2017 International Conference on Frontiers of Characterization and Metrology for Nano-electronics (FCMN), Monterey, CA, March 21-23, 2017

Interfacial Electronic Characterization of Oxides/Metals on High Mobility Semiconductors Using in-situ Synchrotron Radiation Photoemission and the Correlation with the Interfacial Electric Properties

Perfecting the hetero-structural growth

K. Y. Lin, Y. H. Lin, L. B. Young, H. W. Wan, and Minghwei Hong

Grad. Inst. Appl. Phys. and Dept. Phys., National Taiwan University, Taipei, Taiwan, ROC

W. S. Chen and T. W. Pi

National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, ROC

Y. T. Cheng and C. P. Cheng

Department of ElectroPhysics, National ChiaYi University, Chiayi, Taiwan, ROC

J. Kwo

Department of Physics, National Tsing Hua University, Hsinchu, Taiwan, ROC

Outline

- ✓ Perfecting surface and interfacial electronic structures ⟹ High-performance MOS and self-aligned inversion-channel MOSFETs
  - ALD-oxides (Al_2O_3, HfO_2)/InGaAs(001) MOSFET
  - Single crystal ALD-Y_2O_3/GaAs(001) MOS
  - Common gate dielectrics and CMOS compatible process
    - Distinct nature of ionic/covalent bonding → different surface electronic characteristics → interfacial electronic structures/electric properties
- ✓ Surfaces and interfaces studied using *in-situ* synchrotron radiation photoemission
  - ✓ III-V passivation with ALD oxides
    - Understanding/tailoring surfaces of semiconductor, oxide-semiconductor interfaces for advancing device performance
  - ✓ III-V and metal – Schottky barrier heights (SBH)
    - Understanding/tailoring metal-semiconductor interfaces for advancing device performance
    - Origin of SBH, vital for lowering ohmic contacts
- ✓ Single-crystal single-domain complex materials using Sub-Nano-Laminated (*snl*) ALD and substrate induced epitaxy

Multi-chamber MBE/e-beam/ALD/Analysis System

Pioneering work of (In)GaAs MOSFET's using MBE-$Ga_2O_3(Gd_2O_3)$ at Bell Labs

- 1994 [**Appl. Phys. Lett. 66, 625 (1995).**]
  - ✓ novel oxide $Ga_2O_3(Gd_2O_3)$ to effectively passivate GaAs surfaces
- 1995 [**IEDM**]
  - ✓ accumulation and inversion in $Ga_2O_3(Gd_2O_3)$/p- and n-GaAs MOS diodes with a low D_{it}
- 1996 [**IEDM; Appl. Phys. Lett. 69(3), 302 (1996); Solid State Electronics, 41 (11), 1751 (1997).**]
  - ✓ **first e-mode inversion-channel p- and n- GaAs MOSFETs**
  - ✓ Thermodynamically stable, dense, uniform microstructures; smooth, atomically sharp interface; low leakage currents
- 1997 [**DRC, IEEE Electron Device Letters, V. 19, 309 (1998).**]
  - ✓ **e-mode inversion-channel n-InGaAs/InP MOSFET with g_m= 0.19 mS/μm, I_d = 0.35 mA/μm, and mobility of 470 cm^2/Vs**

(In)GaAs MOSFET's using MBE-$Ga_2O_3(Gd_2O_3)$ and Y_2O_3 at Bell Labs and in Taiwan

- 1998 **[IEDM; Invited talk at Symp. Z of Materials Research Soc. 1999 Spring Mtg., April 5-7 at San Francisco, CA. MRS Proceedings volume 573 219 (1999).]**
  - d-mode GaAs MOSFETs with negligible I_d drift and hysteresis (IEDM)
  - e-mode inversion-channel GaAs MOSFETs with improved I_d (100 times over 1996 result)
- 1999 [**Electronics Letters 35, 667 (1999); Science 283, 1897 (1999)**]
  - GaAs power MOSFET
  - **Single-crystal, single-domain Gd_2O_3 epitaxially grown on GaAs**
- 2000 [**27th Intl Symp. on Compound Semiconductors, Proc. pp.345-350 Oct. 2-5, 2000, Monterey, California**.]
  - demonstration of **GaAs CMOS inverter**
- 2008 [**APL 93 033516 (2008)**]
  - Self-aligned inversion-channel InGaAs MOSFET, **g_m= 0.7 mS/μm, I_d = 1.05 mA/μm, L_g = 1μm**
- 2012 [**APEX 4 14202 (2011)**]
  - Self-aligned inversion-channel InGaAs MOSFET with in-situ MBE-Y_2O_3, **g_m= 0.77 mS/mm, I_d = 1.5 mA/μm, L_g = 1μm**

(In)GaAs and GaN MOSFET's using ***ex-situ*** ALD-oxides

- 2003
  - d-mode GaAs MOSFETs using ***ex-situ*** ALD-Al_2O_3 Ye, Hong, Kwo (APL 83, 180, 2003)
- 2005
  - "***Self-cleaning***" and passivation of (In)GaAs using ***ex-situ*** ALD-Al_2O_3 Hong, Kwo (APL 87, 252104, 2005)
- 2006
  - Energy-band parameters of ***ex-situ*** ALD-Al_2O_3/InGaAs, Kwo, Hong (APL 89, 012903, 2006)
- 2007, 2008
  - ***Ex-situ*** ALD HfO_2 on GaN and InGaAs, Hong, Kwo (APL **90**, 232904, 2007; APL **92**, 072901, 2008)
- 2008
  - Inversion-channel GaN MOSFET with ***ex-situ*** ALD-Al_2O_3 as gate dielectric, Hong, Kwo (APL **93**, 053504, 2008)

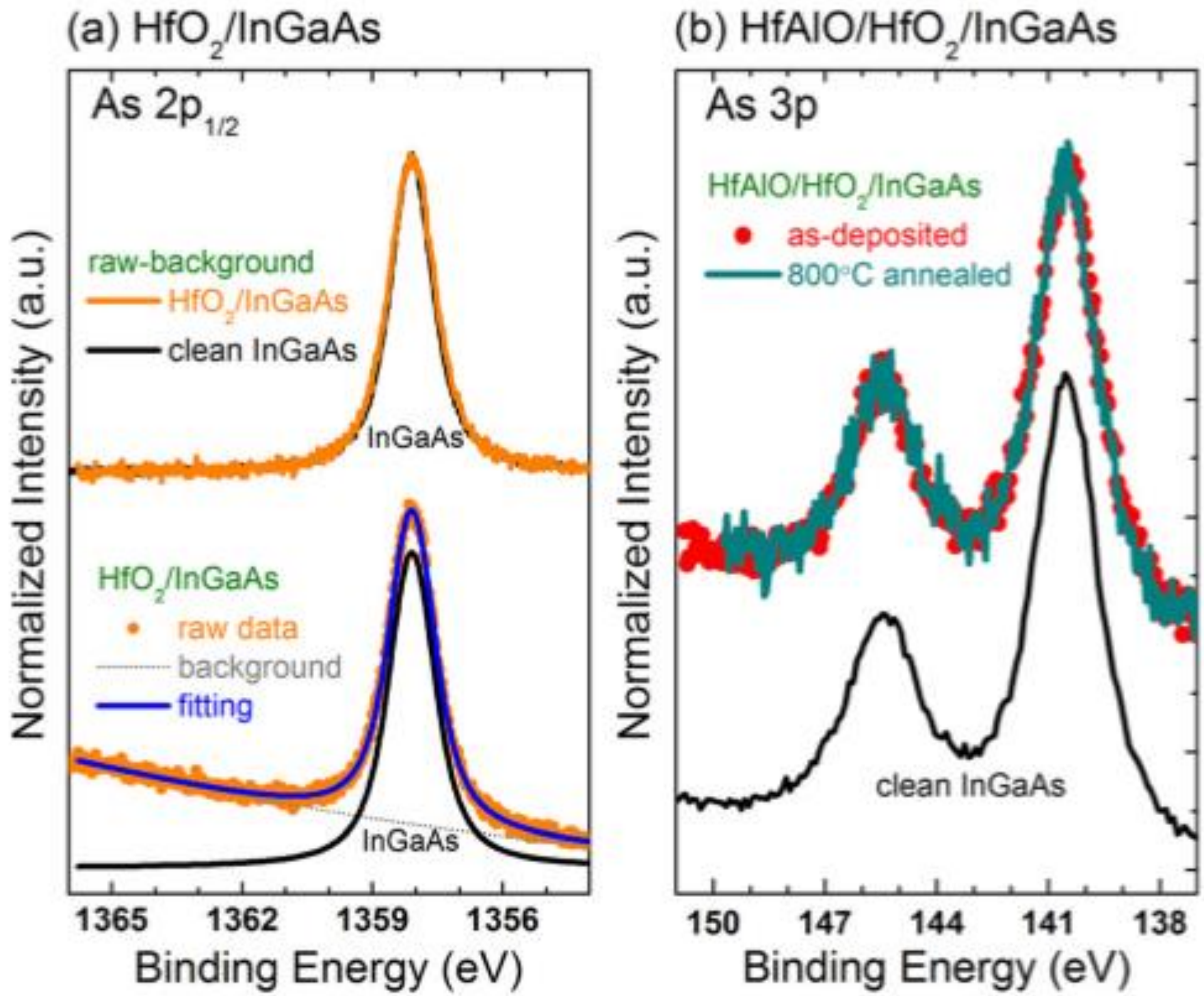
(In)GaAs MOSFET's using *in-situ* ALD-oxides

- 2011
  - ***In-situ*** ALD and synchrotron-radiation photoemission study of Al_2O_3 on pristine n-GaAs(001)-4×6 surface, Pi, Hong, Kwo, (Microelectronic Eng. **88**, 1101, 2011)
- 2012
  - Realization of high-quality ***HfO_2*** on $In_{0.53}Ga_{0.47}As$ by ***In-situ*** ALD, Kwo, Hong, (APL **100**, 172110, 2012)
    - $In_{0.53}Ga_{0.47}As$ surface passivation with **tetra-valence** high κ's recognized as "**MISSION IMPOSSIBLE**"
    - Thin ALD-HfO_2 (0.8nm) initial layer followed by ALD-HfAlO top layer to enhance thermal stability (>800°C).
- 2013
  - High-performance self-aligned inversion-channel $In_{0.53}Ga_{0.47}As$ MOSFET by ***In-situ*** ALD- ***HfO_2***, Kwo, Hong, (APL **103,** 253509, 2013) **g_m= 1.06 mS/μm, I_d = 1.5 mA/μm, L_g = 1μm**
- 2015
  - Single-crystal ***In-situ*** ALD-Y_2O_3 epitaxially on GaAs(001) using ALD, Kwo, Hong, (Materials **8**, 7084, 2015)

XPS studies of InGaAs and in-situ ALD-HfO_2/InGaAs, and 800°C PDA of ALD-HfAlO/HfO_2/InGaAs

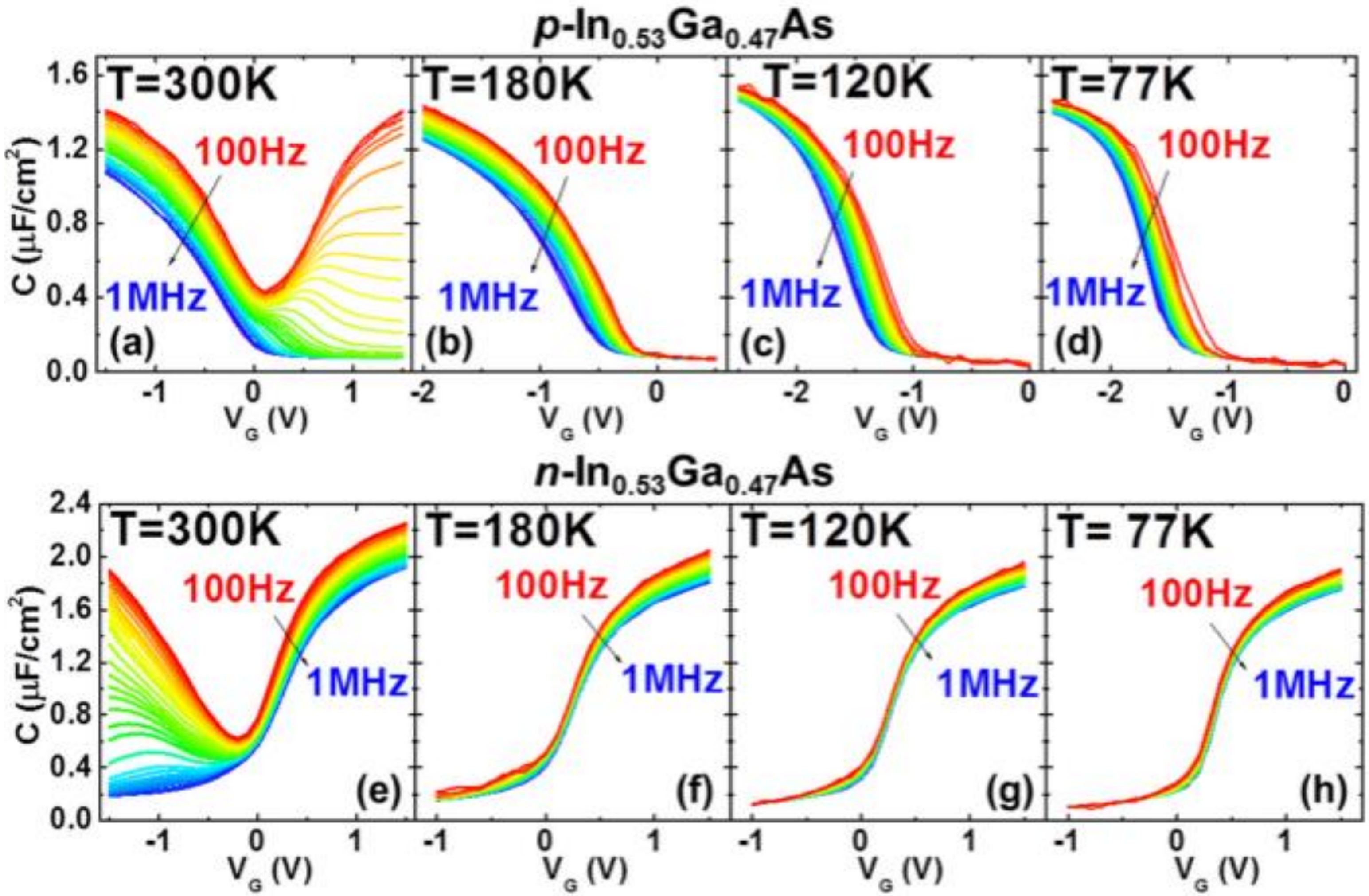
In-situ ALD-HfO_2(0.8nm)/InGaAs interface and clean InGaAs surface

In-situ ALD-HfO_2(0.8nm)/InGaAs **as-deposited** and **800°C PDA (air-exposure)** interfaces



T. D. Lin et al, APL 100, 172110 (2012)

CVs of 800°C PDA of ALD-HfAlO/HfO_2/InGaAs



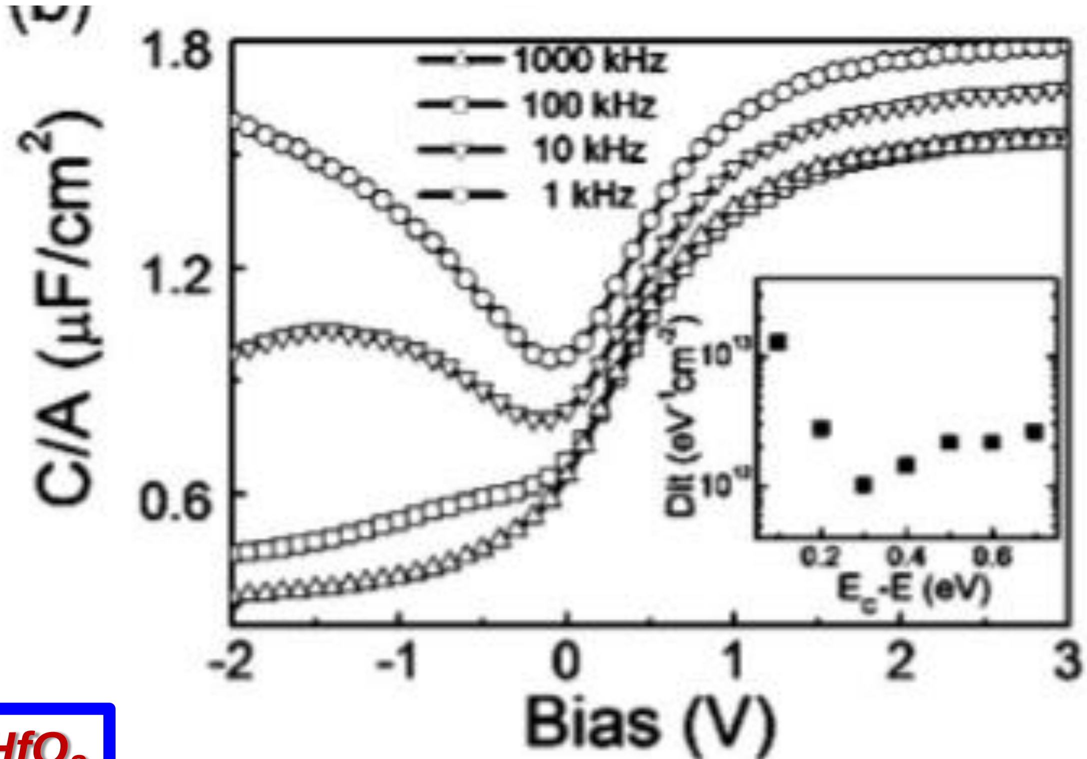
C-Vs of ALD-HfO_2 on (a)-(d) p-$In_{0.53}Ga_{0.47}As$ and (e)-(h) n-$In_{0.53}Ga_{0.47}As$ measured at temperatures from 300 to 77K

T. D. Lin et al, APL 100, 172110 (2012)

APPLIED PHYSICS LETTERS **92**, 072901 (2008)

Atomic-layer-deposited HfO_2 on $In_{0.53}Ga_{0.47}As$: Passivation and energy-band parameters

Y. C. Chang,[1] M. L. Huang,[1] K. Y. Lee,[1] Y. J. Lee,[1] T. D. Lin,[1] M. Hong,[1,a)] J. Kwo,[2,b)] T. S. Lay,[3] C. C. Liao,[4] and K. Y. Cheng[4]
[1]*Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan 30012, Taiwan*
[2]*Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30012, Taiwan*
[3]*Institute of Electro-Optical Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, Taiwan*
[4]*Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA*

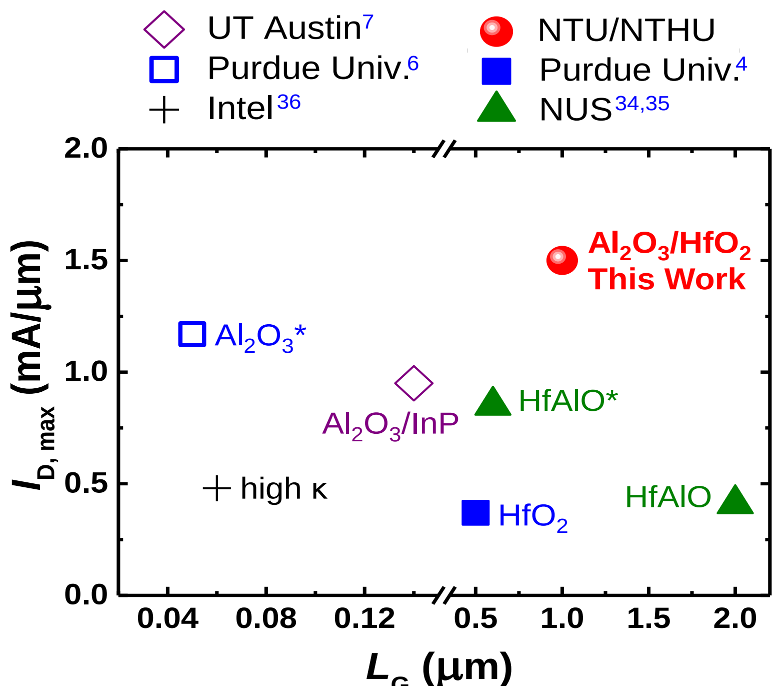


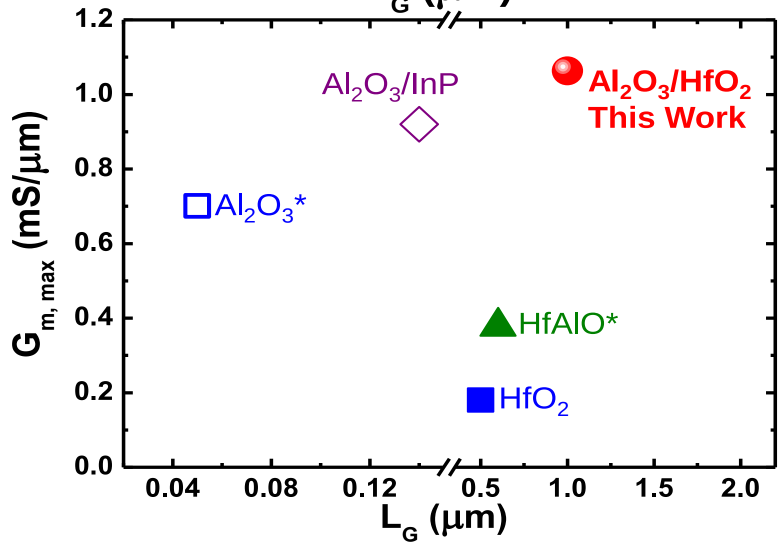
Ex-situ ALD-HfO_2

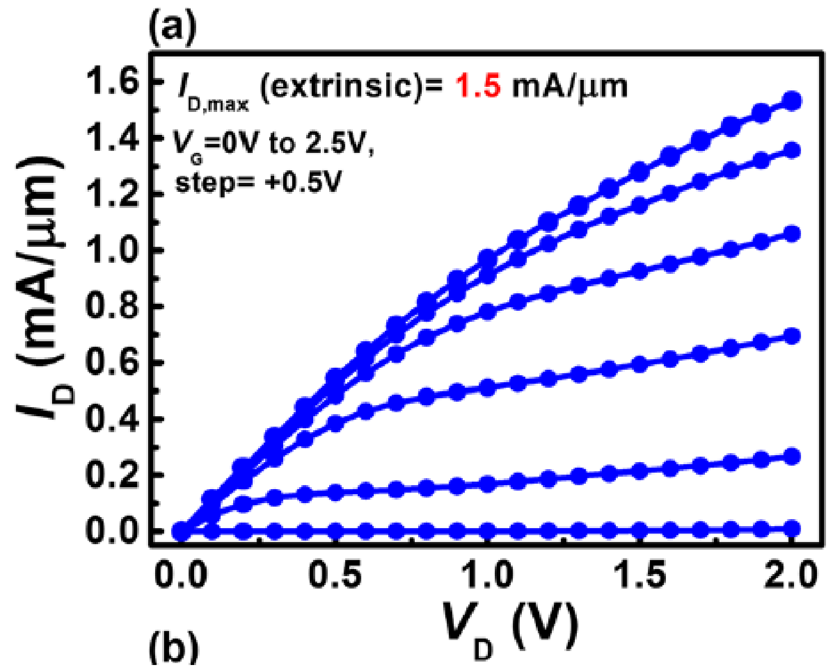
ALD-HfAlO/HfO_2 (0.8nm)/$In_{0.53}Ga_{0.47}As$

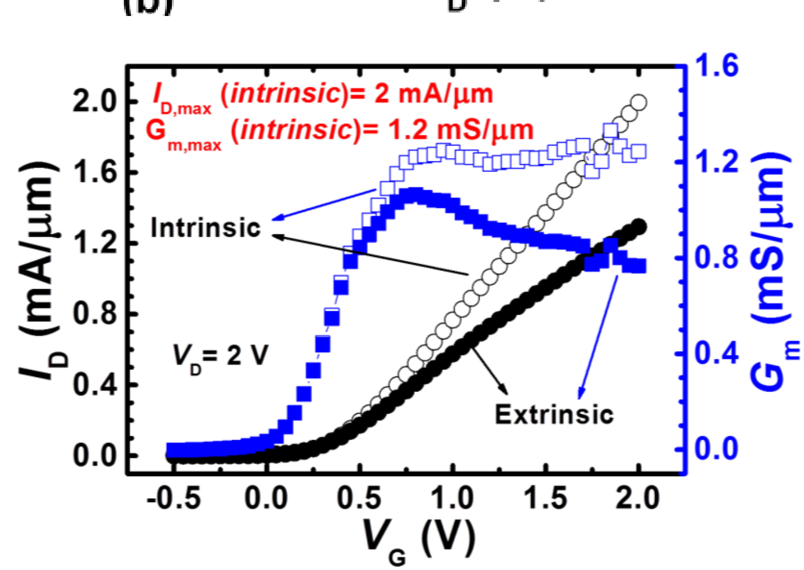
Self-aligned inversion-channel InGaAs n-MOSFET 1um Lg

T. D. Lin, J. Kwo, and M. Hong et al., Appl. Phys. Lett. 103, 253509 (2013)





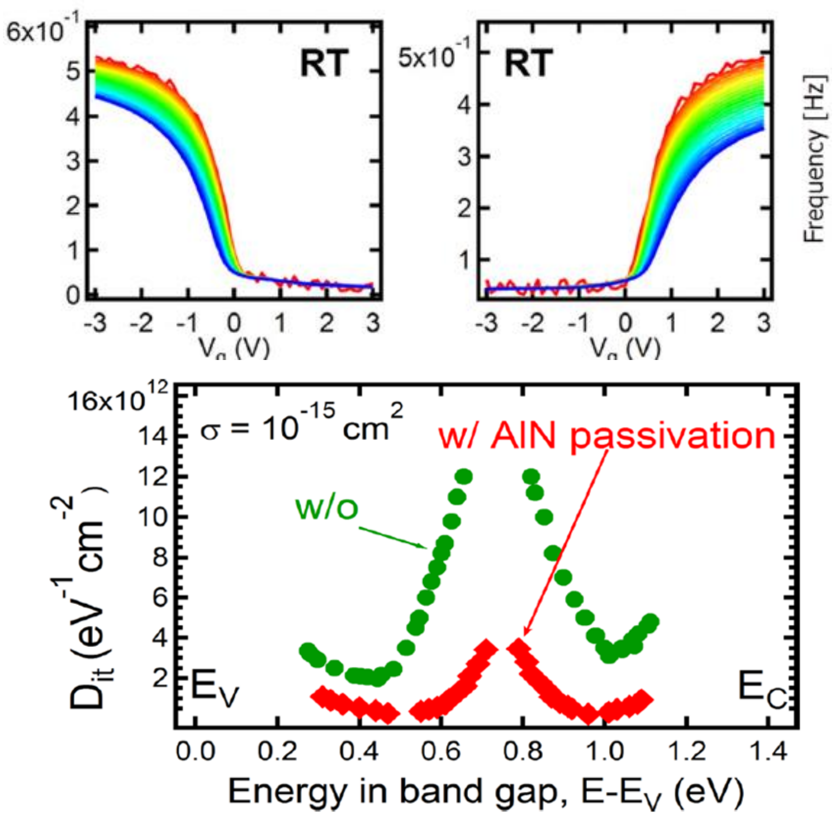




D_{it} Spectrum for *ex-situ* ALD-Al_2O_3/GaAs(001)

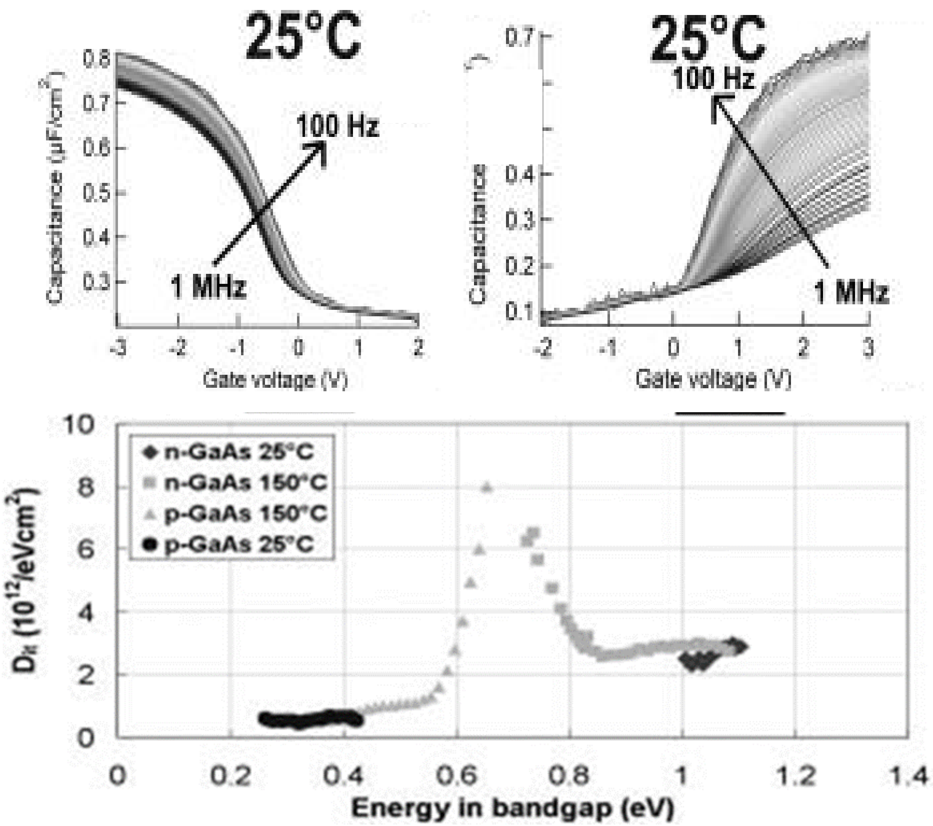
ALD-Al_2O_3/GaAs(001) with AlN interfacial passivation layer

T. Aoki, et al. Appl. Phys. Lett. **105**, 033513 (2014)



ALD-Al_2O_3/GaAs(001) with $(NH_4)_2S$ surface pretreatment

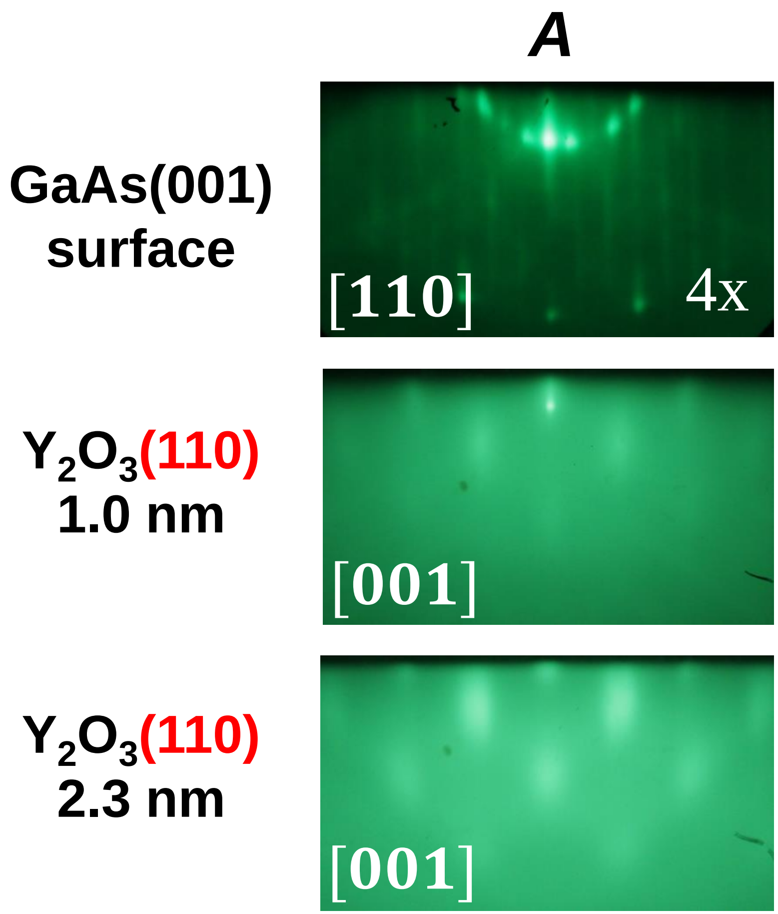
G. Brammertz *et al.* Appl. Phys. Lett. **93**, 183504 (2008)



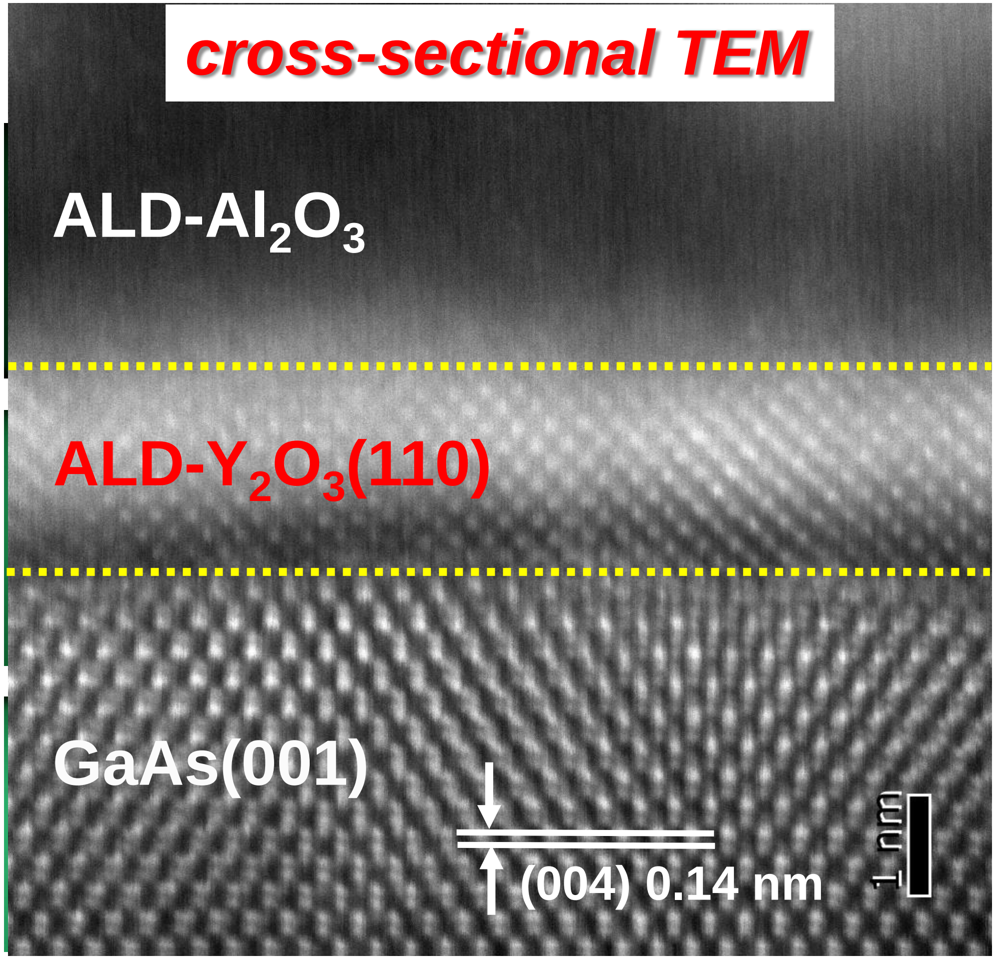
The D_{it} spectrum shows a midgap peak!

In-situ ALD-Al_2O_3/ALD-Y_2O_3/GaAs(001)

RHEED & Cross-sectional TEM

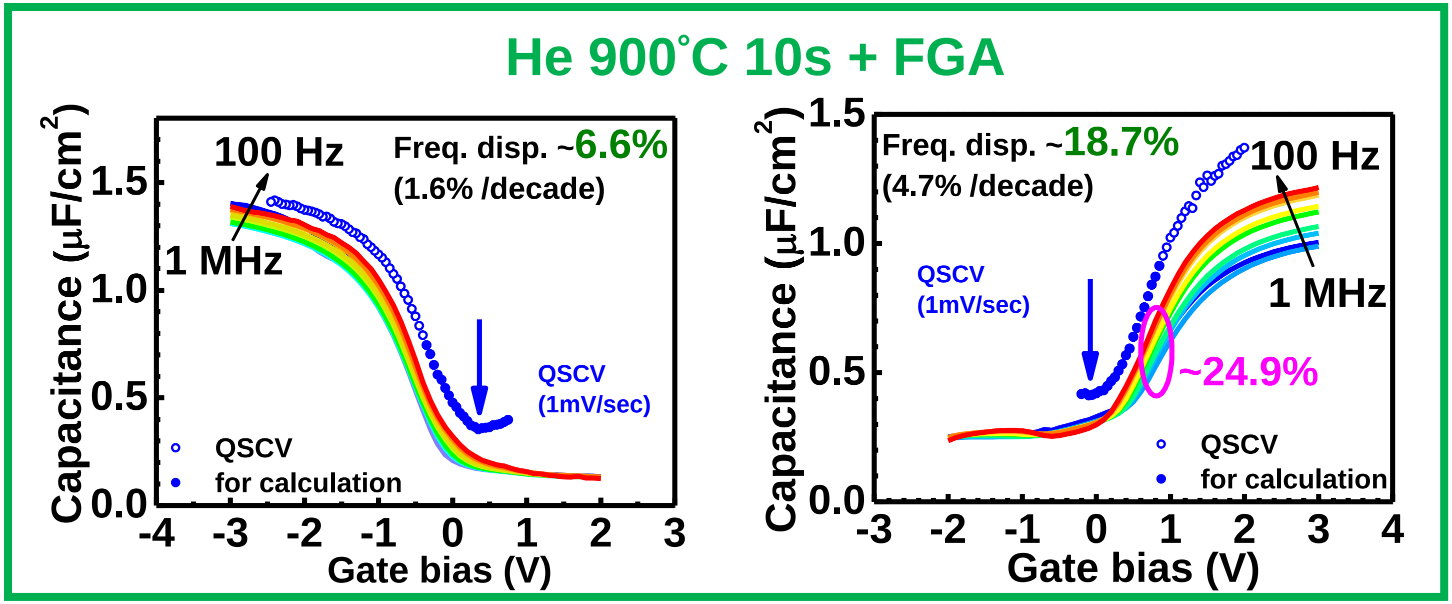


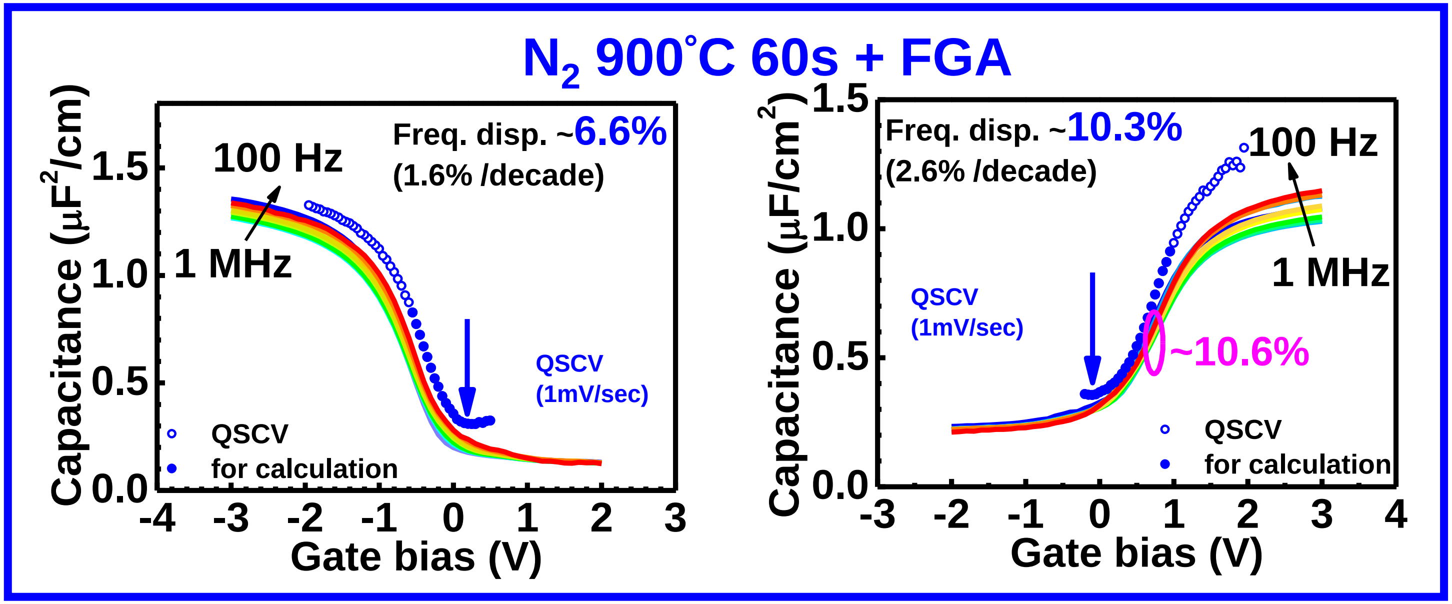
S. Y. Wu, M. Hong, et al, *Microelectron. Eng.* **147**, 310-313 (2015)



K. Y. Lin, L. B. Young, M. Hong, et al Microelectron. Eng. In press (2017)

ALD-Y_2O_3/GaAs(001) - C-V and QSCV





T. W. Chang, M. Hong, et al, Microelectron. Eng. In press (2017)
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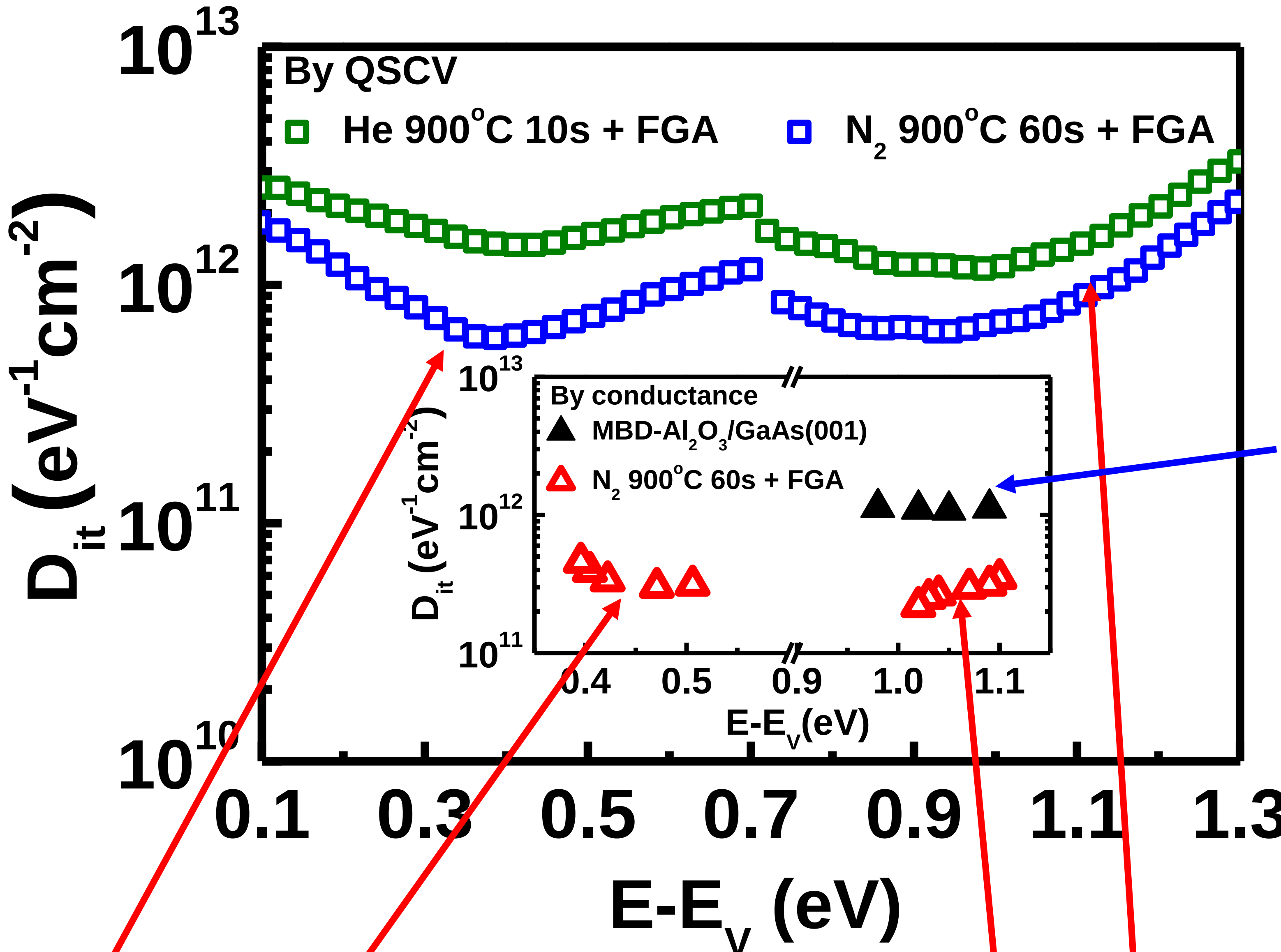
Y. H. Lin, M. Hong, et al, Applied Physics Express 9, 081501 (2016)

D_{it} Spectra for ALD-Y_2O_3/GaAs(001)



Y. C. Chang, C. Merckling, M. Hong, et al, Appl. Phys. Lett. 97, 112901 (2010).

T. W. Chang, M. Hong, et al, Microelectron. Eng. In press (2017).

Y. H. Lin, M. Hong, et al, Applied Physics Express 9, 081501 (2016)

✓ **(In)GaAs passivation using ALD oxides – surfaces and interfaces studied using *in-situ* synchrotron radiation photoemission**

- **Understanding/tailoring surfaces of semiconductor, oxide-semiconductor interfaces for advancing device performance**

Outline

- **Introduction - as-grown over treated (In)GaAs surfaces**
  - **Capacitance-voltage characteristics from related MOSCAPs**
  - **STM and SR-PES**
- **Atomically clean (In)GaAs surfaces**
- **0.5-10 cycles of (TMA+H_2O) on clean (In)GaAs surfaces**
  - **Other precursors**
- **Summary**

goal: low D_{it}

Surface is essential for growth of a dielectric oxide and metal

Q: What kind of the surface?

A: an atomically clean and highly ordered surface

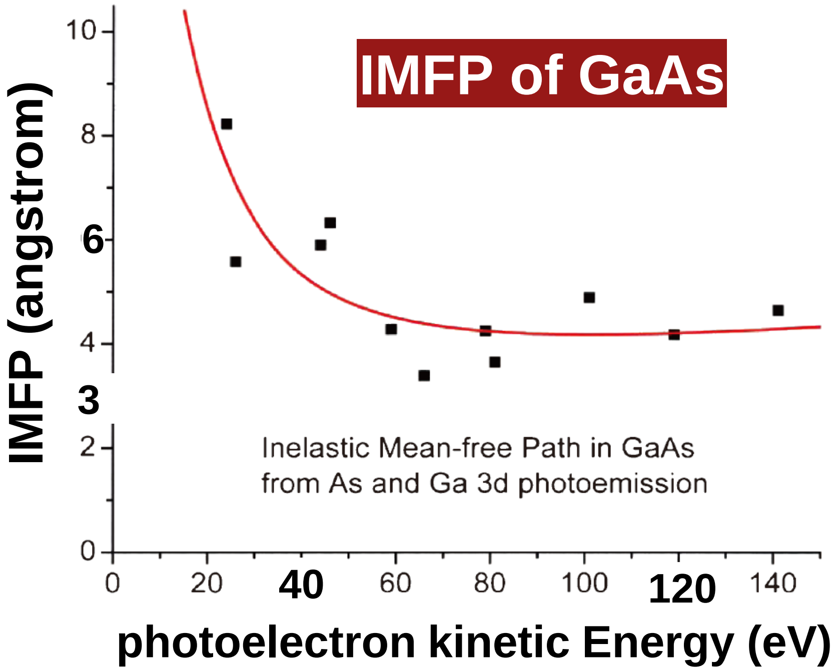
key point: must start with an as-grown surface

Treated methods have yet to come up with a surface quality comparable to that of an as-grown pristine III-V surface

Advantage of photoemission using synchrotron radiation

photon energy selectable, ($E_k = h\nu - E_b - \varnothing$)

✦ high surface sensitivity, short inelastic mean free path (IMFP)



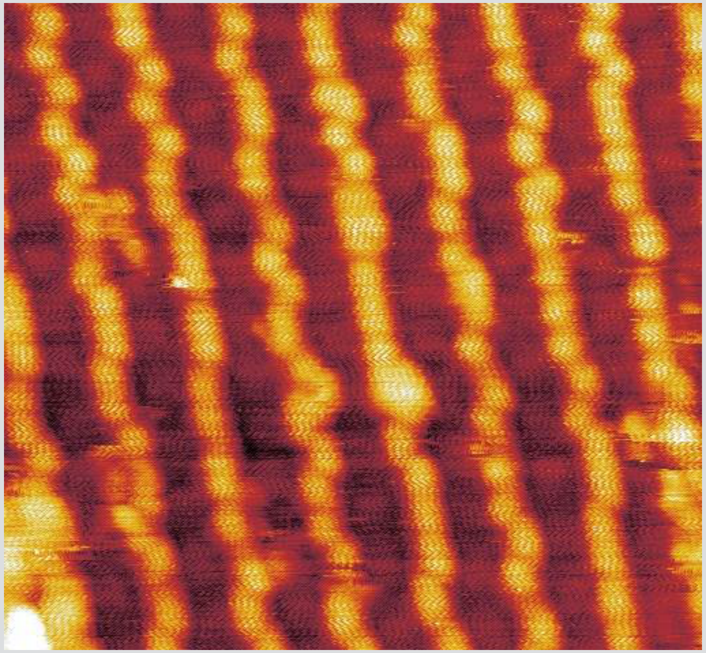
✦ cross section effect

high resolving power ($E/\Delta E$), high brilliance, and small beam size

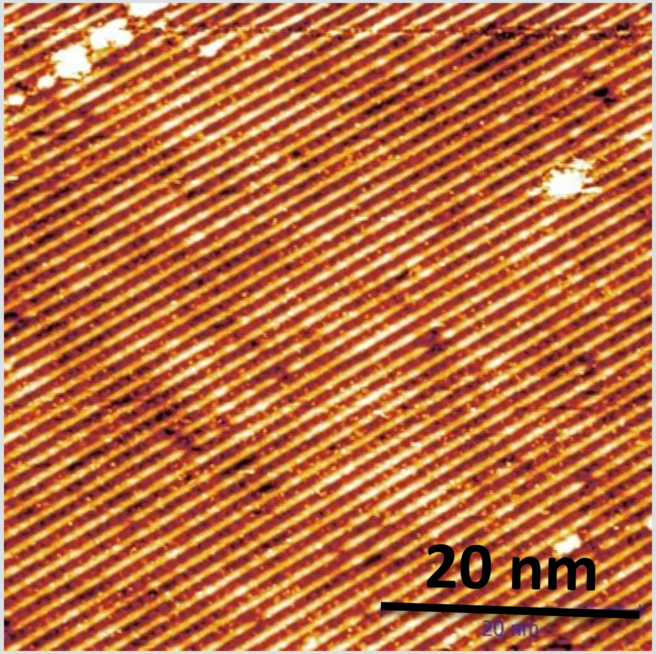
✦ fine structures discernible with a decent S/N ratio

surface characterization: by STM

GaAs(001)-4x6



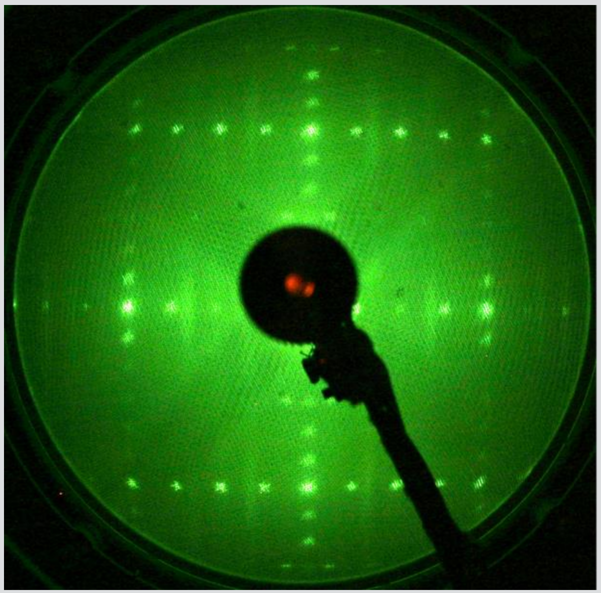
In_xGa_yAs(001)-4x2



In-situ **grown epilayers provide low surface defect densities and smooth surfaces for InGaAs and Ge**

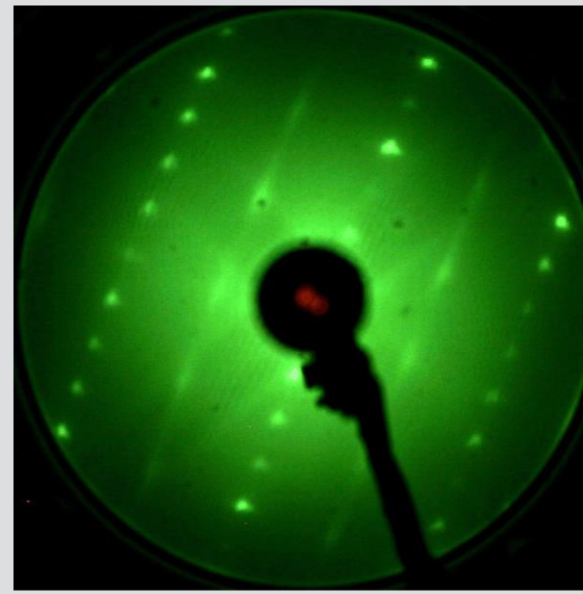
surface characterization: by LEED

GaAs(001)-4x6



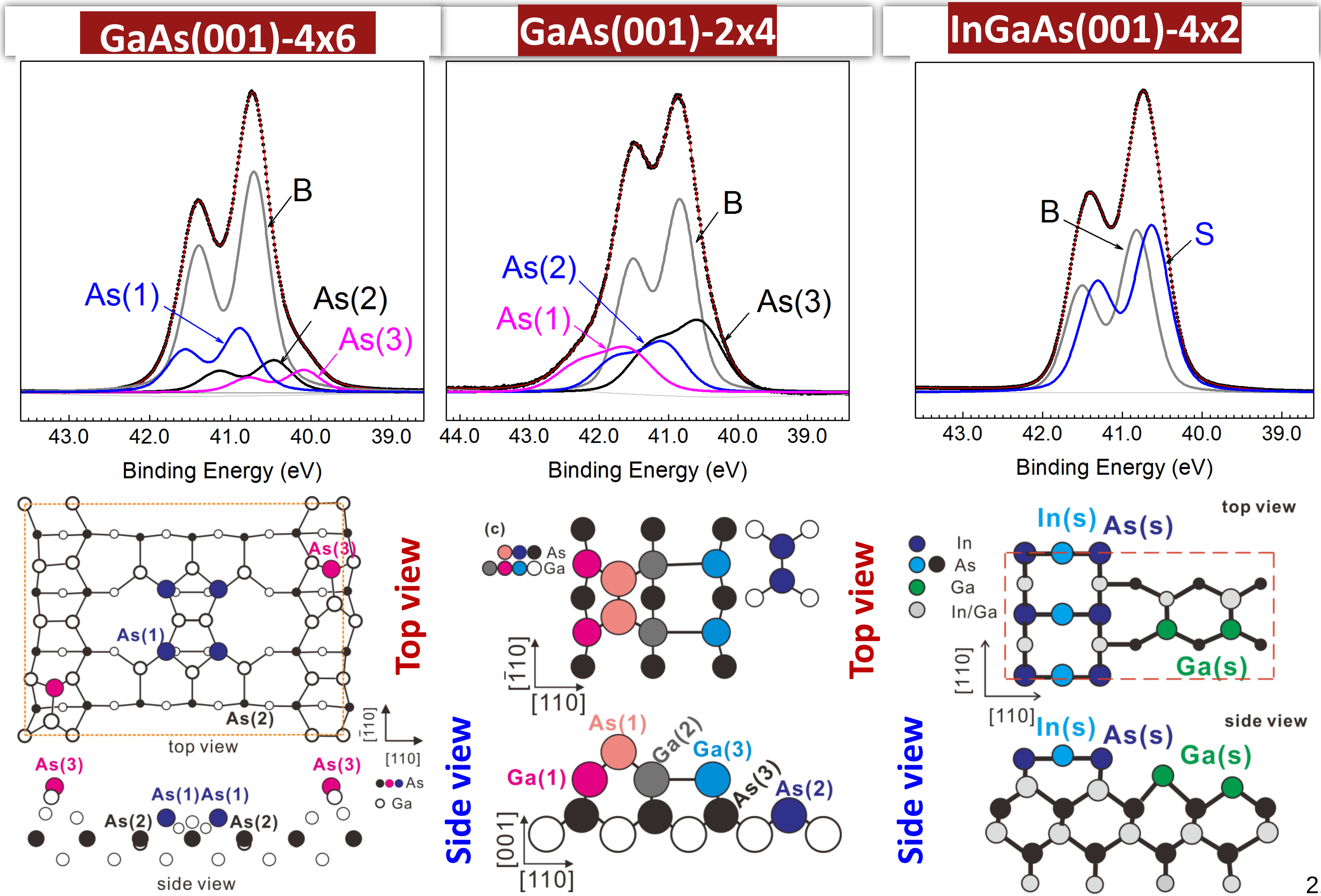
GaAs(001)-2x4

$In_{0.53}Ga_{0.47}As(001)$-4x2

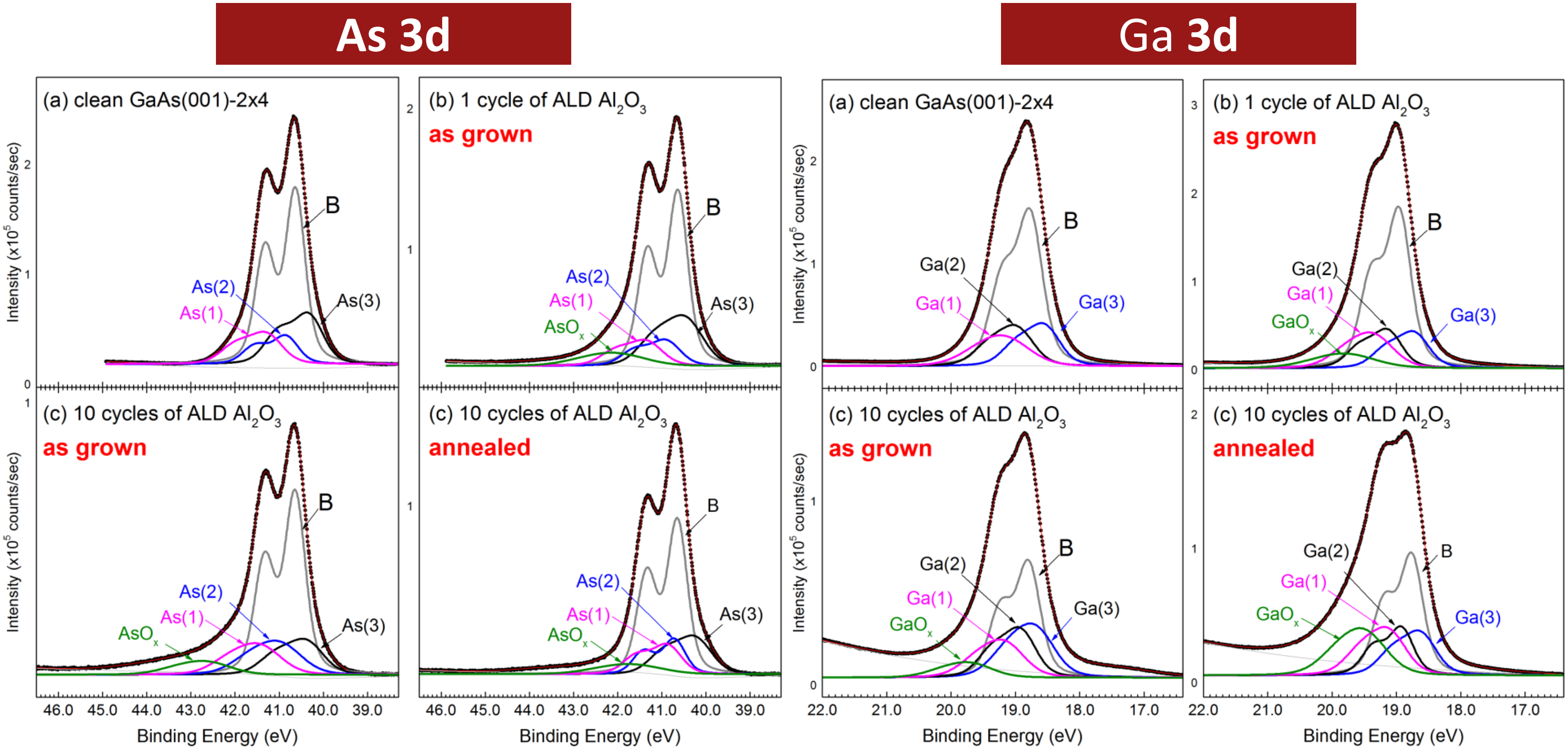


Sharp LEED patterns

core-level spectra of single-crystal III-V surfaces: a fit to As 3d



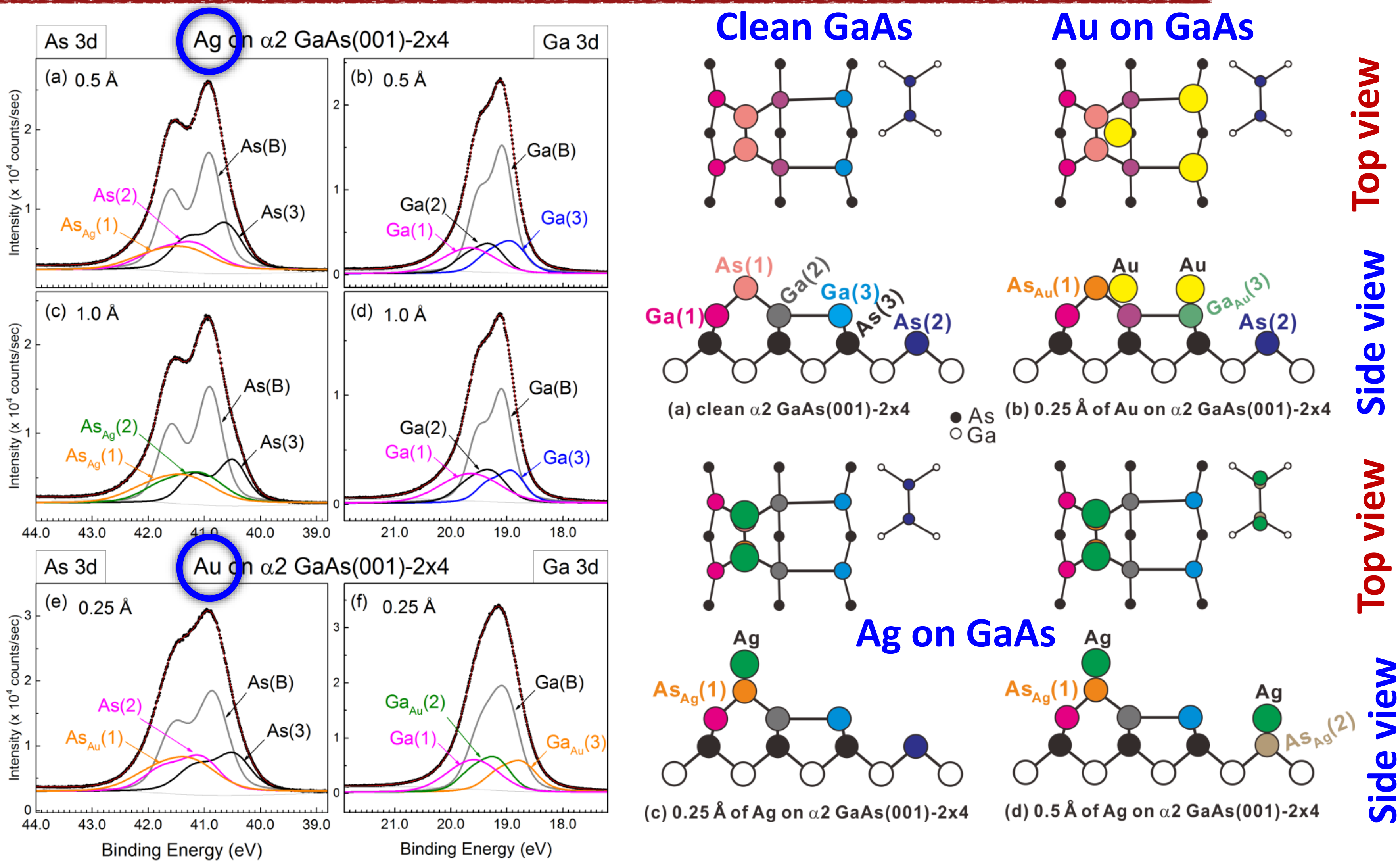
ALD Al_2O_3 on GaAs(001)-2x4



- Some surface As atoms are stripped off by the (TMA+H_2O) precursors
- Stripped As atoms found on surface of Al_2O_3 film and removed by annealing
- Once the surface atoms are removed, interfacial bonding occurs between the precursors and the Ga atoms
- Persistence of surface-related components suggesting that Total passivation of the surface atoms of GaAs is unlikely using **ALD Al_2O_3**
- **ALD and MBE-Y_2O_3 and -HfO_2 on GaAs(001) and InGaAs(001) are very different**

Interface reactivity: noble metals on GaAs(001)-2x4

Pi et al, APL 110, 052107 (2017).



The electronegativity of GaAs(001) surface is greater than that of the noble metals!!! Hence, if the surface atoms are not passivated, they will serve as electron trappers in *n*-type MOS under positive bias.

Summary - ALD Al_2O_3 on GaAs(001) - 2x4 and 4x6

In general

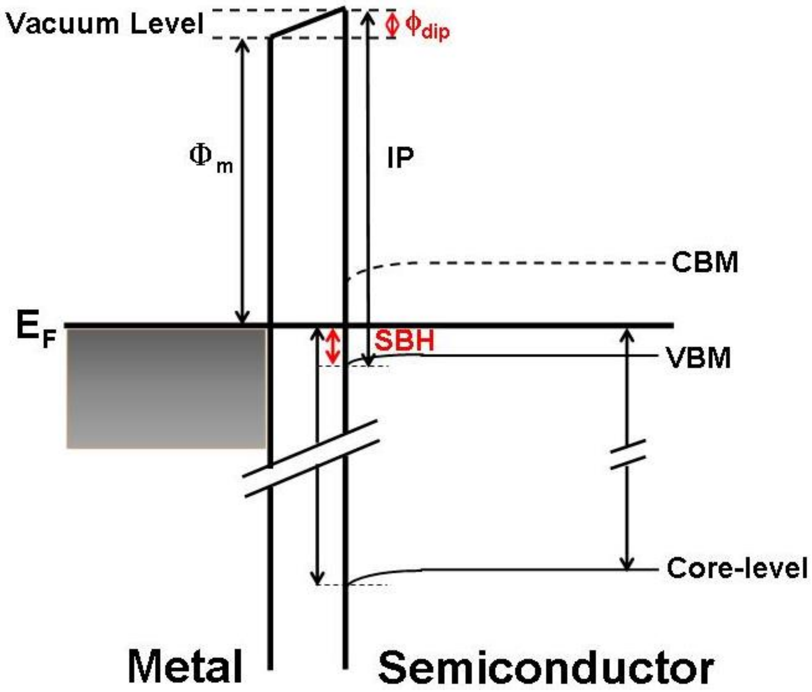
- Precursors adhere on a III-V surface free of a functional group
- Precursors react only with the atoms in the topmost (In)GaAs surface layer
- Total passivation of the surface atoms by the precursors is unlikely to achieve
- Clean (In)GaAs surface does not react with pure H_2O in ~ 10mTorr, but not in air

correlation with the electric characteristics

- Suggesting that high frequency dispersion is caused by the un-passivated surface atoms (**"Relevance of GaAs(001) surface electronic structure for high frequency dispersion on n-type accumulation capacitance", T. W. Pi, W. -S. Chen, Y. H. Lin, Y. -T. Cheng, G. -J. Wei, K. Y. Lin, C. -P. Cheng, J. Kwo, and M. Hong, Appl. Phys. Lett. 110, 052107 (2017).**)

Metal on semiconductor – Schottky barrier height

metal on *p*-semiconductor



Schottky-Mott rule:

(a non-interacting interface and the vacuum-level alignment are assumed)

$$SBH = IP - \Phi_m$$

Modified Schottky-Mott rule:

$$SBH = (IP - \phi_{dip}) - \Phi_m$$

(a non-interacting interface does not exist and the charge rearrangement at the interface due to the M-S bonding regarded as formation of **interfacial dipoles**)

SBH: Schottky barrier height

IP: Ionization potential energy

Φ_m: Metal work function

ϕ_{dip}: Interfacial dipole potential energy

Conventional Method to Obtain SBH

By a fit of a measured I-V curve with thermionic emission model:

An I-V relationship for an ideal metal-semiconductor interface is

$$I = I_0 \exp\left(\frac{q(V - IR_s)}{nk_B T}\right)\left(1 - \exp\left(-\frac{qV}{k_B T}\right)\right), \quad (1)$$

The saturation current I_0 is given by

$$I_0 = AA^{**}T^2 \exp\left(-\frac{q\phi_B}{k_B T}\right), \quad (2)$$

SBH

A: the constant area

A**: the effective Richardson constant

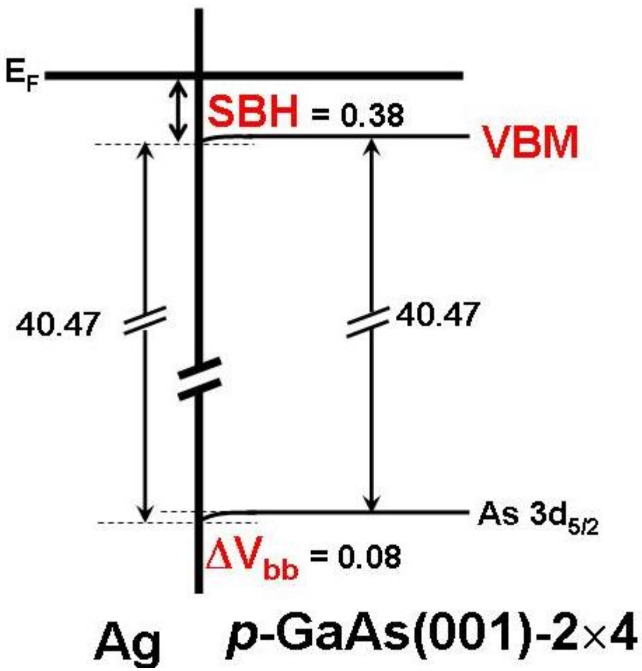
Neglecting R_s, we obtain from Eq. (1) that

$$\ln\{I/[1 - \exp(-qV/k_B T)]\} = \ln(I_0) + \frac{qV}{nk_B T}, \quad (3)$$

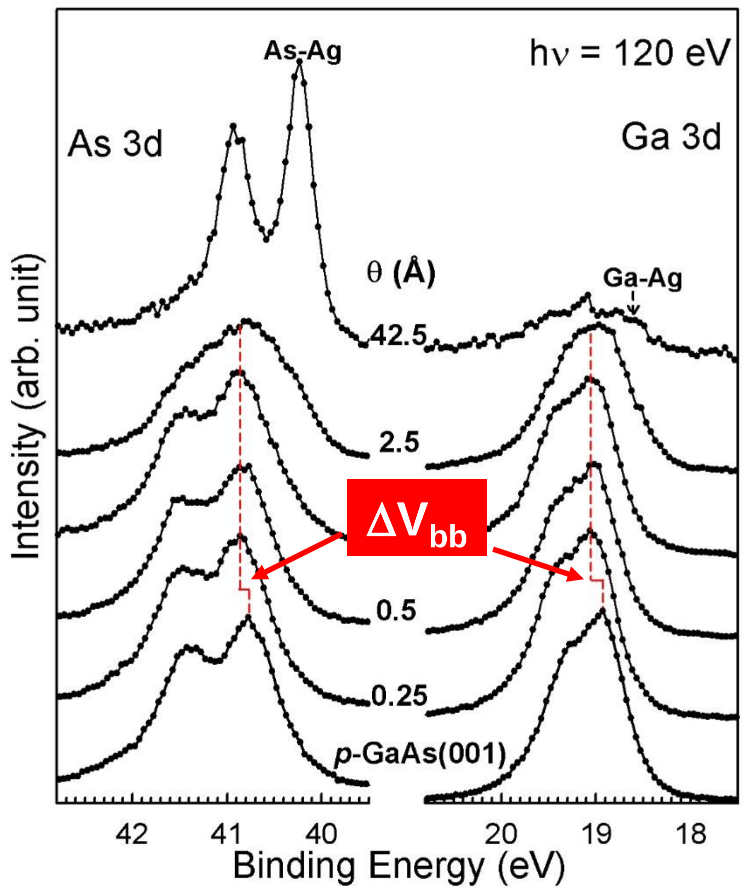
Direct Determination of SBH

ΔV_{bb}: strength of the band bending by the shift in the bulk peak position

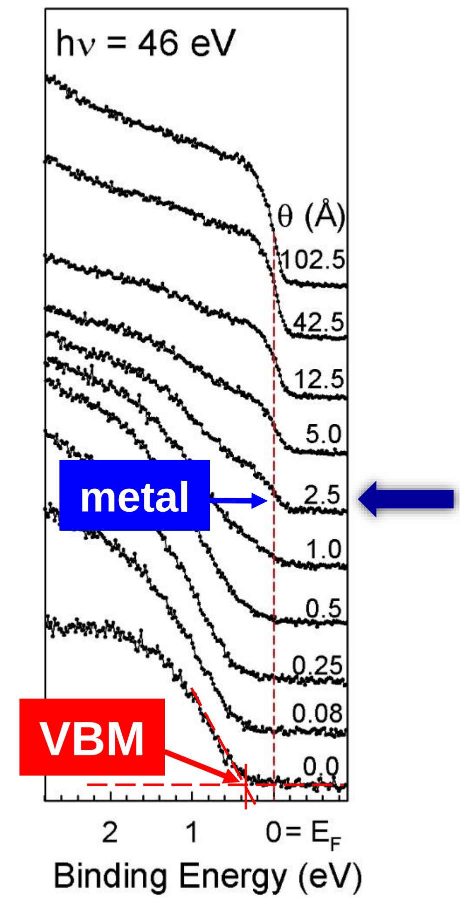
SBH = VBM + ΔV_{bb}



core-level spectra

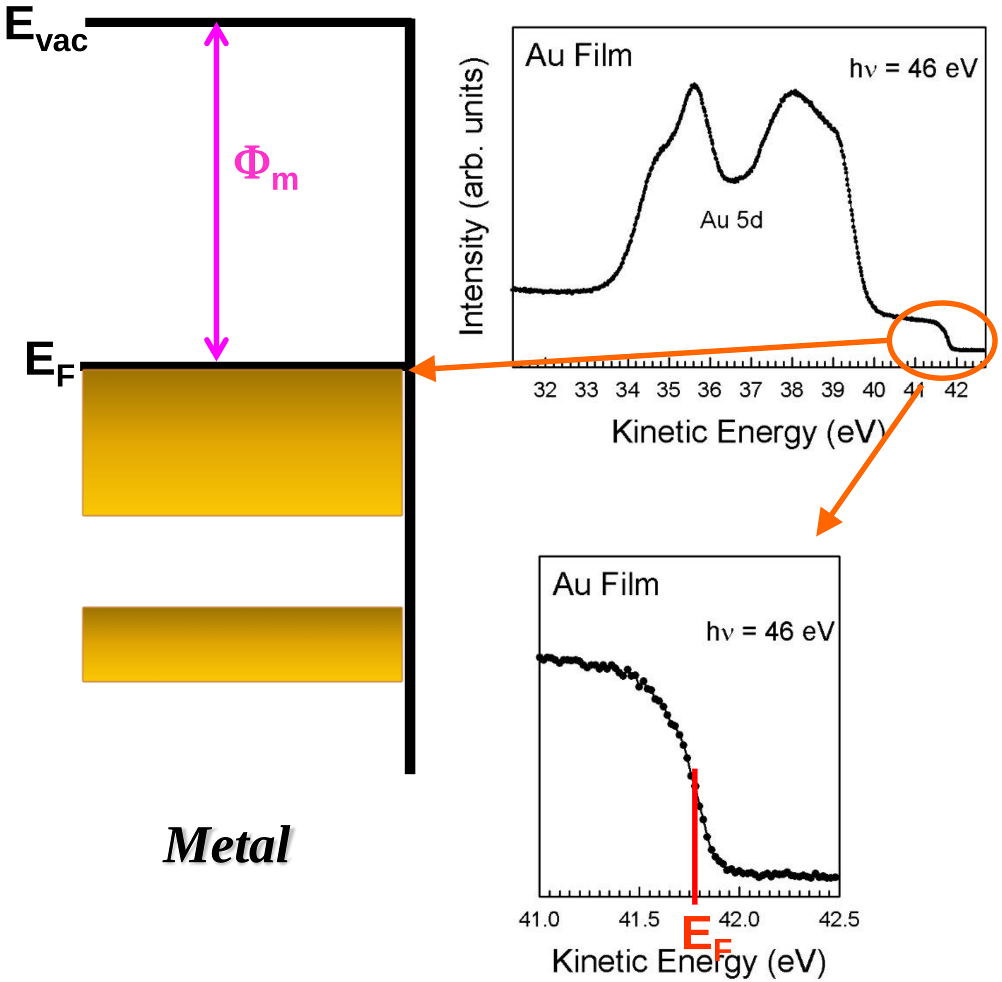


valence-band spectra



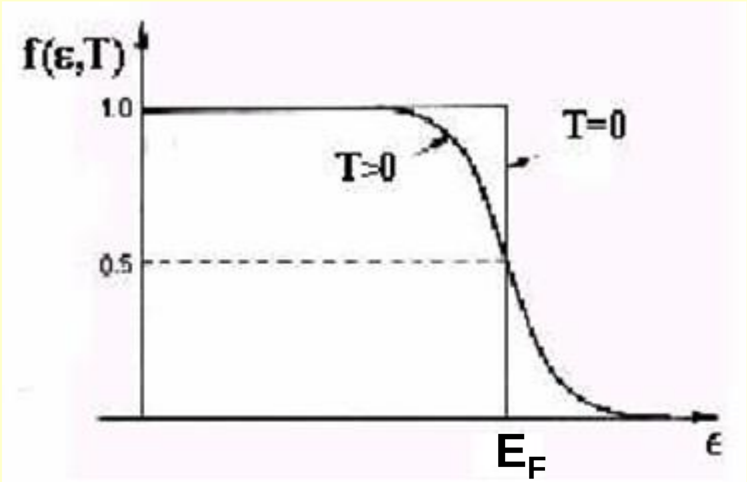
"Atomic nature of the Schottky barrier height formation of the Ag/GaAs(001)-2×4 interface: an in-situ synchrotron radiation photoemission study", **C.-P. Cheng, and M. Hong, et al, Appl. Surf. Sci. 393, 294 (2017).**

Fermi Edge of Metals Detected by PES



Density of electron states:

$$N(\varepsilon,T) = D(\varepsilon) f(\varepsilon,T)$$



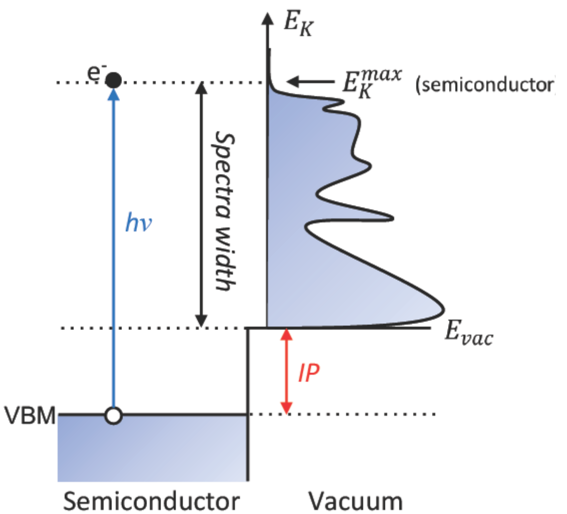
$$f(\varepsilon,T) = \frac{1}{1+\exp(\frac{\varepsilon - E_F}{kT})}$$

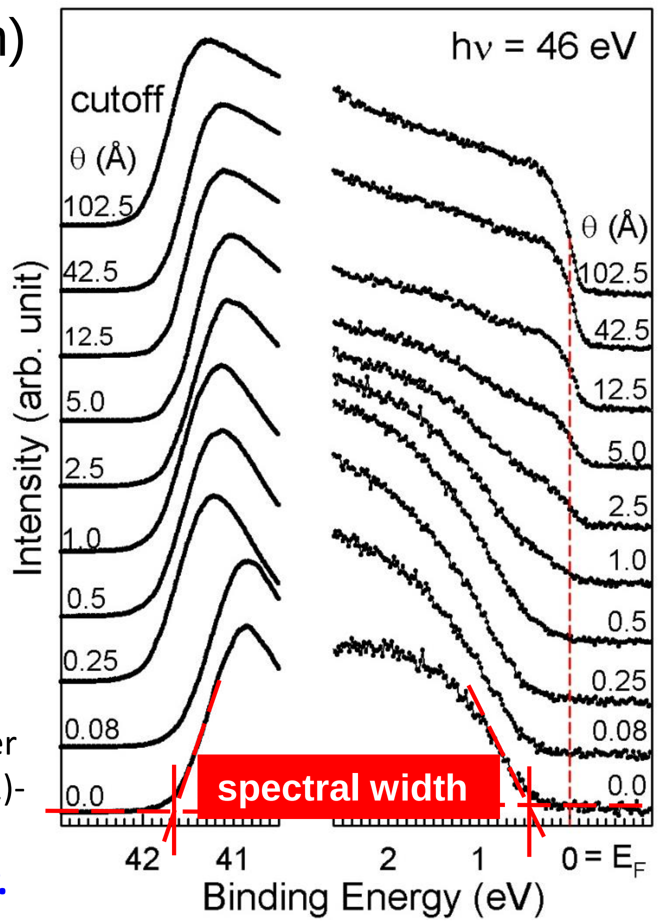
Direct Determination of Dipole Potential

Dipole Potential Energy = $IP_{(GaAs)} - IP'_{(adsobates/GaAs)}$

change in IP induced by the adsorbates

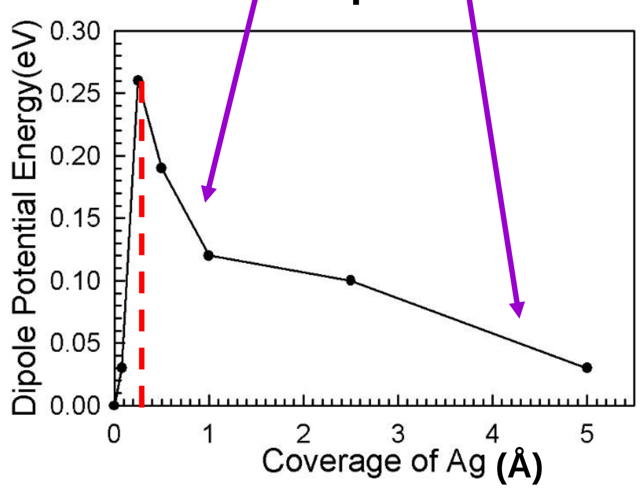
IP = hν - (spectral width)





potential energies drop with increasing coverage, indicating the appearance of opposite dipoles

Evolution of Dipole Potential

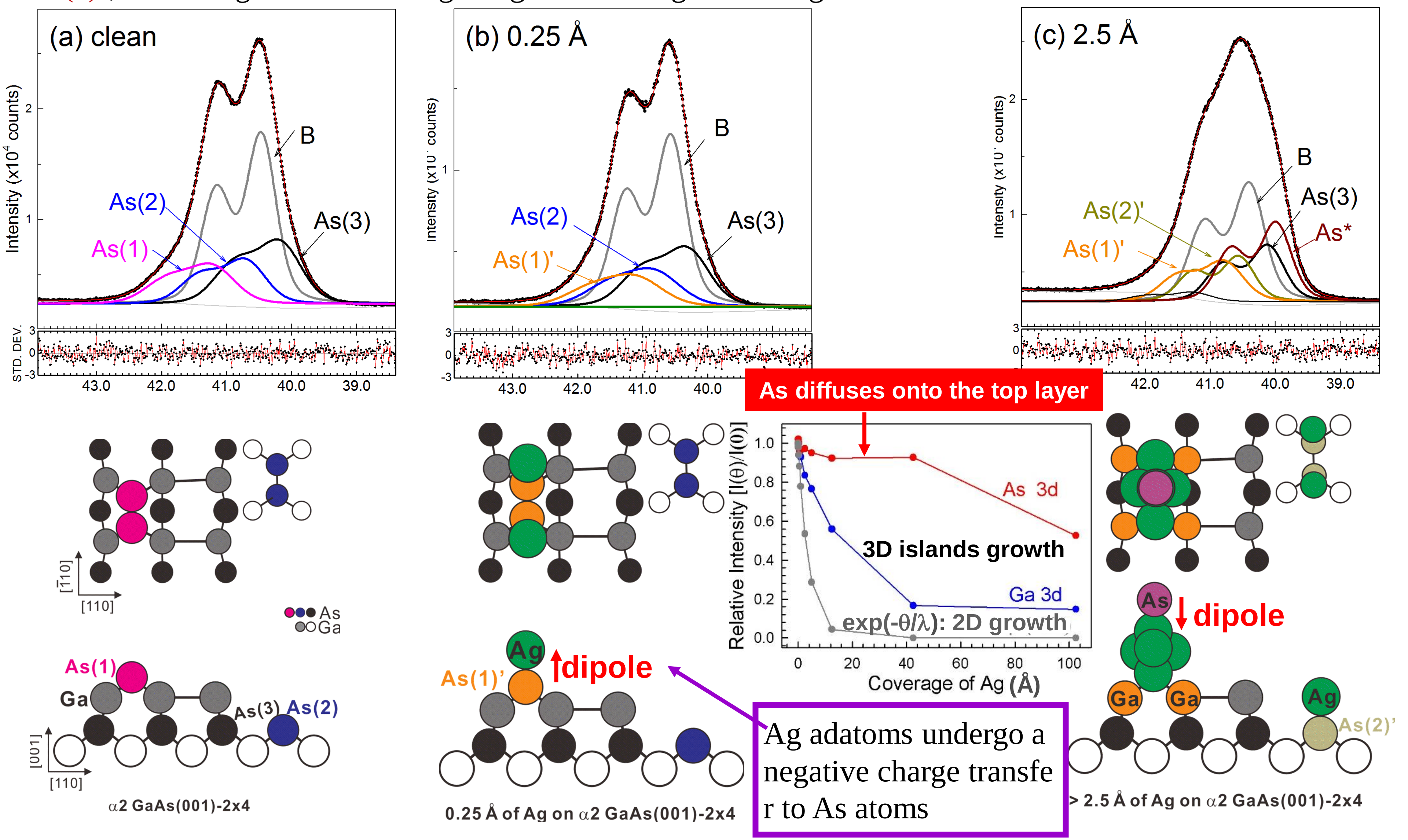


"Atomic nature of the Schottky barrier height formation of the Ag/GaAs(001)-2×4 interface: an in-situ synchrotron radiation photoemission study", **C.-P. Cheng, and M. Hong, et al, Appl. Surf. Sci. 393, 294 (2017).**

IP: Ionization potential energy

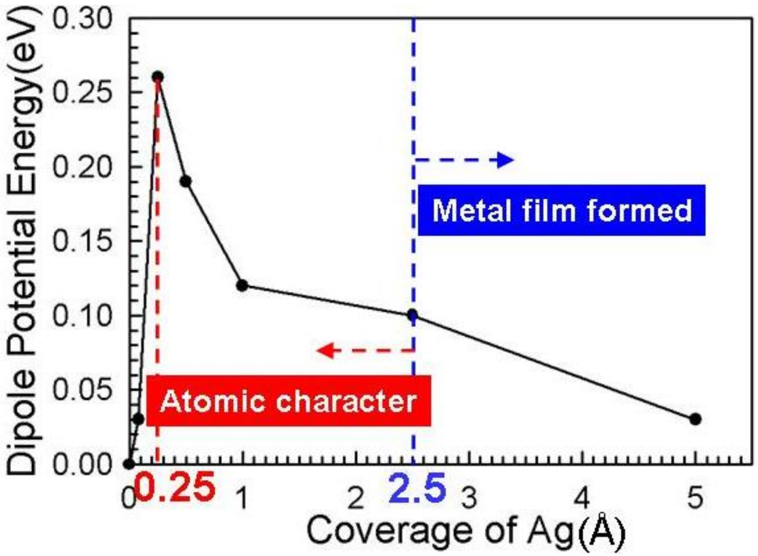
Mechanism of dipole and barrier formation using As 3d Curves of GaAs and Ag/GaAs

Ag adatoms induce **As(1)** component shifted toward lower binding energy, marked **As(1)’**, indicating As-As dimers getting an extra negative charges



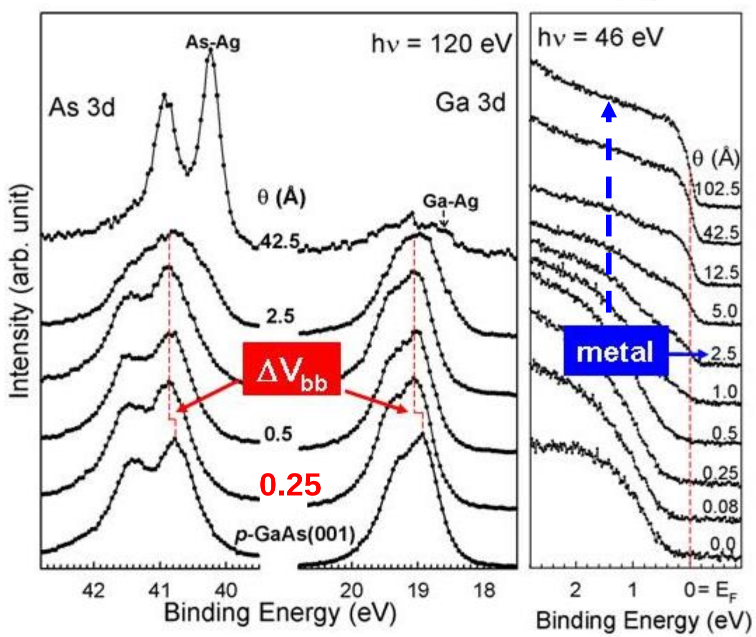
Dipole Formation at the Interface

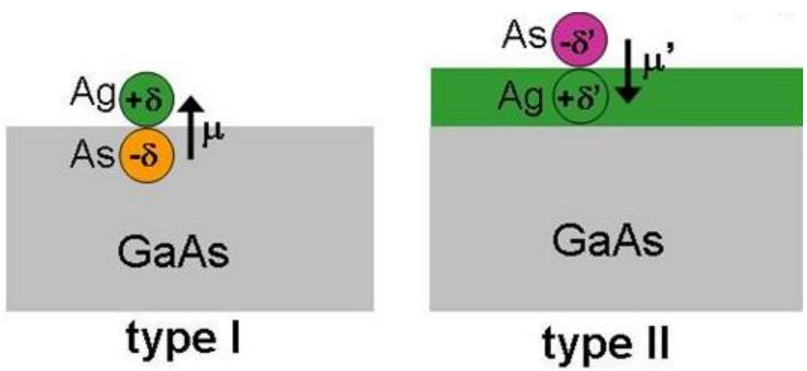
“Atomic nature of the Schottky barrier height formation of the Ag/GaAs(001)-2×4 interface: an in-situ synchrotron radiation photoemission study”, C.-P. Cheng, and M. Hong, et al, Appl. Surf. Sci. 393, 294 (2017).



● At **0.25-Å** coverage:
The dipole potential and the band bending reach the maximal strengths.

● **0.25-Å** coverage ≈
All of the As-As dimers in the topmost layer were passivated.





≤ **0.25-Å** coverage of Ag: type I

> **0.25-Å** coverage of Ag: type I + type II

Conclusion

- ✓ **Perfected growth of high κ dielectrics and metals on (In)GaAs using an in-situ approach**
  - Single-crystal single-domain complex materials using Sub-Nano-Laminated (*snl*) ALD and substrate induced epita
- ✓ **High-performance MOS and self-aligned inversion-channel MOSFETs via perfecting surface and interfacial electronic structures**
  - ALD-oxides (Al_2O_3, HfO_2)/InGaAs(001) MOSFET
    - I_d = 1.5 mA/μm, L_g = 1μm
  - Single crystal ALD-Y_2O_3/GaAs(001) MOS
    - D_{it} of (2-4) x 10^{11} $eV^{-1}cm^{-2}$ without a mid-gap peak
  - Common gate dielectrics using CMOS compatible process on InGaAs and Ge
- ✓ **ALD oxides and metals on Semiconductor (III-V) studied using *in-situ* synchrotron radiation photoemission**
  - Understanding/tailoring **surfaces** of semiconductors and oxide- and metal-semiconductor **interfaces** for advancing device performance
    - ALD half-cycle and cycle-cycle on (In)GaAs
    - Direct determination of Schottky barrier height and interfacial dipoles prior to the metal formation

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