III- Nitride compounds
And other
Wide Band Gap Semiconductors

G. Feuillet - CEA/LETI Grenoble
Outline

GaN : a particular place in the WBG family

PART A –WBG semiconductors

their specificities and comparisons

Part B –the LED case study

pros and cons of GaN vs. other WBG semiconductors
Energy Gap and Bond Length

From: Sproull, R. L., and Phillips, W. A.,
Wide band gap materials and bond length
the common anion representation

Note: alloys can also be made with different anion e.g. ZnSSe or GaNAs
Wide band gap materials and bond length
III-V compounds

Energy gap in eV

Indirect gap
Direct gap

bond length in nm

Wide band gaps
Wide band gap materials and bond length
II- VI compounds

<table>
<thead>
<tr>
<th>Material</th>
<th>Energy gap in eV</th>
<th>Bond length in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>CdO</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>MgS</td>
<td>0.18</td>
<td>0.18</td>
</tr>
<tr>
<td>MgSe</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>MgTe</td>
<td>0.24</td>
<td>0.24</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>CdS</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.34</td>
<td>0.34</td>
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<tr>
<td>CdTe</td>
<td>0.36</td>
<td>0.36</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.38</td>
<td>0.38</td>
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<tr>
<td>ZnTe</td>
<td>0.40</td>
<td>0.40</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.44</td>
<td>0.44</td>
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<tr>
<td>ZnSe</td>
<td>0.46</td>
<td>0.46</td>
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<tr>
<td>ZnTe</td>
<td>0.48</td>
<td>0.48</td>
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<tr>
<td>ZnSe</td>
<td>0.50</td>
<td>0.50</td>
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<tr>
<td>ZnTe</td>
<td>0.52</td>
<td>0.52</td>
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<tr>
<td>ZnSe</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.56</td>
<td>0.56</td>
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<tr>
<td>ZnSe</td>
<td>0.58</td>
<td>0.58</td>
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<tr>
<td>ZnTe</td>
<td>0.60</td>
<td>0.60</td>
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<tr>
<td>ZnSe</td>
<td>0.62</td>
<td>0.62</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.64</td>
<td>0.64</td>
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<tr>
<td>ZnSe</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>ZnTe</td>
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<td>0.68</td>
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<td>ZnSe</td>
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<td>0.70</td>
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<tr>
<td>ZnTe</td>
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<td>0.72</td>
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<tr>
<td>ZnSe</td>
<td>0.74</td>
<td>0.74</td>
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<tr>
<td>ZnTe</td>
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<tr>
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<td>0.78</td>
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<td>ZnTe</td>
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<td>0.80</td>
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<td>ZnSe</td>
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<td>0.82</td>
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<tr>
<td>ZnTe</td>
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<td>0.84</td>
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<td>ZnSe</td>
<td>0.86</td>
<td>0.86</td>
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<tr>
<td>ZnTe</td>
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<td>0.88</td>
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<tr>
<td>ZnSe</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.94</td>
<td>0.94</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.96</td>
<td>0.96</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>ZnTe</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>
Other wide band gap semiconductors

Delafossite structure

p type SC for TCO – \( V_{Cu} \)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cu20</th>
<th>CuAlO2</th>
<th>CuGa2O2</th>
<th>SrCu2O2</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap in eV</td>
<td>2.2</td>
<td>3.5</td>
<td>3.6</td>
<td>3.3</td>
<td>4</td>
</tr>
</tbody>
</table>

Ahmed et Al. PRB 79,104302 (2009)

Cu and Ni oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Cu20</th>
<th>CuAlO2</th>
<th>CuGa2O2</th>
<th>SrCu2O2</th>
<th>NiO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap in eV</td>
<td>2.2</td>
<td>3.5</td>
<td>3.6</td>
<td>3.3</td>
<td>4</td>
</tr>
</tbody>
</table>

Beryllium compounds

<table>
<thead>
<tr>
<th>Be -VI</th>
<th>BeTe</th>
<th>BeSe</th>
<th>BeS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap in eV</td>
<td>2.7</td>
<td>4 / 4.5</td>
<td>&gt; 5.5</td>
</tr>
</tbody>
</table>


Alloying with insulators

An example: BeO: 10.7 eV (insulator), WZ, bond length = 0.163 nm

Solid ZnO – BeO solutions obtained for the whole compo range

Dong and Alpay, PHYSICAL REVIEW B 84, 035315 (2011)
Wide band gap materials and atomic bonding

- Bond energy scales inversely with bond length
- Bond Length scales inversely with energy gap
- (Ionicity /Covalence) ratio relationship with band gap ?

Note that strongly Ionic Compounds are also insulators LiF – 11eV; NaCl – 8.5eV; KBr – 7.5 eV

![Graph showing bond energy and bond length](image)

**Self consistent Band Structure calculations**
(Christiensen et Al. PRB 36, n°3, 1032, 1987)
Vs.
Philips ionicity

**Pauling ionicity as a function of Electronegativity difference**

\[
f_i = 1 - e^{-\frac{(\chi_A-\chi_B)^2}{4}}
\]

\[
f_i = \sin^2 \varphi
\]


**FIG. 6.** The ionicities $f_i^*$ as derived from our calculations plotted against $f_i$, Phillips ionicity values.
### III-V Wide band gap materials and atomic bonding

**For same cation, band gap increases with ionic character** (with electronegativity difference)

\[ \chi_N >> \chi_P > \chi_{As} > \chi_{Sb} \]

except InN

**Model dependent for same anion different cations**

Cf. for instance GaAs, AlAs and InAs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Pauling ionicity</th>
<th>( \phi ) model</th>
<th>Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>0.430</td>
<td>0.449</td>
<td>6.2 d</td>
</tr>
<tr>
<td>AlP</td>
<td>0.086</td>
<td>0.307</td>
<td>2.4 i</td>
</tr>
<tr>
<td>AlAs</td>
<td>0.061</td>
<td>0.274</td>
<td>2.17 i</td>
</tr>
<tr>
<td>GaN</td>
<td>0.387</td>
<td>0.500</td>
<td>3.4 d</td>
</tr>
<tr>
<td>GaP</td>
<td>0.061</td>
<td>0.327</td>
<td>2.3 i</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.039</td>
<td>0.310</td>
<td>1.4 d</td>
</tr>
<tr>
<td>InN</td>
<td>0.345</td>
<td>0.578</td>
<td>0.6 d</td>
</tr>
<tr>
<td>InP</td>
<td>0.039</td>
<td>0.421</td>
<td>1.35 d</td>
</tr>
<tr>
<td>InAs</td>
<td>0.022</td>
<td>0.357</td>
<td>0.35 d</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.668</td>
<td>&gt; 0.9</td>
<td>8.5</td>
</tr>
<tr>
<td>C (Diamond)</td>
<td>0</td>
<td>0</td>
<td>5.4</td>
</tr>
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</table>
### II-VI Wide band gap materials and atomic bonding

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionicity</th>
<th>Gap en eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>0.715 (P)</td>
<td>1.44</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.7 (P)</td>
<td>1.74</td>
</tr>
<tr>
<td>CdS</td>
<td>0.685(P)</td>
<td>2.4</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.62(P)</td>
<td>3.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.73 (P)</td>
<td>3.35</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.63 (P)</td>
<td>2.7</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.61 (P)</td>
<td>2.6</td>
</tr>
<tr>
<td>MgO</td>
<td>0.85 (ϕ)</td>
<td>5.7</td>
</tr>
<tr>
<td>MgS</td>
<td>0.81(ϕ)</td>
<td>4.78</td>
</tr>
<tr>
<td>MgSe</td>
<td>0.79(ϕ)</td>
<td>3.35</td>
</tr>
<tr>
<td>MgTe</td>
<td>0.73(ϕ)</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The good case
The most common crystalline structures of WBG materials

- **Zinc Blende (Sphalerite)**
- **Wurtzite**
- **Rock Salt (NaCl)**

Coordination number: 4 → 6
Wide band gap materials vs. bond length
Crystalline symmetry

Energy gap in eV

Bond length in nm

D: diamond cubic
ZB: Zinc Blende
WZ: Wurtzite
RS: Rock salt

Wide band gap materials vs. bond length
Crystalline symmetry
Crystalline symmetry in WBG materials
Some implications

- If two AC and BC binaries have similar crystal symmetry
  \( A_{1-x} B_x C \) alloys from the two binaries have same crystal symmetry
  Ex
  \begin{align*}
  &\text{GaN / AlN / InN} & \text{WZ} \\
  &\text{or InP / GaP / AIP} & \text{ZB}
  \end{align*}

- Binaries may be synthesized in their non equilibrium form
  through non equilibrium growth processes (e.g. epitaxy)
  and for thin enough films
  Ex
  \begin{align*}
  &\text{MgS on ZnSe (RS\(\rightarrow\) ZB)} & \text{Uesugi et Al APL68, 844 (1996)}
  \end{align*}

- If two AC and BC binaries have different crystal symmetry,
  the phase of one constituent may be preserved up to a certain \( C^\circ \),
  above the solubility limit of the other element
  by using out of equilibrium growth conditions

An example: $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ phase stability

**Diagram:**
- Energy gap in eV vs. bond length in nm
- Thermodynamical MgO/ZnO solubility limit
Doping of WBG materials

Some general background

Simple Hydrogenoid model
where
$Z = \text{charge state}$
$m^* = e^- \text{ or } h^\text{eff. mass}$
n the state $n^0$
band gap independent

$$E_c - E_{dn} = \frac{q^4 Z^2 m^*}{2n^2 (4\pi \varepsilon_0 h)^2}$$

Thermodynamic Model
for the ionised defect formation energy

Donor case
$$E_f (d, q) = E_t (d) - E_t (0) + \mu_{id} + q E_{\text{Fermi}}$$

Acceptor case
$$E_f (d, q) = E_t (a) - E_t (0) + \mu_{ia} - q E_{\text{Fermi}}$$

Cf. for instance: Yan et Wei phys. stat. sol. (b) 245, No. 4, 641–652 (2008)
Doping: the particular case of WBG semiconductors «doping asymmetry»

Formation energies of donors and acceptors as a function of CB and VB positions

compensation in WBG SEmiconductors

As VBM decreases, $E_f$ (donors) decreases and $E_f$ (acceptors) increases

As CBm increases, $E_f$ (donors) increases and $E_f$ (acceptors) decreases
The difficult materials to dope p type: ZnO, AlN, GaN.
N.B. MgO: low electron affinity of < 1eV, gap = 5.7eV ...but n type
The particular case of AlN and Ga$_{1-x}$Al$_x$N alloys
Both types limited

- **p-type Mg doping**

- **n-type Si doping**
The particular case of Hydrogen in Wide band gap materials

Hydrogen counteracts the prevailing conductivity

Hydrogen acts as a donor whatever Ef
Same for InN
Intrinsic point defects in WBG semiconductors

The case of ZnO

- Large variations of intrinsic defect formation energy as $E_f$ moves across gap
  Ex: $\text{Zn}_i$ (double donor) : $\Delta E_f = 2 E_g = 6.8 \text{ eV}$

- Playing with stoechiometry during growth to adjust intrinsic defect formation energies
  Ex.: $V_O$ (the « acceptor killer »)
  Or to facilitate the formation of defect complex
  Ex.: $(\text{As}_{\text{Zn}} - 2\text{V}_{\text{Zn}})$, low $E_f$ and low $E_i$
Doping of WBG materials

<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) Zn ~ 340 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>
</tr>
</tbody>
</table>

* Experimental values
Material availability: a strategic analysis from EU

Critical raw materials for the EU

Report of the Ad-hoc Working Group on defining critical raw materials

The Ad-hoc Working Group is a sub-group of the Raw Materials Supply Group (and is chaired by the European Commission)

The Group recommends that substitution should be encouraged, notably by promoting research on substitutes for critical raw materials in different applications and to increase opportunities under EU RTD Framework Programmes.

Supply risk

Economic importance

Ga, In, Zn
Material availability according to demand

Global demand of the emerging technologies analysed for raw materials in 2006 and 2030 related to today’s total world production of the specific raw material (Updated by BGR April 2010).

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Production 2006 (t)</th>
<th>Demand from emerging technologies 2006 (t)</th>
<th>Demand from emerging technologies 2030 (t)</th>
<th>Indicator 1 2006</th>
<th>Indicator 1 2030</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallium</td>
<td>152</td>
<td>28</td>
<td>603</td>
<td>0,18</td>
<td>3,97</td>
</tr>
<tr>
<td>Indium</td>
<td>581</td>
<td>234</td>
<td>1,911</td>
<td>0,40</td>
<td>3,29</td>
</tr>
<tr>
<td>Germanium</td>
<td>100</td>
<td>28</td>
<td>220</td>
<td>0,28</td>
<td>2,20</td>
</tr>
<tr>
<td>Neodymium (rare earth)</td>
<td>16.800</td>
<td>4,000</td>
<td>27,900</td>
<td>0,23</td>
<td>1,66</td>
</tr>
<tr>
<td>Platinum (PGM)</td>
<td>255</td>
<td>very small</td>
<td>345</td>
<td>0</td>
<td>1,35</td>
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<tr>
<td>Tantalum</td>
<td>1,384</td>
<td>551</td>
<td>1,410</td>
<td>0,40</td>
<td>1,02</td>
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<tr>
<td>Silver</td>
<td>19.051</td>
<td>5,342</td>
<td>15,823</td>
<td>0,28</td>
<td>0,83</td>
</tr>
<tr>
<td>Cobalt</td>
<td>62.279</td>
<td>12,820</td>
<td>26,860</td>
<td>0,21</td>
<td>0,43</td>
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<tr>
<td>Palladium (PGM)</td>
<td>267</td>
<td>23</td>
<td>77</td>
<td>0,09</td>
<td>0,29</td>
</tr>
<tr>
<td>Titanium</td>
<td>7,211.000²</td>
<td>15,397</td>
<td>58,148</td>
<td>0,08</td>
<td>0,29</td>
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<tr>
<td>Copper</td>
<td>15.093.000</td>
<td>1,410.000</td>
<td>3,696.070</td>
<td>0,09</td>
<td>0,24</td>
</tr>
</tbody>
</table>
PART A - An intermediate conclusion

Wide Band Gap Semiconductors

- III Nitrides: the highest gap family ➔ the smallest atomic bonds
  - II Oxides competing
    - Gap and ionic character
- Same cation family with different structures ➔ unstable alloys
  - Doping asymmetry
- III-nitrides: material availability?
Wide Band Gap materials
What for?

For electronics applications
@High power
@High frequency
@High temperature
In caustic environments

For opto-electronic applications
UV LEDs
Blue to red LEDs
White LEDs in SSL
Blue lasers
Solar blind detectors
Photodetectors
Photovoltaics....
Wide band gap semiconductors for electronics applications

<table>
<thead>
<tr>
<th>Semiconductor (Typical Materials)</th>
<th>Silicon</th>
<th>Gallium Arsenide</th>
<th>Indium Phosphide</th>
<th>Silicon Carbide</th>
<th>Gallium Nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic</td>
<td>Unit</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bandgap</td>
<td>eV</td>
<td>1.1</td>
<td>1.42</td>
<td>1.35</td>
<td>3.25</td>
</tr>
<tr>
<td>Electron Mobility at 300 °K</td>
<td>cm²/Vs</td>
<td>1,500</td>
<td>8,500</td>
<td>5,400</td>
<td>700</td>
</tr>
<tr>
<td>Saturated Electron Velocity</td>
<td>× 10⁷ cm/s</td>
<td>1</td>
<td>1.3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Critical Breakdown Field</td>
<td>MV/cm</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W/cm °K</td>
<td>1.5</td>
<td>0.5</td>
<td>0.7</td>
<td>4.5</td>
</tr>
<tr>
<td>Relative Dielectric Constant</td>
<td>ε&lt;sub&gt;r&lt;/sub&gt;</td>
<td>11.8</td>
<td>12.8</td>
<td>12.5</td>
<td>10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35</td>
</tr>
<tr>
<td>200-500</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>1.5</td>
</tr>
</tbody>
</table>
High frequency / high power electronics

Figure of Merit for high frequency/high power

\[ CFOM = \frac{\chi \varepsilon \mu v_s E_B^2}{\left(\chi \varepsilon \mu v_s E_B^2\right)_{\text{silicon}}} \]

\( \chi \) is thermal conductivity
\( E_B \) is breakdown field
\( \mu \) is low field mobility
\( v_s \) is saturation velocity
\( \varepsilon_0 \) is dielectric constant

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>GaAs</th>
<th>GaN</th>
<th>4H-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFM</td>
<td>1</td>
<td>11</td>
<td>790</td>
<td>410</td>
</tr>
<tr>
<td>KFM</td>
<td>1</td>
<td>0.45</td>
<td>1.8</td>
<td>5.1</td>
</tr>
<tr>
<td>BFM</td>
<td>1</td>
<td>28</td>
<td>910</td>
<td>290</td>
</tr>
<tr>
<td>BHFM</td>
<td>1</td>
<td>16</td>
<td>100</td>
<td>34</td>
</tr>
</tbody>
</table>

Cf. C.Brylinsky course
WBG Semiconductors for LED structures

Choosing criteria
- Gap
- Alloying possibilities for gap adjustment in HS
  - Excitons
    - QW excitons and the polarization issue
      - Misfit strain / relaxation processes
        - Substrates
          - Designing an efficient LED
Light Emitting Diode
the most simple case: p / n homojonctions

(a) Homojunction under zero bias
(b) Homojunction under forward bias

Emitted $h\nu = E_g = \text{semiconductor gap energy}$
Light Emitting Diode
Confining carriers to improve radiative recombination

Heterostructures

Quantum wells

Multiple quantum wells

For confinement of h and e
⇒ Improved radiative efficiency
\[ hν \sim Eg : \lambda \text{ control} \]

For stronger localisation of h and e at the same place
⇒ Improved radiative efficiency
\[ hν \sim Eg + Ece + Ech \]
\( \lambda \text{ control} \)

For confining more h and e
⇒ Higher brightness

www.Light Emitting Diodes.org

+ Electron (hole) blocking layer to reduce diffusion of the carriers out of the confinement region
Gap issues
Selection of Wide Band Gap
According to desired wavelength range

Direct gap

Indirect gap

Wide Band Gap (eV)

Relative Eye Sensitivity

Diamond
AIP
SiC
GaP
Si
Ge

AI
GaN
InN
ZnO
ZnSe
Direct band gap: a necessity for efficient light emission and absorption

Using phonons ($T^\circ$) Low radiative efficiency ...

GaN

$\beta$-SiC
Emitting light in indirect semiconductors...?

Using small objects
To enhance e-h wavefunction overlap
Low radiative efficiency...

Cf. for instance, «Light Emission in Si nanostructures»

Defect engineering
Using the strain field around dislocations to prevent NR recombination at surfaces and point defects....
Low efficiency...
Lourenço et Al. APL 87, 201105 (2005)
But indirect WBG diodes have been demonstrated… the case of SiC

6H-Silicon Carbide Light Emitting Diodes and UV Photodiodes

Fig. 1. SEM micrograph of a typical Cree 6H-SiC blue LED

phys. stat. sol. (a) 162, 481 (1997)
Subject classification: 73.40.Lq; 78.66.Li; S6

6H-Silicon Carbide Light Emitting Diodes and UV Photodiodes

J. Edmond, H. Kong, A. Suworov, D. Waltz, and C. Carter, Jr

Cree Research, Inc., 2810 Meridian Pkwy., Durham, NC 27713, USA

Blue emission from radiative phonon assisted recombination between N donors and Al acceptors

Fig. 2. Typical a) emission spectra and b) current-dependent output of 6H-SiC blue LEDs
Associating direct and indirect WBG SC: the case of phosphides for yellow and red LEDs
AlP, GaP indirect and InP direct

AllInGaP LEDs
Designing Quantum Well Heterostructures for light emitters choosing the right combination of materials

- 1- for type I WBG Quantum Well Heterostructures (maximize radiative efficiency)
- 2 - for maximum band offsets (minimize thermal escape)
Part B - WBG Semiconductors for LED structures

Alloys
Choosing the right ternary or quaternary alloys for the right wavelength

![Graph showing the energy gap in eV versus bond length in nm for various materials.](image)
Band gap of WBG « cation » alloys
validity of Vegard law / Bowing

Linear Vegard law
\[ E_g (A_{1-x} B_x C) = 1-x E_g (AB) + x E_g (BC) \]

Non linear law
\[ E_g (A_{1-x} B_x C) = (1-x) E_g (AB) + x E_g (BC) - b x (1-x) \]
with \( b \) : bowing parameter

Alloys : not simply mixing two crystals

Charge exchange (ion/cov)
Structural relaxation (minimum E)
Alloy disorder
→ Not simply linear variation for \( E_g \)

Cf. for instance Bernard and Zunger
PRB n° 34, n°8, 1986, 5992

Eg determined from Absorption
Wu et Al. Solid State Com 127 , 2003, 411
« Universal Band Gap in group III nitrides »

Gorczyca et Al. , APL 98 241905 (2011)
Band gap bowing in quaternary nitride semiconducting alloys
### Bowing parameters

<table>
<thead>
<tr>
<th>Ternary alloy</th>
<th>GaInN</th>
<th>GaAlN</th>
<th>AlInN</th>
<th>ZnMgO (RS)</th>
<th>ZnCdO (ZB)</th>
<th>ZnSSe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bowing parameter ( b ) en eV</td>
<td>1,4</td>
<td>0,7</td>
<td>3,7</td>
<td>5 ( ( x=0,5 ))</td>
<td>1,21 (0 to 25%)</td>
<td>(-4.43x + 1,13)</td>
</tr>
</tbody>
</table>

- Zhang et Al. JAP 103,063721 (2008)

> Strong implication for choosing the right alloy composition Corresponding to the desired emission wavelength
Part B - WBG Semiconductors for LED structures

EXCITONS
**Direct gap semiconductors**

**Excitons binding energies in bulk semiconductors**

<table>
<thead>
<tr>
<th>Compound</th>
<th>GaAs</th>
<th>CdTe</th>
<th>ZnSe</th>
<th>ZnO</th>
<th>GaN</th>
<th>ZnS</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap 300K</td>
<td>1.42</td>
<td>1.44</td>
<td>2.7</td>
<td>3.3</td>
<td>3.4</td>
<td>3.7</td>
<td>6.2</td>
</tr>
<tr>
<td>exciton binding energy in meV</td>
<td>4.2</td>
<td>10</td>
<td>20</td>
<td>60</td>
<td>25</td>
<td>35</td>
<td>48 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80 (2)</td>
</tr>
</tbody>
</table>

Towards a stabilization of excitons above RT°

300K: kT = 25 meV

Monotonous variation $E_x$ with $E_g$ except for ZnO…

From Bastar, Esaki, PRB 26,4, 1974,1982

1- Leute et Al APL 95 ,031903, 2009
2- Li et Al. APL 83, 25, 2003
Excitons and photons
radiative lifetime and oscillator strength

\[ \tau = \text{radiative lifetime}, \quad f = \text{oscillator strength of the optical transition} \]

\[
\tau_{\text{rad}} = \frac{2\pi \varepsilon_0 m_0 c^3}{ne^2 \alpha^2 f}
\]

Deduced from Time Resolved Photoluminescence

ZnO \( \tau = 322 \text{ ps} \), Reynolds et Al., JAP 88, 4, 2152, 2000: bulk Hydrothermal

GaN \( \tau = 220 \text{ ps} \), Reynolds et Al., JAP 88, 3, 1460 2000: thick HVPE samples

ZnSe ?

Bunea et Al, APL 1999
70 \( \mu \text{m} \) thick HVPE samples
Excitons in quantum wells
The case of cubic ZB WBG

QW = Confinement region
⇒ Stronger wave-function overlap between electrons and holes
   Stronger radiative emission
⇒ Increase of the coulomb interaction between e-h (X-binding energy)

G.V. Astakhov PRB 65 165335 2002
The case of hexagonal WZ and of <111> oriented ZB semiconductors
The internal polarization issue

A - Spontaneous polarization

For ZnO: Dal Corso et Al, PRB, 50, 15, 10715, 1994

Fig. 6 Theoretical predictions of the spontaneous polarization in wurtzite compound semiconductors (private communication N. Ashcroft et al.).
The case of hexagonal WZ and <111> oriented ZB semiconductors
The internal polarization issue

**B- Piezoelectric polarization**

\[ \delta P_3 = e_{33}\varepsilon_3 + e_{31}(\varepsilon_1 + \varepsilon_2), \]

With \( \varepsilon_i = \) elastic deformation components in the strained QW
\( e_{ij} = \) piezo tensor

TABLE II. Calculated spontaneous polarization (in units of C/m²), Born effective charges (in units of e), and piezoelectric constants (in units of C/m²) for III-V wurtzite nitrides and II-VI wurtzite oxides.

<table>
<thead>
<tr>
<th></th>
<th>( P_{eq} )</th>
<th>( Z^* )</th>
<th>( du/d\varepsilon_3 )</th>
<th>( e_{33} )</th>
<th>( e_{31} )</th>
<th>( e_{33}^{(0)} )</th>
<th>( e_{31}^{(0)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>-0.081</td>
<td>-2.70</td>
<td>-0.18</td>
<td>1.46</td>
<td>-0.60</td>
<td>-0.47</td>
<td>0.36</td>
</tr>
<tr>
<td>GaN</td>
<td>-0.029</td>
<td>-2.72</td>
<td>-0.16</td>
<td>0.73</td>
<td>-0.49</td>
<td>-0.84</td>
<td>0.45</td>
</tr>
<tr>
<td>InN</td>
<td>-0.032</td>
<td>-3.02</td>
<td>-0.20</td>
<td>0.97</td>
<td>-0.57</td>
<td>-0.88</td>
<td>0.45</td>
</tr>
<tr>
<td>ZnO</td>
<td>-0.057</td>
<td>-2.11</td>
<td>-0.21</td>
<td>0.89</td>
<td>-0.51</td>
<td>-0.66</td>
<td>0.38</td>
</tr>
<tr>
<td>BeO</td>
<td>-0.045</td>
<td>-1.85</td>
<td>-0.06</td>
<td>0.02</td>
<td>-0.02</td>
<td>-0.60</td>
<td>0.35</td>
</tr>
</tbody>
</table>

WZ materials

ZB materials

TABLE III. Piezoelectric constants (in units of C/m²) of several zincblende compounds, calculated via linear response theory in Refs. 17 (III-V), 18 (CdTe) and 19 (other II-VI).

<table>
<thead>
<tr>
<th></th>
<th>( e_{33} )</th>
<th>( e_{31} )</th>
<th>( e_{33} )</th>
<th>( e_{31} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe</td>
<td>0.03</td>
<td>-0.01</td>
<td>AlAs</td>
<td>-0.01</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.10</td>
<td>-0.05</td>
<td>GaAs</td>
<td>-0.12</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.04</td>
<td>-0.02</td>
<td>InAs</td>
<td>-0.03</td>
</tr>
<tr>
<td>AlP</td>
<td>0.04</td>
<td>-0.02</td>
<td>AlSb</td>
<td>-0.04</td>
</tr>
<tr>
<td>GaP</td>
<td>-0.07</td>
<td>0.03</td>
<td>GaSb</td>
<td>-0.12</td>
</tr>
<tr>
<td>InP</td>
<td>0.04</td>
<td>-0.02</td>
<td>InSb</td>
<td>-0.06</td>
</tr>
</tbody>
</table>

Taken from Bernardini et Al, 1997
A tracer Peq + Ppiezo (epsilon)
Excitons in quantum wells
The case of hexagonal WZ and 111 ZB WBG

GaN / Ga$_{0.85}$Al$_{0.15}$N QW $\Delta a/a = 0.5\%$

Calculated Exciton binding energies in « squared » and « inclined » GaN / AlGaN wells With 2 Al C°

Bulutay et Al. IEEE J. of Quantum electronics, 35,n°4,1999
Excitons in quantum wells
The case of hexagonal WZ and 111 ZB WBG

Decrease of the exciton binding energies in polar ZnO / ZnMgO QWs
Because of internal electric field (measured: 0.9 MV/cm)

C. Morhain, PRB 72, 241305 (R) 2005
Measured field = 0.9 MV/cm
Internal polarization effects: not always detrimental…

The HEMT configuration

Internal polarization $\rightarrow$ 2 DEG at the GaN/AlGaN interface
No barrier doping - « Undoped electronics »

Fig. 1. The conduction-band and their related subbands as calculated at room temperature for an AlGaN/GaN HEMT. The inset shows the conductive channel located at the lower AlGaN/GaN heterointerface.

Saidi et Al; Solid State Electronics 61, 20011, 1-6
Part B - WBG Semiconductors for LED structures

Misfit Relaxation issues
Lattice misfit between barriers and QW
Designing Quantum Well Heterostructures
minimum lattice misfit between barriers and QW

If low enough misfit
between barrier and QW materials
Or thin enough QW

Biaxially Elastically Strained QW
With no interfacial defects

Above a certain « critical » thickness
Plastic Strain relaxation ➔ dislocation formation

- Dark lines due to dislocation lines
- Radiative efficiency low at dislocation lines
Critical Thickness: GaN / InGaN heterostructures
InN / GaN $\Delta a/a = 10\%$

Higher critical thicknesses than predicted
- Slip systems with high activation energies in c-oriented hexagonal?
- Work hardening because of pre-existing dislocations?
mechanical strength of different WBG materials

Yonenaga et Al. J. Appl. Phys. 103, 093502 (2008)

The lower the Yield stress, the easier dislocation formation
⇒ Lower critical thicknesses

The lower $E_a$ the easier dislocation glide
⇒ easier annihilation and fewer threadings
⇒ Easier bending at inclined surfaces / regrowth
For a true comparison of the plastic properties
Slip systems

Slip systems in Hexagonal WZ

For c-oriented growth
only
high energy
Pyramidal slip systems
 can be activated

FIG. 4. Slip systems in a hexagonal lattice. Slip planes and directions are as indicated.

Slip systems in FCC / ZB

12 independant
slip systems
Easily activated whatever
the growth orientation

GANEX Summer School 2013      G. Feuillet
mechanical strength of different WBG materials

Cubic vs. Hexagonal

Yonenaga et Al. J. Appl. Phys. 103, 093502 (2008)
Misfit relaxation at GaInN / GaN interfaces
Evidence for « work hardening » effects

C –oriented growth
Pre-existing threading dislocations prevent misfit dislocations to be formed
If no threading dislocations: secondary slip systems on pyramidal planes activated
Srinivasan et Al.; APL 83, 25, 2003

C –oriented growth
Pre-existing threading dislocations: V pits strain relaxation process at GaInN interface
Cheong et Al. J. of Lum. 99(2002) 265
Are interface dislocations detrimental??

Dislocations at GaInN / GaN interfaces: radiative centers at low energy
Less radiative at GaInN QW energy

Huang et Al. APL 98, 261914 (2011)
Are interface dislocations detrimental??

High dislocation density

- decreased strain in the QW
- less piezo field …

Rebane et Al. Applied Surface Sc. 166 (2000) 300
Part B - WBG Semiconductors for LED structures

Substrate Issues
Hetero-substrates for WBG epitaxy
One selection criterion: bond length for reduced mismatch
Designing Efficient Quantum Well Heterostructures
Minimum strain / dislocations in the active region
⇒ The « hetero » substrate limits?

Active layer
Buffer
substrate

$\Delta a/a = 0$
Homoepitaxial growth

$\Delta a/a \neq 0$
Heteroepitaxial growth

Density of dislocations according to misfit :
1 misfit dislocation every $a / (\Delta a/a)$

If all misfit dislocations emerge
⇒ max threading dislocation density $= 1/a^2 \times (\Delta a/a)^2$

With $\Delta a/a = 10^{-3}$ ⇒ $C^\circ \max = 10^9$/cm$^2$...
With $\Delta a/a = 10^{-2}$ ⇒ $C^\circ \max = 10^{11}$/cm$^2$...
With $\Delta a/a = 10^{-1}$ ⇒ $C^\circ \max = 10^{13}$/cm$^2$...

Progressive but very slow dislocation annihilation
GaN on Si
The « other » problem with heteroepitaxial growth of WZ materials

tilt and twist $\Rightarrow$ threading dislocations

Dislocations density: independent upon misfit but rather on nucleation

Screw threading disloc
$\Rightarrow$ tilt accommodation

Edge threading disloc
$\Rightarrow$ Twist accommodation

Lower misfit substrate are not enough

to reduce dislocations density…
The « other » problem with heteroepitaxial growth of WZ materials
tilt and twist \( \rightarrow \) threading dislocations
Dislocations density: independent upon misfit but rather on nucleation

\[ \text{FIG. 3. Two-beam bright-field cross-sectional electron micrographs of the ZnO/\( \alpha \)-plane sapphire near the [2\( \overline{1} \)1\( \overline{0} \)]\( \text{ZnO} \) zone axis with} \ g = 0006 \ (a) \text{ and} \ 1010 \ (b).} \]

GaN on c- Al2O3

GaN on SiC

ZnO on a plane sapphire
Lim et Al. JVST 19, 2601 (2001)
Are threading dislocations a limit for nitride LEDs?

\[ \tau^{-1} = B \cdot \rho_{\text{dis}}^{-1} \cdot j_{\text{cond}}^{-1} \cdot e^{\Delta E / kT} \]

\[ \eta_{\text{rat}} = \frac{1}{1 + \pi^2 \rho_{\text{dis}}^2 \rho_{\text{dis}}^{-1}}. \]

Tsao et al.
IEEE Circuit and Design 20, n°3, 28, 2001

For GaInN QW, alloy instabilities, composition fluctuations ➔ Dislocations are « transparent »
(not the case for binary QW!)
But composition fluctuation still a debate …
# The other option: « homo » substrates

<table>
<thead>
<tr>
<th>GaN</th>
<th>HVPE - FS</th>
<th>Ammonothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disloc density /cm²</td>
<td>$10^6$ [1]</td>
<td>$10^3$ [2]</td>
</tr>
<tr>
<td>Demonstrated size</td>
<td>6&quot; [1]</td>
<td>1.5&quot; [2]</td>
</tr>
<tr>
<td>Available size</td>
<td>(?)</td>
<td>(?)</td>
</tr>
<tr>
<td>Demonstrated Thickness</td>
<td>5-10 mm</td>
<td>&lt;1 mm?</td>
</tr>
<tr>
<td>Available thickness</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>High Price /cm²</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Low price /cm²</td>
<td>?</td>
<td>?</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ZnO</th>
<th>Hydrothermal</th>
<th>Melt</th>
<th>CVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disloc density /cm²</td>
<td>$10^3 - 10^4$ [3]</td>
<td>$10^4 - 10^5$</td>
<td>$10^4 - 10^5$ [2]</td>
</tr>
<tr>
<td>Available size</td>
<td>$\frac{1}{4}$&quot;</td>
<td>1&quot; ?</td>
<td>?</td>
</tr>
<tr>
<td>Demonstrated Thickness</td>
<td>40-50 mm</td>
<td>50 mm</td>
<td>15 mm</td>
</tr>
<tr>
<td>Available thickness</td>
<td>10 mm</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>High Price /cm²</td>
<td>200 €</td>
<td>?</td>
<td>60 € (estimate)</td>
</tr>
<tr>
<td>Low price /cm²</td>
<td>50 €</td>
<td>500-600 € [8]?</td>
<td>30 € (estimate)</td>
</tr>
</tbody>
</table>
The other option: « homo » substrates

GaN ELOG, Epitaxial Lateral Overgrowth

**Figure 4.** TEM vertical cross-section micrograph of GaN ELO sample.

**Figure 3.** Cross-sectional TEM picture displaying the bending of the threading dislocations over the window area.

**FIG. 2.** Cross-sectional TEM picture displaying the bending of the threading dislocations over the window area.

**Sublimation GaN**

**SiO₂**

**MOCVD GaN**

**Sapphire Substrate**

ELOG + HVPE

« free-standing » GaN

**Low Dislocation Density GaN ELO**

**High Dislocation Density GaN Buffer Layer**

**GaN ELO**

**Insulator Stripe**

**1 mm**

**1 µm**

**Thickness of GaN (µm)**

**Dislocation Density (cm²)**
The other option: “homo” substrates

the case of ZnO

Tokyo Denpa Japon
Hydrothermal growth

3 inches
The other option: "homo" substrates: ZnSe

2004 - Growth of large ZnSe single crystal by R-CVT method
Shinsuke Fujiwara, Yasuo Namikawa, Takao Nakamura and Masami Tatsumi
Sumitomo Electric Industries, Semiconductor R&D Laboratories, 1-1-1, Koyakita, Itami, Hyogo, 664-0016 Japan

EPD : 5×103 to 3×104
Other methods
-Seeded PVT
-Sublimation …

But GaAS: a serious contender
GaAs match to ZnSSe
Part B - WBG Semiconductors for LED structures

Designing efficient LED
Efficiency « droop » and peak wavelength shift at high current density

- Auger effects
- Dislocations
- Internal Polarisation or carrier overflow
A - Efficiency droop and Auger effects

Carrier Recombination rate $\sim An + Bn^2 + Cn^3$

- Non radiative
- Deep levels
- Extended defects

Radiative

Auger

Two solutions:

1 - use materials with Smaller Auger Coefficient

2 – increase active zone width to decrease carrier density
A - Efficiency droop and Auger effects

1 – Use materials with Smaller Auger Coefficient


\[ \Delta (BC \Gamma) \]

\[ E_g \]

\[ \begin{array}{c|ccc|ccc|ccc|ccc} 
 & \text{AlN} & \text{GaN} & \text{InN} & \text{AlN} & \text{GaN} & \text{InN} & \text{AlN} & \text{GaN} & \text{InN} \\
\hline
E_g & 6.47 & 3.24 & 0.69 & 6.53 & 3.07 & 0.53 &  \text{ZnO} \\
\Delta & 2.65 & 2.50 & 3.12 & 8.62 & 9.07 & 10.12 & \text{ZnO} \\
\end{array} \]

TABLE I. Band gap \( E_g \), gap between the first and the second conduction band at \( \Gamma(\Delta) \) and crystal-field splitting \( \Delta_c \) calculated with the OEPx(cLDA)\(+G_0W_0\) approach for AlN, GaN, and InN.

A - Efficiency droop and Auger effects

2 - Increasing active region width to decrease carrier density

Applicable as long as critical thickness is not exceeded ➔ GREEN led??
A - Efficiency droop and Auger effects

2 - Increasing active region width to decrease carrier density

X-ray diffraction rocking curves

Reciprocal space maps

Strained Heteroepitaxial ZnMgO/ ZnO growth up to large thicknesses

\[ \Delta a/a [0-15\%]: 5 \times 10^{-4} \]
B - Efficiency droop and dislocations

Schubert et Al. APL 91, 231114 (2007)
MOVPE on different GaN / Al203 templates

Beneficial effects of dislocation reductions
- on the optical power
But not on the efficiency droop …
B - Efficiency droop and dislocations

Reduction in efficiency droop in InGaN/GaN MQWs light-emitting diodes grown on free standing GaN substrate

<table>
<thead>
<tr>
<th>Material</th>
<th>HVPE - FS</th>
<th>Ammonothermal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disloc density /cm²</td>
<td></td>
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</tbody>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>$10^3 - 10^4$ [3]</td>
<td>$10^4 - 10^5$</td>
<td>$10^4 - 10^5$ [2]</td>
</tr>
<tr>
<td>Disloc density /cm²</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
C - Efficiency droop and polarisation

1st solution - Use non polar heterostructures

On non polar and semi-polar HVPE GaN substrates from Mitsubishi
C - Efficiency droop and polarisation

1st solution - Use non polar heterostructures

With present day ZnO CVT boules:
Available sizes for m oriented wafers: 50 x 15 mm² and up…

GaN non polar LEDs structures on ZnO substrates

Whole ZnO non polar LEDs structures on ZnO substrates
C - Efficiency droop and polarisation
Demonstrated benefit of oxide non polar homoepitaxy

A result from CRHEA: MBE homoepitaxy of non polar ZnO/ZnMgO quantum well (collab. LETI)

Strong benefits of homoepitaxy on the properties of nonpolar ZnMgO/ZnO quantum wells on a-plane ZnO substrates

\[ \frac{I_{\text{int}}(12K)}{I_{\text{int}}(300K)} = \sim 65\% \]

TEM defects in heteroepitaxial Non polar

Morhain et Al
Phys. Rev. B 72
241305 R (2005)
C - Efficiency droop and polarisation

Kim et Al. Appl.Phys.Let. 91 183507, 2007C

WPE
18.5 % $\rightarrow$ 24.9%

$\lambda = 440$ nm
$T = 300K$
Area = 1 mm$^2$

Oxides?
- Strain always compressive in ternary layers
- No need of quaternaries for lattice match
Part B  WBG semiconductors for LEDs

Conclusion

- WBG : Gap adapted to visible – UV emission
- WBG alloys : band gap bowing
  - WBG : strong exciton binding energy, high oscillator strength
- WBG heterostructures : internal polarization limits on X binding energies
  - WBG heterostructures : Misfit strain / relaxation processes
- Substrates for WBG : homo rather than hetero (misfit and nucleation)
- Designing an efficient WBG LED : droop always a problem / solutions
In conclusion

- III-N: the most prominent Wide Band Gap materials

Now just behind Si in terms of revenues (in terms of publications?)

Opto applications on the market, but still challenges for huge penetration (SSL)

- Incremental fabrication steps ➔ steady improvements

- Material Research for WBG should focus on:
  - doping
  - bulk or quasi bulk crystals
  - alternative materials
  - alternative solutions: nanowires, disordered materials
Thank you for your attention
This report reflects citations to source items indexed within All Databases.

GaN + LED

ZnO + LED

ZnSe + LED

Taken from ISI WOS

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GaN + Power

SiC + power

1990  2000  2010
GaN + excitons

ZnO + Excitons