Local Electronic and Chemical Structure at GaN, AlGaN and SiC Heterointerfaces

- Wide Band Gap Semiconductors
- Low Energy Electron-Excited Nanoscale Luminescence (LEEN) Spectroscopy
- Metal/AlGaN Schottky Barriers: Nanoscale Alloy Changes
- GaN/Al₂O₃ Heterojunctions: Interdiffusion, Impurity Complexes, and Localized States
- Metal/4H-SiC Schottky Barriers: Interface States vs. Defects
- Interface Chemical and Electronic Trends

YoramFest 10.10.04
Tel Aviv, Israel
Once upon a time in Tel Aviv and Rochester . . . .
Investigation of InP surface and metal interfaces by surface photovoltage and Auger electron spectroscopies

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Auger depth profiling studies of interdiffusion and chemical trapping at metal–InP interfaces

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InP surface states and reduced surface recombination

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Cathodoluminescence spectroscopy studies of laser-annealed semiconductor interfaces


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NASA:
Dr. Robert Okojie 4H-SiC Interfaces

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GaN Applications

- UV/Blue/white LED (traffic signals, automotive, full color displays, interior lighting, ...)
- Blue/violet LDs. (4-8 GB CD-ROM storage, high resolution printers...)
- UV solar blind Detectors (sterilization sensor, missile tracking/guiding sensor ...)
- Microwave High power HEMTs (radar, cell phones...)
- Low noise, radiation hard transistors (high temperature sensors, space-flight instrumentation...)

[Images of radar, tactical UAV, CD-ROMs, traffic signals, decoys, jammers, seekers]
Nanoscale Electronic Structures

Schottky Barrier

Quantum Well

2 DEG Junction

Insulator-SC Template

Need To Probe Local Band Structure and Defects
Nanoscale Electronic Structures

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Need To Probe Local Band Structure and Defects
Low Energy Electron-Excited Nanometer Scale Luminescence Spectroscopy

Energy-Dependent Depth of Excitation Enables Probe of Localized States, Heterojunction Band Gaps, New Compounds, and Ultra-Thin Layers on a nm Scale

\[ E_{\text{Beam}} = 0.1 - 4.0 \text{ keV} \]
\[ I \approx 1 \mu A, \text{ Spot Size } \approx 500 \mu m \]
GaN Depth Dependence of Electron-Excited Nanoscale Luminescence Spectroscopy

After Everhart and Hoff, J. Appl. Phys. 42, 5837 (1971)
Depth-Resolved CLS: Si-SiO₂

- Interface Defect: 2.0 eV
- SiO₂ E₂' Defect: 2.7 eV
- Si Feature: 4.3 eV

Transition Region:
- \( R_B \approx 18 \text{ nm}, U_0 \approx 6 \text{ nm} \)
- \( R_B \approx 10 \text{ nm}, U_0 \approx 3 \text{ nm} \)
UHV CLS Using Auger Microprobe

- Quantum-Scale (5 nm) Analysis of Electronic States and Morphology
- UHV Control of Surface and Interface
- 0.5 - 25 keV Electron Probe Energy
- 8×10^{-11} Torr
- 0.5 nm Resolution for UV/IR CL Spectra 10K-300K
- 50 meV Resolution Auger Electron Spectroscopy

JEOL 7800F
Schottky Contacts to III-N materials

• Schottky contacts to AlGaN and AlGaN/GaN devices: Crucial for device operation
  – High barrier for leakage current reduction/ better gate control

• Carrier transport through AlGaN/GaN Schottky contacts is not well explained

• Experimental Approach:
  – UHV Metal Deposition on Representative, Chemically-Cleaned Surfaces
  – Internal Photoemission Spectroscopy (IPE)
  – Nanoscale Depth-Resolved Cathodoluminescence Spectroscopy (LEEN)
  – Secondary Ion Mass Spectrometry (SIMS)

Use IPE, CLS, and SIMS to Correlate Changes in Schottky Barrier Height with Chemistry/Processing
UHV Ohmic and Schottky Deposition

- $1 \times 10^{-10}$ Torr Base Pressure
- Thermal and E-beam Sources
- Ti/Al/Ti/Au Ohmic Contacts
  - 850 °C UHV Anneal, 30 seconds
- 1 mm and 0.5 mm Ni Schottky Contacts

**Different Surface Treatments Applied before Ni Deposition**

- Organic + HCl + Buffered HF
- + UV/O$_3$ Cleaning (Hg lamp + O$_2$
- + UV/O$_3$ Cleaning + Buffered HF

UHV Annealing Performed after Diode Deposition

<table>
<thead>
<tr>
<th></th>
<th>$\text{Al mole fraction}$</th>
<th>Mobility (300 K)</th>
<th>$\text{AlGaN FWHM}$</th>
<th>YL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1235 (Wafer 1)</td>
<td>0.33</td>
<td>805</td>
<td>140 meV</td>
<td>Little</td>
</tr>
<tr>
<td>1041 (Wafer 2)</td>
<td>0.35</td>
<td>730</td>
<td>330 meV</td>
<td>Higher</td>
</tr>
</tbody>
</table>
Internal Photoemission Spectroscopy (IPE)

- **IPE**: Yields True Barrier Height(s)
- **I-V, C-V**: SBH(s) Weighted Averages

\[ Y \propto (h \nu - q \phi_B)^2 \]

X-intercept of \( Y^{1/2} \) plot gives Schottky barrier height

Fowler, Phys. Rev. 38, 45 (1931)

More than One SBH Measurable

(Parallel Schottky Contacts to Si Observed with IPE (Okumura, et al. J. Appl. Phys. 54, 922 (1983)))
Wafer 1 IPE Schottky Barriers

- **Two Thresholds → Multiple SBH’s**
  - Not observed until 325 °C Anneal
- **Marked SBH increase with 325 °C Anneal**

- Two Thresholds Common to Solvent/HF and UV/O₃ Diodes with 325 °C Anneal

- UV/O₃ Diodes Yield Larger SBH’s
  → Surface Oxidation Enhances Observed SBH (essentially MOS)

Wafer 2 IPE Schottky Barriers

- Similar Marked Increase in SBH with 325 °C Anneal for HCl+HF Etch
- I-V Reverse Current Consistent with Increase in SBH with Anneal

Wafer 2 Low Temperature Interface LEEN Spectra: *Through the Metal*

- *Two* AlGaN NBE Emissions
- Lower AlGaN NBE Peak Increases with UV/O$_3$ + HF cleaning
- AES vs. Process Shows:
  - UV/O$_3$ Process Oxidizes Surface
  - Subsequent HF Treatment Removes O
- SIMS Reveals: $\geq$ 30% Lower AlN$^-$/GaN$^-$ Ion Yield and Less Abrupt Ni/AlGaN Interface for UV/O$_3$ -Treated Diodes
- Low Temperature LEEN Reveals Broadening of Peaks → Compositional Disorder

Shift in AlGaN Emission Correlates with Changes in SBH → Local Al Alloy Variation
PHI TRIFT III Time-of-Flight SIMS

- ~ ppb Sensitivity for Some Elements, 1-2 milli-amu Mass Resolution
- Depth Profiling and Imaging Capability
Ni/AlGaN Interface Chemistry

- Top 20% of AlGaN Oxidized as AlO and GaO
- Top 20% of AlGaN Contains NiN and NiO Reaction Products
Ni/AlGaN Interface Chemical Changes with Processing

HCL+HF

\[ \Phi_{b1} \]  
\[ \text{Al}_{0.3}\text{Ga}_{0.7}\text{N} \]  
\[ \text{GaN} \]

HCL+HF, 325°C Anneal

Ni penetrates adventitious layer

HCL+HF+UV/O\textsubscript{3}, 325°C Anneal

Thicker (AlO>GaO) oxide layer forms; Al/Ga composition in AlGaN changes.

HCL+HF+UV/O\textsubscript{3} + HF, 500°C Anneal

AlO>GaO) layer largely removed; Ni contacts both Al-deficient AlGaN layer and AlGaN layer
Ni/AlGaN Schottky Barrier Summary

- Chemical and Thermal Treatments Alter SBH’s over Range of 100’s of meV
- IPE Detects Double Barriers (200 meV separation)
- LEEN Detects Dual Al Content AlGaN
- SIMS Reveals > 30% Al Content Changes Consistent with CLS and IPE
  - Interfacial Carbon Also Affects SBH’s; Cl, F Much Less So

→ Al Content Changes Dominate SBH Variation
**GaN/Al$_2$O$_3$ Interfaces: Background**

**Highly n-Type Layer Near HVPE GaN-Sapphire Interface**


**O Diffuses into GaN**


**X-Sectional Micro-CLS Reveals New Donor Bound Exciton at Degenerate Interface - Extends 1-2 $\mu$m**


**New Donor Emission Correlates Spatially with SIMS**
Low-T CL GaN/Al₂O₃ Depth Profile: New Interface Donors & Reaction Products

- 34 meV O Donor
- Band Tailing & Filling at Highest Doping

Above-GaN Energy Shoulder: AlGaN Formation


Auger Images of Sample TH1011-1,3 (E=10 keV, I=3.3 nA)
Cross-Sectional SIMS Images at GaN-Al$_2$O$_3$ Interfaces

- Filamentary GaO Image $\rightarrow$ O Grain Boundary Diffusion
- GaO, GaON, AlGaO & AlGaON Fragments $\rightarrow$ Ga-O Bonding
- AlN, AlGaN Fragments $\rightarrow$ AlGaN Alloy Formation
GaN/Al₂O₃ Interface Summary

• New Shallow Donor Transition Tracks with Interface SIMS [O] Concentrations → High n_{int} Due to O Diffusion from Al₂O₃ Into GaN

• Interface Defects Can Extend Microns Into GaN and Al₂O₃

• Al-N-O Complex Formation→ N Indiffusion and Defect Emission

• Evidence for GaN-Al Alloying: Al Indiffusion, High Energy Emission
SiC Schottky Barrier Formation: Background

- Localized States Influence Charge Transfer & Barrier Height
- Until Now: Moderate Interface State Density Only Inferred from Band Bending vs. $\Phi_M$ since:
  
  Conventional Techniques (e.g., C-V, DLTS) Can’t Probe nm-Scale Interface Region

- Now: Near-Interface States Measured Directly By Nanoscale Depth-Resolved CL

Au – Induced 4H-SiC Interface States (0.5 keV)

- Au Deposition introduces 1.7 – 2.0 eV Deep Level Emission
- Emission highly localized to interface region

Au-Deposited vs. Bare 4H-SiC Comparison
Only Au-Covered Area Changes with Annealing
Unreactive Metals: Au, Ag/ 4H-SiC Interface States

- 4 nm Au, ~3 nm Ag Induce 1.7-2.0 eV Emissions
- 800 - 900°C Anneals Decrease 1.7-2.0 eV Emissions
  → Au and Ag Exhibit Analogous Behavior with Deposition and Annealing

4 nm Au on SiC(Si face)
$E_B = 1$ keV ($U_0 = 4\text{-}5$ nm)

~3 nm Ag/4H-SiC
$E_B = 500$ eV ($U_0 = 2\text{-}4$ nm)
UHV Thermally-Activated Deep Level Emission

- Highly N-doped (> 2 x 10^{19} \text{ cm}^{-3})
  4H-SiC(0001) Annealed in UHV

- New Emissions Appear at 2.47 eV and ~ 1.9 eV

- Similar Activation Energy as Oxidized 4H-SiC(0001)

- 1.9 eV Transition Appears After Emergence of 2.47 eV Peak

→ Both Related to Stacking Faults

Electroluminescence of Electrically-Stressed 4H-SiC

- 2.65-2.9 eV Associated with Triangular Stacking Faults
  [Single Stacking Faults Produced under Electrical Stress]

- 1.7-1.9 eV Emission From Partial Dislocations Bounding
  Stacking Fault Planes

- 2.45 eV and 1.9 eV Similar to Double Stacking Faults Produced
  Under Thermal Stress


Reactive Metals: Ti, Ni/4H-SiC Interface States

• ~3 nm Ti or Ni Deposition Induce No Major Changes

• 800-900 °C Anneals Introduce New 2.85 eV Emission

→ Ti and Ni Interfaces Are Qualitatively Different from Au and Ag Interfaces
4H-SiC Schematic Energy Level Transitions

$E_G = 3.2 \text{ eV}$

- 2.7-2.9 eV
- 2.5 eV
- 1.7-1.9 eV
- ~2.4 eV
- ~2.3 eV

- Multiple Deep Defect Levels with Energies Near $\Phi_B$ Fermi Levels
- Role of Morphological Defects or Mobile Point Defects

$\Phi_B$ Range

- 1.1-1.8 eV
Metal/4H-SiC Schottky Barrier Summary

- **No** Metal-Specific Interface States Observed
- Metal-Induced States Similar to States Associated with Dislocations or Stacking Faults
- **Major** Effect with Non-Reactive Metals – Consistent with Diffusion Processes
- **Minor** Effect with High Reactivity Metals – Consistent with Limited or Si/C Balanced Reactions
- Mobile Native Defects vs. Extrinsic Metal-Induced States Are Dominant SiC-Metal Interface States
Overall Summary

• Depth-Resolved Optical Emission from Localized Electronic States and Band Structure on Nanometer Scale

  → Multiple Deep Levels / New Phases at Wide Gap Semiconductor Surfaces and Interfaces

• Three Types of Wide Gap Interface Electronic Phenomena:

  1. Ni/AlGaN: Ternary Alloy Changes That Correlate with Schottky Barriers

  2. GaN/Al₂O₃: Interdiffusion That Produces Impurity Complexes, Localized States & Degenerate Carrier Concentrations

  3. 4H-SiC(100)/Metal Interfaces: Defect Movements That Depend on Metal Diffusion vs. Reaction

  → Key Role of Chemical Interactions at the Nanoscale Interfaces
Happy Birthday, Yoram!
Possible Mechanisms for Au-Induced Electronic States

**Interdiffusion:** Increase in 1.7-1.9 eV Emission After Au Deposition and Before Annealing → Au Film May Induce Si-Au Mixing → *New Native Defects* (e.g., $V_{Si}$ and $Au_I$)

SIMS Shows Au Diffuses ~ 10 nm Into Si After 800°C /900°C Annealing

**Defect Complex Formation:**
Decrease in 1.7-2.0 eV Emission After Annealing → Au May Complex with Native Defects → **Passivate**

Before annealing  

After annealing (more diffusion)

**Ec**

$Au$ level

$Si$

$Ev$

Vacancy complex $V_{Si}$

SF complex

Interstitial

$Au$

$C$

$Si$
Low Temperature LEEN/CL Maps: Wafer 1

- Maps Reveal Regions of AlGaN Near Band Edge Nonuniformity
- Complementary Maps Correlate with Multiple AlGaN Near Band Edge Emissions

Low Al% AlGaN NBE (3.85 eV)  
High Al% AlGaN NBE (3.94 eV)  

5 µm