Polarization charges

Spontaneous polarization due to crystal asymmetry in wurtzite

Debdeep Jena Ph.D dissertation
Polarization charges – bulk GaN

Debdeep Jena Ph.D dissertation
Polarization charges – AlGaN/GaN

AlGaN/GaN (strained to GaN)

Debdeep Jena Ph.D dissertation
Piezoelectric polarization
(polarization caused by strain)

\[ P_{PE} = e_{33} \varepsilon_z + e_{31} (\varepsilon_x + \varepsilon_y) \]

\[ \varepsilon_z = (c - c_0)/c_0, \quad \varepsilon_x = \varepsilon_y = (a - a_0)/a_0. \]

Also, \[ \varepsilon_z = -2 \frac{C_{13}}{C_{33}} \varepsilon_x \]

Therefore, \[ P_{PE} = 2 \frac{a - a_0}{a_0} \left( e_{31} - e_{33} \frac{C_{13}}{C_{33}} \right) \]

(e_{31} - e_{33} C_{13} / C_{33}) is always –ve, as e_{31} is always –ve, and others are +ve.

<table>
<thead>
<tr>
<th>Material</th>
<th>e_{31} (C/m^2)</th>
<th>e_{33} (C/m^2)</th>
<th>C_{13} (Gpa)</th>
<th>C_{33} (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN</td>
<td>-0.49^a</td>
<td>0.73^a</td>
<td>103^b</td>
<td>405^b</td>
</tr>
<tr>
<td>AlN</td>
<td>-0.60^a</td>
<td>1.46^a</td>
<td>108^b</td>
<td>373^b</td>
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</tbody>
</table>

- Spontaneous and piezoelectric polarization aid each other for tensile strain and oppose for compressive strain
Spontaneous and piezoelectric polarization under different conditions of the GaN and AlGaN layers
Surface and interface energy

Frank-van der Merwe (FM)  Volmer-Weber (VW)  Stranski-Krastanov (SK)

\[ \Delta \gamma_n < 0 \]  \[ \Delta \gamma_n > 0 \]  \[ \Delta \gamma_n < 0 \]

\[ \Delta \gamma_n > 0 \]

\[ \Delta \gamma_n = \gamma_{FV} + \gamma_{FS} - \gamma_{SV} \], where \( n \) refers to \( n^{th} \) layer growth
\( \gamma_{FV} \) = surface energy of film-vapor interface
\( \gamma_{FS} \) = interfacial energy between film and substrate
\( \gamma_{SV} \) = substrate surface energy

Note: Difference between FM and SK arises primarily due to elastic strain associated with the film
Other epitaxial growth modes, summary

Supersaturation vs. misfit percentage
Common growth techniques

- **Bulk crystal growth**
  - Czochralski: Liquid to solid (Si, GaAs)
  - Bridgman: Liquid to solid (CdTe, other II-VI compounds)
  - Sublimation: Vapor to solid (SiC, GaN?)

- **Epitaxial crystal growth**
  - Liquid phase epitaxy: substrate moves from one melt to another (Ex: GaAs)
    - Adv: Simple, high quality defect free layers, equilibrium growth
    - Disadv: Multiple layers difficult, QW structure difficult, poor layer interface
  - Chemical vapor deposition (Ex: all compound semiconductors, Si)
    - Adv: Very high quality, high throughput
    - Disadv: Toxic gases, non-uniform, not as abrupt as MBE
  - Molecular beam epitaxy (Ex: all compound semiconductors)
    - Adv: Very high quality, no toxic gases, very abrupt
    - Disadv: Low throughput, can be unstable from run to run
Partial pressure curves for III-Nitrides

For same temperature, the partial pressure of InN is the highest and AlN the lowest.
MBE growth system

RHEED techniques for growth study
General MBE growth features

• Advantages
  – Precise layer by layer growth process
  – Excellent in-situ growth rate monitoring possible
  – Very abrupt (one atomic layer) growth possible
  – Can replicate starting layers in excellent manner

• Disadvantages
  – Growth occurs far from equilibrium and is not thermodynamically favorable
  – Growth temperature lower and so film quality is not as good
  – Slower growth rate than MOCVD; difficult design for multiple wafers
MOCVD growth system
General MOCVD growth features

**Advantages**
- Faster growth than MBE, can be a few microns per hour; multi-wafer capability easily achievable
- Higher temperature growth; growth process is thermodynamically favorable
- Quality of layers usually better than MBE

**Disadvantages**
- Difficult to monitor growth rate exactly (no Rheed possible due to higher pressure)
- Not as abrupt a process as MBE due to gas flow issues and memory effects
- Toxic gases are to be handled
Various problems associated with mismatches

**Substrate Property**

1. Lateral lattice constant (a-lattice constant) mismatch
2. Vertical lattice constant (c-lattice constant) mismatch
3. Coefficient of thermal expansion mismatch
4. Low thermal conductivity
5. Different chemical composition of the epitaxial film
6. Non-polar surface

**Consequence**

1. All problems typically associated with high dislocation density
2. Anti-phase boundaries, inversion domain boundaries
3. Thermally induced stress, cracks in epitaxial films
4. Poor heat conduction; unsuitability for high power devices
5. Contamination, interface states, poor wetting of surface during growth
6. Mixed polarity; inversion domains
Formation of dislocations

• Dislocations are formed in the epitaxial layers due to
  – **Transfer of defects/dislocations already present in the substrate:** Happens when substrate has high density of defects (example: dislocation in GaN epilayers when SiC is used as a substrate)
  – **Misfit dislocation:** When dislocations are caused by a difference in the lattice constant of the epitaxial layer and the substrate (Ex: dislocations in AlGaN layer \( d_{\text{AlGaN}} > d_{\text{critical}} \) grown on GaN)
  – **Imperfections resulting from island coalescence** (example: dislocations in GaN buffer layers grown on AlN nucleation layer)

• Main types of defects in GaN
  – Point defects (vacancies, self-interstitials, and antisites)
  – Threading edge dislocation
  – Threading screw dislocation
  – Mixed screw-edge dislocations
Dislocations

Simple cubic lattice

Extra half plane of atoms

Displaced plane faces

Edge dislocation

Screw dislocation

Crystal Planes and Directions

Planes inside crystals are represented by a set of numbers called Millers Indices \((h, k, l)\).

- Determine intercepts on crystal axes
- Take reciprocal of it
- Multiply by an integer to convert to integers

These are called Millers Indices \((h, k, l)\)

Crystalline directions are represented by three integers with the same relations as a vector in that direction \([a, b, c]\).
Major techniques to reduce dislocations

• Bulk growth
  – By direct synthesis (from Ga metal and nitrogen)
  – By sublimation (by using GaN powder as starting material, and by vapor transport of Ga, which later reacts with NH\textsubscript{3})

• Exotic substrates
  – Si
  – ZnO
  – Lithium niobate
  – Lithium gallate

• Lateral epitaxial overgrowth (LEO) or epitaxial lateral overgrowth (ELO)

• Pendeo-epitaxial growth (*pendeo* means *suspended*)

• Quasi-bulk growth by HVPE on sapphire
Reduction of dislocations: LEO growth

1. One of the most commonly used techniques to reduce dislocation density in nitride films (both c-plane and a-plane).

2. Advantage: Simple fabrication procedure, can be easily implemented.

3. Disadvantage: Dislocation density only reduced in selected areas. The stripes free of dislocation not very suitable for large scale device fabrication.
Quasi-bulk GaN: Hydride Vapor Phase Epitaxy

Ga (melt) + HCl = GaCl + ½ H₂

GaCl + NH₃ = GaN + HCl + H₂  (forward reaction)

GaN + HCl = GaCl + ½ N₂ + ½ H₂  (reverse reaction)

“Hydride (not halide)” because of the use of NH₃. If NCl₃ is used then it becomes “Halide”

• Usually requires MOCVD templates or LEO substrates (not easy to grow smooth layers just by itself)
• Usual growth rates few tens of microns per hour resulting in rougher but low dislocation density films
• Low cost technique
# Doping of Wide Bandgap Semiconductors

<table>
<thead>
<tr>
<th></th>
<th>GaN</th>
<th>SiC</th>
<th>ZnO</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-type dopant</strong></td>
<td>Si on Ga site (~ 15 meV)</td>
<td>N on C site (~ 85 meV)</td>
<td>B on Zn (~30-60 meV)</td>
<td>N (~ 1.7 eV)</td>
</tr>
<tr>
<td><strong>p-type dopant</strong></td>
<td>Mg on Ga site (160 meV)</td>
<td>Al on Si site (~ 200 meV)</td>
<td>N on O site (~ 170-200 meV)</td>
<td>B (~ 370 meV)</td>
</tr>
<tr>
<td><strong>n-conductivity</strong>*</td>
<td>~ 0.002 Ωcm</td>
<td>~ 0.01 Ωcm</td>
<td>~ 0.02 Ωcm</td>
<td>&gt; 1000 Ωcm</td>
</tr>
<tr>
<td><strong>p-conductivity</strong>*</td>
<td>0.2-2 Ωcm</td>
<td>0.5-2 Ωcm</td>
<td>0.5-40 Ωcm</td>
<td>10-100 Ωcm</td>
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</table>

* Experimental values

<table>
<thead>
<tr>
<th></th>
<th>GaAs</th>
<th>Si</th>
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<tbody>
<tr>
<td><strong>Si</strong></td>
<td>6meV</td>
<td></td>
</tr>
<tr>
<td><strong>P</strong></td>
<td>45meV</td>
<td></td>
</tr>
<tr>
<td><strong>C (Be)</strong></td>
<td>~28 meV</td>
<td></td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>40meV</td>
<td></td>
</tr>
<tr>
<td><strong>Diamond</strong></td>
<td>~ 0.001 Ωcm</td>
<td></td>
</tr>
</tbody>
</table>
Hydrogenic model for impurities

Ionization of acceptor or donor impurities can be considered in the same fashion as the electron energy levels and radii are calculated for an isolated hydrogen atom.

The impurity levels $E_{dn}$ are given by:

$$E_c - E_{dn} = \frac{q^4 Z^2 m^*}{2n^2 (4\pi\epsilon\hbar)^2}$$

where $n$ is a positive integer and $Z$ is the number of unit charge of the ionized donor atom, i.e. $Z = 2$, for a doubly ionized donor.

In terms of hydrogen atom ionization energies:

$$\Delta E_{dn} = E_c - E_{dn} = 13.6 \left( \frac{Z}{n\epsilon_r} \right)^2 \left( \frac{m^*}{m} \right)$$

The orbital radii of the electrons are given by:

$$r_{dn} = 0.53 \left( \frac{n^2 \epsilon_r}{Z} \right) \left( \frac{m}{m^*} \right) \text{ Å}$$
p and n type doping of GaN

• N-type doping for GaN is simple and similar to other common semiconductors
  – Si has $E_a \sim 20$ meV (mobility $\sim 800 - 1000$ cm$^2$V$^{-1}$s$^{-1}$), Ge not so good for doping due to low incorporation

• P-type doping is complicated and quite different from other semiconductors
  – Mg has activation energy of $\sim 0.2$ eV (mobility few tens of cm$^2$V$^{-1}$s$^{-1}$)
  – Mg forms complexes with hydrogen which has to be broken first, for Mg to act as acceptors
  – Mg-H complexes can be broken down by
    • Annealing in nitrogen atmosphere
    • Low energy electron beam irradiation (LEEBI); $\sim 10$KeV, 60 $\mu$A

Variation of resistivity with annealing temperature
Processing

Pattern Transfer Method 1:
- Film Deposition
- PR Ashing & clean
- Lithography
- Etching

Subtractive

Pattern Transfer Method 2:
- Substrate
- PR Ashing & clean
- PR Masking
- Film Deposition

Additive

Directionality of Etching Process:
- Isotropic Etch
- Directional Etch
- Vertical Etch

Two Kinds of Etching Method:

**Wet Etching**
- by Wet chemical solution
- Isotropic etching

**Dry Etching**
- by Plasma
- Anisotropic etching

Vertical E/R ≠ Horizontal E/R
Pure Chemical Reaction
High Selectivity
CD Loss or Gain

Vertical E/R >> Horizontal E/R
Ion assisted
Relatively low Selectivity
No CD bias

Hynix semiconductor
Common Techniques for Ohmic contacts

(i) Ohmic contact by band alignment

\[ \phi_M < \chi + E_c - E_F = \phi_S \]

For n-type semiconductor.
Reverse for p-type

(ii) Ohmic contact by high doping

- Usually for compound semiconductors the ohmic contact by band alignment is hard to realize due to surface states and Fermi pinning. For p-type, the problem is caused by unavailability of metals with large enough work function.
- High n-type doping required for ohmic contacts to n-type semiconductors, which can also be realized by interfacial layer reaction chemistry.
Schottky contacts

- Schottky contacts are formed when
  - Doping in the semiconductor is not very high i.e. > ~5x10^{18} cm^{-3}
  - The metal work function is greater than the n-type semiconductor work function
  - The metal work function is lower than p-type semiconductor work function
  - Very high density of surface states “pinning” the Fermi level at the surface w.r.t. the conduction band (Example: GaAs)

\[
\phi_M > \chi + E_c - E_F = \phi_S
\]

For n-type semiconductor and reverse for p-type
Conduction mechanisms in Schottky contacts

- **Thermionic emission**
  - Electrons emit over the barrier
  - Low probability of direct tunneling
  - Valid for low doping ($N_D < \sim 10^{17} \text{ cm}^{-3}$)

- **Thermionic-field emission**
  - Electrons use thermal energy to tunnel through the thin barrier in the upper end of the conduction band
  - Valid for intermediate doping ($\sim 10^{17} \text{ cm}^{-3} < N_D < \sim 10^{18} \text{ cm}^{-3}$)

- **Field emission**
  - Direct tunneling, as depletion region is very narrow
  - Valid for heavy doping ($N_D > \sim 10^{18} \text{ cm}^{-3}$); almost ohmic

- **Leakage current**
  - High probability of defect-assisted tunneling and simple conduction
  - Occurs in poor material/interface quality; dislocations

Slide # 27
Evaporation systems

Contact Metallization (Ti, Al, Ni, Au etc)
Metal Electron-Beam Evaporation System

Rapid Thermal Annealing System from 20 °C to 1000 °C in seconds
Nitride thin film characterization

- Hall measurement
  - Mobility
  - Sheet carrier density
- Capacitance-voltage measurements (CV)
  - Carrier conc. vs. distance
  - Trap densities
- Deep level transient spectroscopy (DLTS)
  - Deep trap levels
- Atomic force (AFM) and transmission electron microscopy (TEM)
  - Surface and interface studies
- Photoluminescence (PL)
  - Bandgap
  - Purity of material and uniformity
- X-ray diffraction (XRD)
  - Lattice constant and composition
  - Structure and defects
Homework Discussion