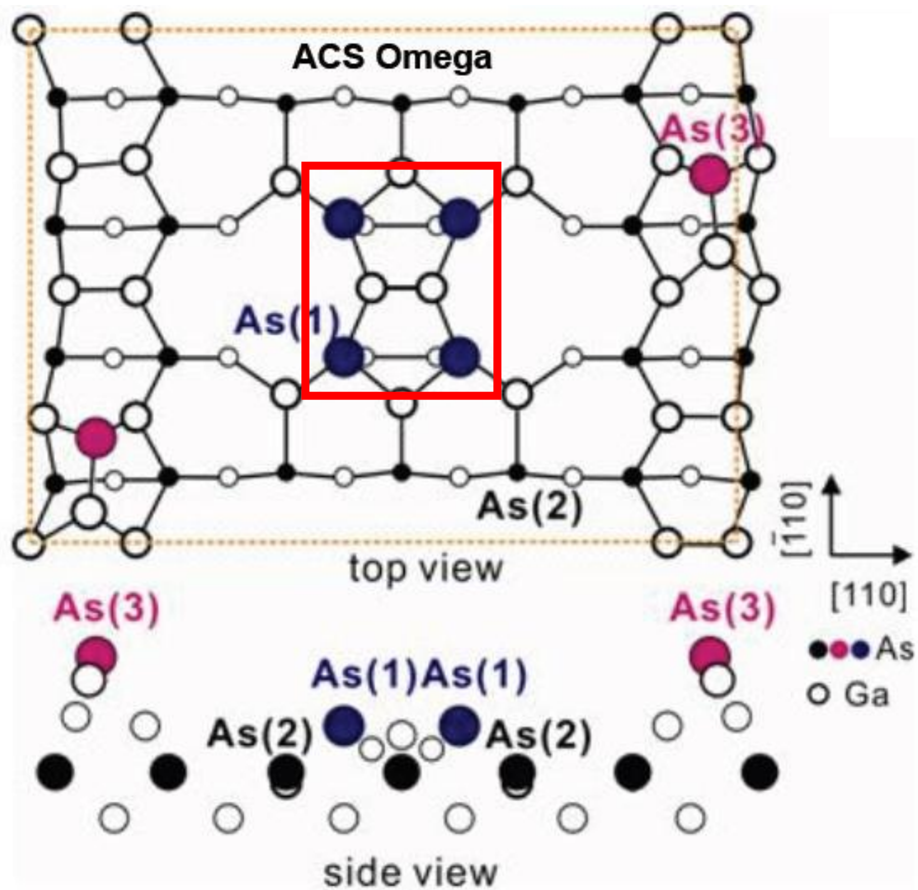
$\frac{I_{0,As}}{I_{0,Ga}} = 0.53$

$\frac{I_{As}}{I_{Ga}}(23Å) = 0.45$ Å

$$x \sim 18\%$$

Growth mode

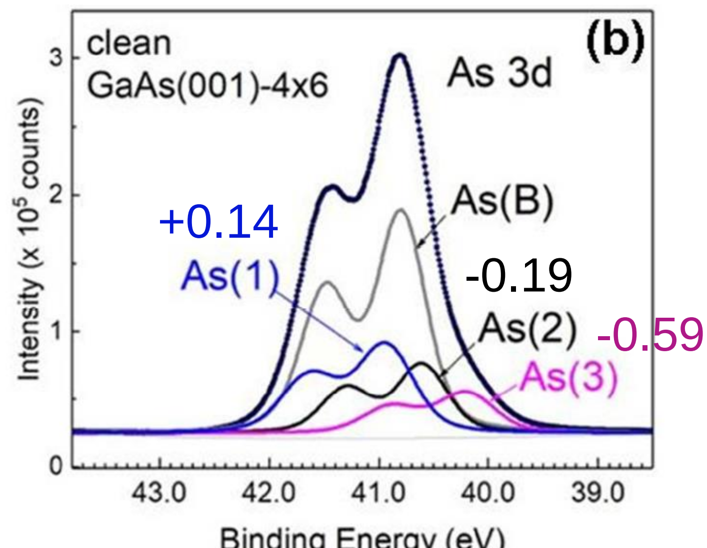
GaAs(001)-4x6 $Theoretical\ calculation \rightarrow x\sim18\%$



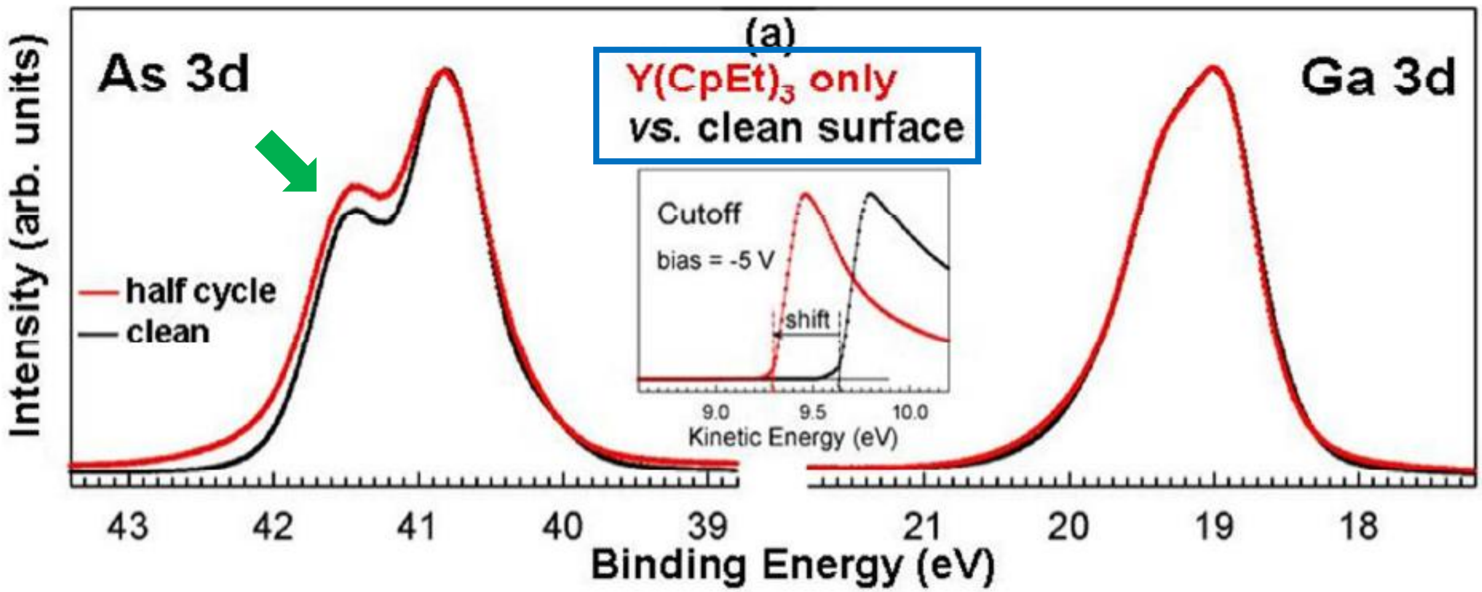
As(1) : 17%

As(2) ∶ 25%

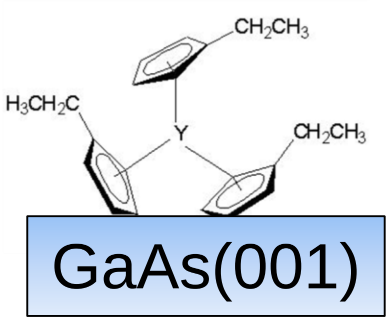
As(3) ∶ 8%

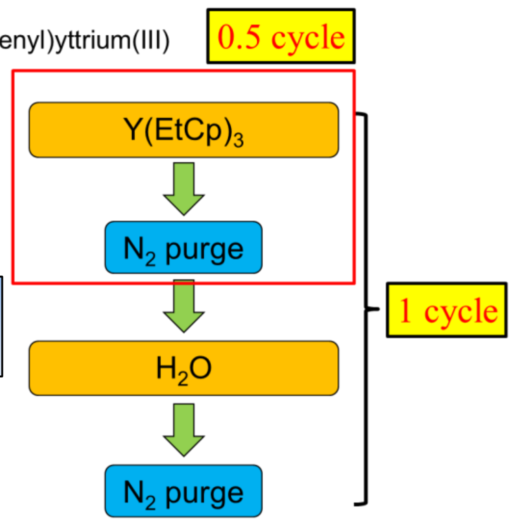


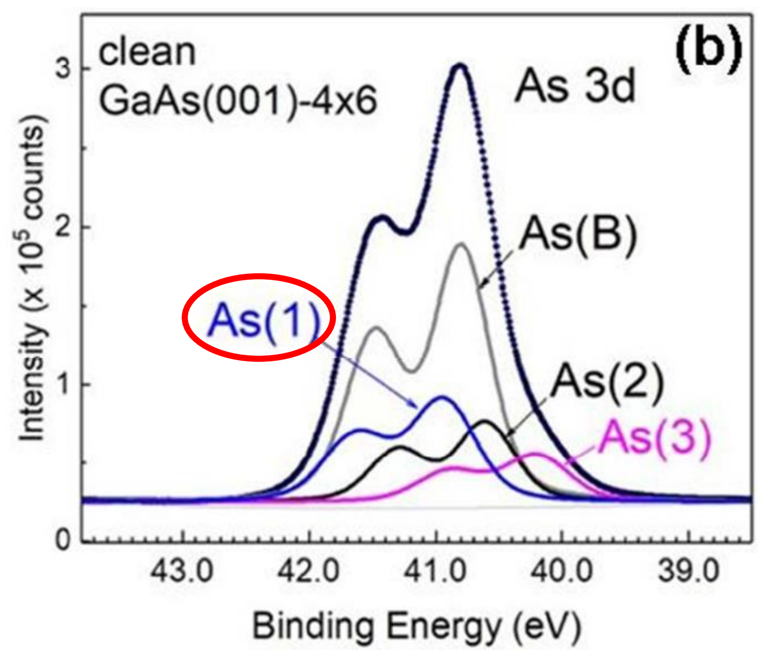
Atom-to-atom interaction



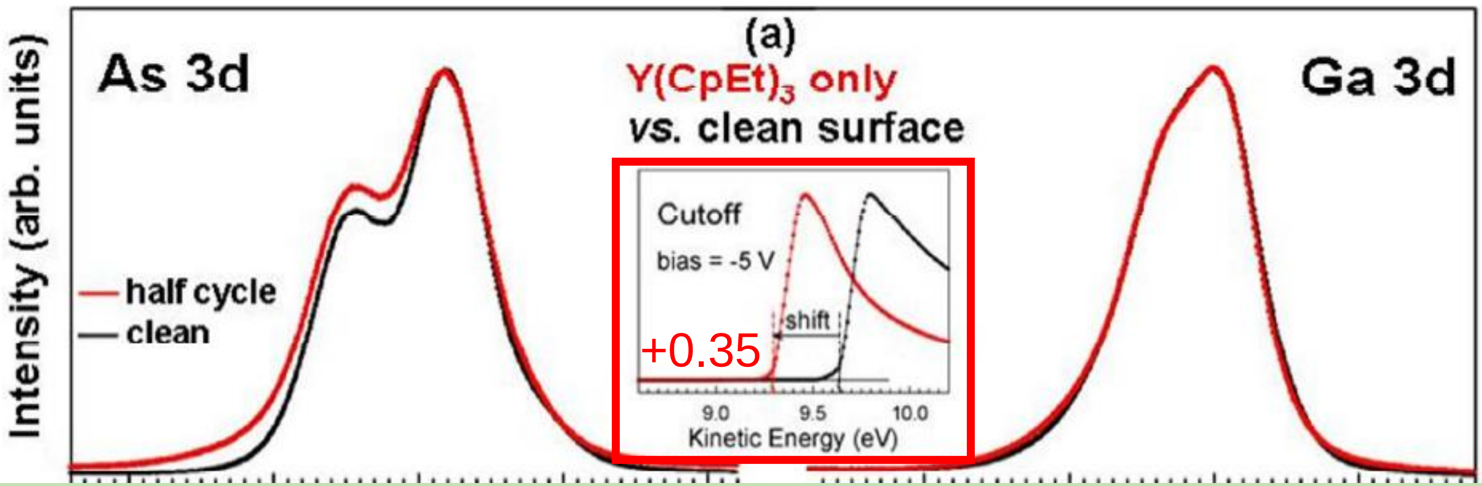
Y(EtCp)$_3$ → Tris(ethylcyclopentadienyl)yttrium(III)





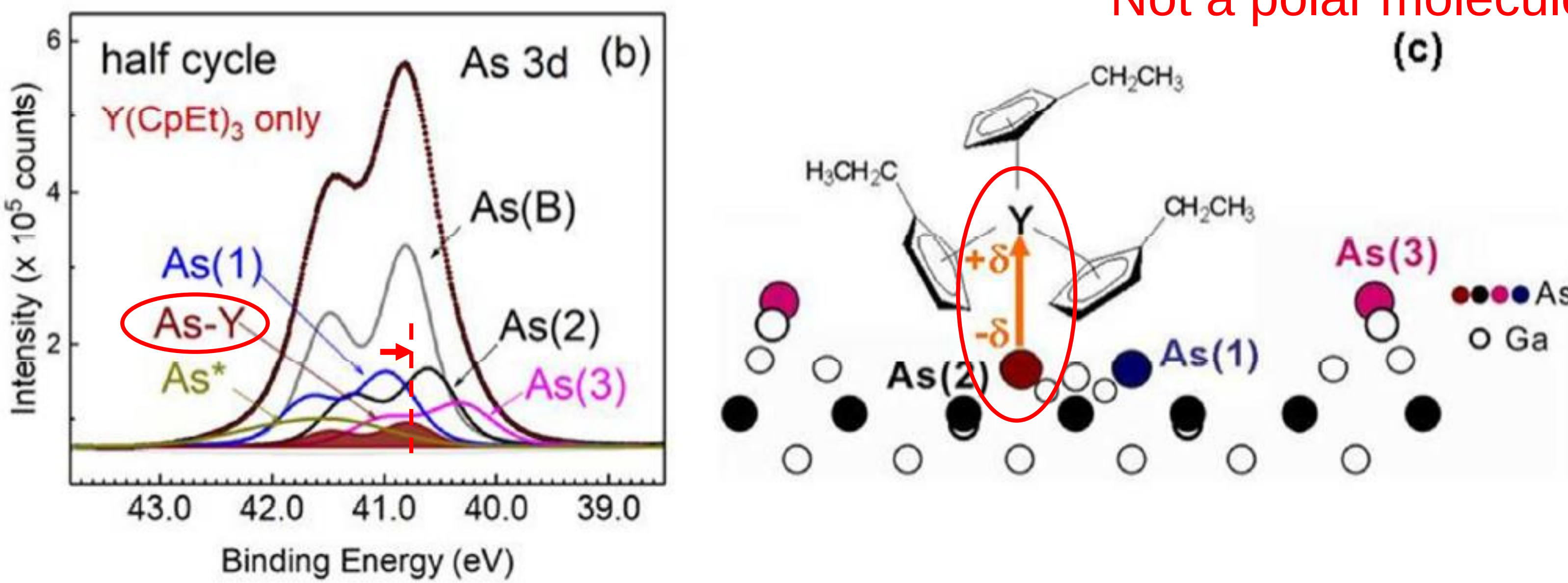


Atom-to-atom interaction

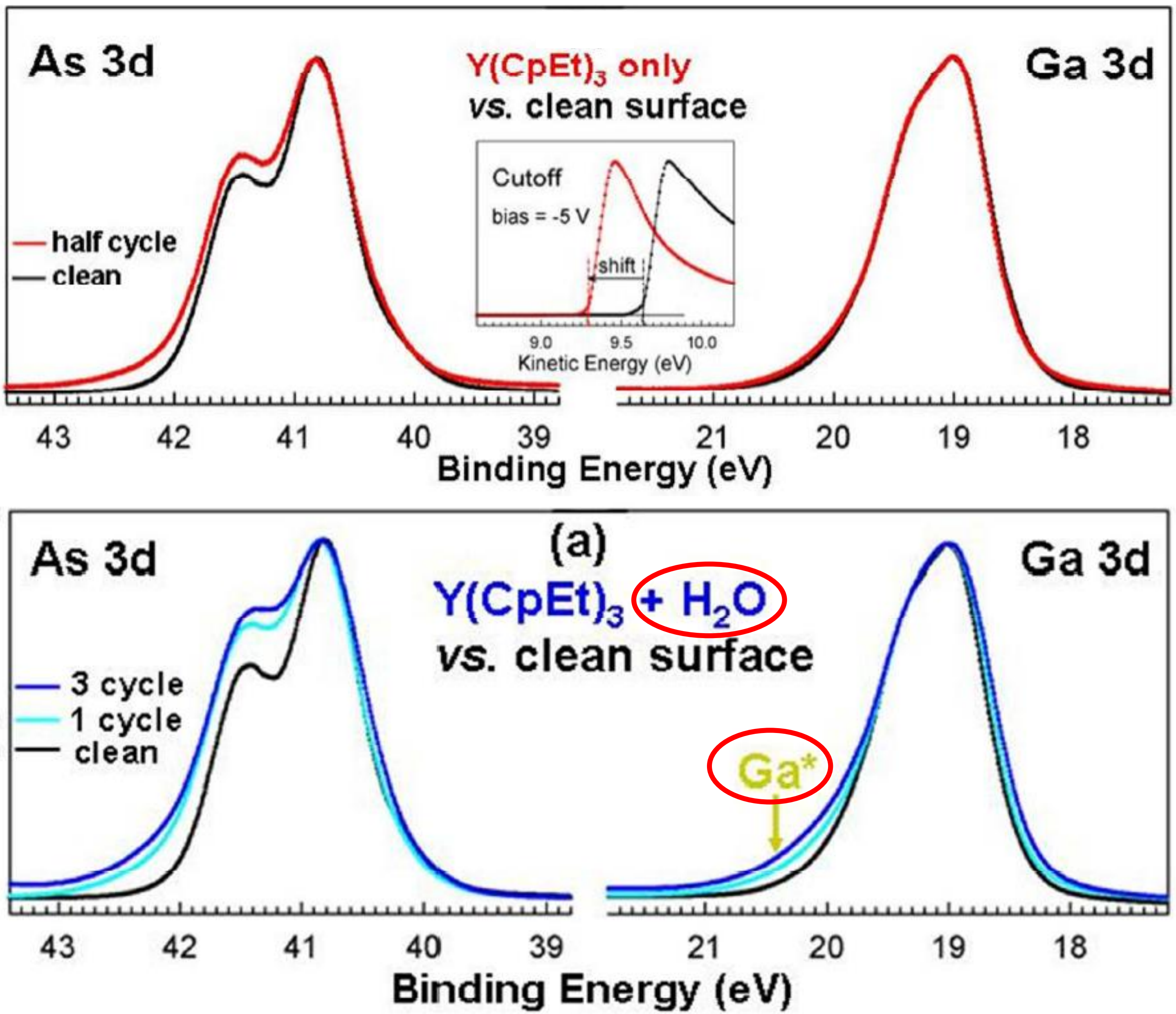


Interfacial dipole potential energy = $IP_{GaAs} - IP_{Y_2O_3/GaAs}$

Not a polar molecule

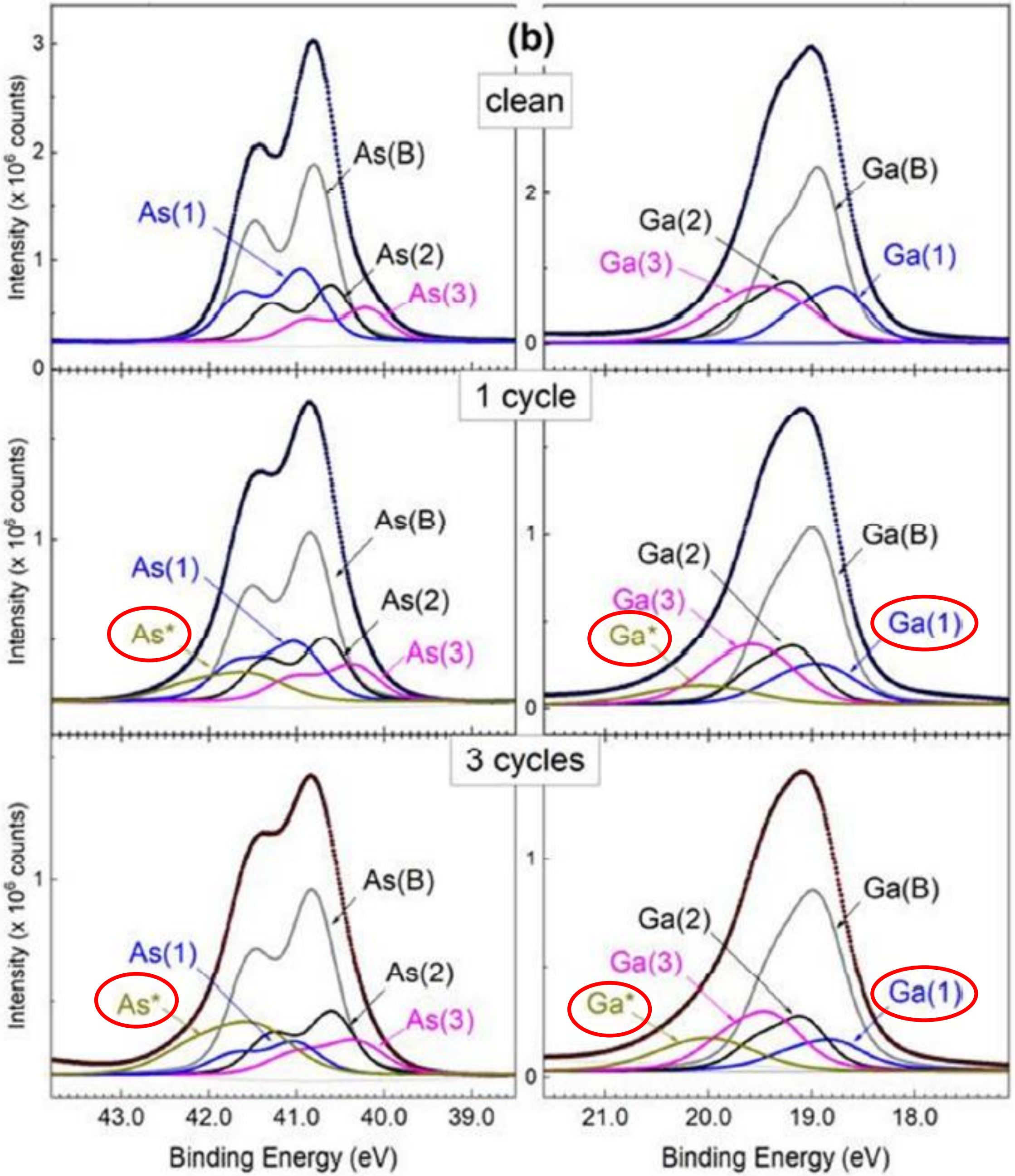


Atom-to-atom interaction



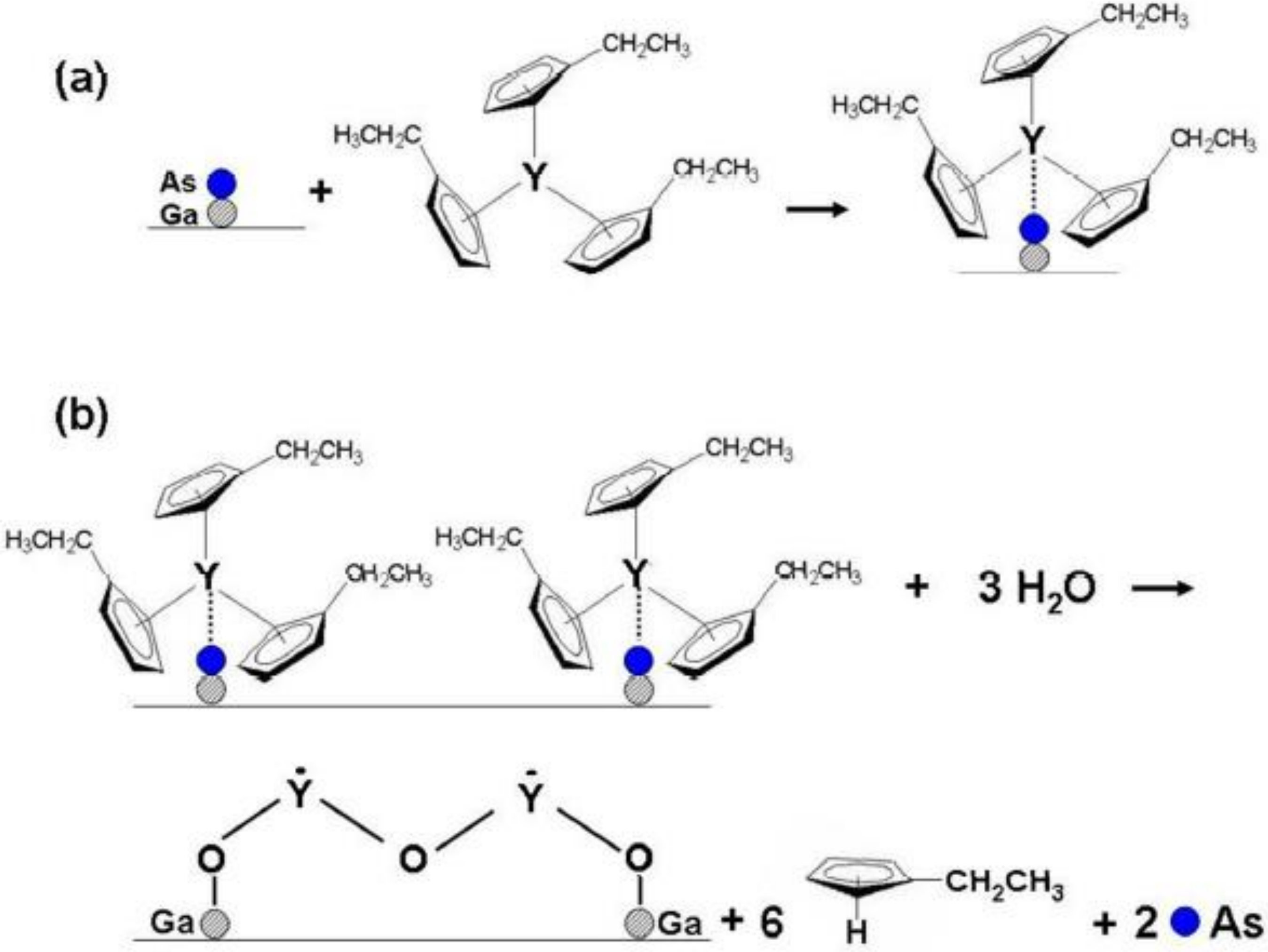
Atom-to-atom interaction

As* = As atom



Ga* = Ga_2O

ALD Y_2O_3/GaAs(001)-4x6



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Atomic Nature of the Growth Mechanism of Atomic Layer Deposited High-κ Y_2O_3 on GaAs(001)-4 × 6 Based on in Situ Synchrotron Radiation Photoelectron Spectroscopy

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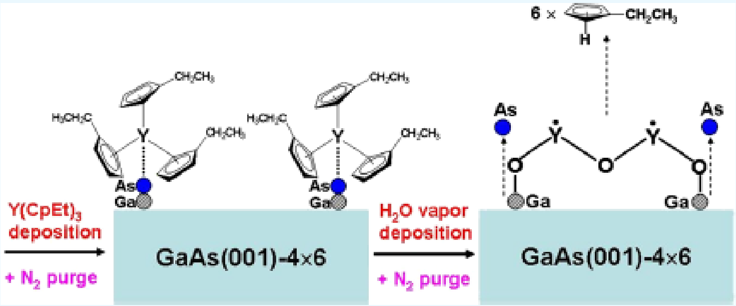

ABSTRACT: Y_2O_3 was in situ deposited on a freshly grown molecular beam epitaxy GaAs(001)-4 × 6 surface by atomic layer deposition (ALD). In situ synchrotron radiation photoemission was used to study the mechanism of the tris-(ethylcyclopentadienyl)yttrium [$Y(CpEt)_3$] and H_2O process. The exponential attenuation of Ga 3d photoelectrons confirmed the laminar growth of ALD-Y_2O_3. In the embryo stage of the first ALD half-cycle with only $Y(CpEt)_3$, the precursors reside on the faulted As atoms and undergo a charge transfer to the bonded As atoms. The subsequent ALD half-cycle of H_2O molecules removes the bonded As atoms, and the oxygen atoms bond with the underneath Ga atoms. The product of a line of Ga−O−Y bonds stabilizes the Y_2O_3 films on the GaAs substrate. The resulting coordinatively unsaturated Y−O pairs of Y_2O_3 open the next ALD series. The absence of Ga_2O_3, As_2O_3, and As_2O_5 states may play an important role in the attainment of low interfacial trap densities (D_{it}) of $<10^{12}$ cm^{-2} eV^{-1} in our established reports.

Summary

- Our unique approach of combining MBE/ALD with SRPES *in-situ* is a must to characterize interfacial chemistry for high-k/(In)GaAs hetero-structures.

- High surface sensitivity and high energy resolution of SRPES enable an atomic-scale interface study down to atom-to-atom interaction.

Thank You