Valence Band Anticrossing in III-Bi-V Alloys

LBNL and UC Berkeley

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Students, UC Berkeley
Collaborations

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- **C. Skierbiszewski**, Unipres (InGaAs(N))
- **A. Ramdas**, Purdue University (ZnTe(Se), ZnTe(S)...) 
- **I. K. Sou**, UST, Hong Kong (ZnSe(Se), ZnS(Se)) 
- **I. Suemune**, Hokkaido University (InGaAs(N)) 
- **T. Kuech**, University of Wisconsin (GaN(As)) 
- **Y. Nabetani**, University of Yamanashi (ZnSe(O), ZnTe(O)) 
- **J. A Gupta**, NRC, Canada (GaAs(Sb)) 
- **S. Watkins**, Simon Frasier (GaAs(Sb)) 
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- **J. Blacksberg**, JPL (Ge(Sn)) 
- **T. Foxon, S. Novikov**, University of Nottingham (GaN(As)) 
- **J. Furdyna**, University of Notre Dame (GaAs(Mn))
Outline

- Highly Mismatched Semiconductor Alloys
- Conduction and Valence Band Anticrossing
- Key examples of highly mismatched alloys (HMAs)
  - $\text{GaN}_x\text{As}_{1-x}$
  - $\text{ZnO}_x\text{Se}_{1-x}$
- Group III-Bi-V highly mismatched alloys
- Electronic Band Structure Engineering of HMAs
- Potential applications of HMAs (including bismides)
- Conclusions and outlook
Normal alloying: well matched alloys

Relatively easy to grow in the whole composition range

Small deviations from linear interpolation between end point compounds
## Anion Site Alloys

Electronegativities, X and atomic radii, R

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- A large variety of potential alloys.
- Well matched alloys: replacing atoms with similar properties.
- What happens when As is replaced with very much different N or Se with O?
III-Vs and II-VIs HMAs

Drastic deviation from linear interpolation between end point compounds

Band Anticrossing in HMA: Dilute nitride alloys: GaAs$_{1-x}$N$_x$

- Interaction of localized N levels with extended states of the conduction band.
- Homogenous broadening within coherent potential approximation

\[ E_{\pm}(k) = \frac{1}{2} \left\{ [E^C(k) + E^L] \pm \sqrt{[E^C(k) - E^L]^2 + 4C_{NM}^2} \right\} \]

W. Shan et al., Phys. Rev. Lett. 82, 1221-1224 (1999);
Highly mismatched Alloys

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- A large variety of potential highly mismatched alloys.
  - III-N_x-V_{1-x}
  - II-O_x-VI_{1-x}
- **Compared to normal alloys, they are difficult to synthesize**
- **Require non-equilibrium synthesis**
Synthesis of HMAs by ion implantation and pulsed laser melting (II-PLM)

- N ions
- GaAs ion induced damage
- GaAs ion induced damage
- Homogenized excimer laser pulse ($\lambda=248$ nm, 30 ns FWHM, $\sim0.2-0.8$ J/cm$^2$)
- GaNAs
- GaAs
- RTA
- GaNAs
- GaAs

- Liquid phase epitaxy at submicrosecond time scales
- Supersaturation of implanted species
- Suppression of secondary phases
Alloys with local level below the direct CBE

Oxygen level in ZnTe and MnTe is \(~0.2\) eV below the conduction band (CB) edge. Can it be used to form a separate band?
An isolated intermediate band is formed in Zn$_{1-y}$Mn$_y$O$_x$Te$_{1-x}$ by PLM.
Highly Mismatched Alloy
Valence Band Anticrossing (VBAC)

Electronegativities, $X$ and atomic radii, $R$

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- Highly electronegative anions are partially replaced with more metallic isovalent atoms e.g. N-rich $\text{GaN}_{1-x}\text{As}_x$.
- *The metallic atoms form localized states close to the valence band that interact with the valence band*
Band anticrossing in the whole composition range: GaNAs
HMAs over a wide composition range

GaN$_{1-x}$As$_x$ alloys over the entire composition range were grown by a highly non-equilibrium synthesis method: low temperatures plasma-assisted MBE

- Alloys are amorphous for 0.15<x<0.8
- Sharp optical absorption gives well-defined bandgaps
- Bandgap and band edge tunable in a broad range

Red curve: BAC prediction
\( \text{ZnO}_{1-x}\text{Se}_x \)

Group II-VI compound analog of \( \text{GaN}_y\text{As}_{1-y} \)

\[ E_{\text{Se}} = E_{\text{VBM}} + 0.9 \text{ eV}, \quad C = 1.2 \text{ eV} \]
ZnO$_x$Se$_{1-x}$: Electronic Structure

Blue curve: weighted interpolation of CBAC (Se-rich) and VBAC O-rich
Optical Properties of GaBi\textsubscript{x}As\textsubscript{1-x}

Band gap and spin orbit splitting energies

Large bandgap reduction with increase in impurity concentration

Giant spin orbit bowing*

Not readily explained by the virtual crystal approximation (VCA)

Apply a valence band anticrossing (VBAC) model to understand the origin of the bowing in bandgap and spin orbit splitting energies in GaBi\textsubscript{x}As\textsubscript{1-x}

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Bismuth Level in III-V Compounds

$E_{Bi}(GaP) = E_{VBM} + 0.2\ eV$

$E_{Bi}(GaAs) = E_{VBM} - 0.35\ eV$
Impurities of low ionization energy

Defect states located near the valence band

Anticrossing interaction between host and impurity $p$-like states

Bi introduces 6 $p$-like localized states
### Valence Band Anticrossing Hamiltonian

12x12 matrix, Six valence bands and six p-symmetry impurity states

\[
H_V = \begin{pmatrix}
H & \alpha & \beta & 0 & \frac{i\alpha}{\sqrt{2}} & -i\sqrt{2}\beta & V(x) & 0 & 0 & 0 & 0 & 0 \\
\alpha^* & L & 0 & \beta & \frac{iD}{\sqrt{2}} & i\sqrt{2}\alpha & 0 & V(x) & 0 & 0 & 0 & 0 \\
\beta^* & 0 & L & -\alpha & -i\sqrt{2}\alpha^* & \frac{iD}{\sqrt{2}} & 0 & 0 & V(x) & 0 & 0 & 0 \\
0 & \beta^* & -\alpha^* & H & -i\sqrt{2}\beta^* & \frac{-i\alpha^*}{\sqrt{2}} & 0 & 0 & 0 & V(x) & 0 & 0 \\
\frac{-i\alpha^*}{\sqrt{2}} & \frac{-iD}{\sqrt{2}} & i\sqrt{2}\alpha & \frac{i\alpha}{\sqrt{2}} & S & 0 & 0 & 0 & 0 & 0 & V(x) & 0 \\
\frac{i\sqrt{2}\beta^*}{\sqrt{2}} & \frac{i\sqrt{2}\alpha^*}{\sqrt{2}} & \frac{-iD}{\sqrt{2}} & \frac{i\alpha}{\sqrt{2}} & 0 & S & 0 & 0 & 0 & 0 & V(x) & 0 \\
V(x) & 0 & 0 & 0 & 0 & 0 & E_{imp} & 0 & 0 & 0 & 0 & 0 \\
0 & V(x) & 0 & 0 & 0 & 0 & E_{imp} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_{imp} & 0 & 0 & 0 & 0 \\
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0 & 0 & 0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_{imp} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_{imp} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & V(x) & 0 & 0 & 0 & 0 & E_{imp-so} \\
\end{pmatrix}
\]

\[
\alpha = \sqrt{3}\frac{\hbar^2}{m_0}[k_z(k_x - ik_y)\gamma_3], \quad \beta = \frac{\sqrt{3}}{2}\frac{\hbar^2}{m_0}[(k_x^2 - k_y^2)\gamma_2 - 2ik_xk_y\gamma_3], \quad V = C_A\sqrt{x}
\]
Valence Band Anticrossing Model

Interaction described by a 12 x 12 Hamiltonian

Includes
6 $p$-like states of host
6 $p$-like states of the impurity

Parameters
Location of defect states $E_{Bi}$ and $E_{Bi-SO}$
Coupling parameter $C_p$ (adjustable)

Restructured valence band
HH-like ($E_+$ and $E_-$)
LH-like ($E_+$ and $E_-$)
SO-like ($E_+$ and $E_-$)
Photomodulated Reflectance of GaBi$_x$As$_{1-x}$

$E_{CB} - HH/LH E_+$
Moves downward quickly with $x$

$E_{CB} - SO E_+$
Moves downward slowing with $x$

**Optical Transitions**

$HH/LH E_+$
$SO E_+$
GaAs $E_g$
GaAs $E_g + \Delta_0$

**PR Spectra of GaBi$_x$As$_{1-x}$**

$x = 0.08$
$x = 0.07$
$x = 0.06$
$x = 0.04$
$x = 0$

Energy (eV)
Restructuring of the Valence Band in GaBi$_x$As$_{1-x}$

Bandgap bowing in GaBi$_x$As$_{1-x}$ is due to the upward movement of the valence band edge
Bandgap Energy
Decreases by \(~90\) meV per \(x = 0.01\)

Spin-Orbit Splitting Energy
Increases by \(~50\) meV per \(x = 0.01\)
Bismuth in III-Nitrides: GaN$_{1-x}$Bi$_x$

\[ E_{\text{Bi}}(\text{GaP}) = E_{\text{VBM}} + 0.2 \text{ eV} \]
\[ E_{\text{Bi}}(\text{GaAs}) = E_{\text{VBM}} - 0.35 \text{ eV} \]
\[ E_{\text{Bi}}(\text{GaN}) = E_{\text{VBM}} + 1.7 \text{ eV} \]
Band Structure Engineering of HMAs

- Localized level above CBE and interaction with CB
  - GaAs(N), ZnSe(O), CdTe(O)
- Localized level below CBE and interaction with CB
  - GaAsP(N), ZnTe(O)
- Localized level above VBE and interaction with VB
  - GaN(As), GaN(Bi), ZnO(Se), ZnSe(Se), ZnS(Se), GaAs(Mn)
- Localized level below VBE and interaction with VB
  - GaAs(Bi), GaAs(Sb), Ge(Sn)
Highly Mismatched Alloys for Intermediate Band Cells

The intermediate band serves as a “stepping stone” to transfer electrons from the valence to conduction band.

Photons from broad energy range are absorbed and participate in generation of current.

Major technological advantage: requires single p/n junction only
Intermediate band cell
Intermediate band cell

Sun
Intermediate band cell
Intermediate band cell
Intermediate band cell

Two small energy photons produce single electron-hole pair contributing to large $V_{oc}$
Photoelectrochemical Cells (PECs)

Material requirements
- Band gap must be at least 1.8-2.0 eV but small enough to absorb most sunlight
- Band edges must straddle Redox potentials
- Fast charge transfer
- Stable in aqueous solution

\[ 2hv + H_2O \rightarrow H_2(g) + \frac{1}{2} O_2 (g) \]
Group III-Nitride PECs (GaN$_{1-x}$Sb$_x$)

Bi level too high but Sb level lies low enough below oxygen redox potential H$_2$O/O
Ferromagnetic coupling in Ga$_{1-y}$Mn$_y$N$_{1-x}$Bi$_x$?

Energy level of the Mn impurity is expected to lie close to the Bi level.

Strong coupling between Mn holes and the Bi derived valence band.
Conclusions and Outlook

Conclusions

- A large number of HMAs synthesized and studied.
- Electronic band structure described by the band anticrossing model.
- HMAs allow for an independent control of the location of CBE and VBE.
- Band anticrossing for electrically active impurities (III-Mn-Vs).

Outlook

- Potential applications for solar power conversion devices.
- HMAs for controlled ferromagnetic coupling.
- GaInNAs based photoelectrochemical cells.
- Energy selective contacts for hot electron solar cells.

Key role of highly mismatched III-Bi-V alloys