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
Perfecting surface and interfacial electronic structures → High-performance MOS and self-aligned inversion-channel MOSFETs

- ALD-oxides (Al₂O₃, HfO₂)/InGaAs(001) MOSFET
- Single crystal ALD-Y₂O₃/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$_2$O$_3$(Gd$_2$O$_3$) at Bell Labs

  ✓ novel oxide Ga$_2$O$_3$(Gd$_2$O$_3$) to effectively passivate GaAs surfaces

- 1995 [IEDM]
  ✓ accumulation and inversion in Ga$_2$O$_3$(Gd$_2$O$_3$)/p- and n-GaAs MOS diodes with a low $D_{it}$

  ✓ first e-mode inversion-channel p- and n- GaAs MOSFETs
  ✓ Thermodynamically stable, dense, uniform microstructures; smooth, atomically sharp interface; low leakage currents

  ✓ 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$_2$O$_3$(Gd$_2$O$_3$) and Y$_2$O$_3$ at Bell Labs and in Taiwan

  - 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$_2$O$_3$ epitaxially grown on GaAs

  - 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, $L_g = 1$ µm

- 2012 [APEX 4 14202 (2011)]
  - Self-aligned inversion-channel InGaAs MOSFET with in-situ MBE-Y$_2$O$_3$, $g_m = 0.77$ mS/mm, $I_d = 1.5$ mA/µm, $L_g = 1$ µm
(In)GaAs and GaN MOSFET’s using \textit{ex-situ} ALD-oxides

- **2003**
  - d-mode GaAs MOSFETs using \textit{ex-situ} ALD-$\text{Al}_2\text{O}_3$ Ye, Hong, Kwo (APL 83, 180, 2003)

- **2005**
  - “\textit{Self-cleaning}” and passivation of (In)GaAs using \textit{ex-situ} ALD-$\text{Al}_2\text{O}_3$ Hong, Kwo (APL 87, 252104, 2005)

- **2006**
  - Energy-band parameters of \textit{ex-situ} ALD-$\text{Al}_2\text{O}_3$/InGaAs, Kwo, Hong (APL 89, 012903, 2006)

- **2007, 2008**
  - \textit{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 \textit{ex-situ} ALD-$\text{Al}_2\text{O}_3$ 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 Al₂O₃ on pristine n-GaAs(001)-4×6 surface, Pi, Hong, Kwo, (Microelectronic Eng. **88**, 1101, 2011)

**2012**

- Realization of high-quality HfO₂ on In₀.₅₃Ga₀.₄₇As by *In-situ* ALD, Kwo, Hong, (APL **100**, 172110, 2012)
  - In₀.₅₃Ga₀.₄₇As surface passivation with tetra-valence high κ’s recognized as “MISSION IMPOSSIBLE”
  - Thin ALD-HfO₂ (0.8nm) initial layer followed by ALD-HfAlO top layer to enhance thermal stability (>800°C).

**2013**

- High-performance self-aligned inversion-channel In₀.₅₃Ga₀.₄₇As MOSFET by *In-situ* ALD- HfO₂, Kwo, Hong, (APL **103**, 253509, 2013)
  \[ g_m = 1.06 \, \text{mS/μm}, \, I_d = 1.5 \, \text{mA/μm}, \, L_g = 1\, \mu\text{m} \]

**2015**

- Single-crystal *in-situ* ALD-Y₂O₃ epitaxially on GaAs(001) using ALD, Kwo, Hong, (Materials **8**, 7084, 2015)
In-situ ALD-HfO\textsubscript{2}(0.8nm)/InGaAs interface and clean InGaAs surface

In-situ ALD-HfO\textsubscript{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)
Atomic-layer-deposited HfO$_2$ on In$_{0.53}$Ga$_{0.47}$As: Passivation and energy-band parameters


$^1$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 1μm Lg


- UT Austin
- NTU/NTHU
- Purdue Univ.
- Purdue Univ.
- Intel
- NUS

(a) $I_{D,\text{max}}$ (extrinsic) = 1.5 mA/μm
$V_g$ = 0V to 2.5V, step = +0.5V

(b) $I_D$ (mA/μm) vs $V_D$ (V)

Intrinsic
Extrinsic

$G_{m,\text{max}}$ (intrinsic) = 1.2 mS/μm

$V_D = 2$ V

$G_E = 1.6$ mS/μm
The $D_{it}$ spectrum shows a midgap peak!
**In-situ ALD-Al$_2$O$_3$/ALD-Y$_2$O$_3$/GaAs(001)**

**RHEED & Cross-sectional TEM**

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**GaAs(001) surface**

- [110] 4x

**Y$_2$O$_3$(110) 1.0 nm**

- [001]

**Y$_2$O$_3$(110) 2.3 nm**

- [001]

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ALD-$\text{Y}_2\text{O}_3$/GaAs(001) - C-V and QSCV

He 900°C 10s + FGA

N$_2$ 900°C 60s + FGA


D_{it} Spectra for ALD-Y_{2}O_{3}/GaAs(001)

By QSCV
- He 900°C 10s + FGA
- N_{2} 900°C 60s + FGA

By conductance
- MBD-Al_{2}O_{3}/GaAs(001)
- N_{2} 900°C 60s + FGA

✓ (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+H₂O) on clean (In)GaAs surfaces
  - Other precursors
- Summary
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

In\textit{-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

**GaAs(001)-4x6**

**GaAs(001)-2x4**

**InGaAs(001)-4x2**
Some surface As atoms are stripped off by the (TMA+H$_2$O) precursors

Stripped As atoms found on surface of Al$_2$O$_3$ 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$_2$O$_3$

ALD and MBE-Y$_2$O$_3$ and -HfO$_2$ on GaAs(001) and InGaAs(001) are very different
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 Al₂O₃ 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 H₂O in ~10mTorr, but not in air

**Correlation with the electric characteristics**

Metal on semiconductor – Schottky barrier height

Schottky-Mott rule:
(a non-interacting interface and the vacuum-level alignment are assumed)

\[
SBH = IP - \Phi_m
\]

Modified Schottky-Mott rule:
(a non-interacting interface does not exist and the charge rearrangement at the interface due to the M-S bonding regarded as formation of \textit{interfacial dipoles})

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

- \( SBH \): Schottky barrier height
- \( IP \): Ionization potential energy
- \( \Phi_m \): Metal work function
- \( \phi_{dip} \): 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

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

Equation (1)

The saturation current $I_0$ is given by

$$I_0 = AA^{**}T^2 \exp(-\frac{q\Phi_B}{k_B T}),$$

Equation (2)

$A$: the constant area
$A^{**}$: the effective Richardson constant

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

$$\ln\left\{\frac{I}{1 - \exp(-qV/k_B T)}\right\} = \ln(I_0) + \frac{qV}{nk_B T},$$

Equation (3)
Direct Determination of SBH

\[ \text{SBH} = \text{VBM} + \Delta V_{bb} \]

\( \Delta V_{bb} \): strength of the band bending by the shift in the bulk peak position

Fermi Edge of Metals Detected by PES

Density of electron states:

\[ N(\varepsilon, T) = D(\varepsilon)f(\varepsilon, T) \]

\[ f(\varepsilon, T) = \frac{1}{1 + \exp\left(\frac{\varepsilon - E_F}{kT}\right)} \]
Direct Determination of Dipole Potential

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

decrease in \( IP \) induced by the adsorbates

\[ IP = h\nu - \text{(spectral width)} \]

Evolution of Dipole Potential


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.

As diffuses onto the top layer.

Ag adatoms undergo a negative charge transfer to As atoms.
Dipole Formation at the Interface


- 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 (Al₂O₃, HfO₂)/InGaAs(001) MOSFET
    - $I_d = 1.5 \text{ mA/µm, } L_g = 1\mu m$
  - Single crystal ALD-$Y_2O_3$/GaAs(001) MOS
    - $D_{it}$ of (2-4) x 10¹¹ eV⁻¹cm⁻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
Acknowledgements

✓ Ministry of Science and Technology (MOST), Taiwan
✓ TSMC/NTU Center with grants from MOST and TSMC