Semiconductor Materials for Intermediate Band Solar Cells

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GCEP Solar Energy Workshop
Stanford, CA

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Outline

- New materials for multijunction solar cells: $Ga_xIn_{1-x}N$
- 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

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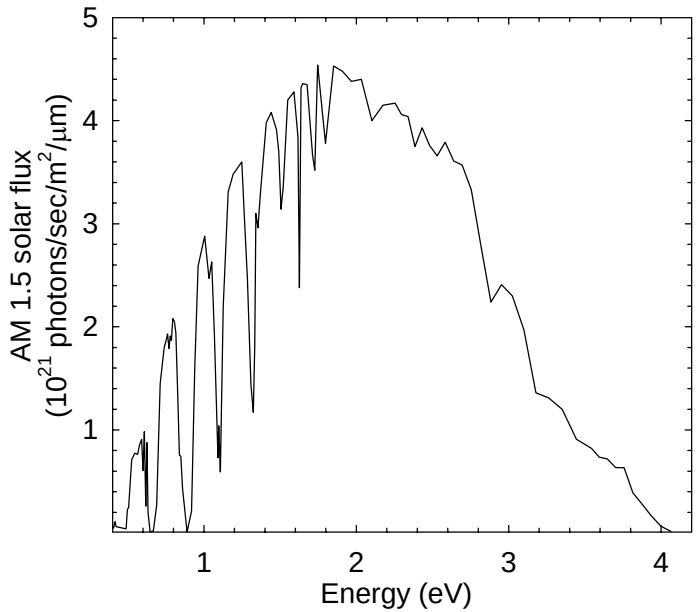
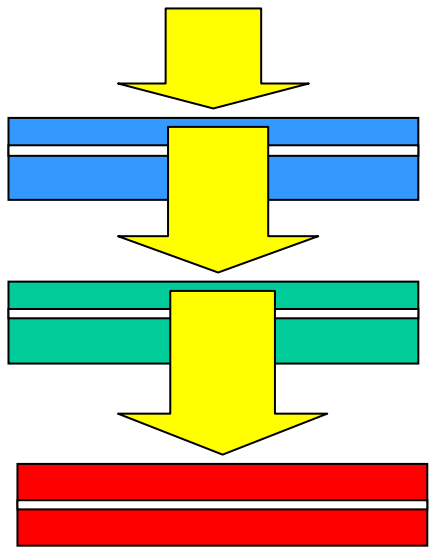
- **Intrinsic efficiency limit for a solar cell using a single semiconducting material is 31%.**
  - **Light with energy below the bandgap of the semiconductor will not be absorbed**
  - **The excess photon energy above the bandgap is lost in the form of heat.**
  - **Single crystal GaAs cell: 25.1%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





$E_{g1} > E_{g2} > E_{g3}$

Cell 1 (E_{g1})

Cell 2 (E_{g2})

Cell 3 (E_{g3})

Multijunction Solar Cells

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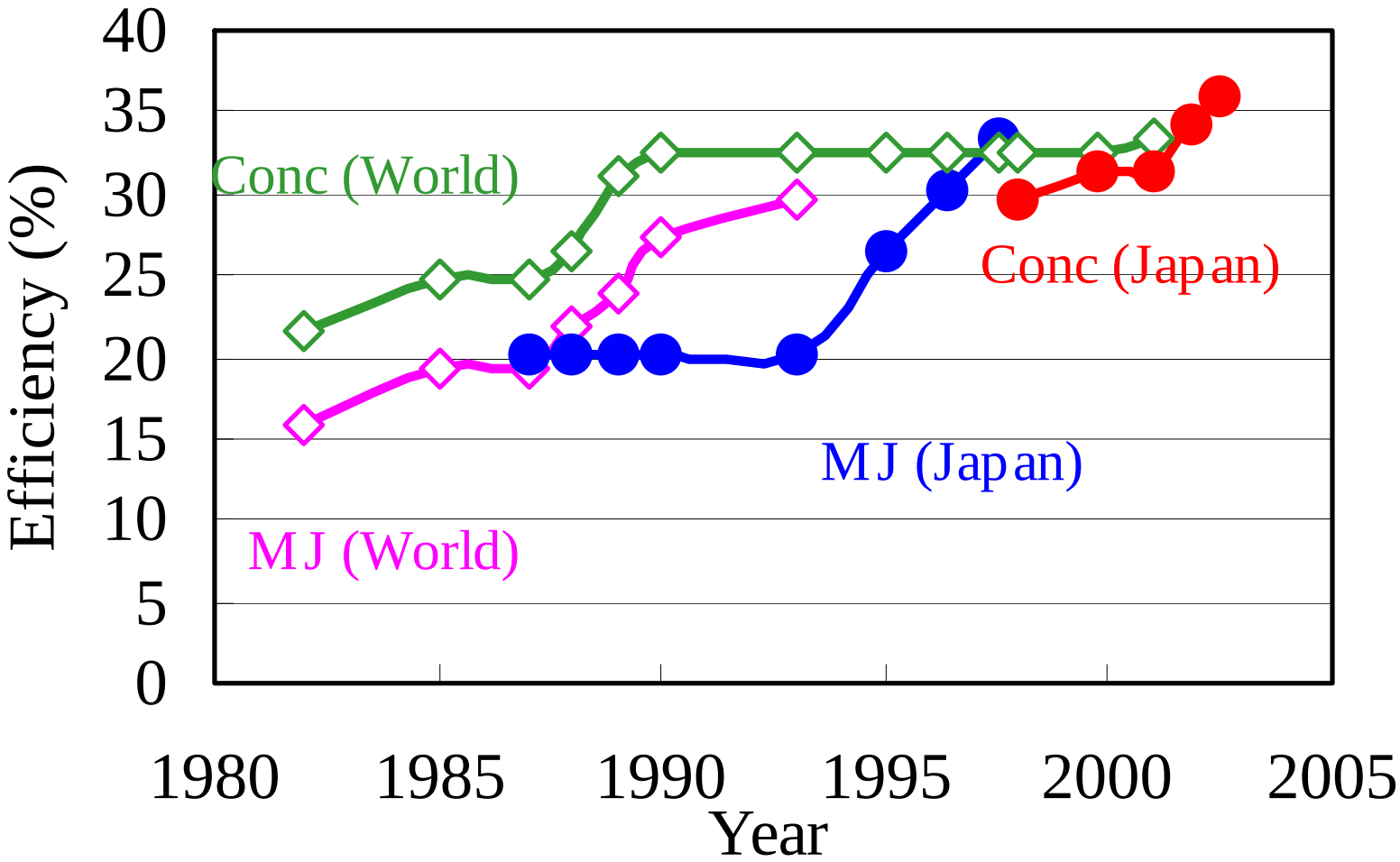
State-of-the art 3-junction GaInP/Ga(In)As/Ge solar cell: 36 % efficient



M. Yamaguchi *et. al.* – Space Power Workshop 2003

Direct bandgap tuning range of $In_{1-x}Ga_xN$
Potential material for MJ cells

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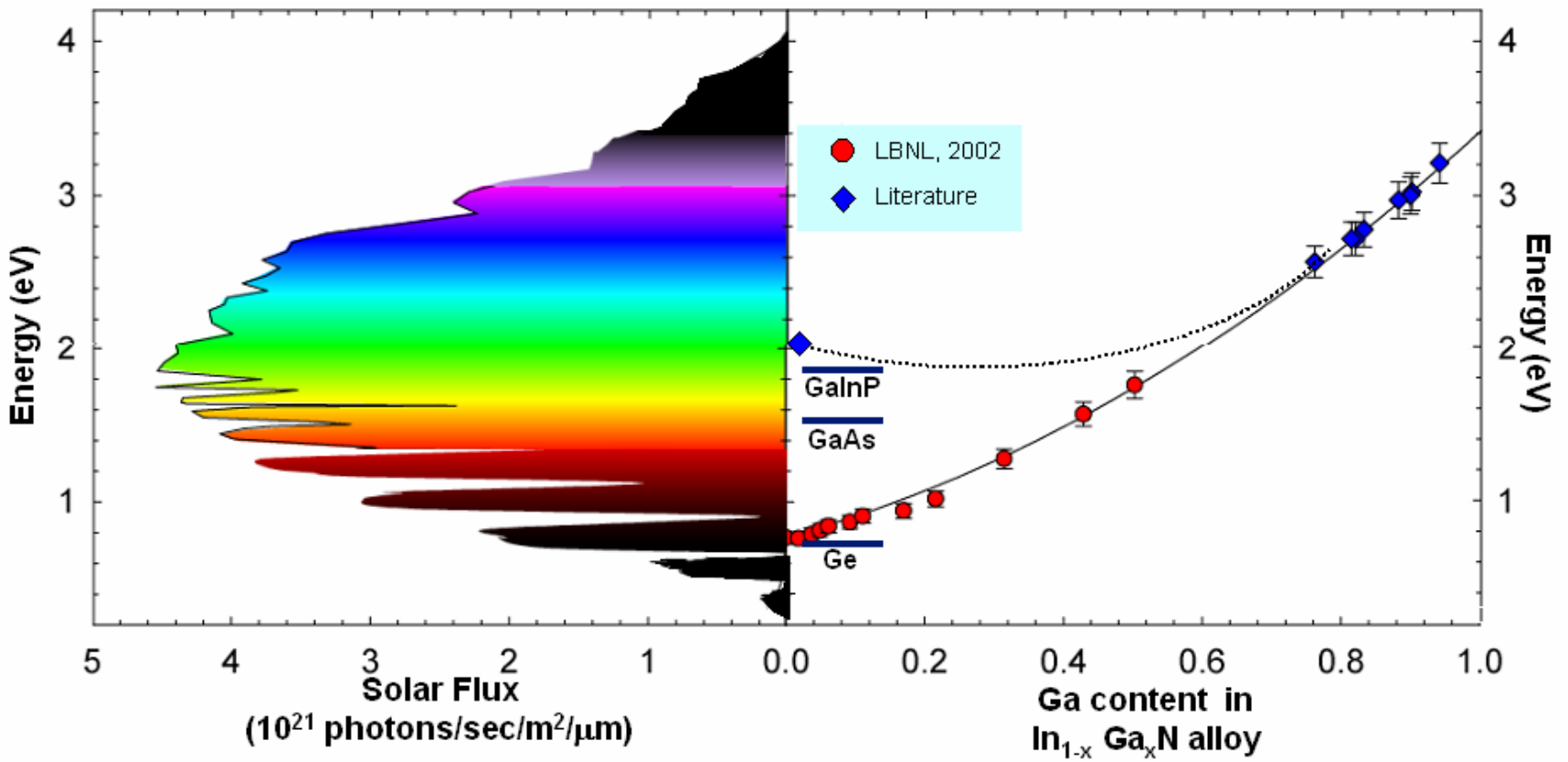

- The direct energy gap of $In_{1-x}Ga_xN$ covers most of the solar spectrum
- Multijunction solar cell based on this single ternary could be very efficient

LBNL/Cornell work: J. Wu *et al.* APL **80**, 3967 (2002)

InGaN is radiation hard

electron, proton, and alpha irradiation

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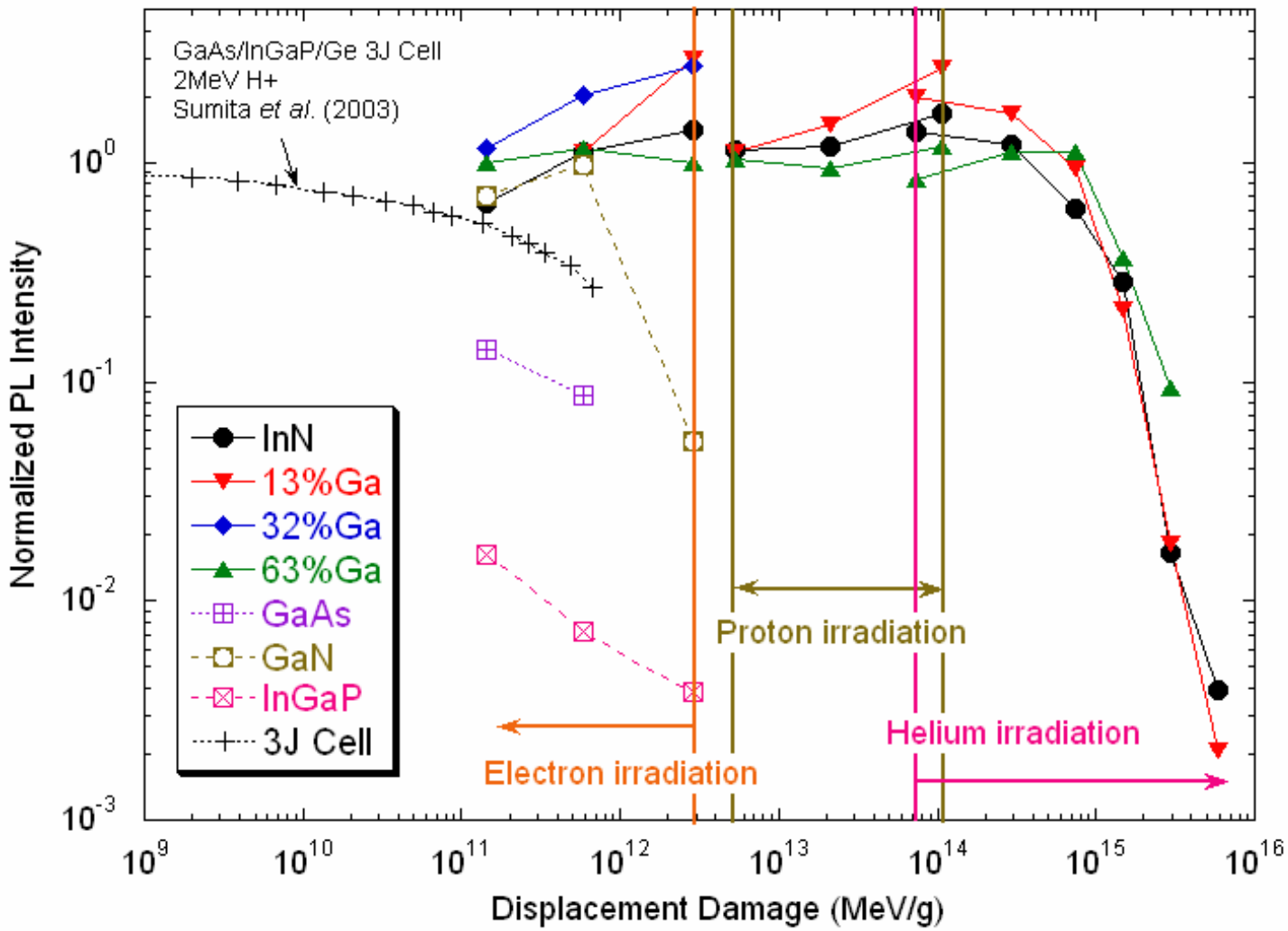

$In_{1-x}Ga_xN$ alloys as solar materials

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

- ***Surface electron accumulation in In-rich alloys***

Intermediate band solar cells

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VOLUME 78, NUMBER 26 PHYSICAL REVIEW LETTERS 30 JUNE 1997

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

P. Wurfel Sol. Energy Mater. Sol. Cells ***29****, 403 (1993),*

M. A. Green, Prog. Photov. :Res. Appl., ***9****, 137, (2001)*

Multijunction vs. Multiband

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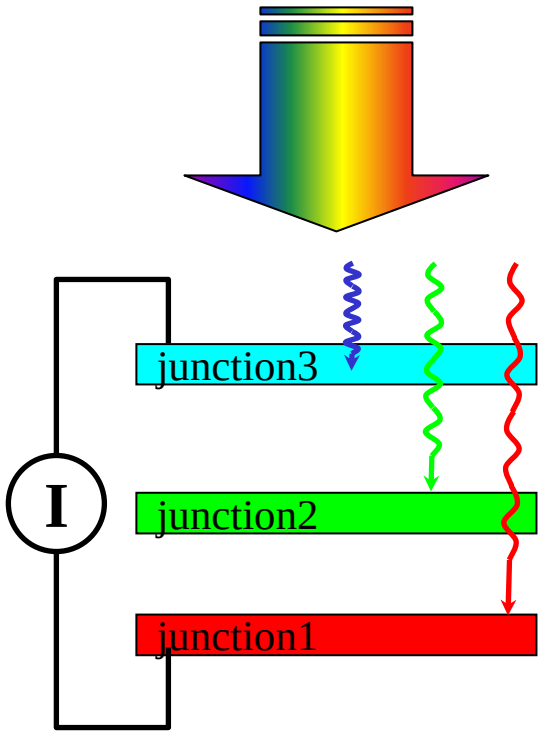

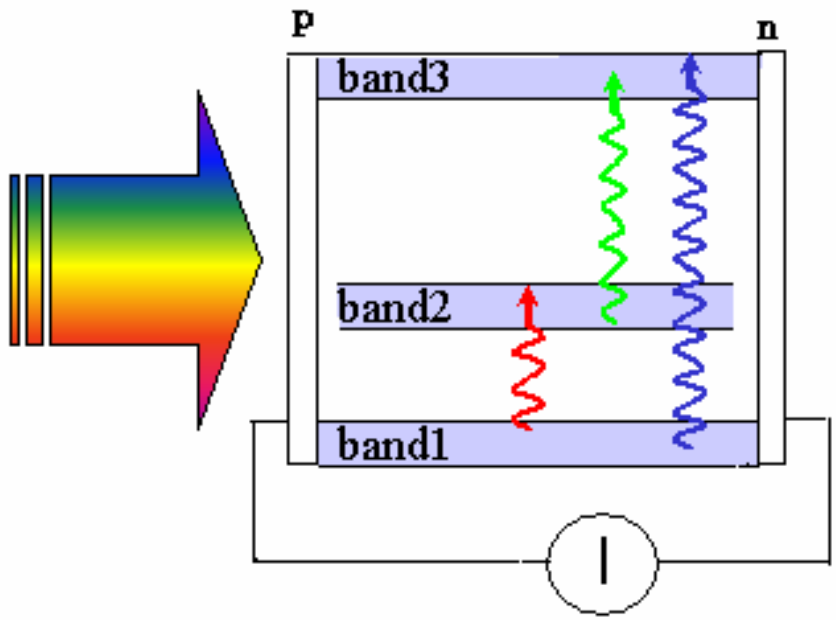

Multi-junction

- Single gap (two bands) each junction
- N junctions ⇒ N absorptions
- Efficiency~30-40%

Multi-band

- Single junction (no lattice-mismatch)
- N bands ⇒ N·(N-1)/2 gaps
  ⇒ N·(N-1)/2 absorptions
- Add one band ⇒ add N absorptions

Intermediate Band Solar Cell

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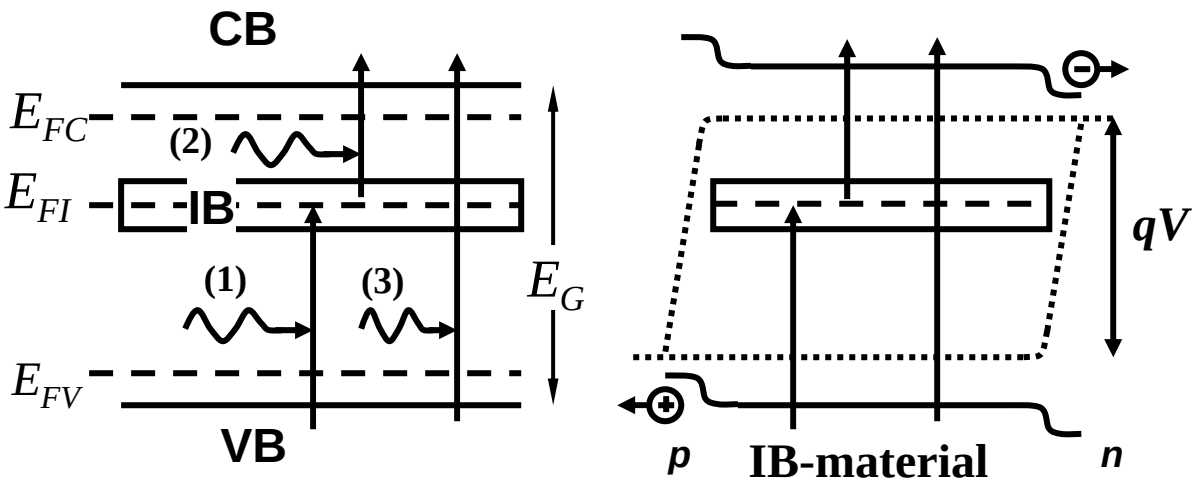
L. Cuadra, et. al., Thin Solid Films, 451-452, 593 (2004)



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

E_{FC}, E_{FV}, E_{FI}
quasi-Fermi levels for the electrons in respective bands

Theoretical efficiency of Intermediate band solar cells

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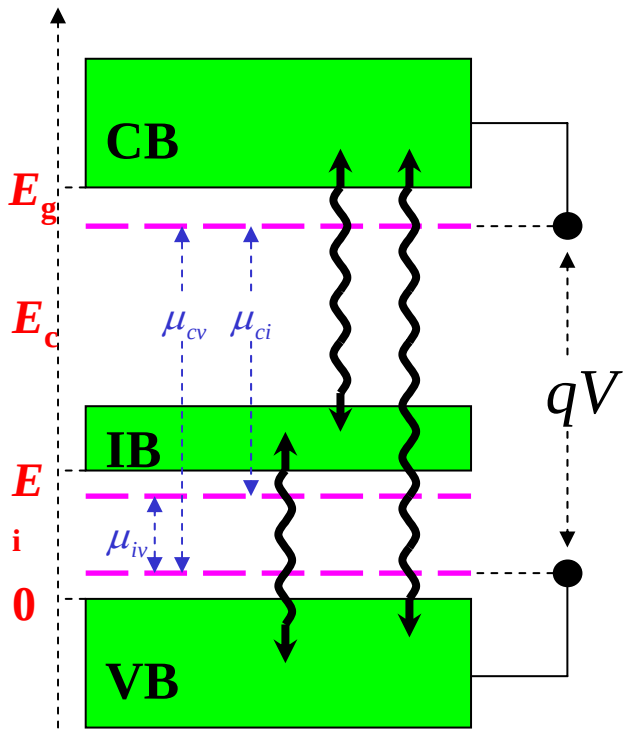

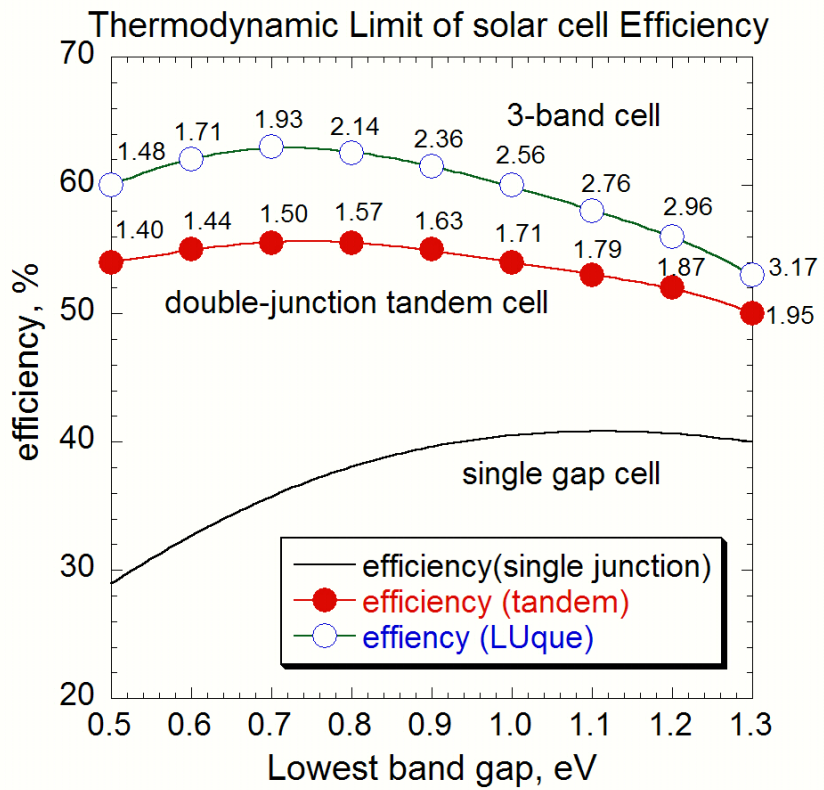

- **Intermediate Band Solar Cells can be very efficient**
  - **Max. efficiency for a 3-band cell=63%**
  - **Max. efficiency for a 4-band cell=72%**
  - **In theory, better performance than any other ideal structure of similar complexity**

But NO multi-band materials realized to date

*Luque et. al. PRL, **78**, 5014 (1997)*

But how to make the intermediate band(s)?

ELSEVIER

Thin Solid Films 451–452 (2004) 593–599

Present status of intermediate band solar cell research

L. Cuadra*, A. Martí, A. Luque

Instituto de Energía Solar – Universidad Politécnica de Madrid, ETSI Telecomunicación, Ciudad Universitaria sn, 28040 Madrid, Spain

- **Impurity bands**
- **Porous materials**
- **Superlattices**
- **Quantum dots**

No successful demonstrations

Well-Matched semiconductor alloys
III-V, and II-VI semiconductors

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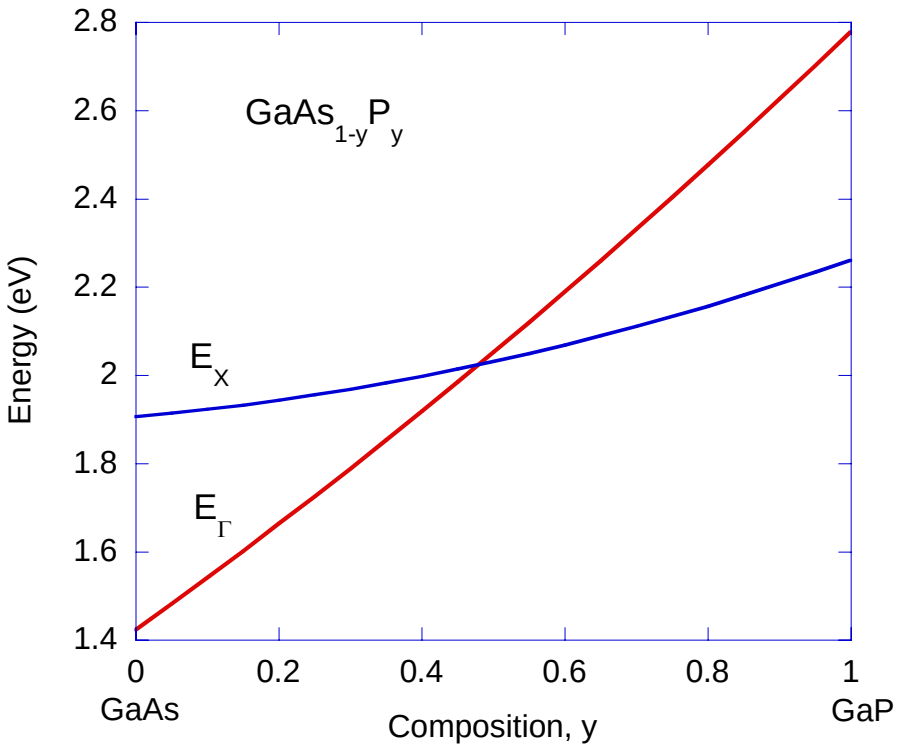

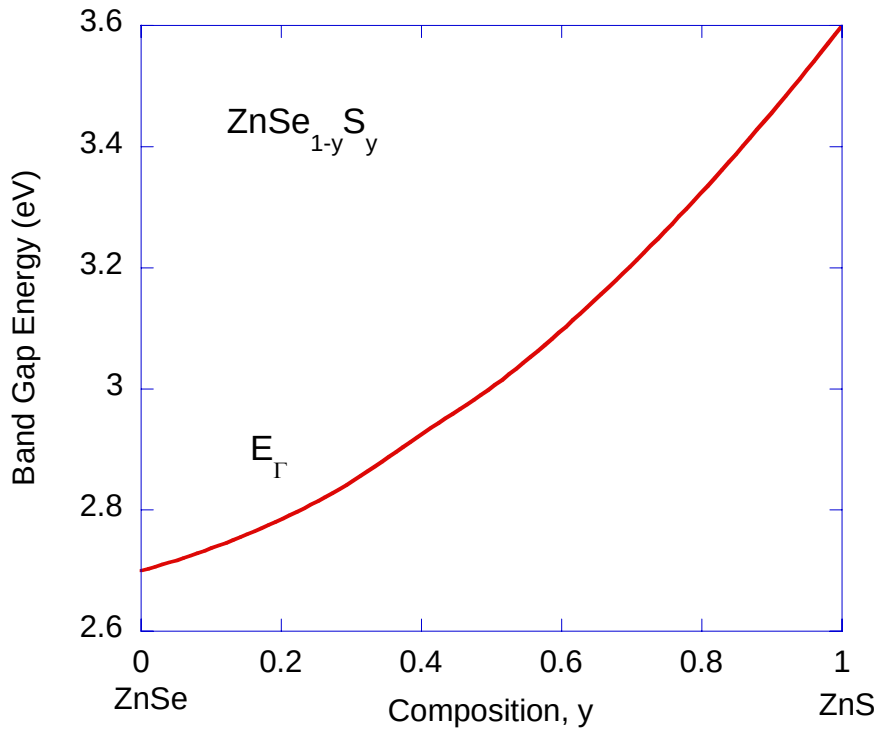

Electronegativity

X_{As}=2.18; X_P=2.19

Atomic radius

R_{As}=0.13nm; R_P=0.12nm

Electronegativity

X_{Se}=2.55; X_S=2.58

Atomic radius

R_{Se}=0.12.; R_S=0.11

Relatively easy to synthesize in the whole composition range

Highly Mismatched Alloys: III-N-Vs

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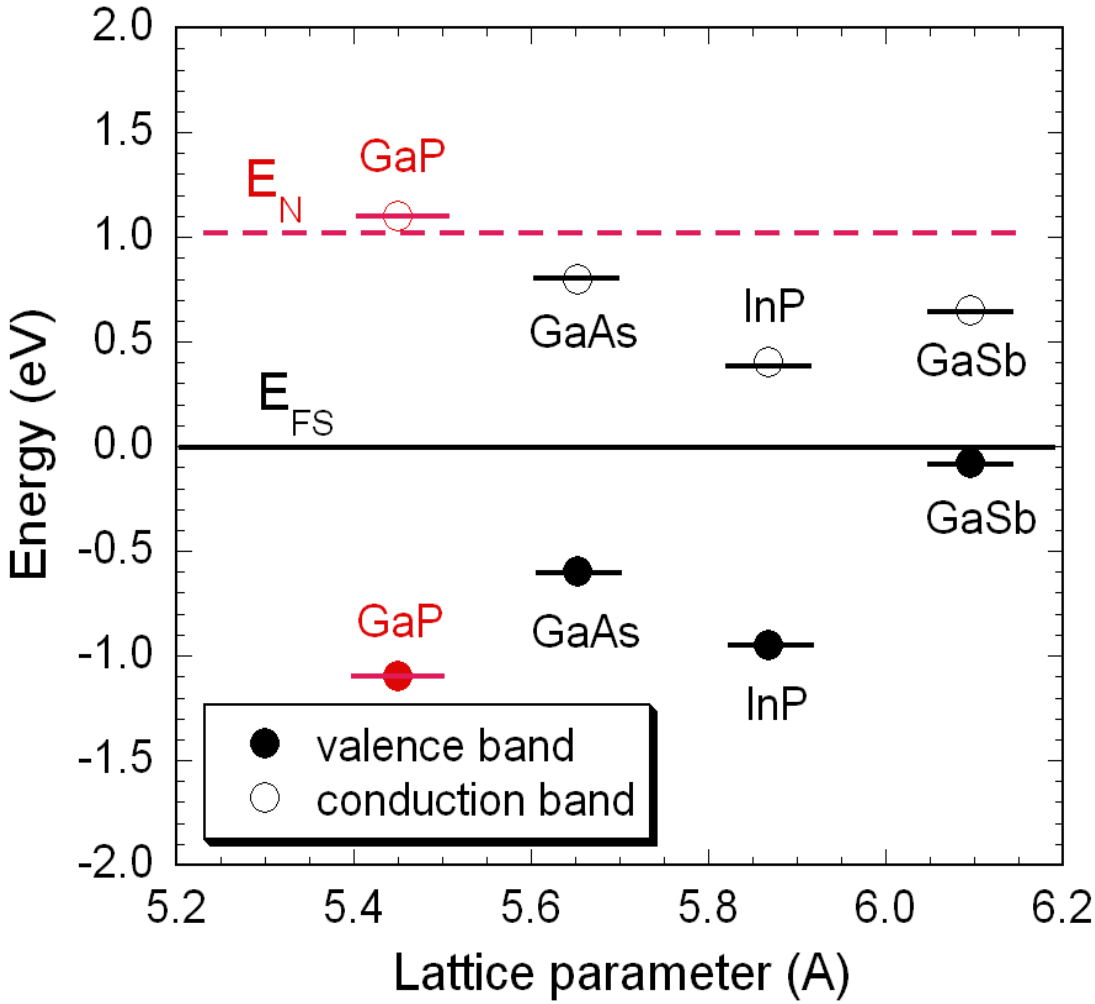


Electronegativity

$X_N = 3.0$

$X_P = 2.2$

$X_{As} = 2.2$

$X_{Sb} = 2.05$

Atomic radius

$R_N = 0.075$ nm

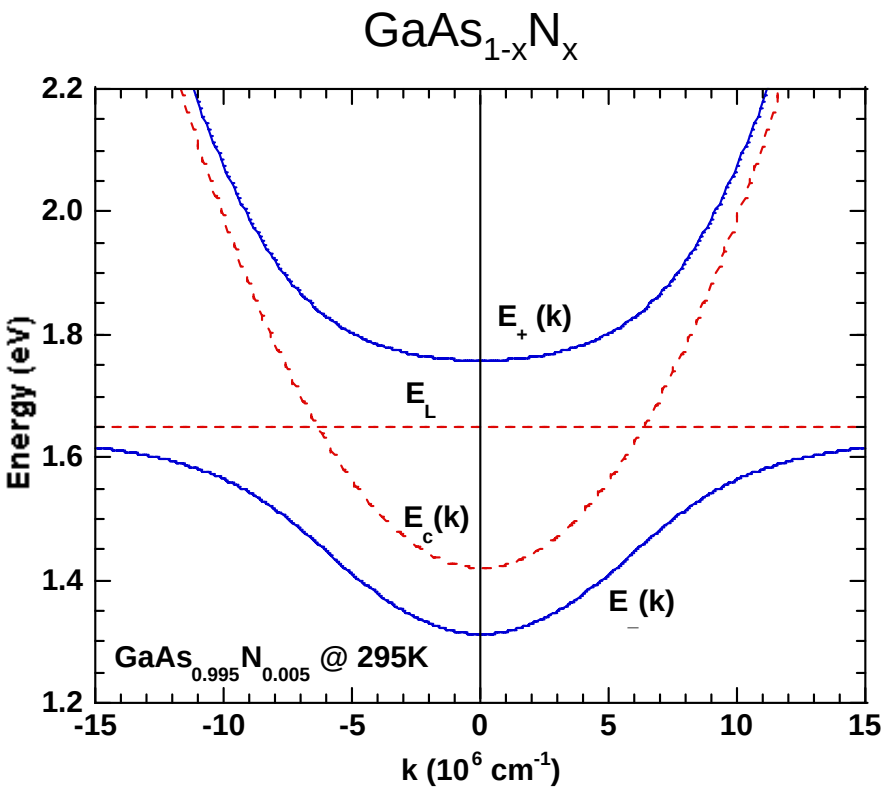
$R_P = 0.123$ nm

$R_{As} = 0.133$ nm

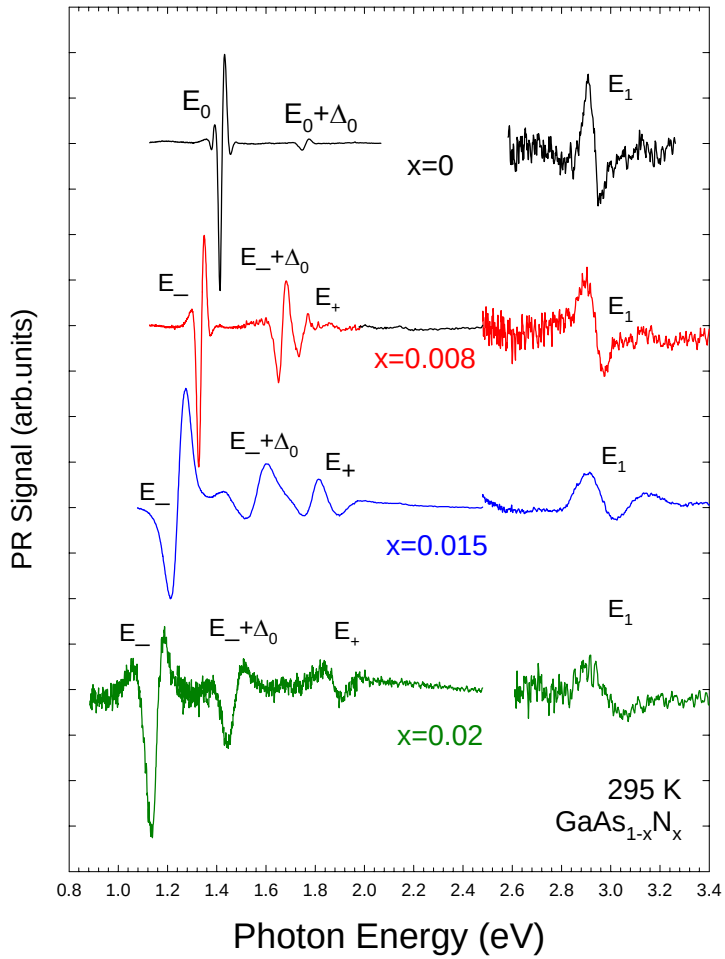
$R_{Sb} = 0.153$ nm

Nitrogen in III-V compounds introduces a localized N level close to the conduction band edge

Unique HMA effect
Band Anticrossing



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



Fundamental band gap is reduced and a new optical transition is formed…

Bandgap tuning with HMAs

$GaAs_{1-x}N_x$

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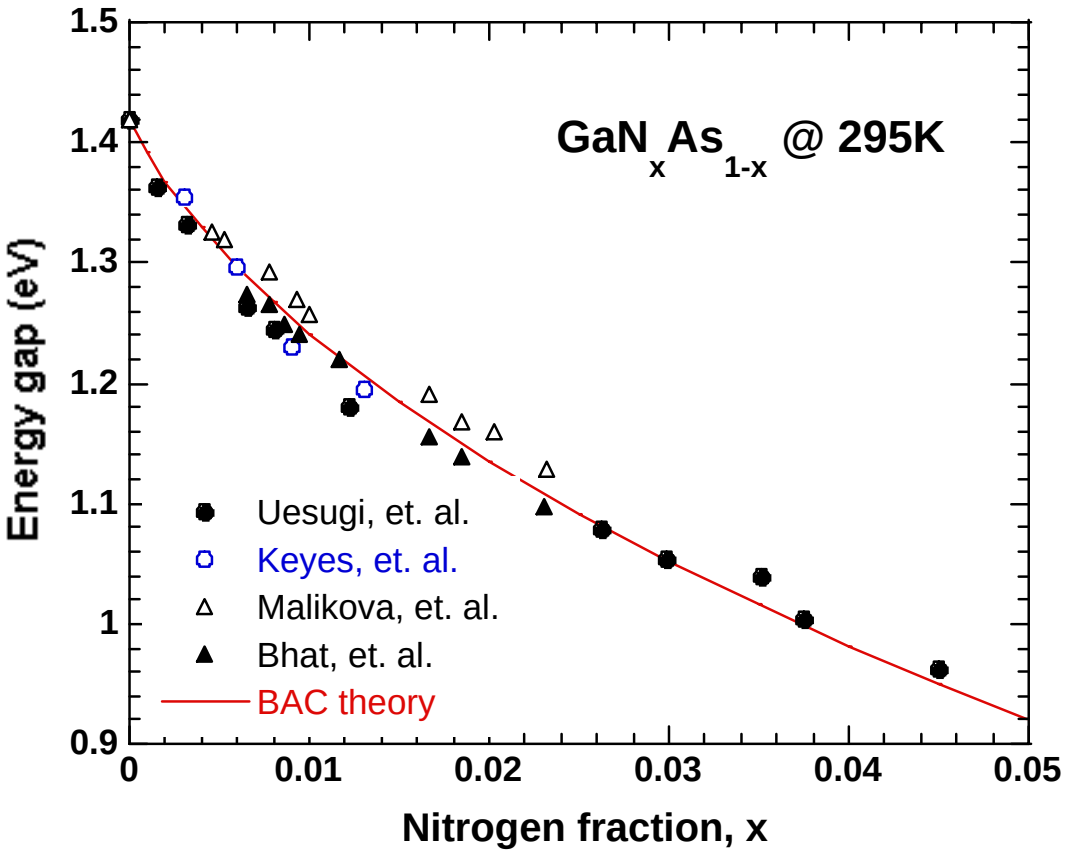

- N localized level situated above GaAs conduction band edge
  - Anticrossing pushes CB edge down
- Effect is large
  - 4% N reduces gap by 0.4 eV

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

How to synthesize an HMA?
Implantation + pulsed laser melting

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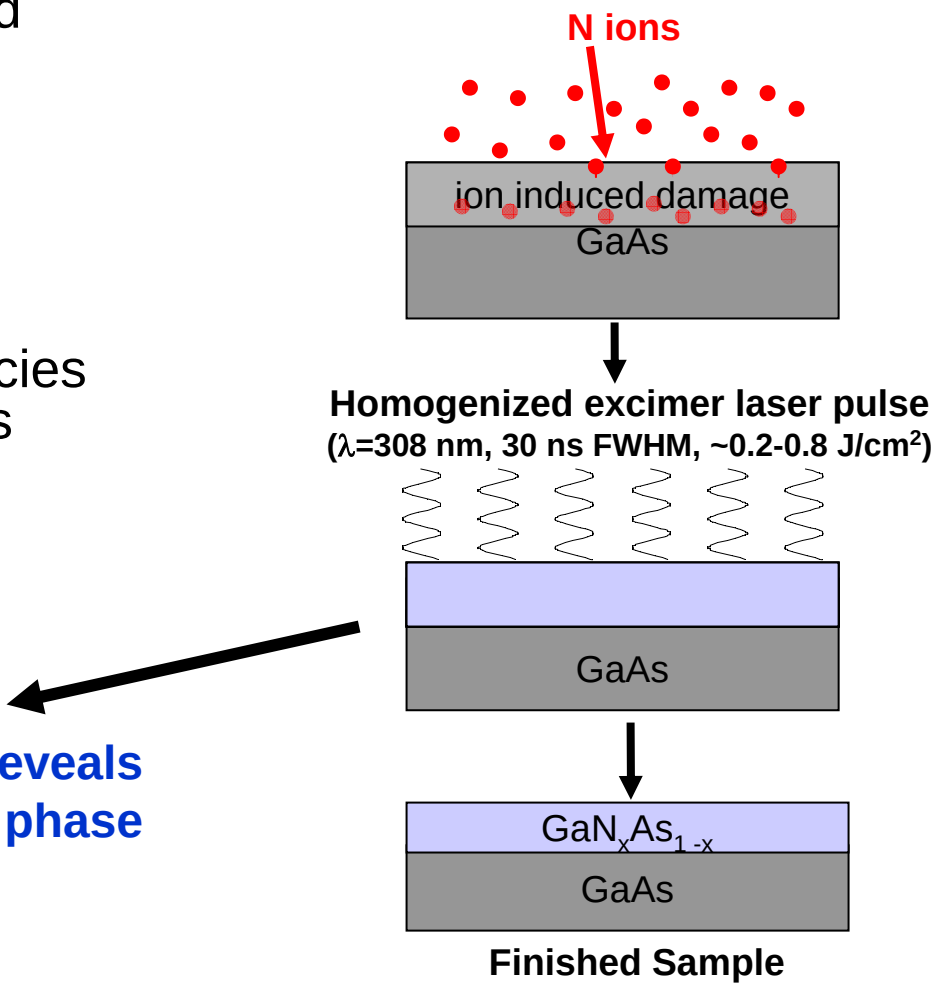
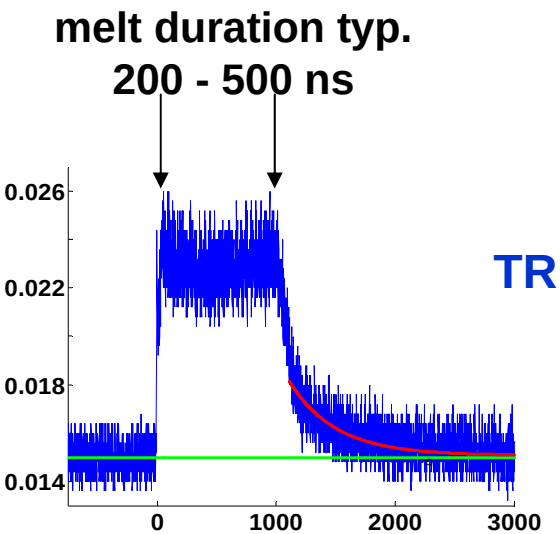
- Ion implantation of diluting species
- Pulsed-laser melting (PLM): liquid phase epitaxy at submicrosecond time scales

Outcome

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

Example: N ion implanted GaAs





TRR data reveals liquid phase

PLM epilayer quality

III-N-Vs

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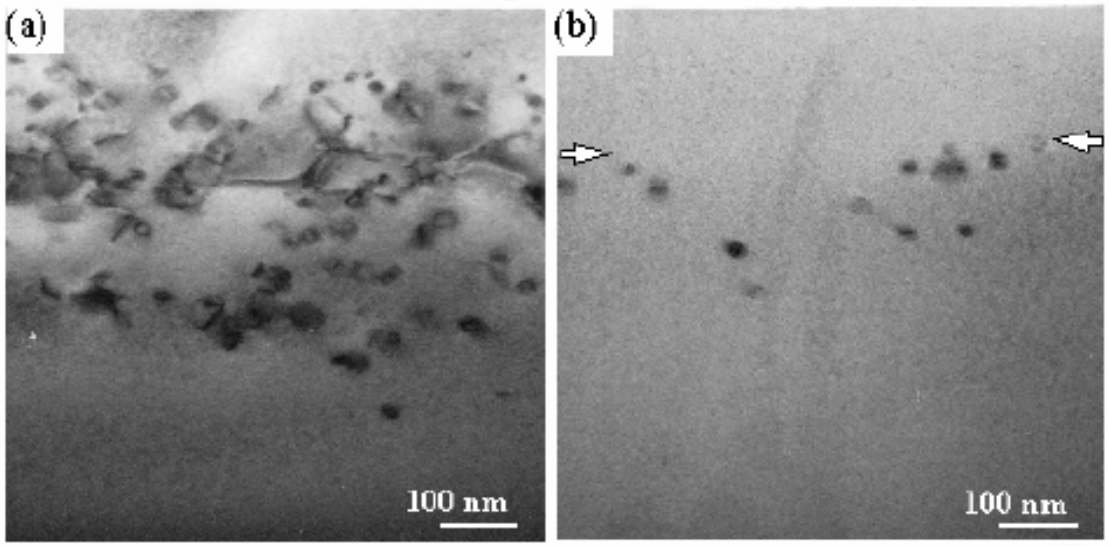
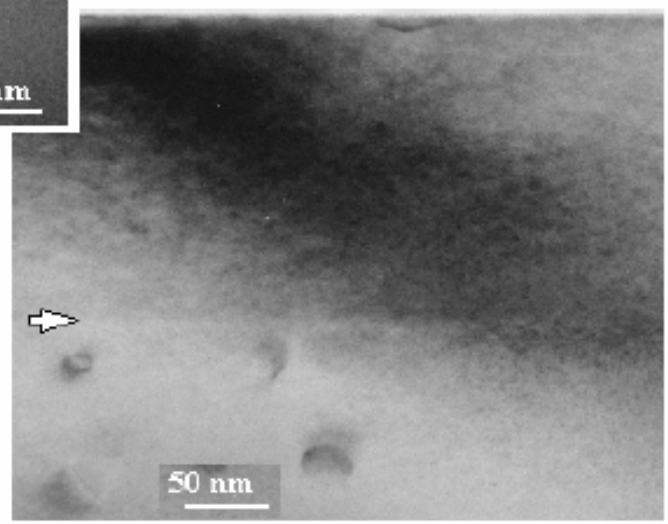
2% N implanted GaAs



RTA

PLM: 0.35 Jcm^{-2}



- **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

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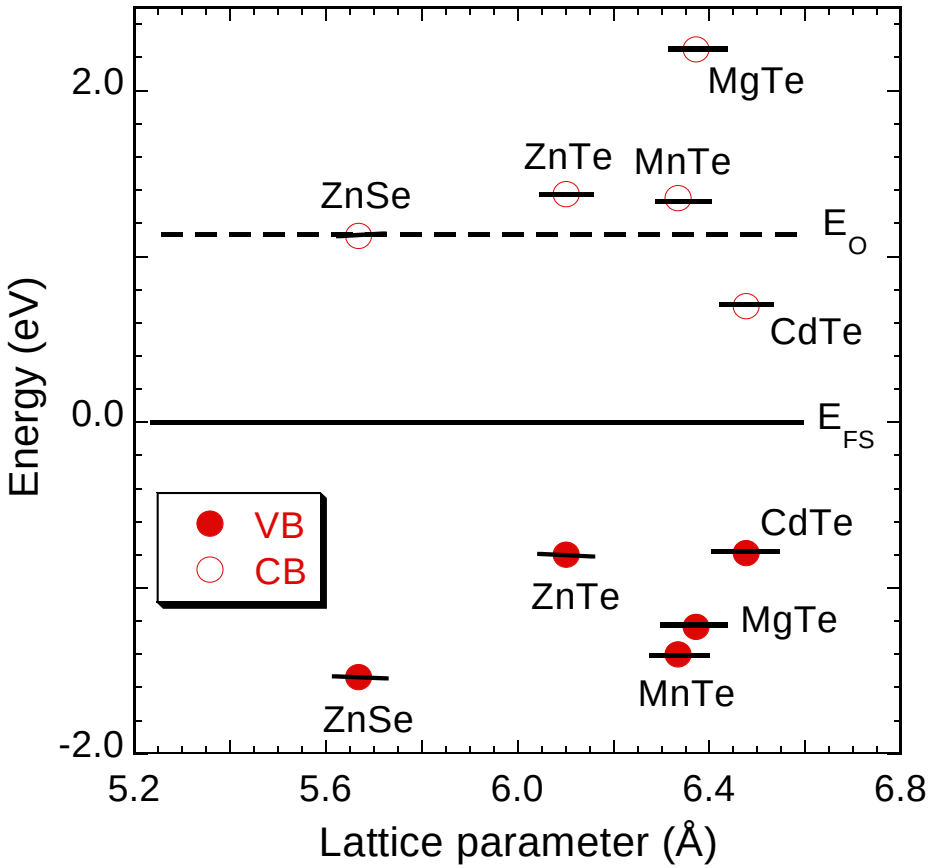

- **Oxygen in II-VI compounds has the requisite electronegativity and atomic radius difference**
  - $X_O = 3.44$; $R_O = 0.073$ nm
  - $X_S = 2.58$; $R_S = 0.11$nm
  - $X_{Se} = 2.55$; $R_{Se} = 0.12$ nm
  - $X_{Te} = 2.1$; $R_{Te} = 0.14$
- **Oxygen level in ZnTe is 0.24 eV <u>below</u> the CB edge**
  - ***Can this be used to form an intermediate band?***
- **Synthesis**
  - **Very low solid solubility limits of O in II-VI compounds**
  - **Nonequilibrium synthesis required**

PLM synthesis of II-O-VIs

X-ray diffraction

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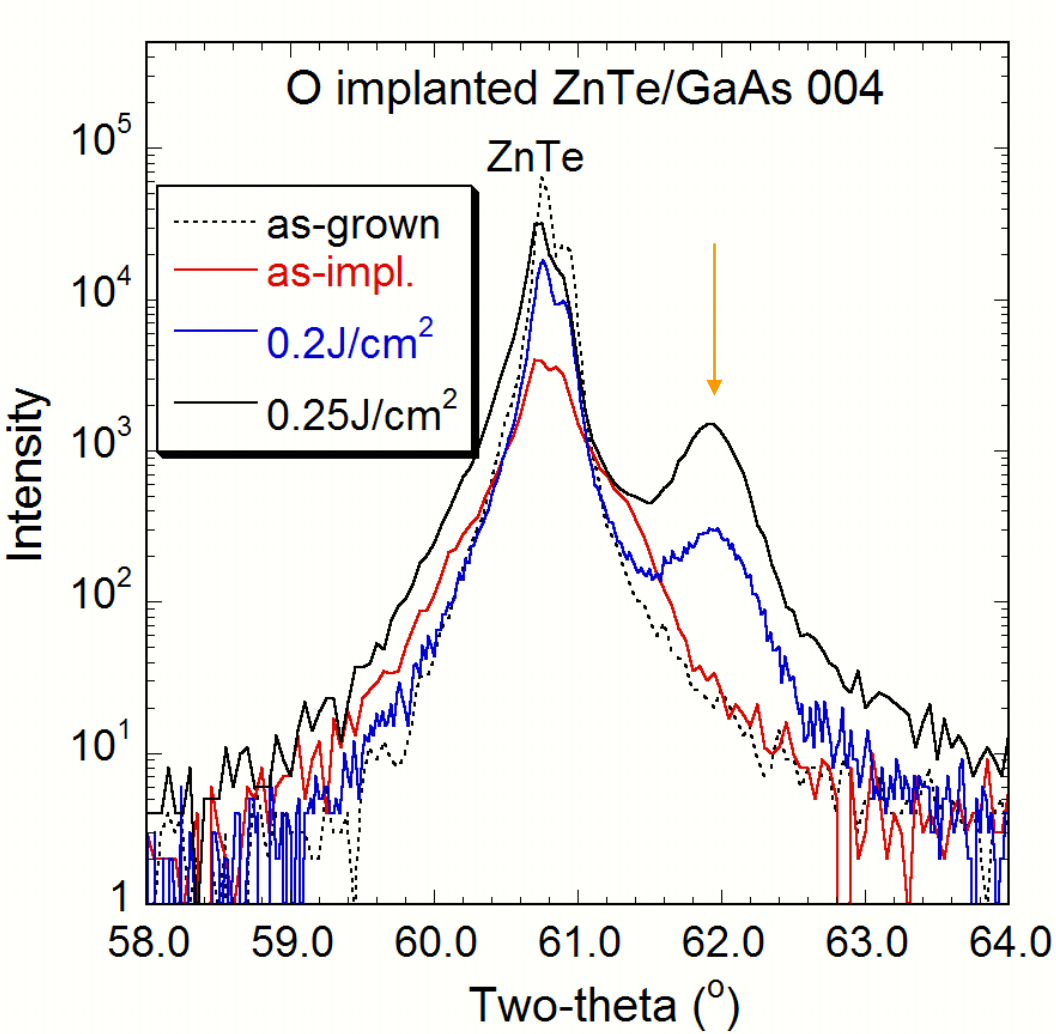

- **As-grown and as-implanted samples show diffraction peaks of the ZnTe only**
- **O implanted ZnTe/GaAs followed by PLM shows a layer of ZnOTe with lattice parameter 0.60 nm**

Is there an intermediate band?

$Zn_{1-y}Mn_yO_xTe_{1-x}$

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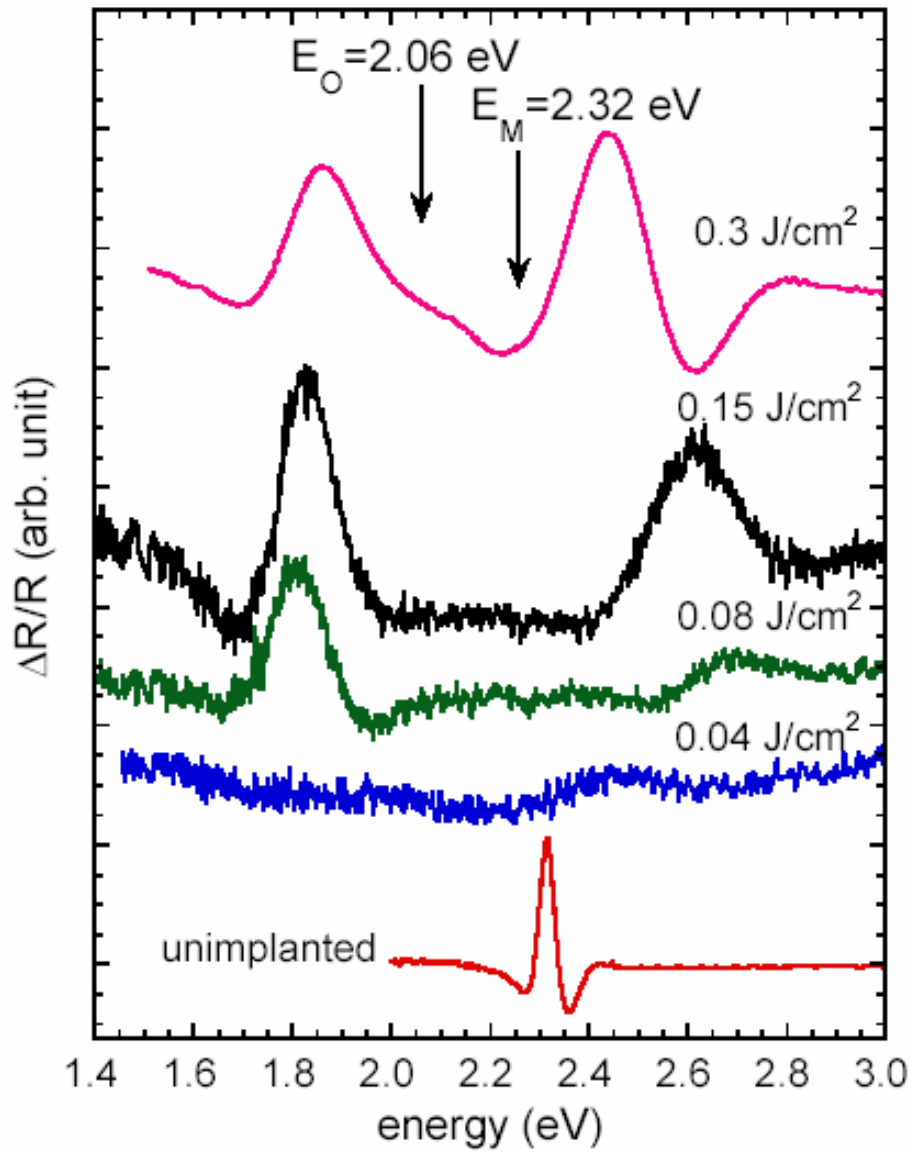

K. M. Yu *et. al.*, *Phys. Rev. Lett.,* **91**, 246403 (2003)

Predicted PV operation

$Zn_{1-y}Mn_yO_xTe_{1-x}$

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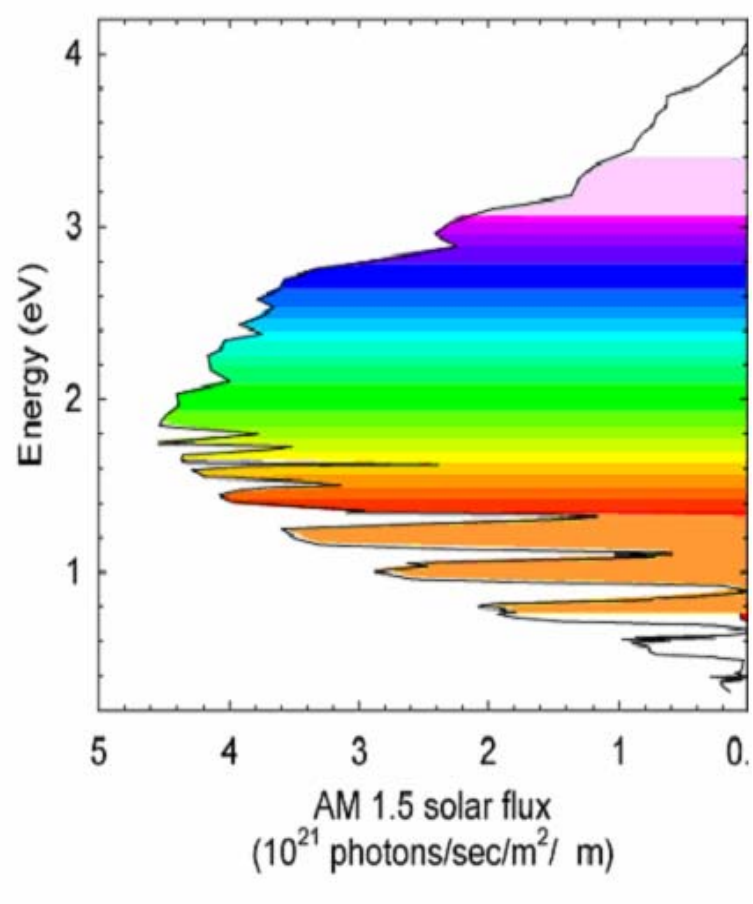
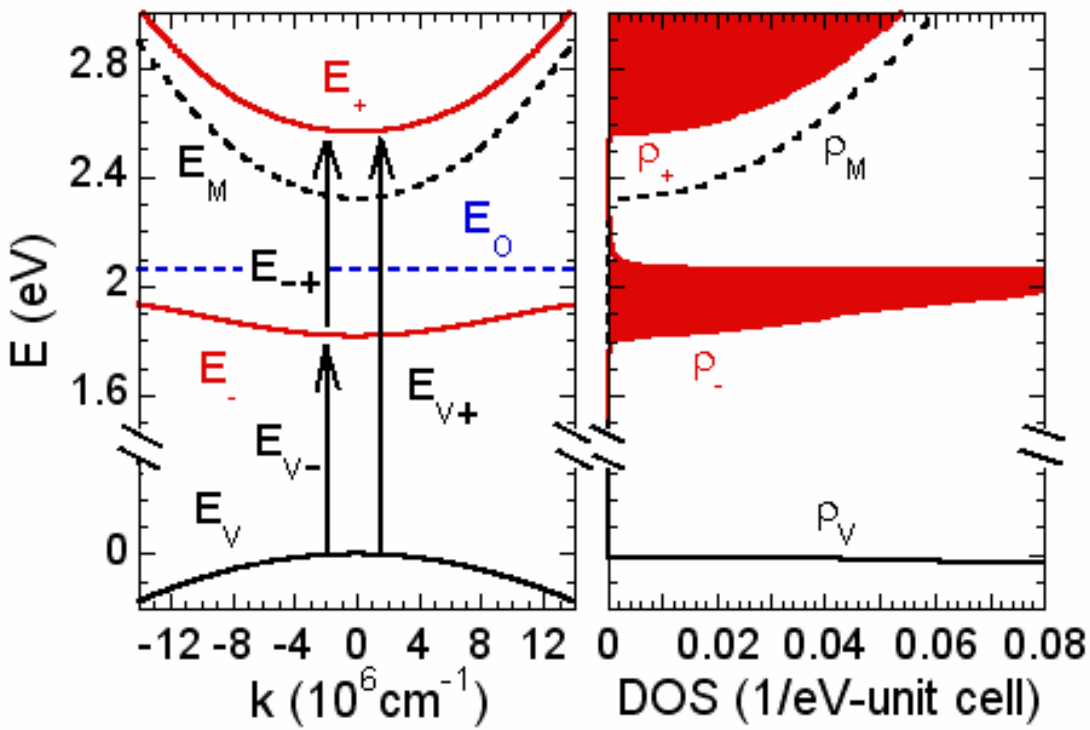
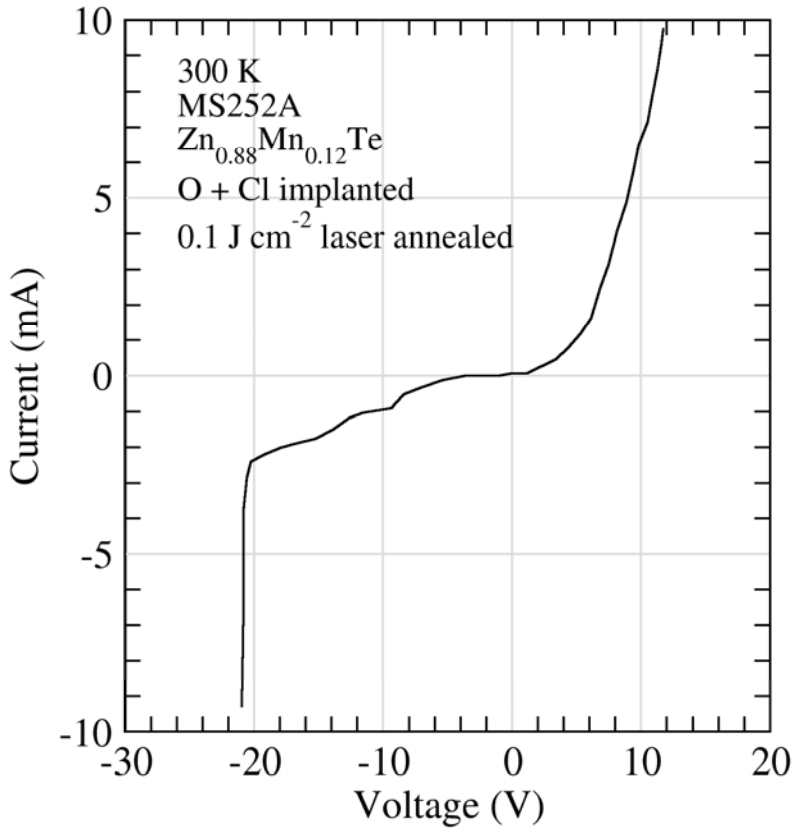
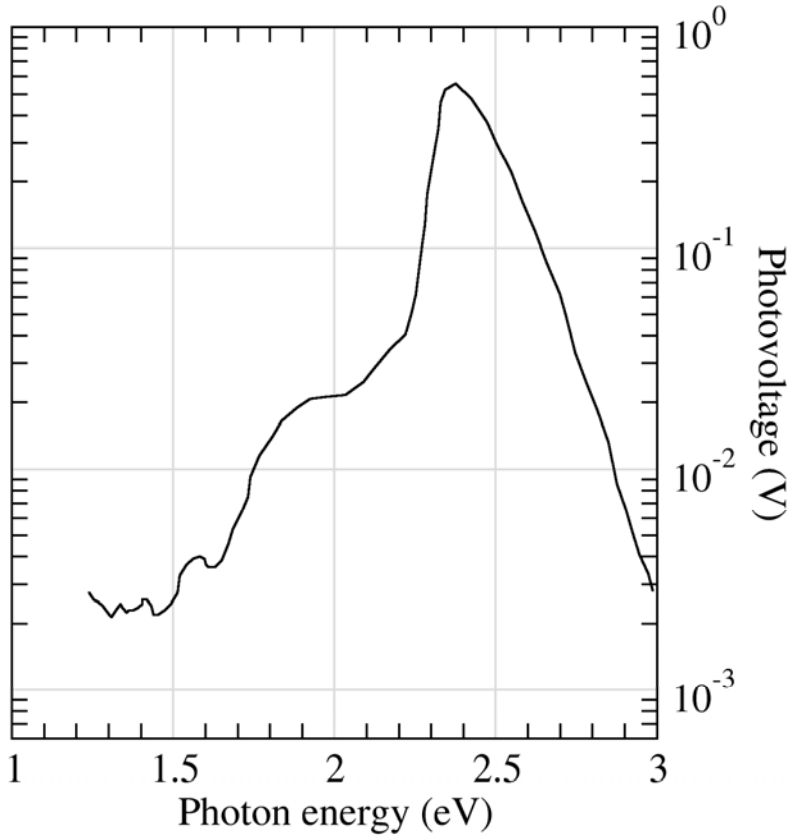




Photovoltaic action





How efficient can they be?

Multi-band ZnMnOTe alloys

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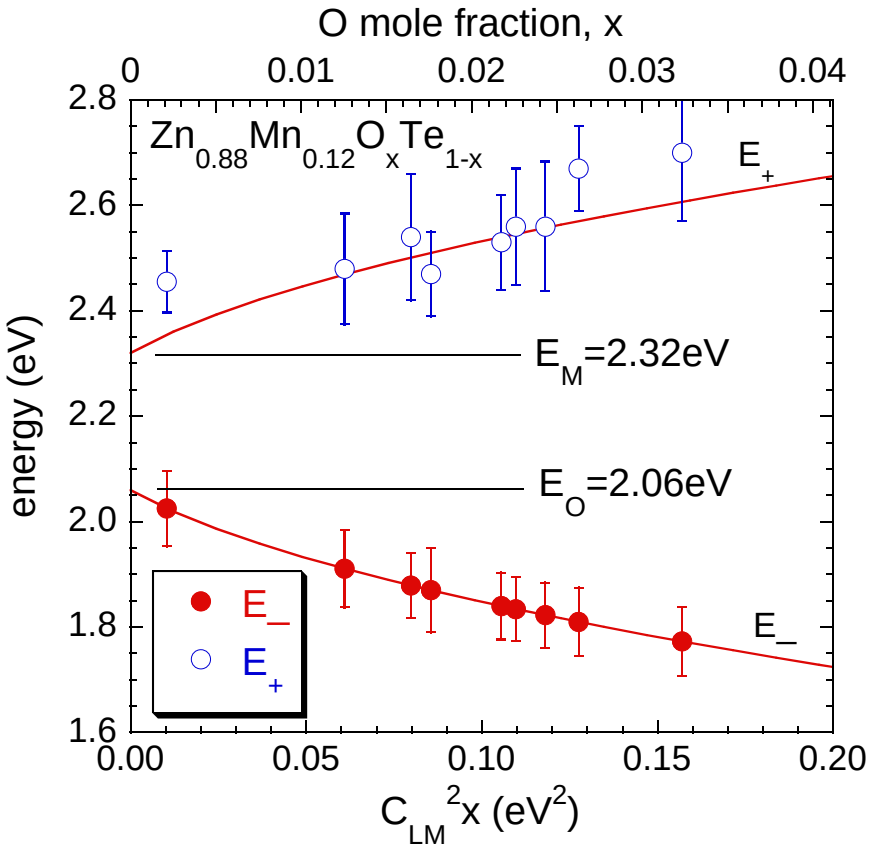

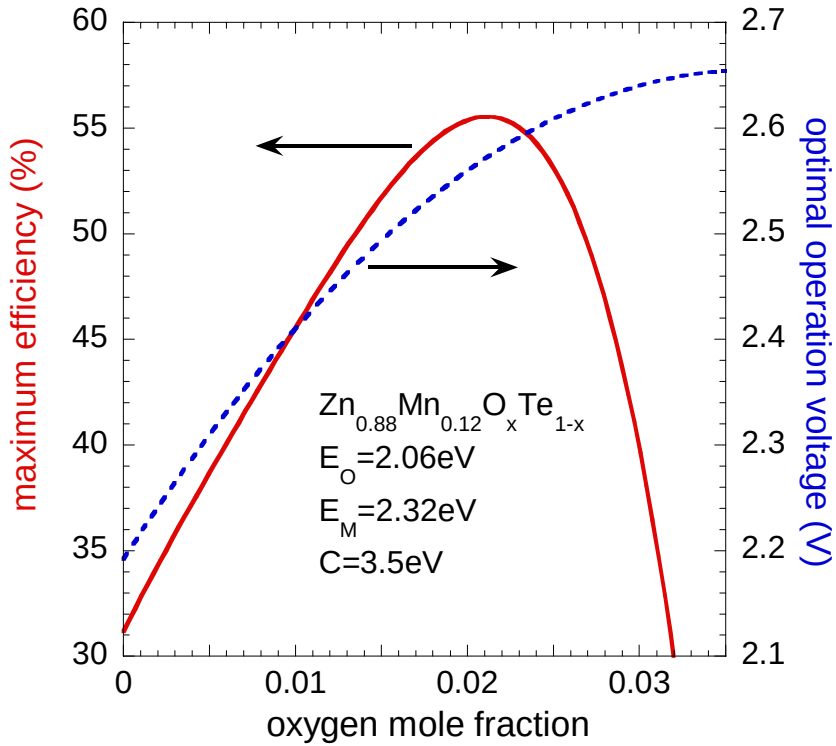

- The location and the width of the intermediate band in ZnMnOxTe1-x is determined by the O content, x
- Can be used to maximize the solar cell efficiency

- 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_xSe_{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: $GaP_yN_xAs_{1-x-y}$**
- **Fundamentals**
  - **Nature of the intermediate band: localized vs. extended**
  - **Carrier relaxation processes**

Collaborators

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