Semiconductor Materials for Intermediate Band Solar Cells

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Outline

- New materials for multijunction solar cells: $\text{Ga}_x\text{In}_{1-x}\text{N}$
- Intermediate (impurity) band solar cell materials
  - Intermediate band solar cell concept
  - Highly mismatched alloys (HMAs)
  - Non-equilibrium synthesis of HMAs
  - II-O$_x$-VI$_{1-x}$ HMAs as intermediate band materials
- Challenges and prospects
Solar Cells
Ultimate Efficiency Limits

- Intrinsic efficiency limit for a solar cell using a single semiconducting material is 31%.
  - Light with energy below the bandgap of the semiconductor will not be absorbed
  - The excess photon energy above the bandgap is lost in the form of heat.
  - Single crystal GaAs cell: 25.1% AM1.5, 1x

- Multijunction (MJ) tandem cell
  - Maximum thermodynamically achievable efficiencies are increased to 50%, 56%, and 72% for stacks of 2, 3, and 36 junctions with appropriately optimized energy gaps
Multijunction Solar Cells

State-of-the-art 3-junction GaInP/Ga(In)As/Ge solar cell: 36% efficient

M. Yamaguchi et al. – Space Power Workshop 2003
Direct bandgap tuning range of In$_{1-x}$Ga$_x$N
Potential material for MJ cells

- The direct energy gap of In$_{1-x}$Ga$_x$N covers most of the solar spectrum
- Multijunction solar cell based on this single ternary could be very efficient

LBNL/Cornell work: J. Wu et al. APL 80, 3967 (2002)
InGaN is radiation hard electron, proton, and alpha irradiation.
$\text{In}_{1-x}\text{Ga}_x\text{N}$ alloys as solar materials

- Significant progress in achieving p-type doping
- Exceptional radiation hardness established

- *Surface electron accumulation in In-rich alloys*
Intermediate band solar cells

Increasing the Efficiency of Ideal Solar Cells by Photon Induced Transitions at Intermediate Levels

Antonio Luque and Antonio Martí
Instituto de Energía Solar, Universidad Politécnica de Madrid, 28040 Madrid, Spain
(Received 7 February 1997)

Recent attempts have been made to increase the efficiency of solar cells by introducing an impurity level in the semiconductor band gap. We present an analysis of such a structure under ideal conditions. We prove that its efficiency can exceed not only the Shockley and Queisser efficiency for ideal solar cells but also that for ideal two-terminal tandem cells which use two semiconductors, as well as that predicted for ideal cells with quantum efficiency above one but less than two. [S0031-9007(97)03454-6]

Several other groups analyzed different aspects of the multiband solar cell concept

M. A. Green, Prog. Photov. :Res. Appl., 9, 137, (2001)
Multijunction vs. Multiband

**Multi-junction**
- Single gap (two bands) each junction
- N junctions $\Rightarrow$ N absorptions
- Efficiency~30-40%

**Multi-band**
- Single junction (no lattice-mismatch)
- N bands $\Rightarrow$ N·(N-1)/2 gaps
- $\Rightarrow$ N·(N-1)/2 absorptions
- Add one band $\Rightarrow$ add N absorptions
Intermediate Band Solar Cell


CB – conduction band
VB – valence band
IB – intermediate band

$E_{FC}, E_{FV}, E_{FI}$

quasi-Fermi levels for the electrons in respective bands
Intermediate Band Solar Cells can be very efficient

- Max. efficiency for a 3-band cell = 63%
- Max. efficiency for a 4-band cell = 72%
- In theory, better performance than any other ideal structure of similar complexity

But NO multi-band materials realized to date

Luque et. al. PRL, 78, 5014 (1997)
But how to make the intermediate band(s)?

- Impurity bands
- Porous materials
- Superlattices
- Quantum dots

No successful demonstrations
Well-Matched semiconductor alloys
III-V, and II-VI semiconductors

Electronegativity
\( X_{\text{As}} = 2.18 \); \( X_{\text{P}} = 2.19 \)

Atomic radius
\( R_{\text{As}} = 0.13 \text{nm}; \) \( R_{\text{P}} = 0.12 \text{nm} \)

Relatively easy to synthesize in the whole composition range

Electronegativity
\( X_{\text{Se}} = 2.55 \); \( X_{\text{S}} = 2.58 \)

Atomic radius
\( R_{\text{Se}} = 0.12 \text{nm}; \) \( R_{\text{S}} = 0.11 \text{nm} \)
Highly Mismatched Alloys: III-N-Vs

Electronegativity

- $X_N = 3.0$
- $X_P = 2.2$
- $X_{As} = 2.2$
- $X_{Sb} = 2.05$

Atomic radius

- $R_N = 0.075 \text{ nm}$
- $R_P = 0.123 \text{ nm}$
- $R_{As} = 0.133 \text{ nm}$
- $R_{Sb} = 0.153 \text{ nm}$

Nitrogen in III-V compounds introduces a localized N level close to the conduction band edge.
Unique HMA effect
Band Anticrossing

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

Fundamental band gap is reduced and a new optical transition is formed…
Bandgap tuning with HMAs
\( \text{GaAs}_{1-x}N_x \)

- N localized level situated above GaAs conduction band edge
  - Anticrossing pushes CB edge down
- Effect is large
  - 4% N reduces gap by 0.4 eV

\[
E_{\pm}(k) = \frac{1}{2} \left\{ E^C(k) + E^L \right\} \pm \sqrt{\left[ E^C(k) - E^L \right]^2 + 4C_{NM}^2 \cdot x}
\]
How to synthesize an HMA?
Implantation + pulsed laser melting

- Ion implantation of diluting species
- Pulsed-laser melting (PLM): liquid phase epitaxy at submicrosecond time scales

Outcome

- Growth of epitaxial, single crystal
- Supersaturation of implanted species
- Suppression of secondary phases

Example: N ion implanted GaAs

Ion induced damage

Homogenized excimer laser pulse ($\lambda=308$ nm, $30$ ns FWHM, $\sim0.2$-$0.8$ J/cm$^2$)

TRR data reveals liquid phase

melt duration typ. 200 - 500 ns

Finished Sample
PLM epilayer quality
III-N-Vs

- **RTA** only: a highly defective layer with numerous dislocations loops; a high density of nanometer-sized bubbles
- **PLM**: the subsurface layer is free from structural defects; a sharp melt/substrate interface at ~0.2 mm below the surface
How to optimize an intermediate band material?
II-O-VI HMAs

- Oxygen in II-VI compounds has the requisite electronegativity and atomic radius difference
  - $X_O = 3.44; \quad R_O = 0.073 \text{ nm}$
  - $X_S = 2.58; \quad R_S = 0.11 \text{ nm}$
  - $X_{Se} = 2.55; \quad R_{Se} = 0.12 \text{ nm}$
  - $X_{Te} = 2.1; \quad R_{Te} = 0.14$

- Oxygen level in ZnTe is 0.24 eV below the CB edge
  - *Can this be used to form an intermediate band?*

- Synthesis
  - Very low solid solubility limits of O in II-VI compounds
  - Nonequilibrium synthesis required
As-grown and as-implanted samples show diffraction peaks of the ZnTe only.

O implanted ZnTe/GaAs followed by PLM shows a layer of ZnOTe with lattice parameter 0.60 nm.
Is there an intermediate band?

Zn$_{1-y}$Mn$_y$O$_x$Te$_{1-x}$

Predicted PV operation
$\text{Zn}_{1-y}\text{Mn}_y\text{O}_x\text{Te}_{1-x}$
Photovoltaic action

300 K
MS252A
Zn$_{0.88}$Mn$_{0.12}$Te
O + Cl implanted
0.1 J cm$^{-2}$ laser annealed
How efficient can they be?
Multi-band ZnMnO\textsubscript{1-x}Te alloys

- The location and the width of the intermediate band in ZnMnO\textsubscript{x}Te\textsubscript{1-x} is determined by the O content, x
- Can be used to maximize the solar cell efficiency
- Calculations based on the detailed balance model predict maximum efficiency of more than 55% in alloys with 2% of O
Intermediate band semiconductors
Challenges an prospects

- Synthesis of suitable materials with scalable epitaxial techniques (*MBE growth of ZnO$_x$Se$_{1-x}$ achieved*)
- N-type doping of intermediate band with group VII donors (Cl, Br)
- Control of surface properties of the PLM synthesized materials
- Other highly mismatched alloys: GaP$_y$N$_x$As$_{1-x-y}$
- Fundamentals
  - Nature of the intermediate band: localized vs. extended
  - Carrier relaxation processes
Collaborators

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