Advances in Intermediate Band Solar Cell Research

IES:1979-2009
30 years
developing PV

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IBPOWER IBPOWER, European Commission

GENESIS-FV, Consolider Ingenio 2010
National Programmes (Spain)

nanogefes NANOGEFES, MICINN (Spain)

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Contents

- Introduction
- Deep level IB materials
  - IB and SRH recombination
  - Proven bulk IB materials and cells
- QD implementation
  - Current enhancement
  - Voltage preservation
  - Experimental proof of concept and some implications
    - Proof of concept
    - The need of two photons
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Contents

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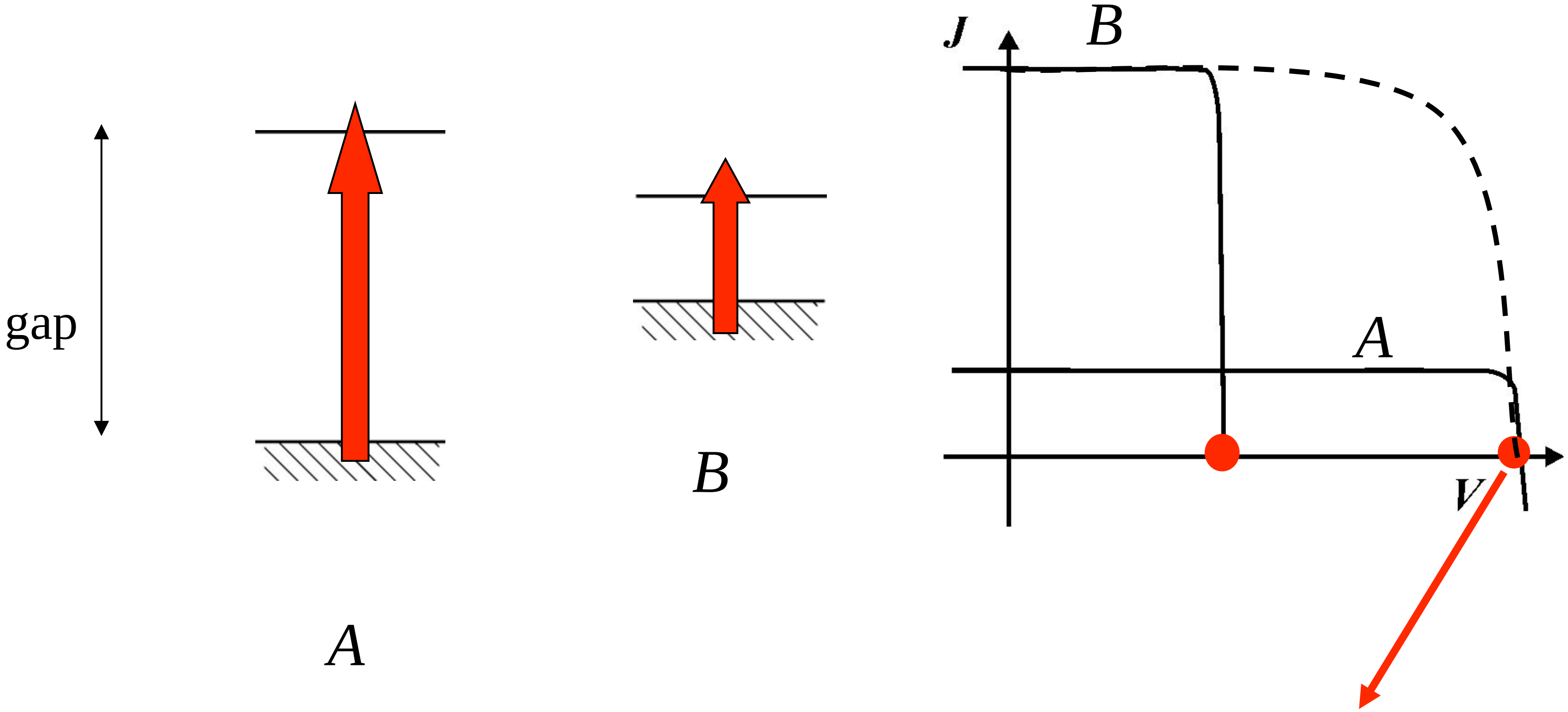
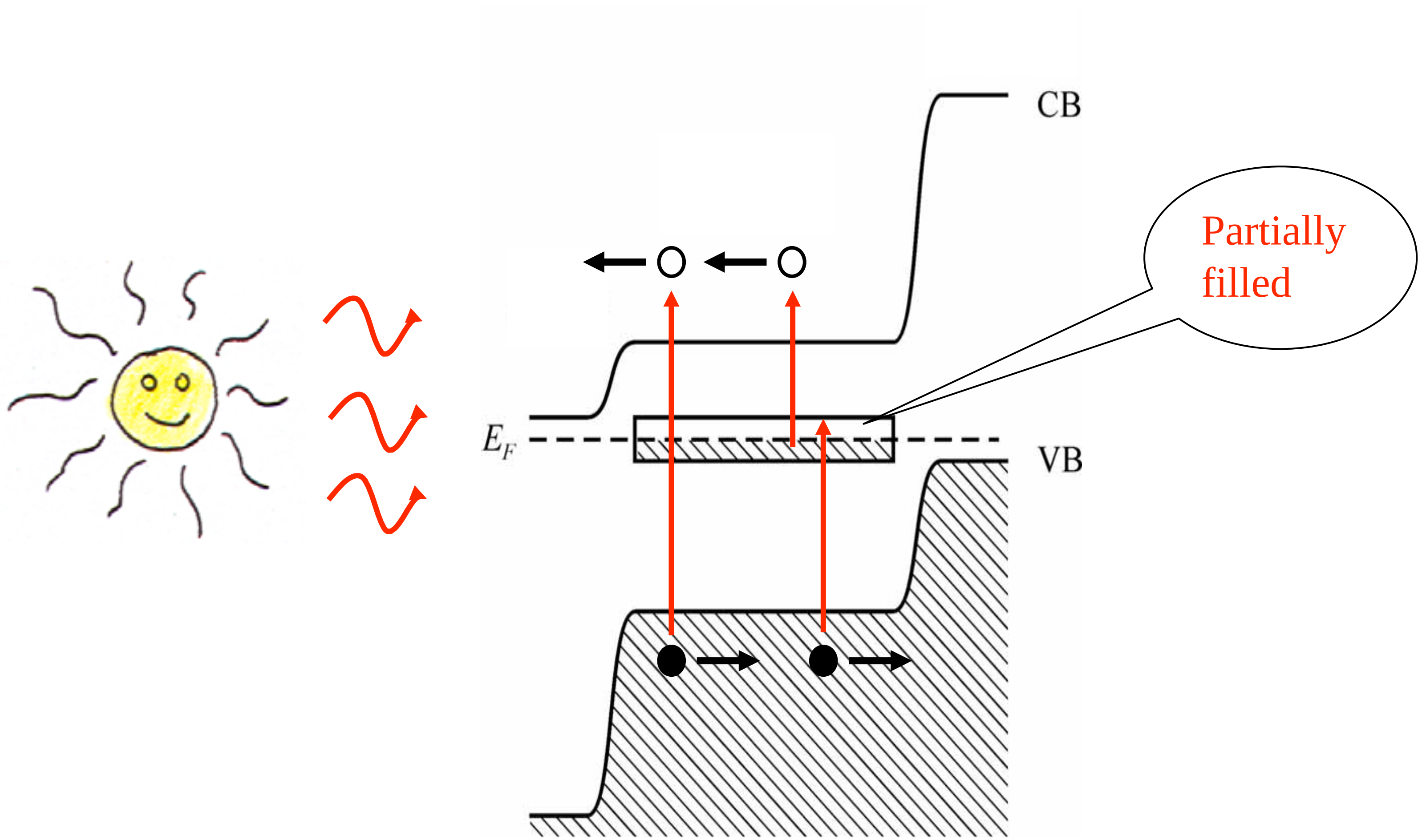
I_{SC}-V_{OC} trade-off

Intermediate band solar cell !



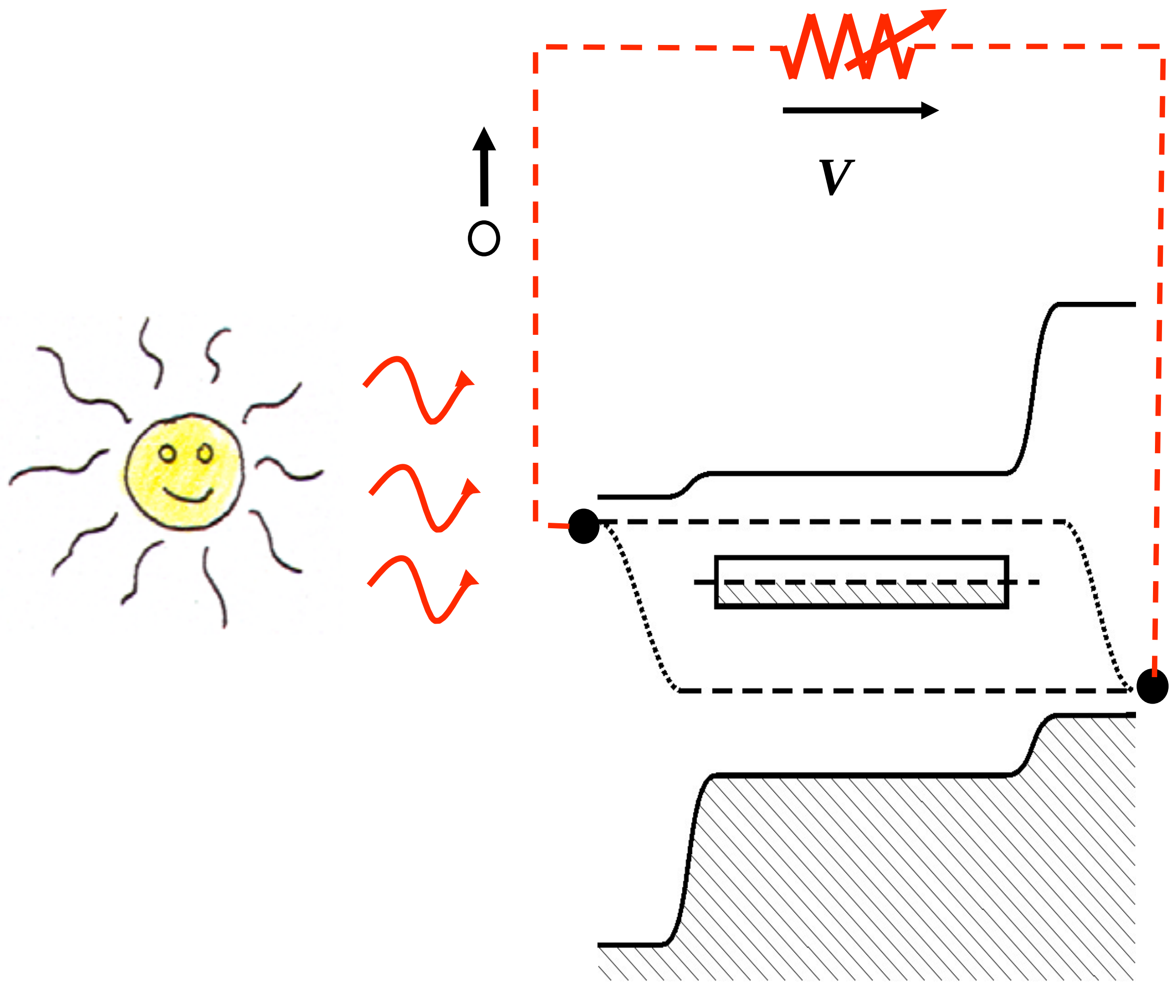
$eV_{OC} <$ gap

Photocurrent gain



A. Luque y A. Martí, Phys. Rev. Lett. 78(26) 5014–5017 (1997).
A. Luque and A. Martí, Prog. in Photov, Res. and Appl. 9(2) 73–86 (2001).

Voltage preservation



A. Luque y A. Martí, Phys. Rev. Lett. 78(26) 5014–5017 (1997).

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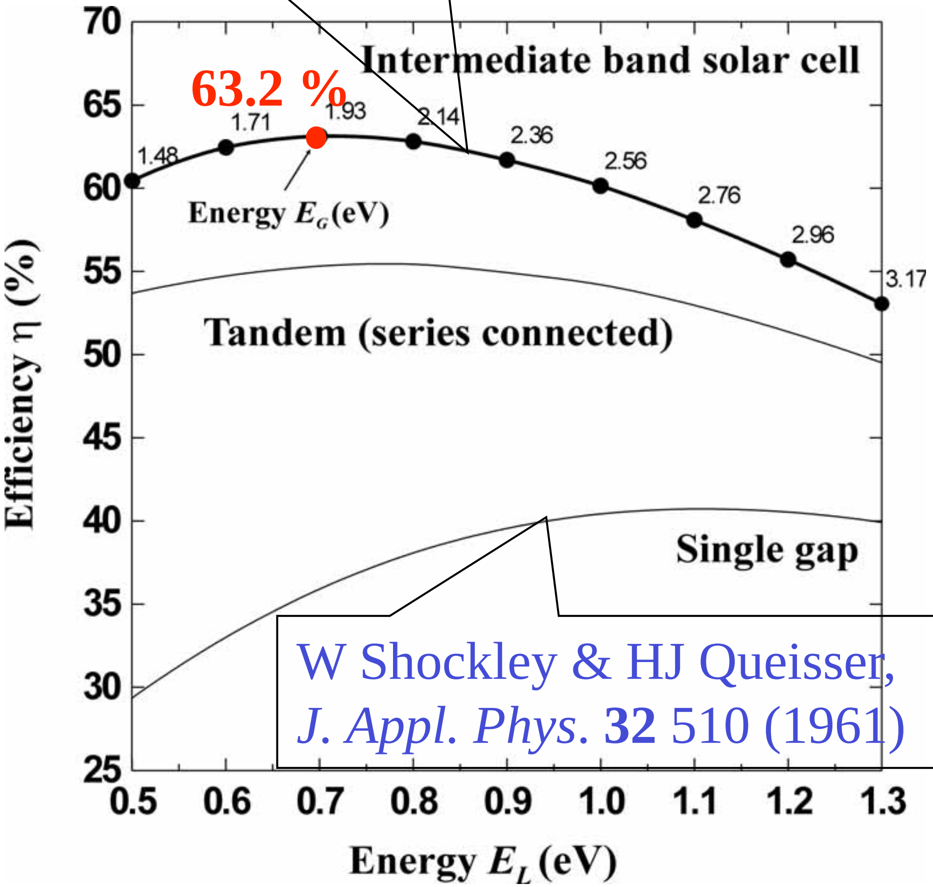
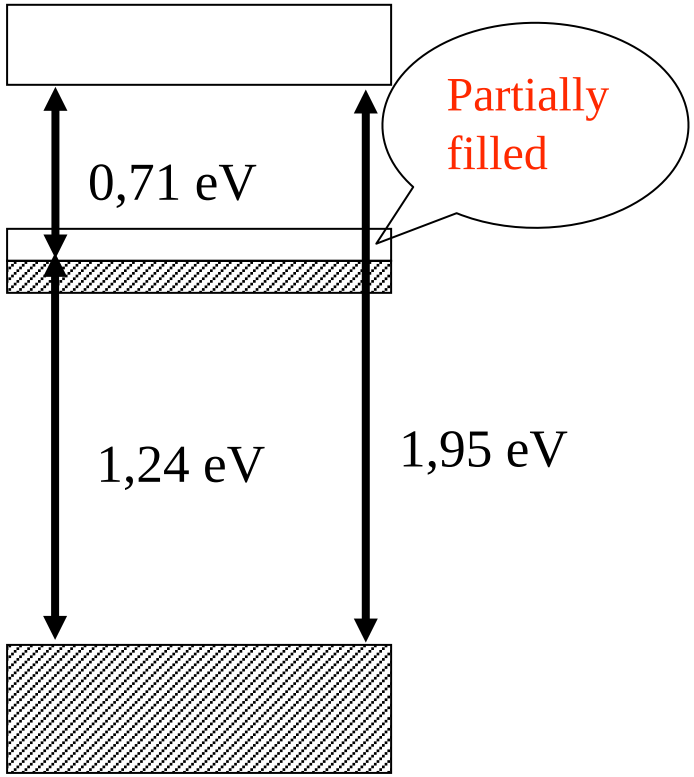
Optimum gaps

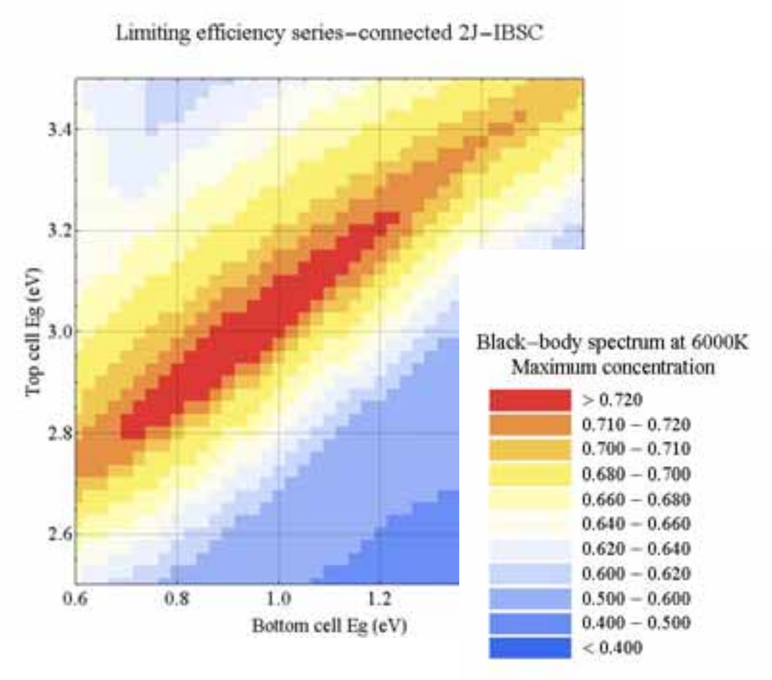
A. Luque & A. Martí, *Phys. Rev. Lett.* **78** 5014 (1997)

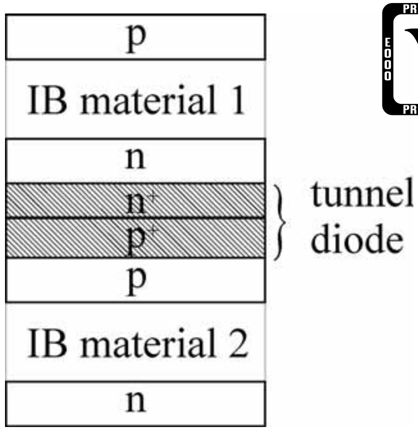


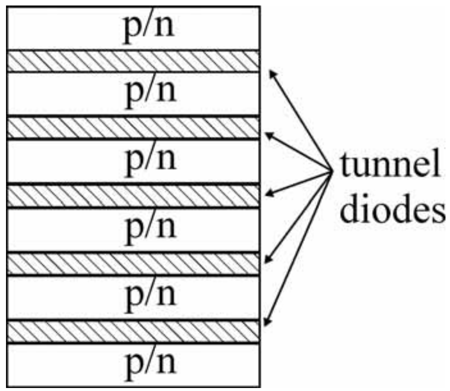
W Shockley & HJ Queisser, *J. Appl. Phys.* **32** 510 (1961)



IBSC & Tandems







Series-interconnected 2J-IBSC
Absolute limit: 72.7 %

tandem of 2 IBSC:
6 gaps only one
tunnel junction

conventional 6
gaps tandem
5 tunnel junctions

E. Antolín, A. Martí, and A. Luque, in Proc. of the 21st European Photovoltaic Energy Conference, 2006, pp. 412--415.
E. Antolín, , A. Martí, P. G. Linares, I. Ramiro, E. Hernández, and A. Luque. In Proc. 5 PV World Conf. in press.

Two-photon mechanism necessary

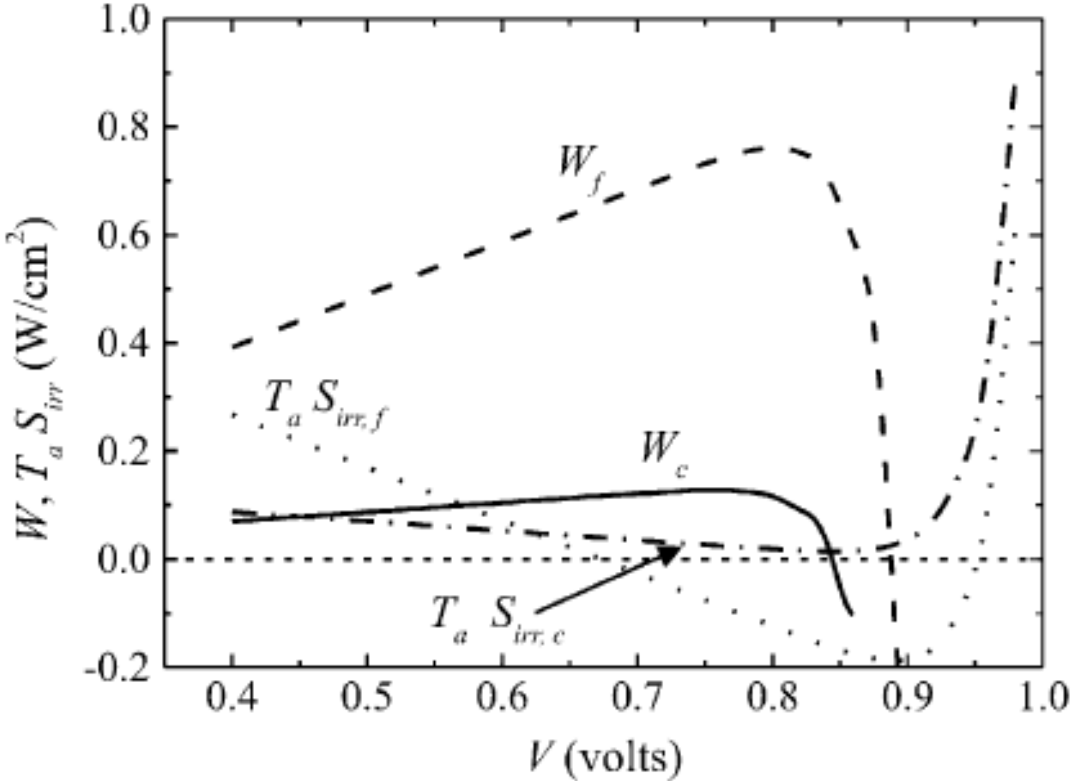


Fig. 2. Power (W) and entropy multiplied by temperature ($T_a S_{irr}$) for an ordinary cell (c) of gap 1 eV and one violating thermodynamics (f) with barrier energy 1 eV and well energy 0.7 eV. The radiator and cell temperatures have been assumed at 1491 and 298 K, respectively.

A. Luque, A. Martí, and L. Cuadra, Physica E **14**, 107 (2002).

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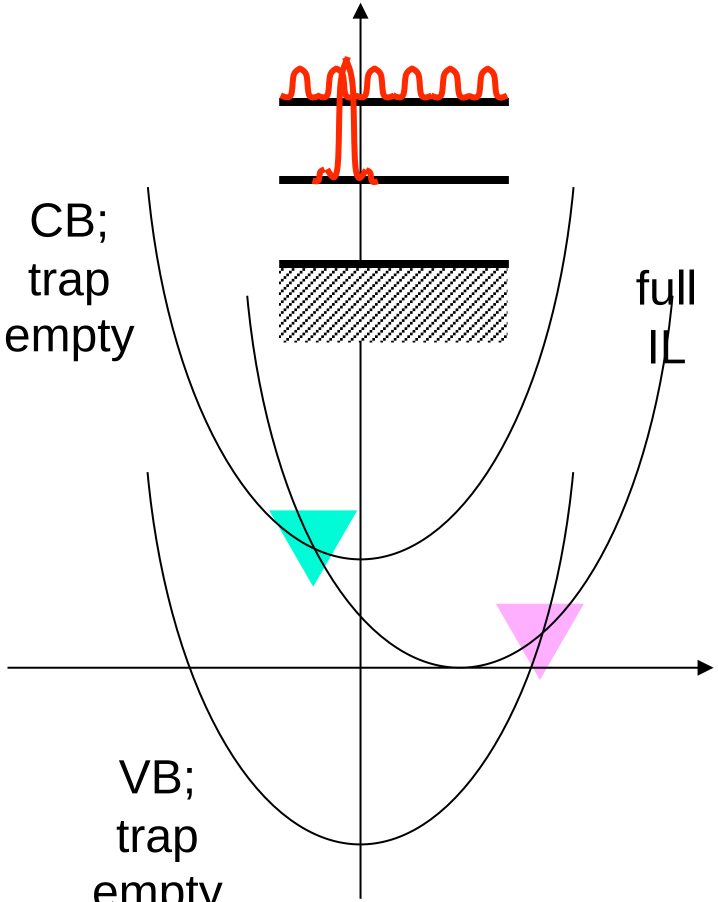
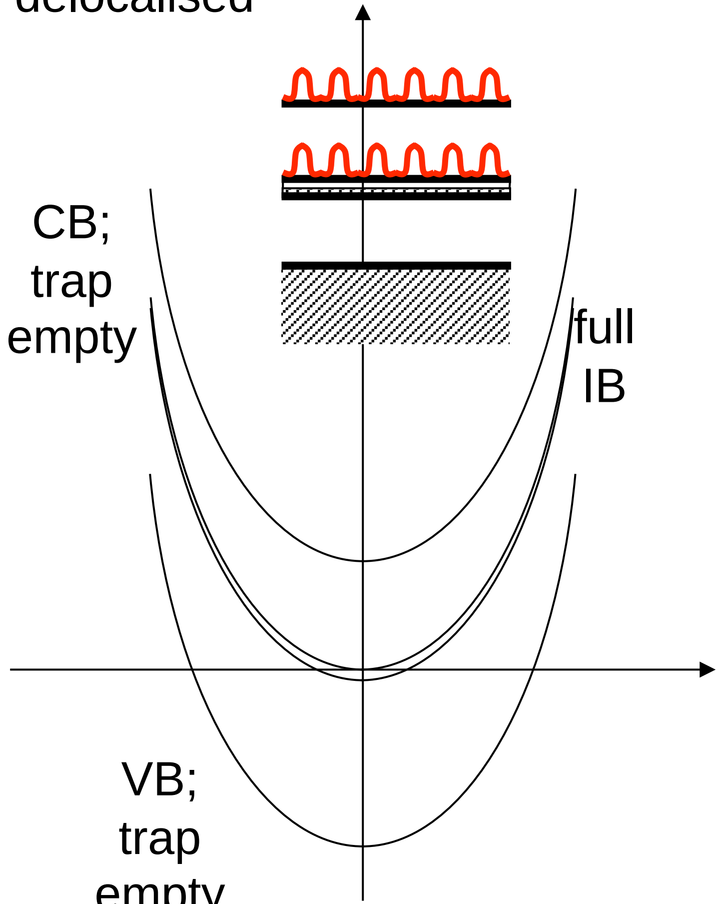
Deep levels induce SRH recombination. Why is the IBC going to be different?

With a low density of impurities, the wavefuntion is localised



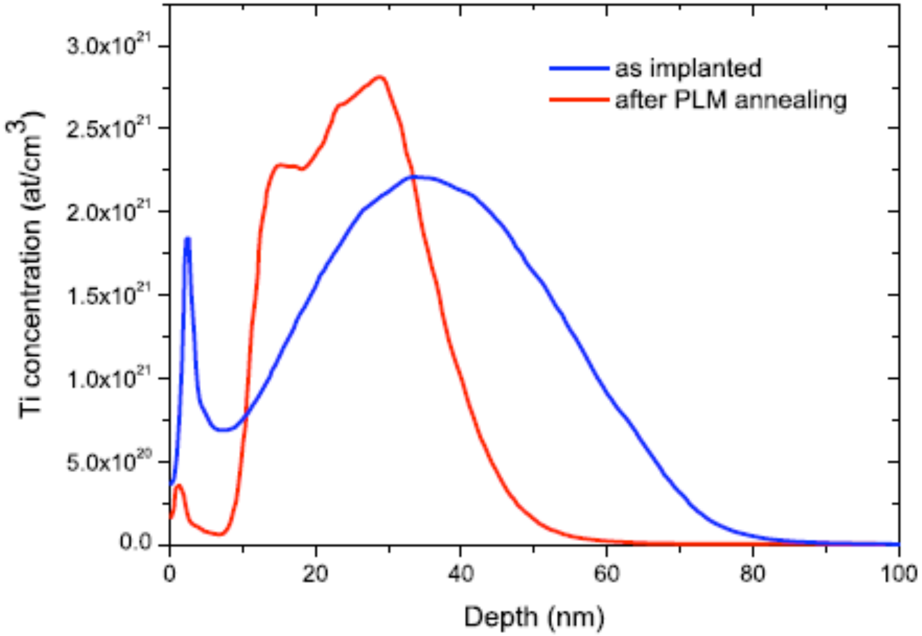
Beyond the density given by the Mott transition the wavefunction becomes delocalised

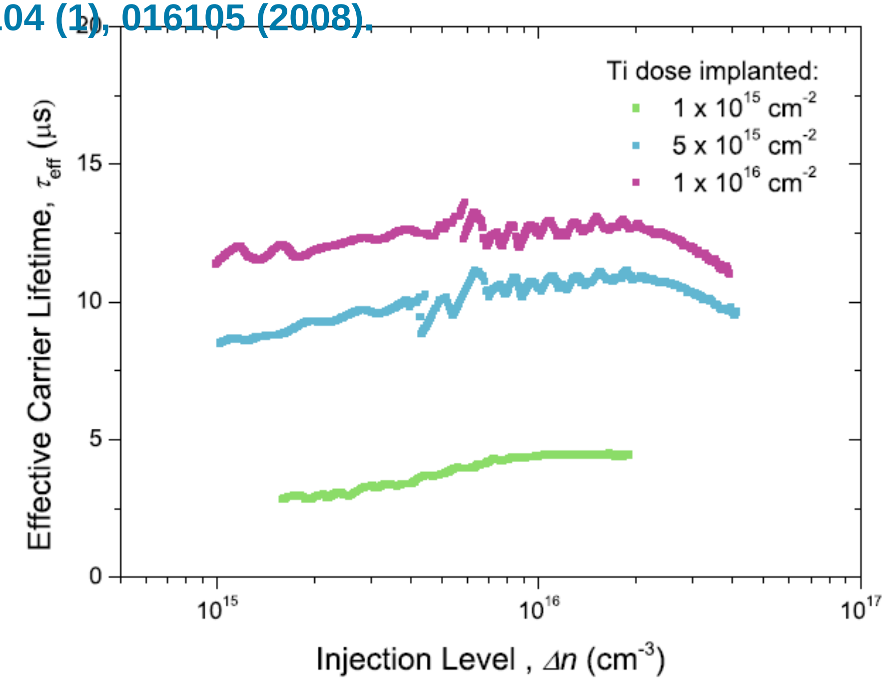


A. Luque, A. Martí, E. Antolín, and C.Tablero, Physica B, vol. 382, pp. 320-327, 2006.

Lifetime increase in heavy Ti implanted Si

Samples prepared by: J. Olea, M. Toledano-Luque, D. Pastor et al., "Titanium doped silicon layers with very high concentration," Journal of Applied Physics 104 (1), 016105 (2008).





Ti concentration profile. Ti concentration vs. depth in the implanted layer, from ToF-SIMS measurements. The blue line as-implanted; red line: sample annealed with 2 laser pulses of 0.6 J/cm2. Both samples implanted with 10^{16} cm^{-2} Ti.

Effective lifetime of wafers with different Ti implantation doses. Carrier lifetime measurement of PLM annealed Si samples implanted with Ti doses of 10^{15}, 5×10^{15} and 10^{16} cm-2. Samples measured by back

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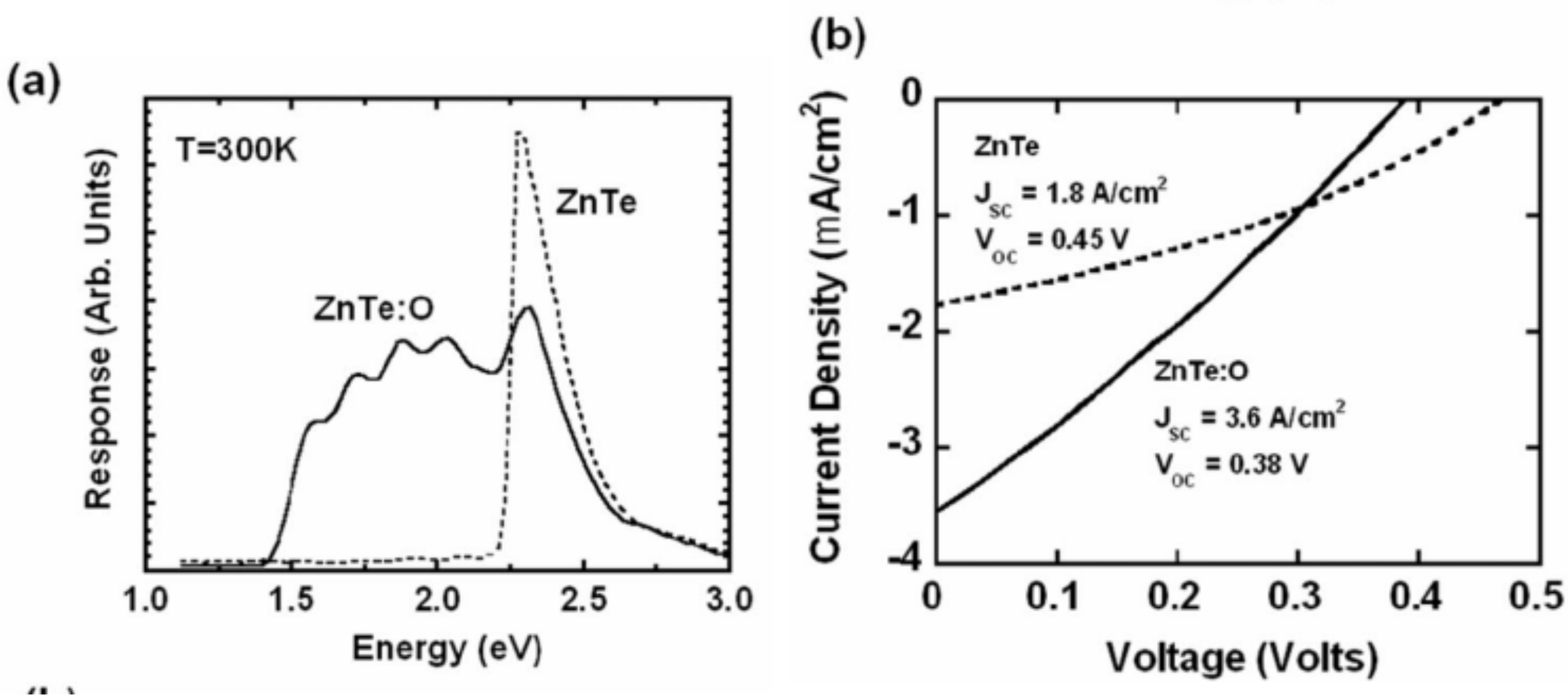
Some proven IB bulk materials and cells

- $Zn_{0.88}Mn_{0.12}Te_{0.987}O_{0.013}$ detected by photo-reflectance
  - K. M. Yu *et al.*, Physical Review Letters **91**, 246403 (2003)
- $GaN_xAs_{1-x-y}P_y$ alloys with $y>0.3$ detected by photo-reflectance
  - K. M. Yu *et al.*, Applied Physics Letters **88**, 092110 (2006)
- **$V_{0.25}In_{1.75}S_3$ detected by absorption coefficient (intrisically half filled)**
  - P. Palacios *et al.*, Phys. Rev. Lett. **101**, 046403 (2008)
  - R. Lucena *et al.*, Chem. Mat. **20**, 5125 (2008)
- Si:Ti ([illegible]5%) detected by Hall experiments
  - G. Gonzalez-Dıaz et al., Solar Energy Materials & Solar Cells, doi: 10.1016/j.solmat.2009.05.014 (2009).
- ZnTe:O solar cell
  - W. Wang, et al, Applied Physic Letters **96**, 011103 (2009)

Bulk IB solar cell

University of Michigan



W. Wang, A. S. Lin, J. D. Phillips, *Applied Physics Letters* ***2009, 96, 011103.***

Contents

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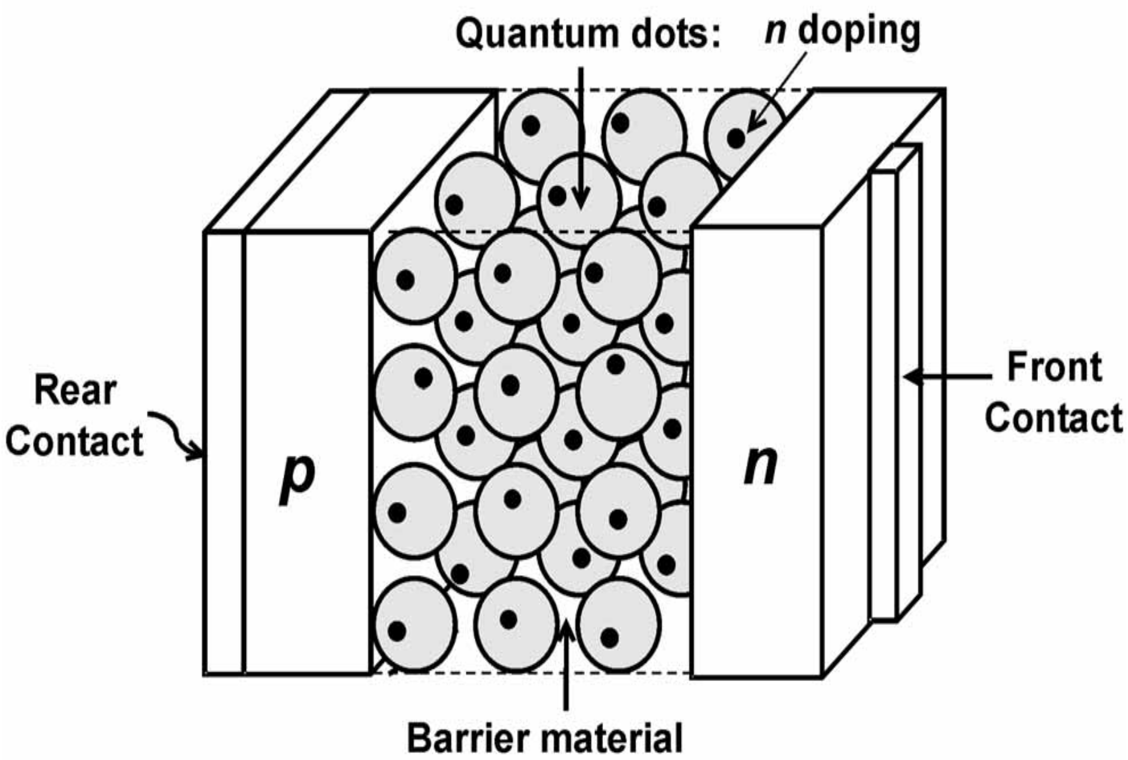
Quantum dots for the IBSC



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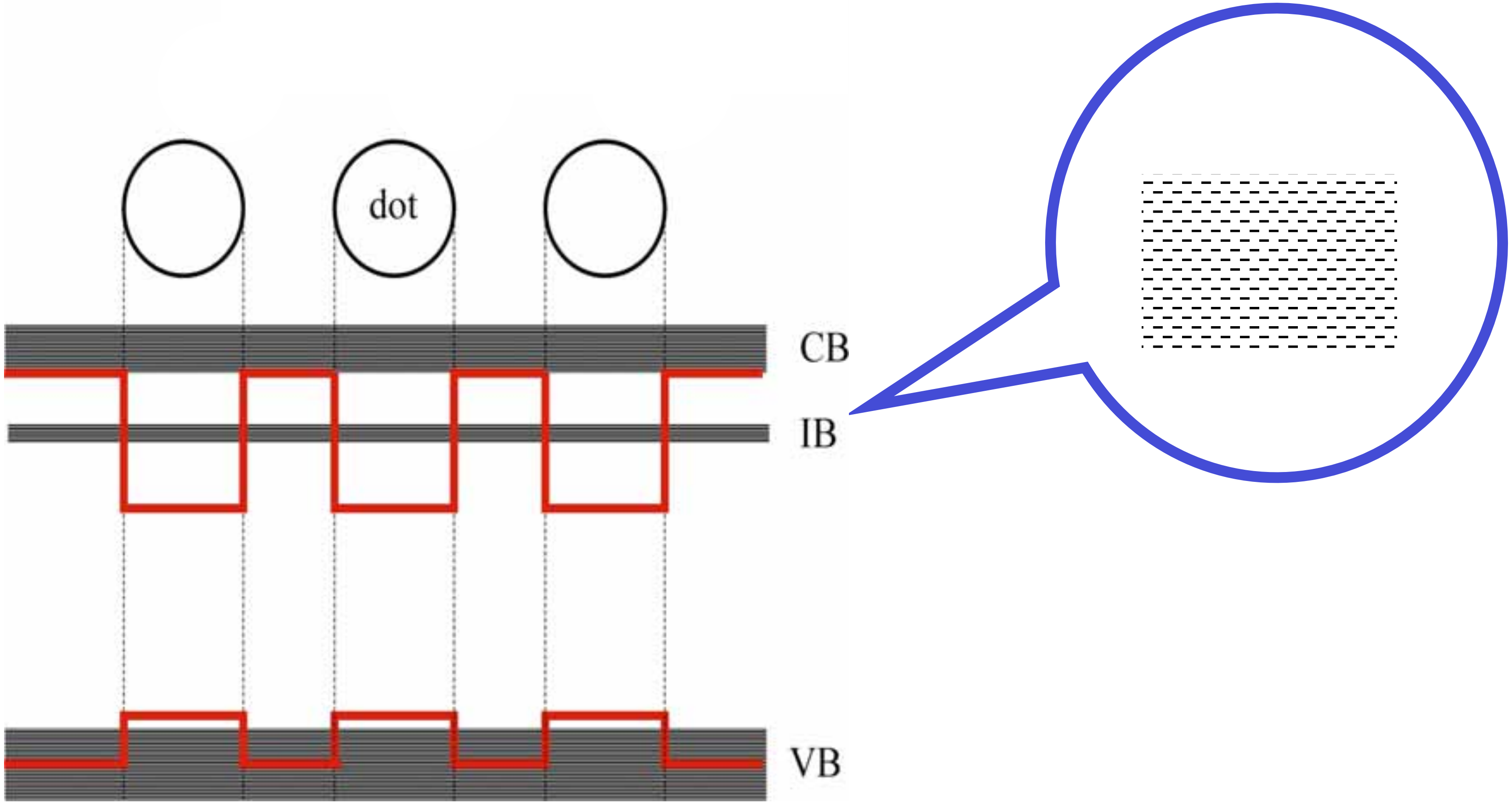
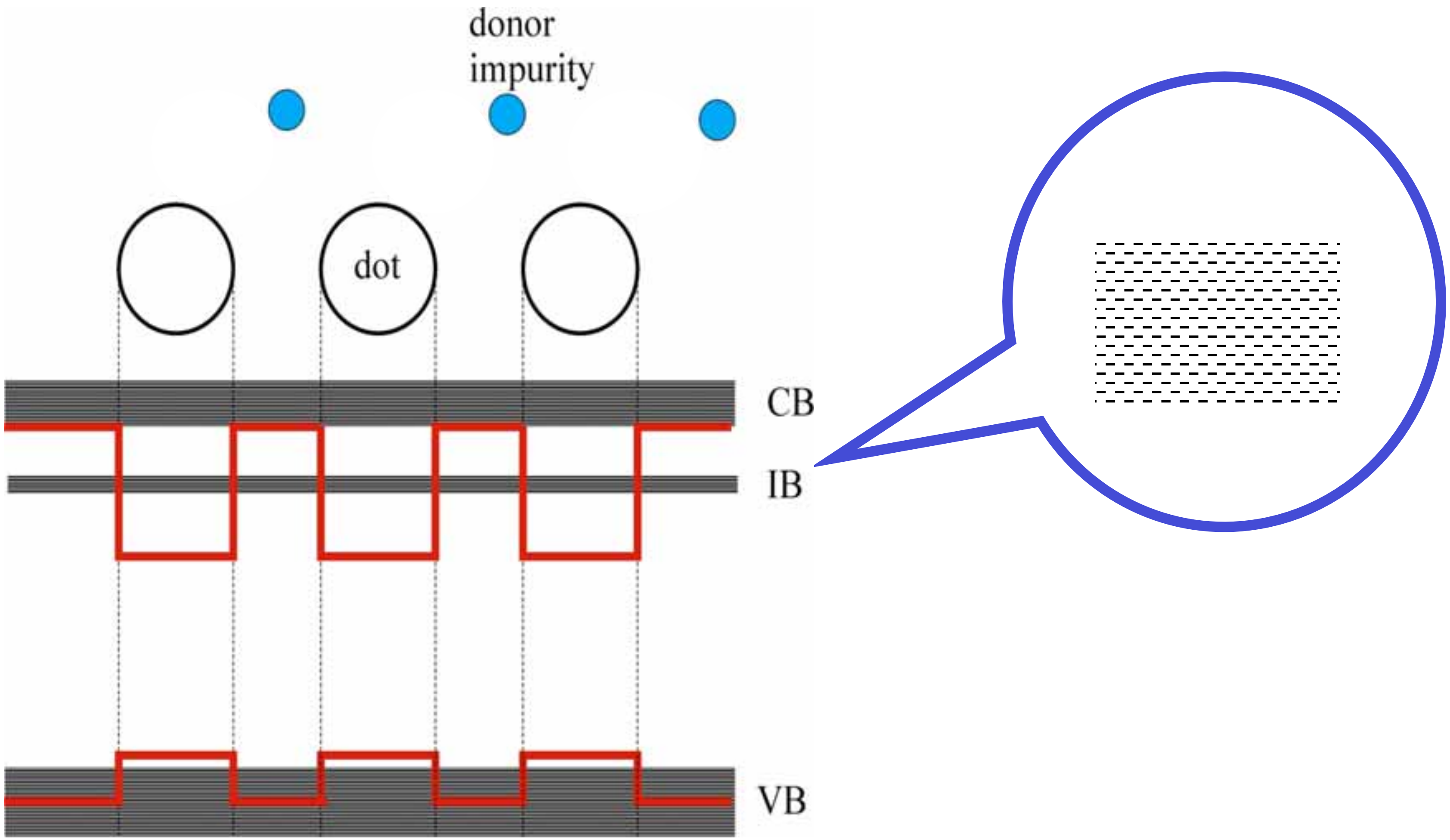
QD-IBSC



A. Martí, L. Cuadra, and A. Luque, in NEXT GENERATION PHOTOVOLTAICS: High Efficiency through Full Spectrum Utilization (Institute of Physics Publishing, Bristol, 2003), pp. 140.

QD-IBSC



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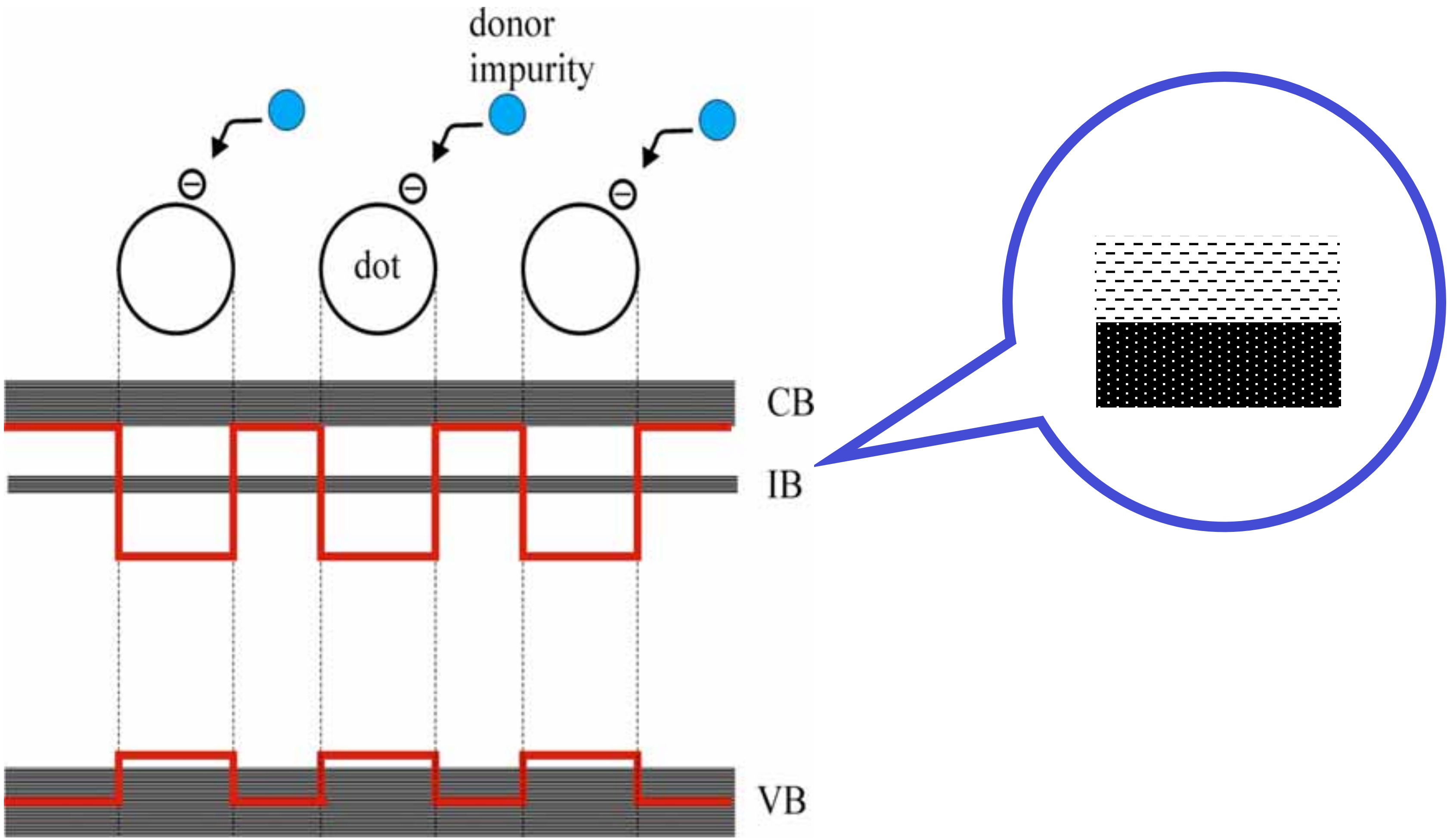
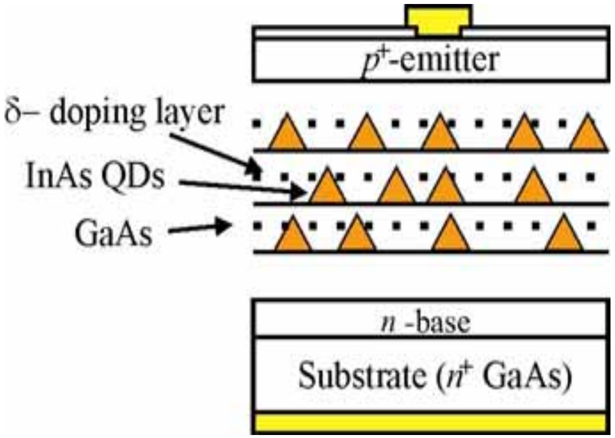


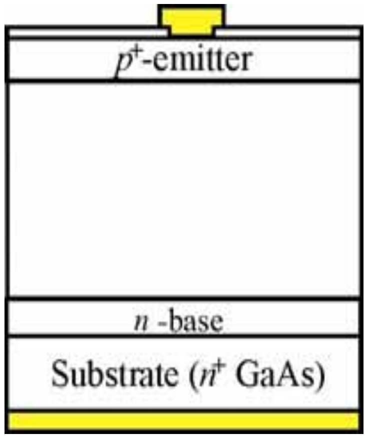
A. Martí, L. Cuadra, and A. Luque, in NEXT GENERATION PHOTOVOLTAICS: High Efficiency through Full Spectrum Utilization (Institute of Physics Publishing, Bristol, 2003), pp. 140.

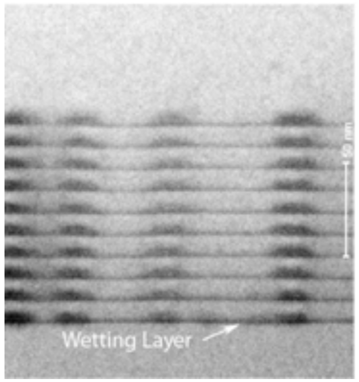
First IB solar cell

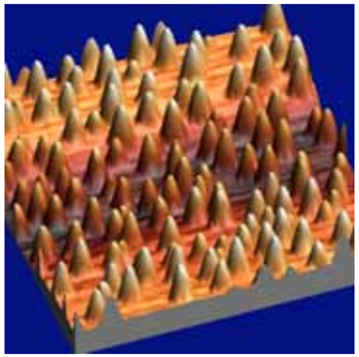
In collaboration with:
University of Glasgow

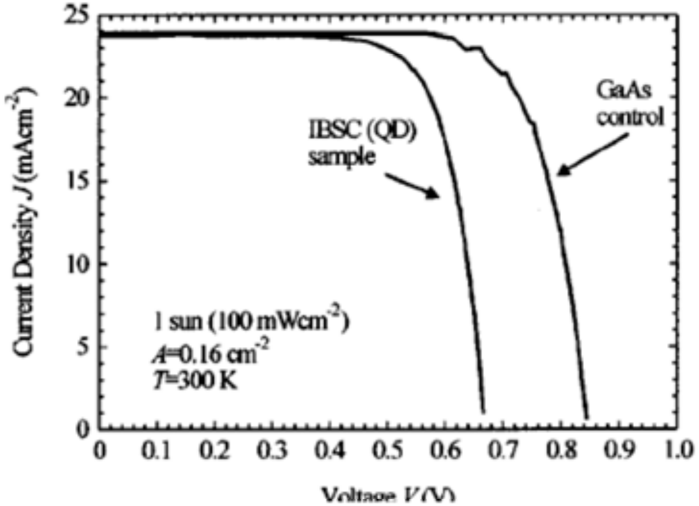
Grown in MBE, in Stranski-Krastanov mode

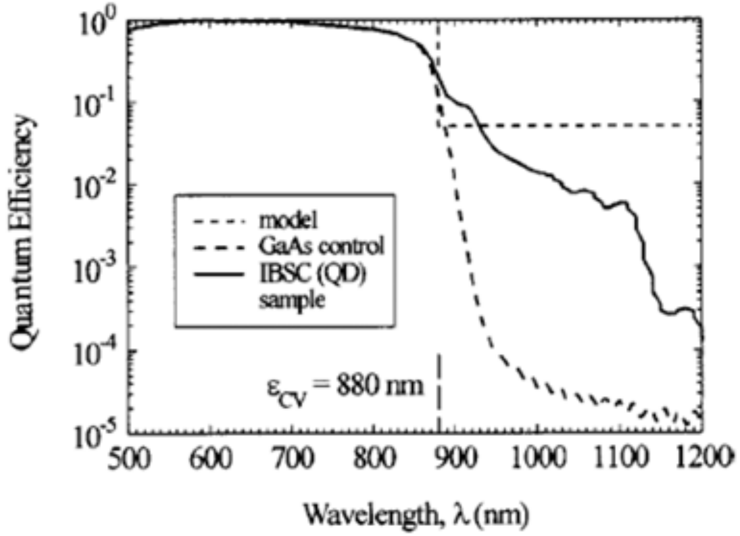








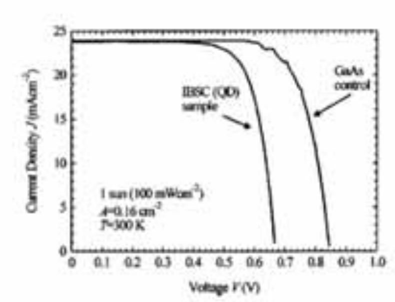




A. Luque, A. Martí, C. Stanley, N. López, L. Cuadra, D. Zhou y A. Mc-Kee, J. Appl. Phys. 96(1) 903, 2004.

QD-IB solar cells worldwide

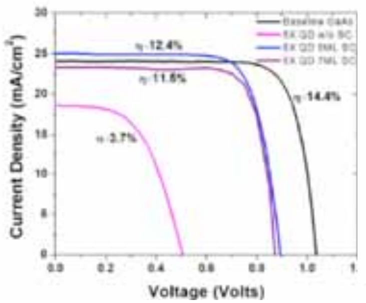
InAs/GaAs



•IES-UPM
•University of Glasgow

A. Luque et al., Journal of Applied Physics 96, 903 (2004).

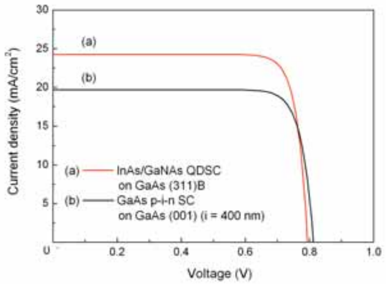
InAs/GaAs-GaP



•Rochester Institute of technology
•NASA

S. M. Hubbard et al., Applied Physics Letters 92, 123512 (2008).

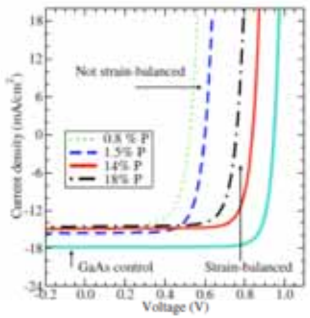
InAs/Ga(N)As



•University of Tokyo
•Univesity of Tsukuba

R. Oshima, A. Takata, and Y. Okada, Applied Physics Letters 93, 083111 (2008).

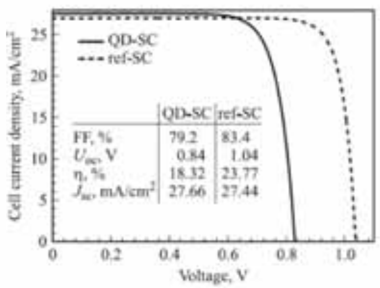
InAs/GaAs-GaP



•NREL

V. Popescu et al., Phys. Rev. B 78, 205321 (2008).

InAs/GaAs-GaP



•St. Petesrburg Tech. Institute
•IOFFE
•Innolume

C. A. Блохин et al., Physics and semiconductors technique 43, 537 (2009).

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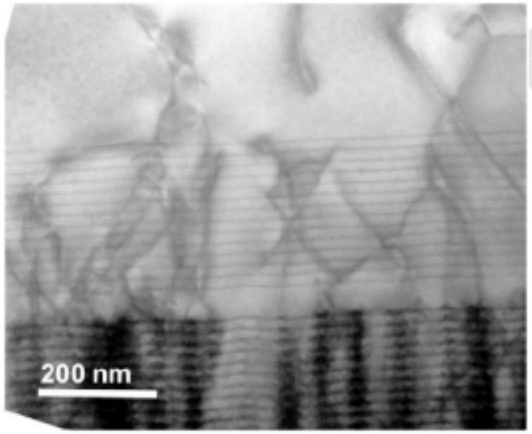
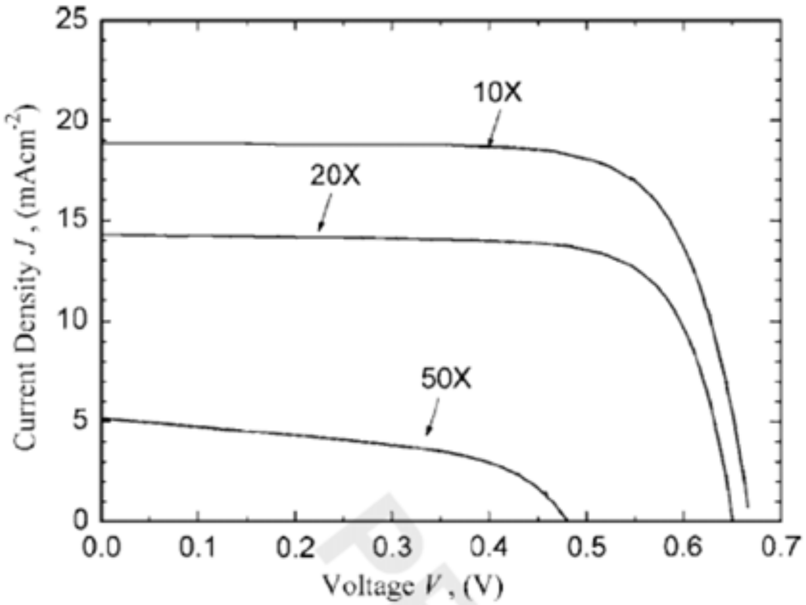
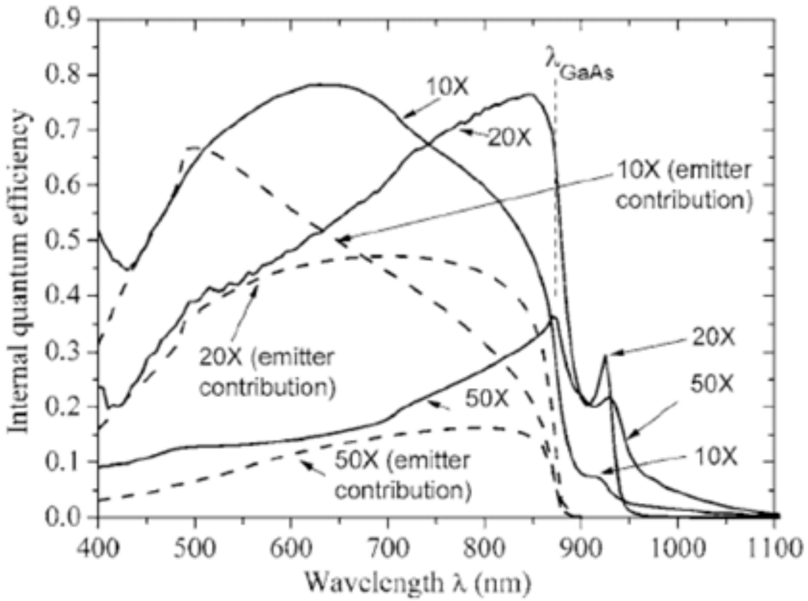
Strain destroys the emitter



In collaboration with:
University of
Glasgow

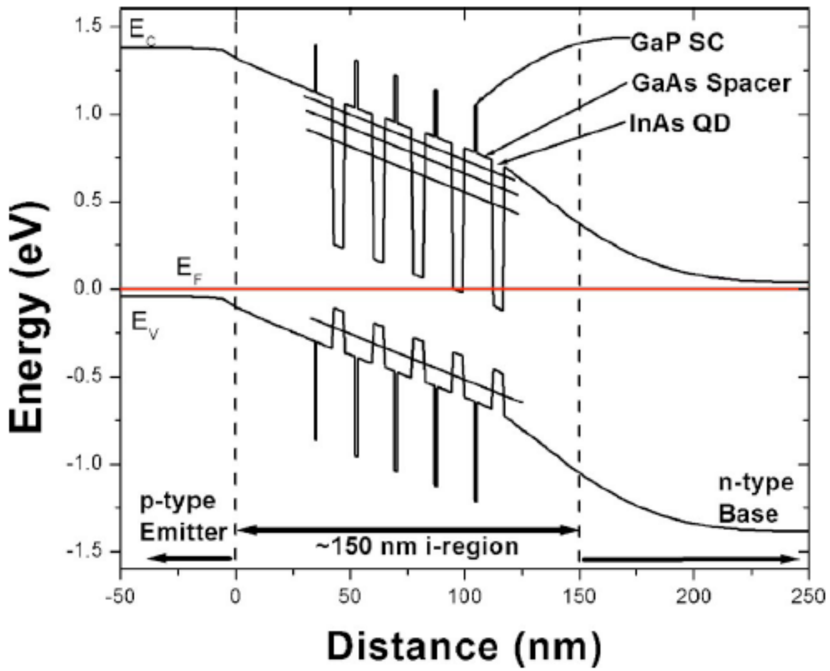


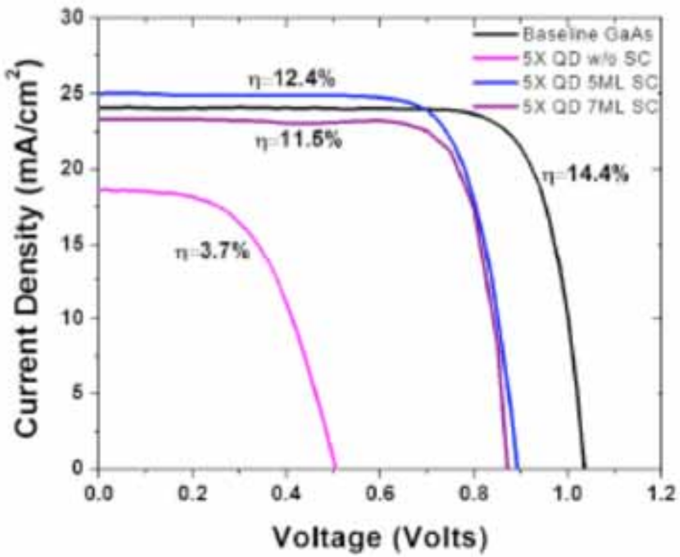


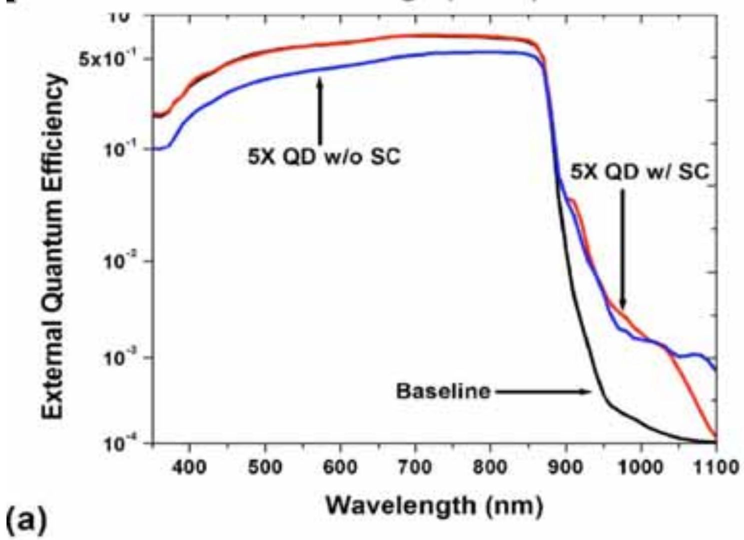
A. Marti et al., Applied Physics Letters **90**, 233510 (2007)

Better results with strain compensated QD

Rochester Inst. Tech + Nasa Glen



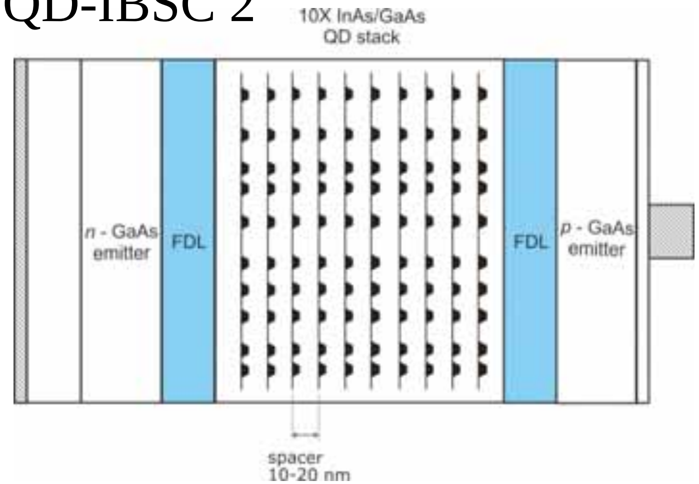




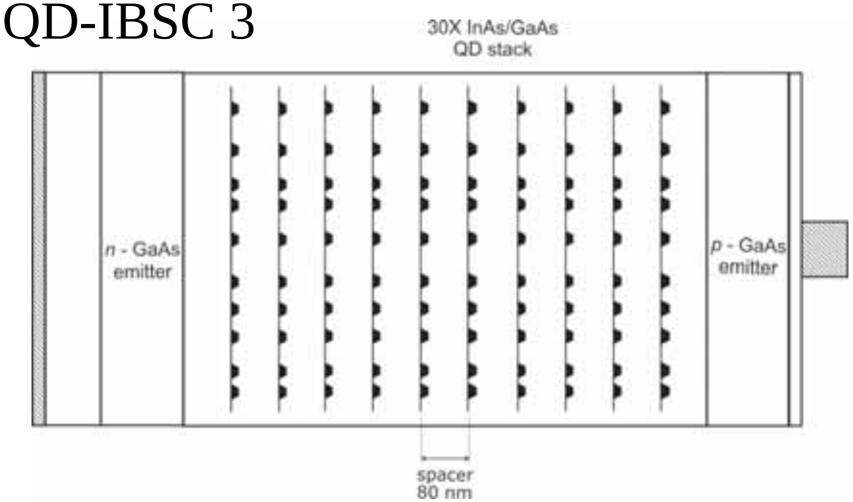
S. M. Hubbard, C. D. Cress, C. G. Bailey, R. P. Raffaelle, S. G. Bailey, and D. M. Wilt, APL 92 (2008)
S. M. Hubbard, C. G. Bailey, C. D. Cress, et al. Short circuit current enhancement… 33st IEEE PVSC, 2008

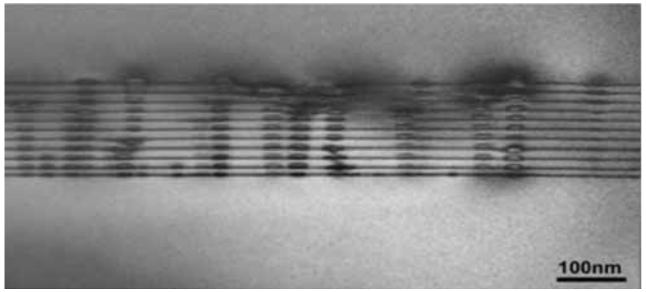
Alternative: stress relief by separating the QDs

QD-IBSC 2

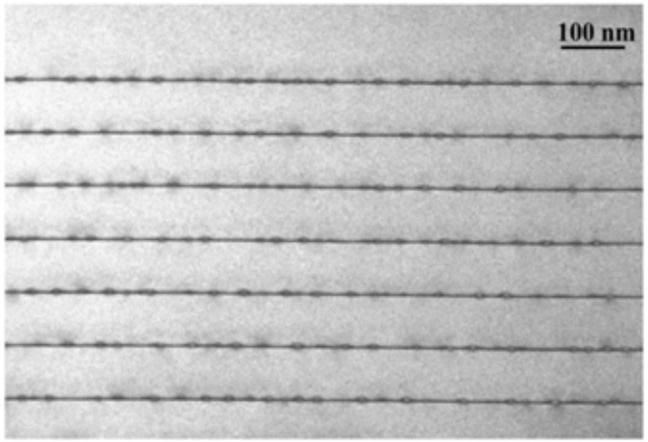


QD-IBSC 3



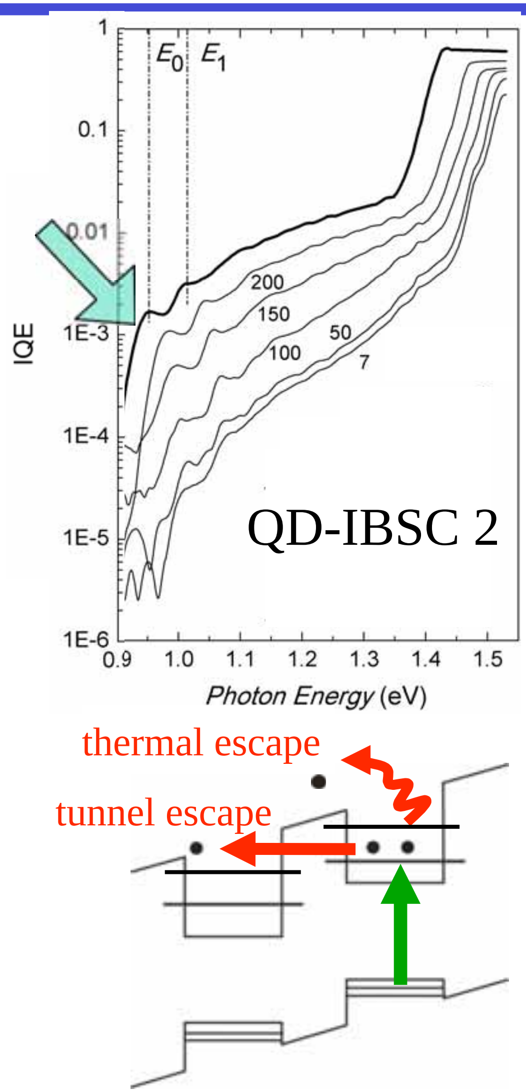


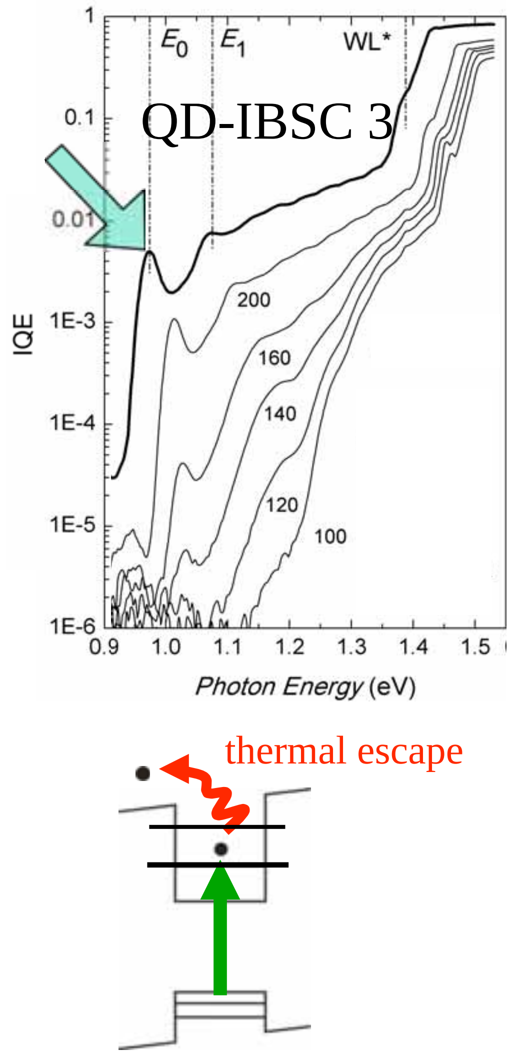
University of Glasgow UCA Universidad de Cádiz

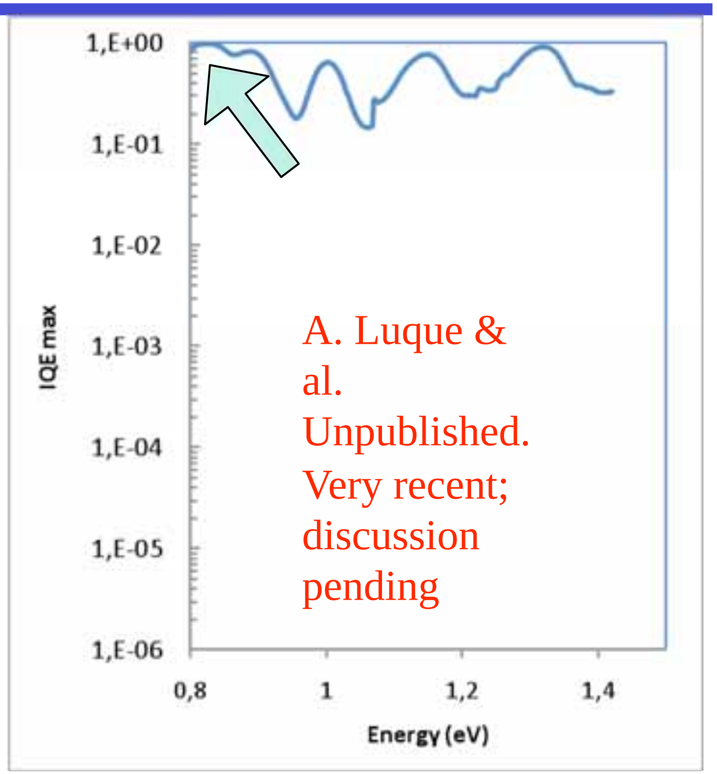


E. Antolín, A. Martí, C.D. Farmer *et al*. to be published in J. Appl. Phys (2010).

Increase of the IQE by spacer increase







Calculated absorption for full extraction

E. Antolín, A. Martí, C.D. Farmer *et al*. to be published in J. Appl. Phys (2010).

Envelope wavefuctions of the highest absorption states

Four band k·p method

$\left\|\Phi^{(cb)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(cb,S)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(cb,X)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(cb,Y)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(cb,Z)}_{1,1,1}\right\|^2$
$\left\|\Phi^{(hh)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(hh,S)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(hh,X)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(hh,Y)}_{1,1,1}\right\|^2$	$\left\|\Psi^{(hh,Z)}_{1,1,1}\right\|^2$

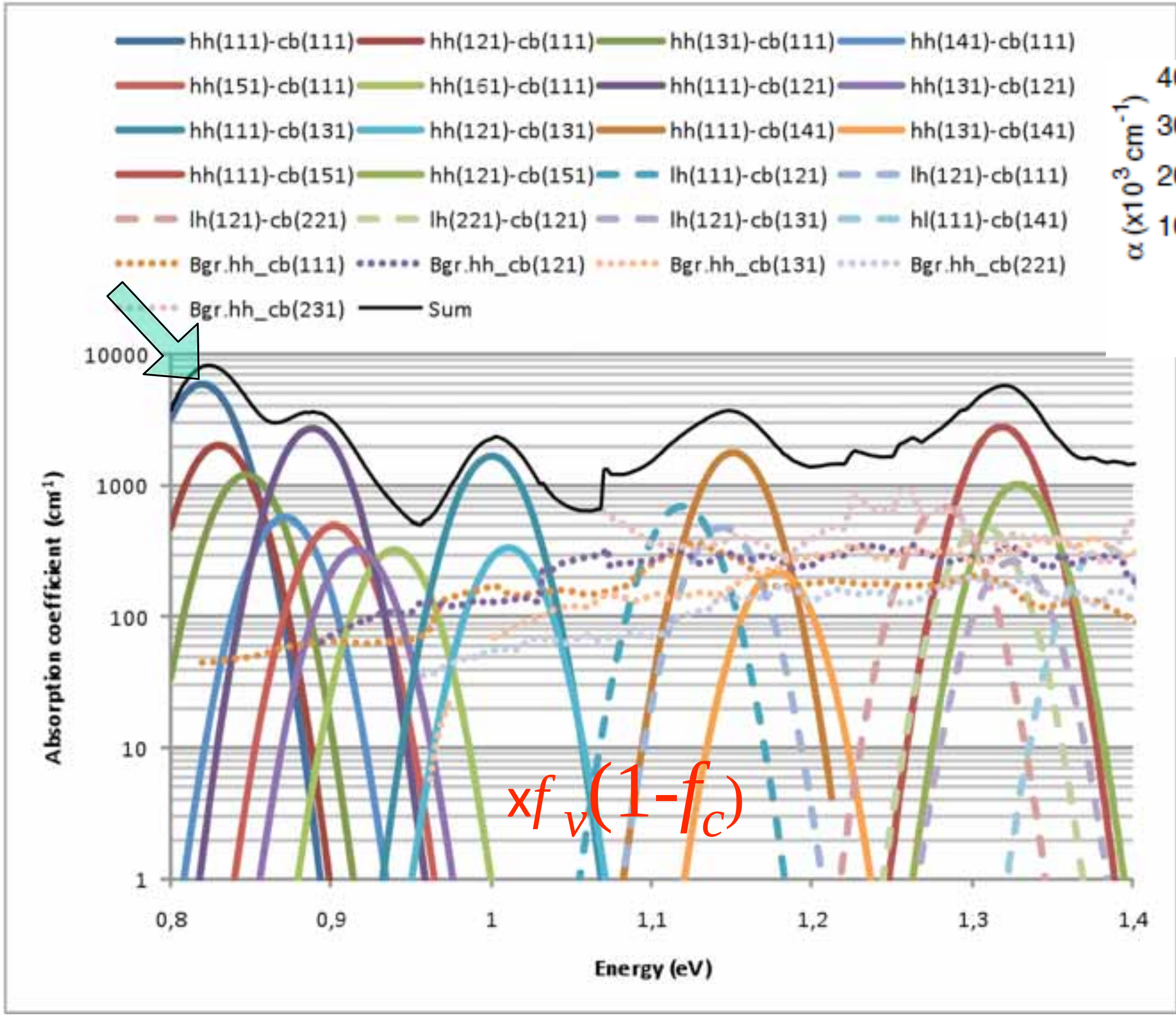
Figure 1. Contour plots of the wavefunction Φ of the diagonalized Hamiltonian in the fundamental state for the CB (cb) and the first excited sate for the light hole band (lh) and the envelope functions Ψ that project them onto $|S\rangle, |X\rangle, |Y\rangle, |Z\rangle$. The contours correspond to the 0.4% or the maximum density of probability (for Φ) for the (cb) and the (hh) bands respectively. The eight red dots are the corners of the QD. Contour not appearing means null or negligible projection

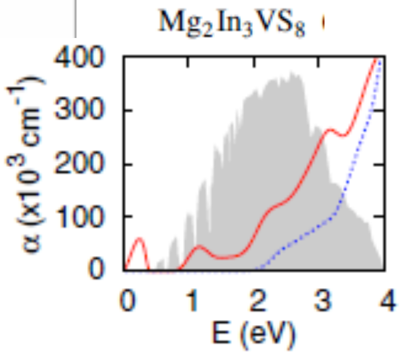
A. Luque & al. Unpublished

Quantum calculation of the sub-bandgap absorption

Coresponding to a layer density of QD of 10^{10} cm^{-2} and a separation between layers of 40 nm

delta E 25 meV, F=0.5



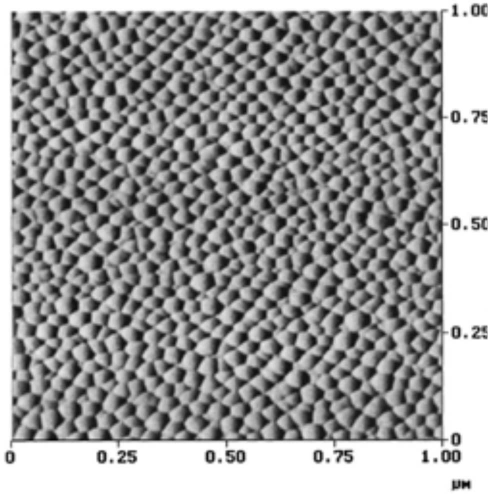


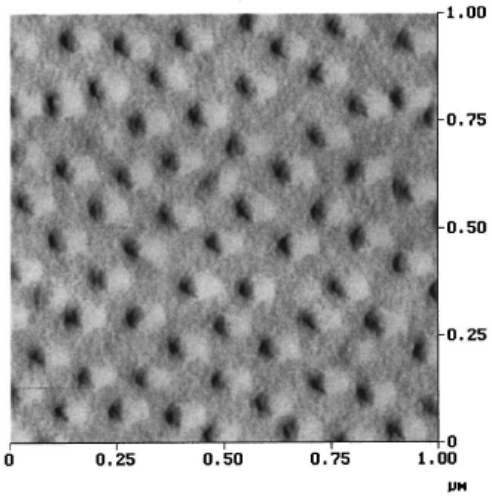
[P. Palacios, I. Aguilera, K. Sanchez, J.C. Conesa, and P. Wahnon, Transition-metal-substituted indium thiospinels as novel intermediate-band materials: Prediction and understanding of their electronic properties. Physical Review Letters 101 (2008) 046403

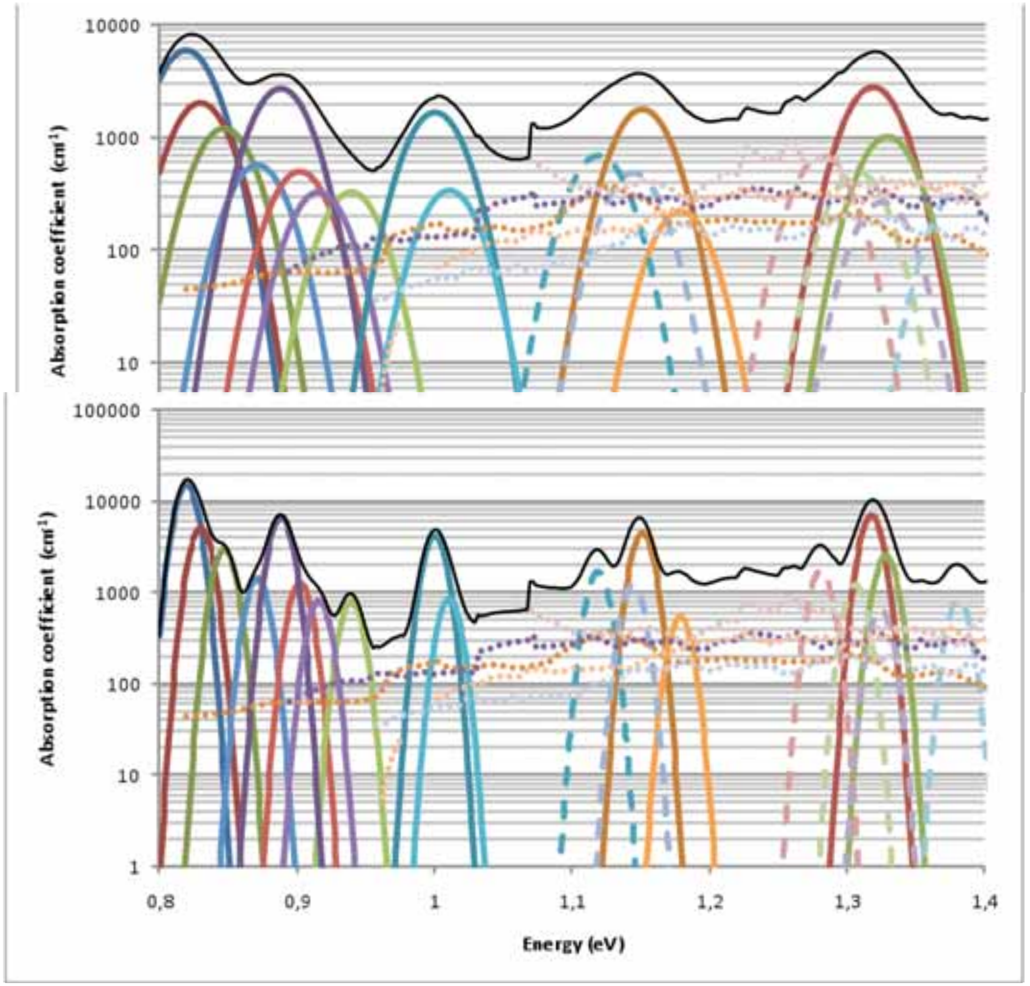
A. Luque & al. unpublished; Very recent; discussion pending

Preliminary discusion

THE UNIVERSITY OF TOKYO





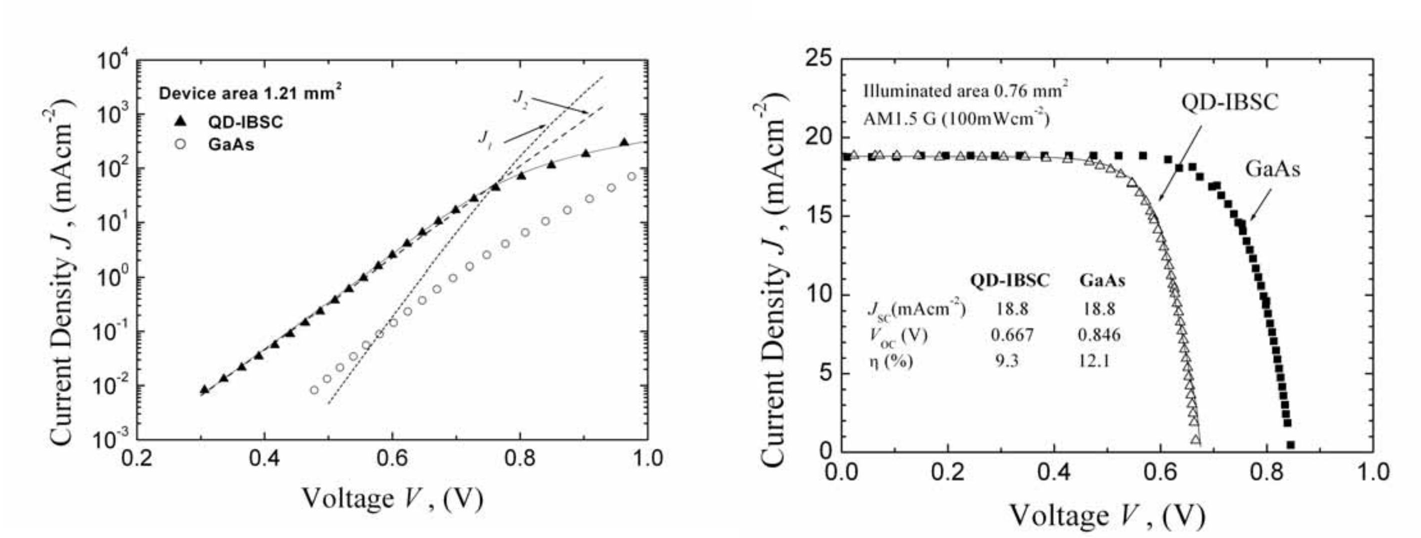


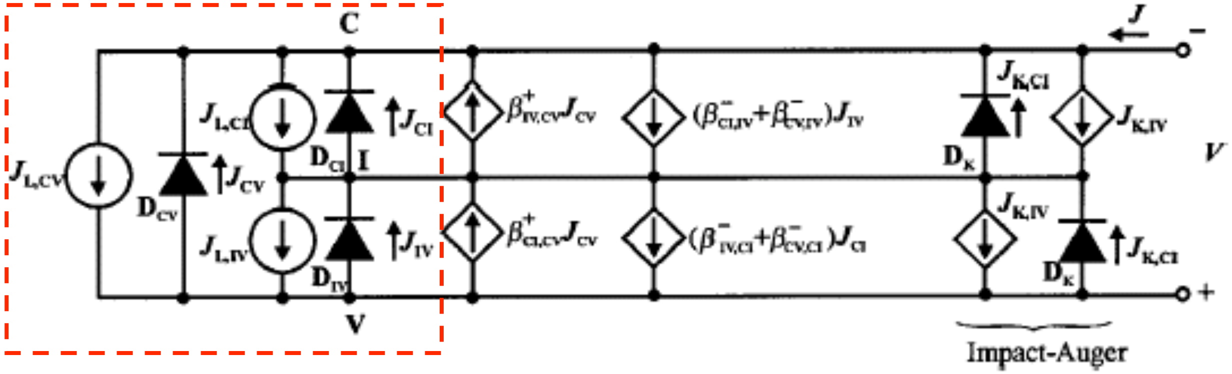
Delta
25 mev,
F=0.5

Delta
10 mev,
F=0.5

A. Luque, unpublished; K. Akahane *et al.*, *Applied Physics Letters* ***73, 3411 (1998).***

Generalized SRH model and explanation of the low IQE



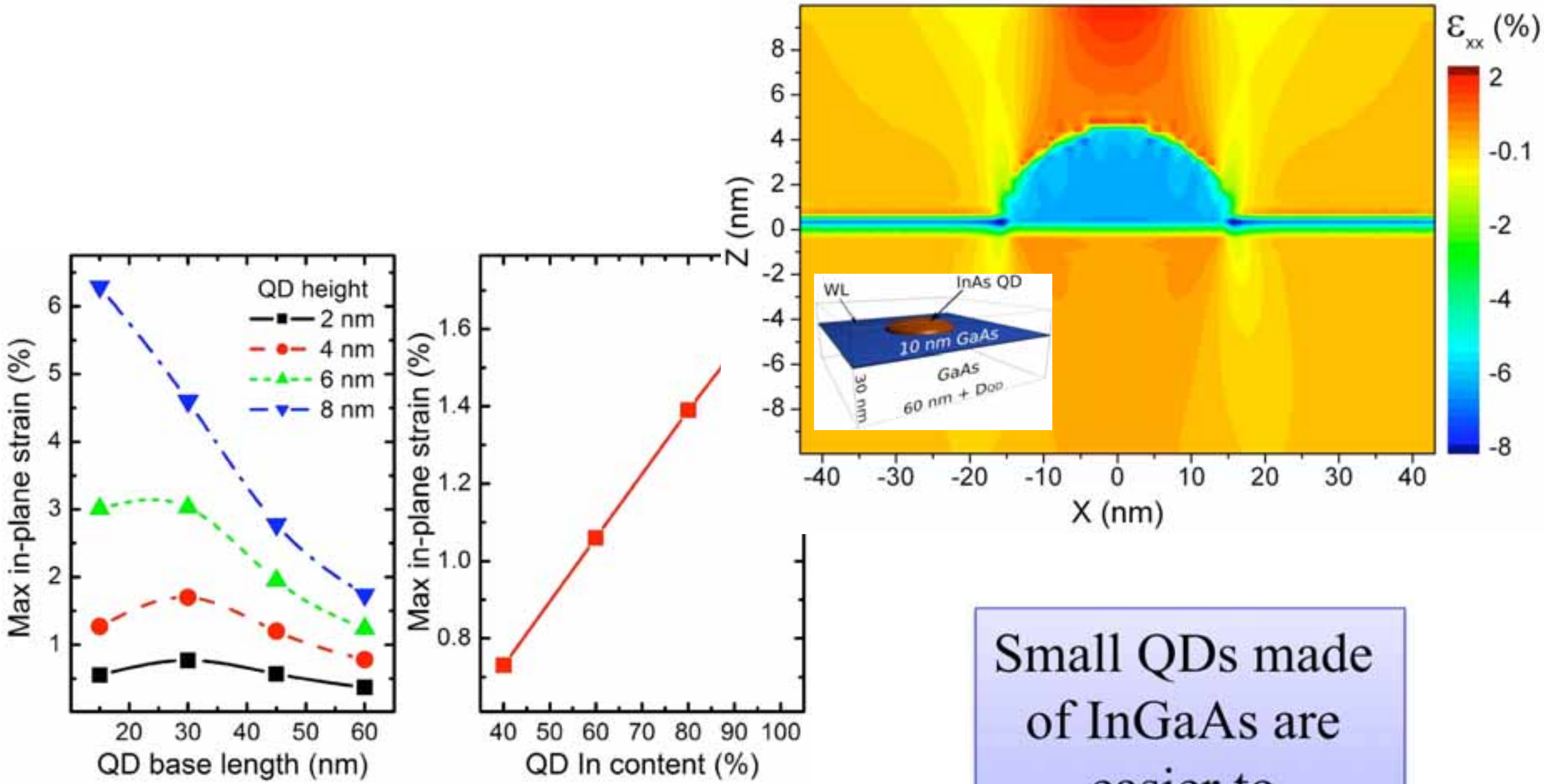


Hole lifetime (ps),	40.0
Electron lifetime (ps),	0.5

Better strain control needed?

A. Luque, A. Martí, N. López, et al., Journal of Applied Physics 99, 094503, (2006)

The inhomogeneous strain field



Small QDs made of InGaAs are easier to compensate

D. Alonso-Álvarez, J. M. Ripalda, B. Alén, A. G. Taboada, J. M. Llorens, Y. González, L. González, F. Briones, *Instituto de Microelectrónica de Madrid & Genesis FV Project meeting 2010/09/21*

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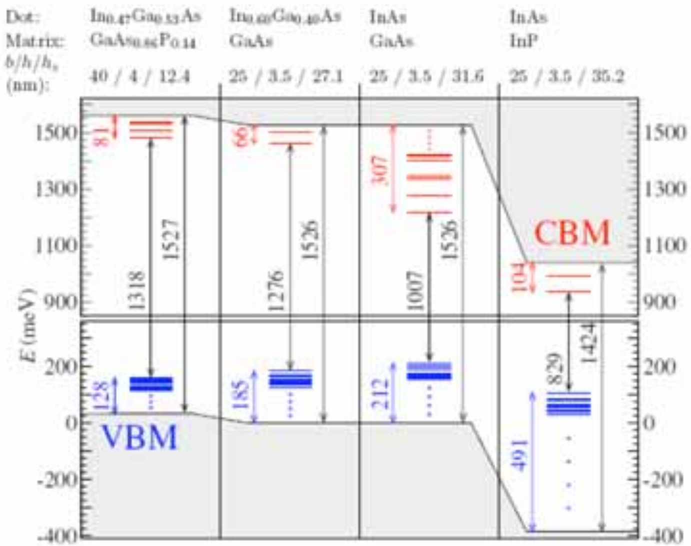
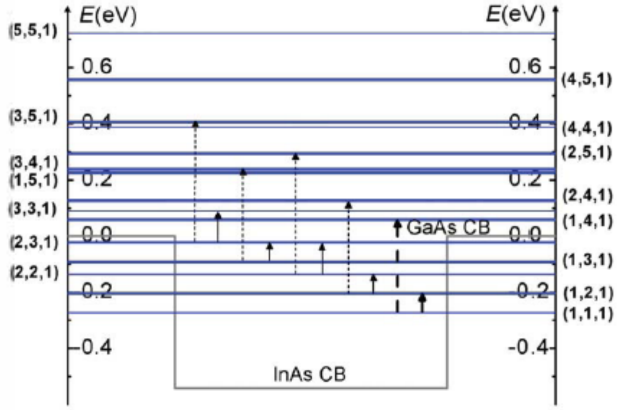
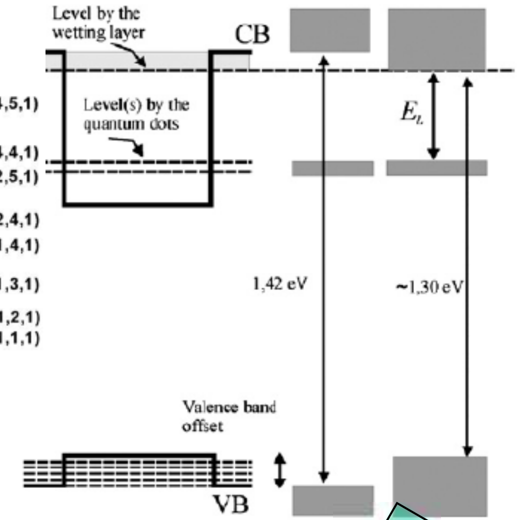
Bandgap spectroscopy and shrinkage

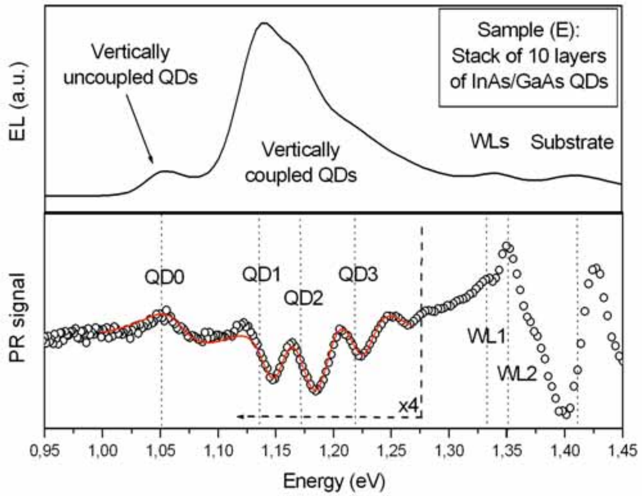


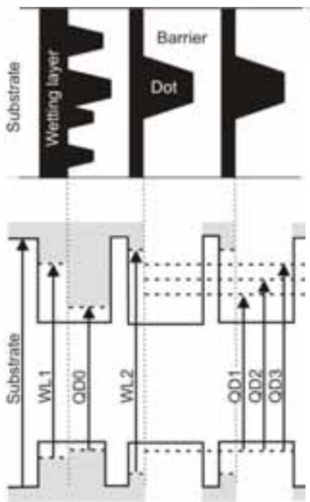
A. Luque et al, *Solar Energy Materials & Solar Cells* **94** (2010) 2032–2035.



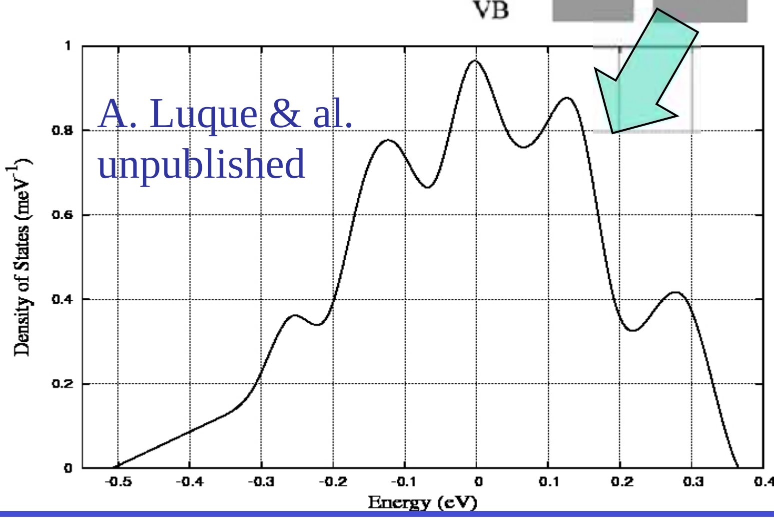
A. Marti *et al.*, *Thin Solid Films* ***516, 6716 (2008).***







A. Luque & al.
unpublished



E. Cánovas, A. Martí, N. López, et al, Thin Solid Films 516, 6943 (2008).

V. Popescu, G. Bester, M. C. Hanna, A. G. Norman, and A. Zunger, Physical Review B 78, 205321 (2008).

DB multilevel IB solar cell

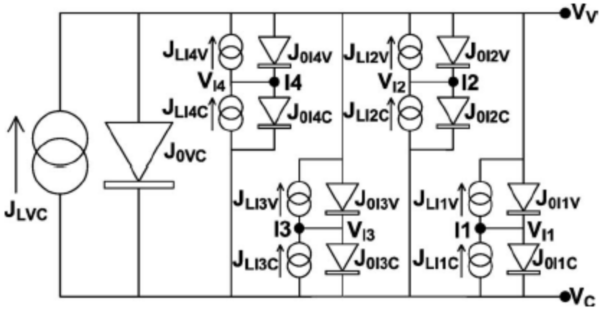


FIG. 2. Equivalent circuit for a four-level IBSC. The voltages correspond to the QFL at the different energy levels or bands, with a change of sign ($E_F = -eV$).

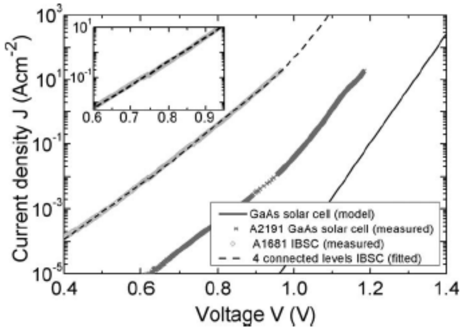


FIG. 5. Experimental J_L-V_{OC} of A2191, a single junction GaAs SC and A1681, a QD-IBSC. The fitted curve of a two exponential characteristic with the single QFL four-IB levels is also presented.

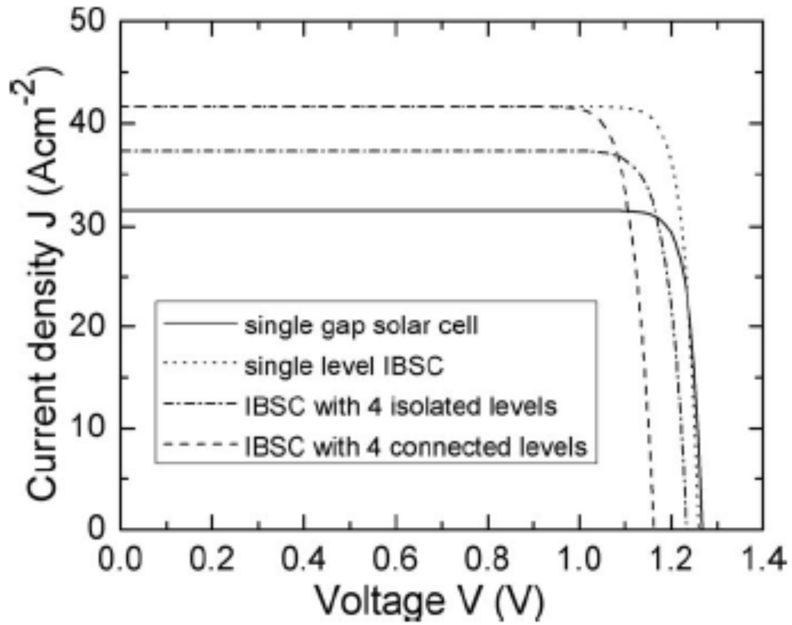
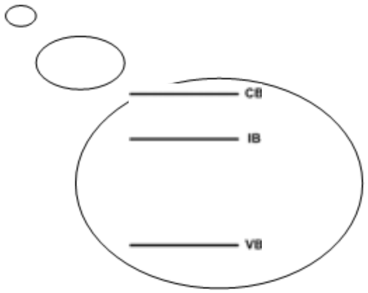


FIG. 3. Detailed balance *J*-*V* calculations for a single junction cell at C=1000 suns with an equivalent band gap of 1.35 eV for the following cases: IBSC with one level at 1.052 eV; IBSC with four isolated levels (and four QFLs) with energies at 1.052, 1.137, 1.175, and 1.225 eV; single QFL IBSC. A single gap SC *J*-*V* calculation without QD levels is also presented.

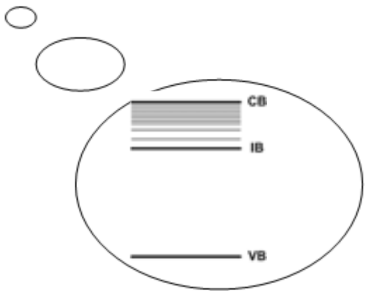
A. Luque, P. G. Linares, E. Antolín, E. Cánovas, C. D. Farmer, C. R. Stanley, and A. Martí, Applied Physics Letters **96, 013501 (2010).**

IB-CB strong thermal contact

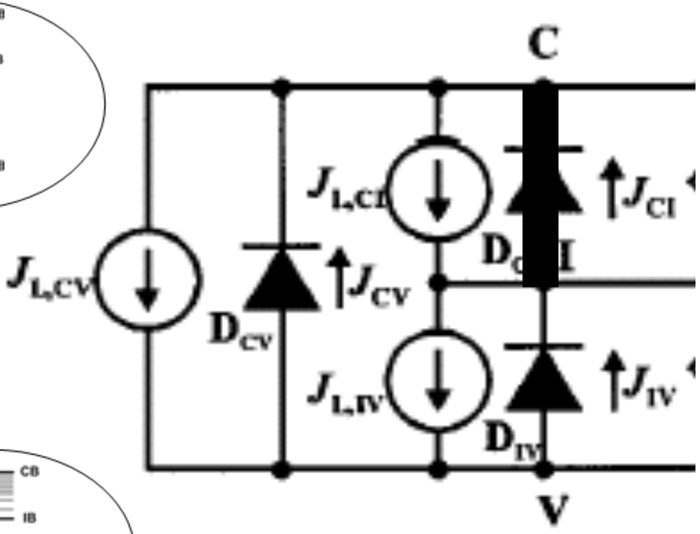
Disconnected:
$\sigma_e \sim 10^{-18}$ [cm^2]

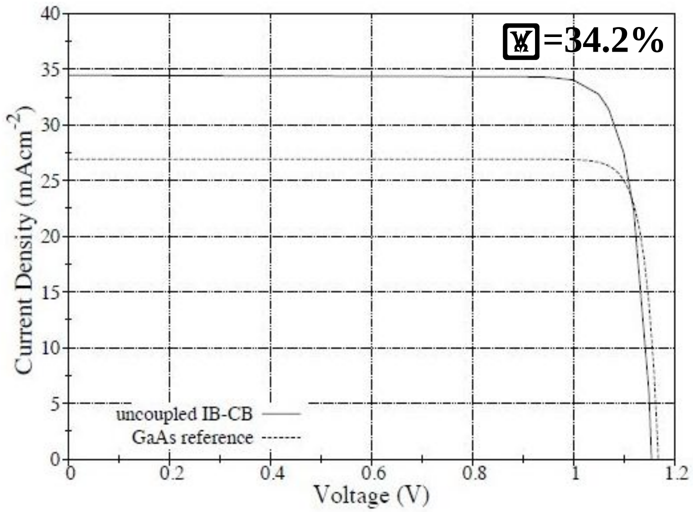


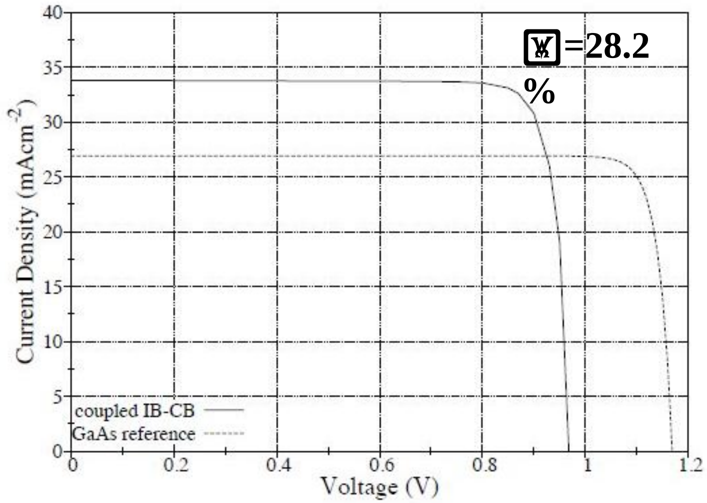
Connected:
$\sigma_e \sim 10^{-13}$ [cm^2]



Capture cross section







A. Luque and A. Martí, IEEE (2010)

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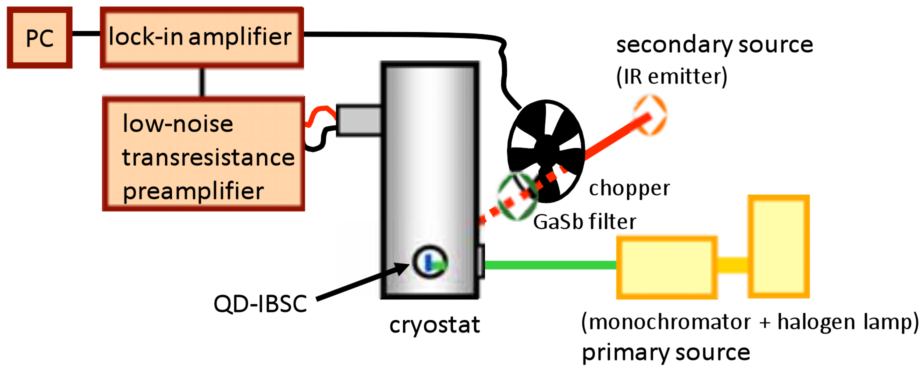
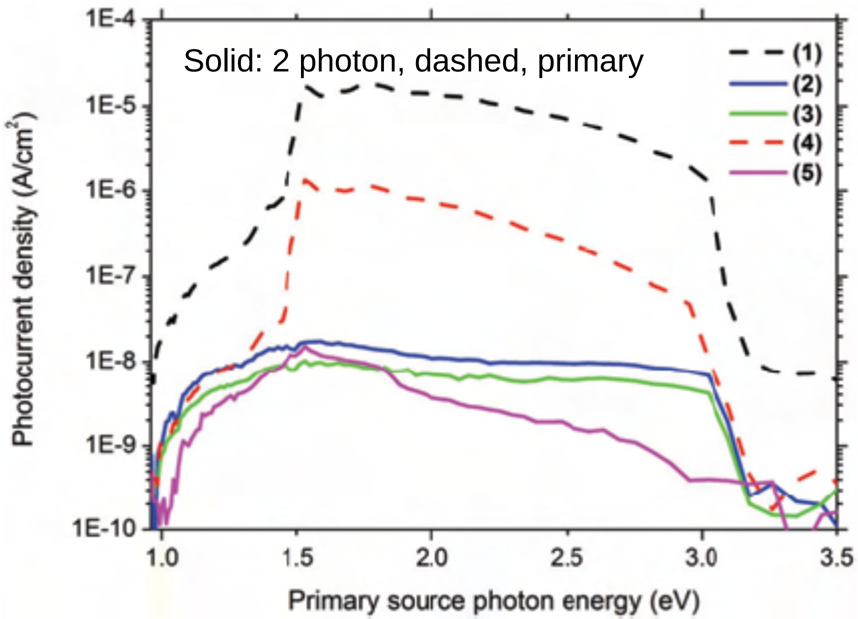
Evidence of two-photon photocurrent





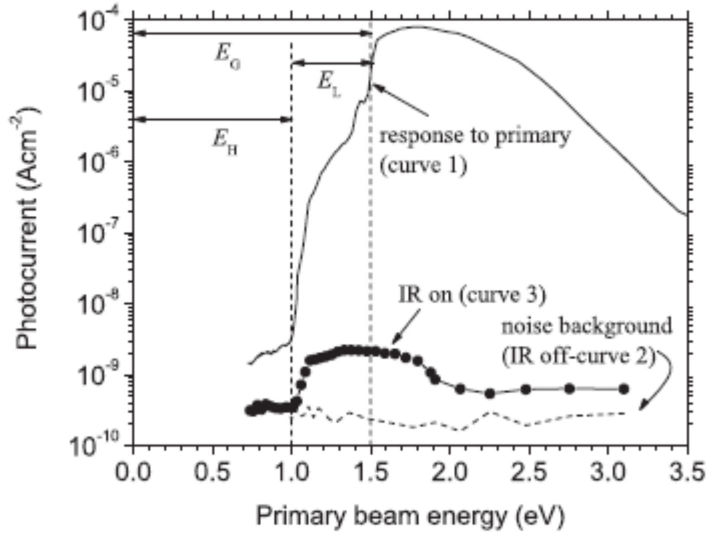


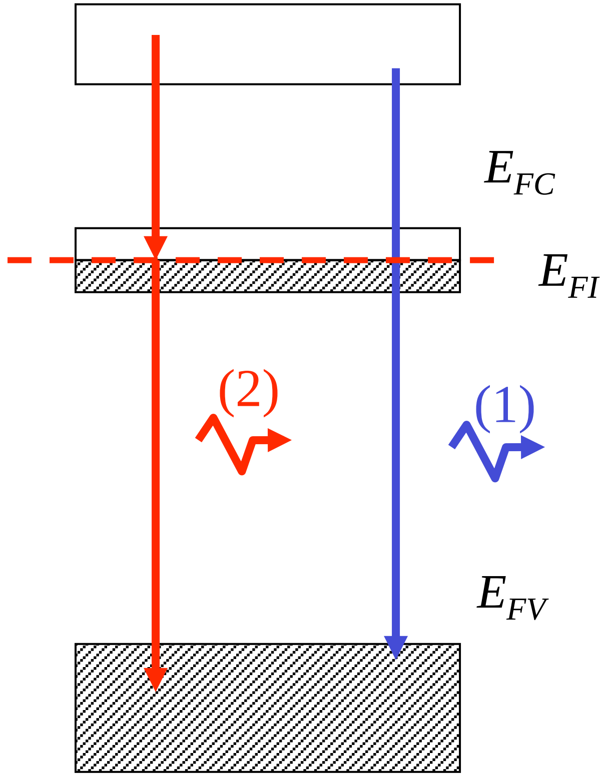
FIG. 3. Photocurrent produced in the QD-IBSC samples as a function of the energy of the photons of the primary light source. Curve 1 (response to primary) represents the photocurrent produced when pumping with the chopped primary source only ($V = -1.5$ V, $T = 4.2$ K). Curve 2 (noise background) is the photocurrent measured when the IR source is off while the chopper, located in front the of the IR source, is kept spinning ($V = 0$ V, $T = 36$ K). Curve 3 (IR on) is the photo-generated current when the IR source is turned on and chopped ($V = 0$ V, $T = 36$ K). Device junction area is 4 mm [2].

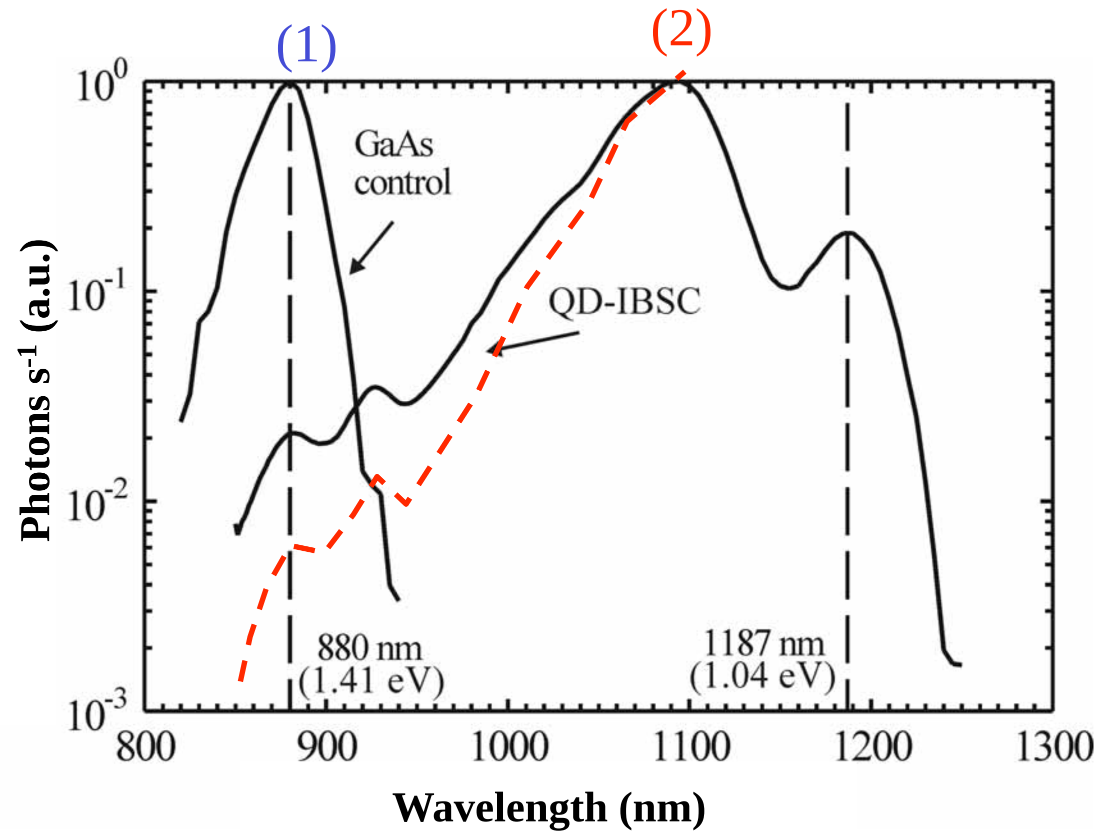
2 photon: blue, reference; green, reduced IR; purple, reduced primary

A. Marti, E. Antolin, C. R. Stanley, C. D. Farmer, N. Lopez, P. Diaz, E. Canovas, P. G. Linares, and A. Luque, Physical Review Letters **97, 247701-4 (2006).**

E. Antolín, A. Martí, C. R. Stanley, C. D. Farmer, E. Cánovas, N. López, P. G. Linares, and A. Luque, Thin Solid Films **516, 6919–6923 (2008).**

Quasi-Fermi level split

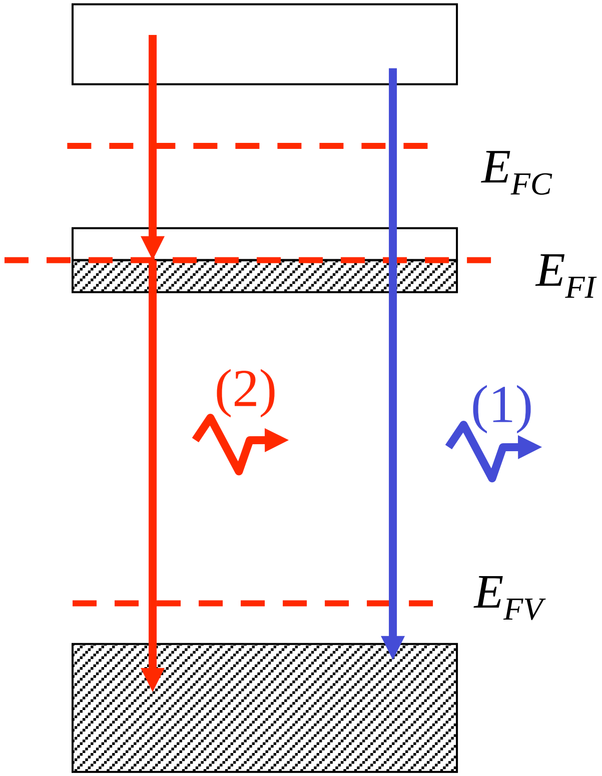


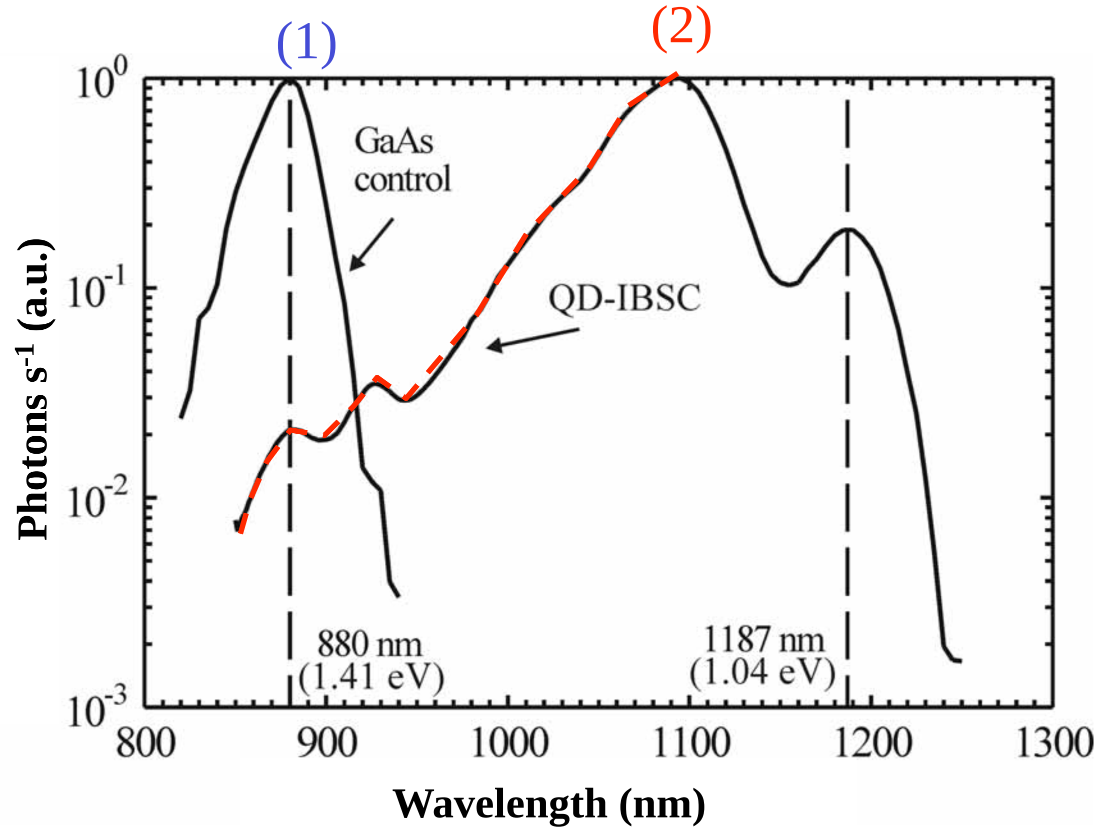


In collaboration with:
University of Glasgow

A. Luque, A. Martí, N. López, E. Antolín, E. Cánovas, C. Stanley, C. Farmer, L. J. Caballero, L. Cuadra y J. L. Balenzategui, Appl. Phys. Lett, 87(8):083505–7, 2005.

Quasi-Fermi level split





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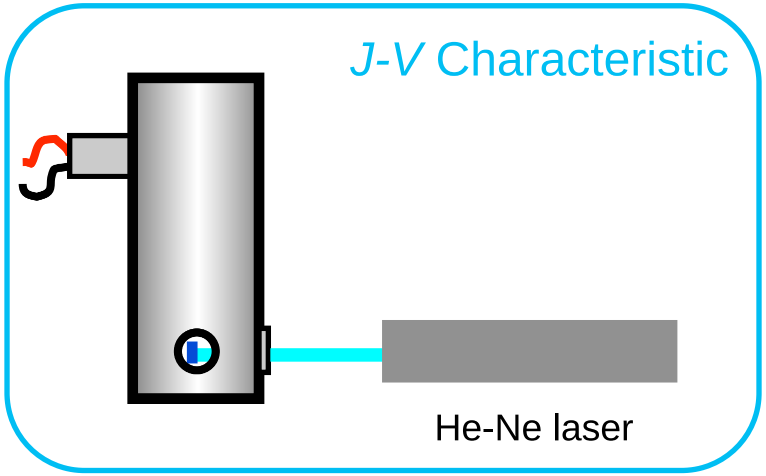
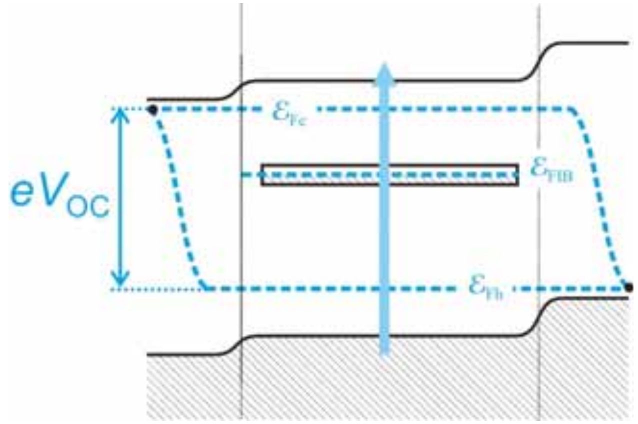
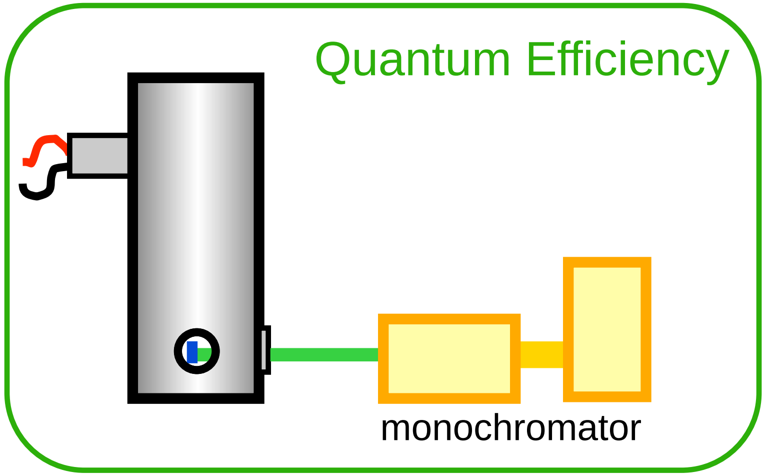
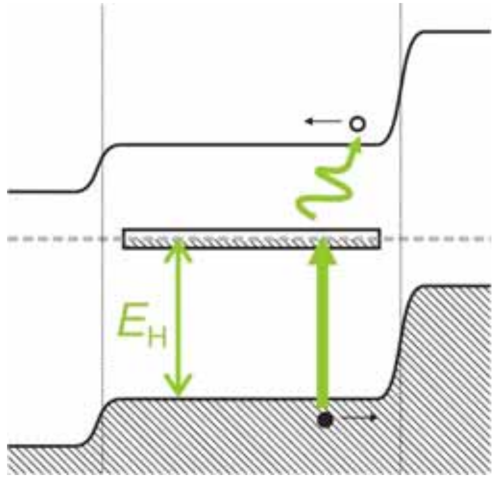
A. Luque, A. Martí, N. López, E. Antolín, E. Cánovas, C. Stanley, C. Farmer, L. J. Caballero, L. Cuadra y J. L. Balenzategui, Appl. Phys. Lett, 87(8):083505–7, 2005.

Test of voltage preservation



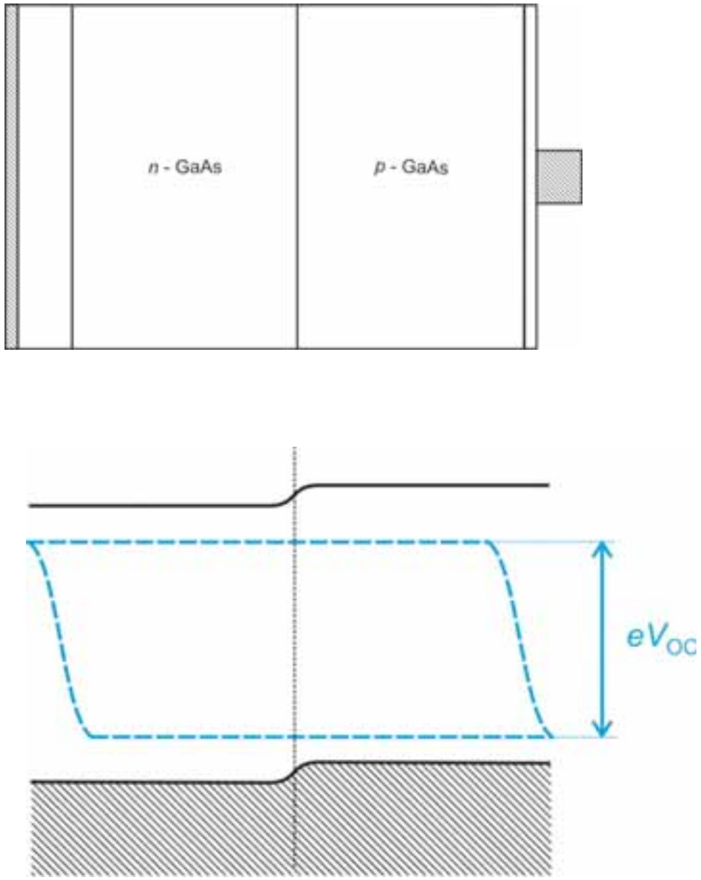




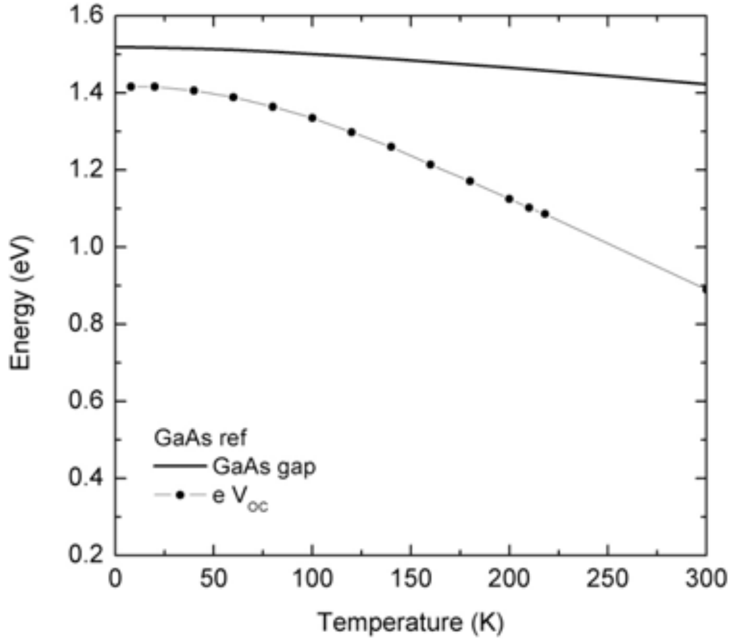


E. Antolín, A. Martí, P. G. Linares, I. Ramiro, E. Hernández, C. D. Farmer, C. R. Stanley, and A. Luque, in Proc.25 Photovoltaic Specialists Conference (IEEE, Honolulu, 2010).

Test of voltage preservation



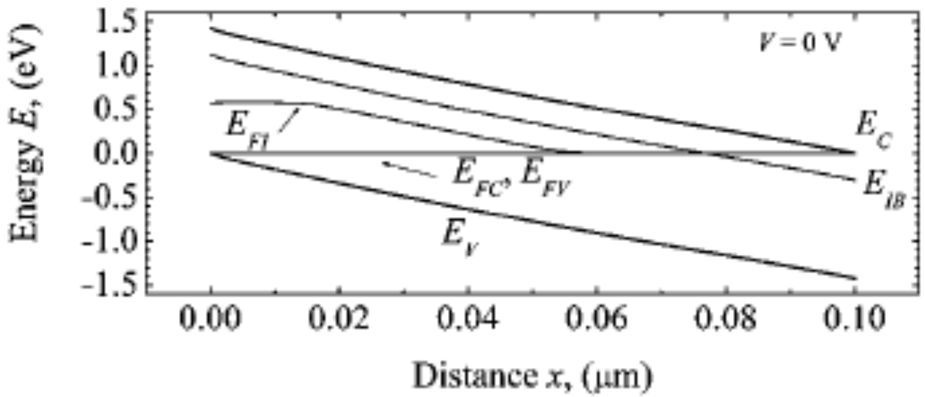
GaAs reference cell

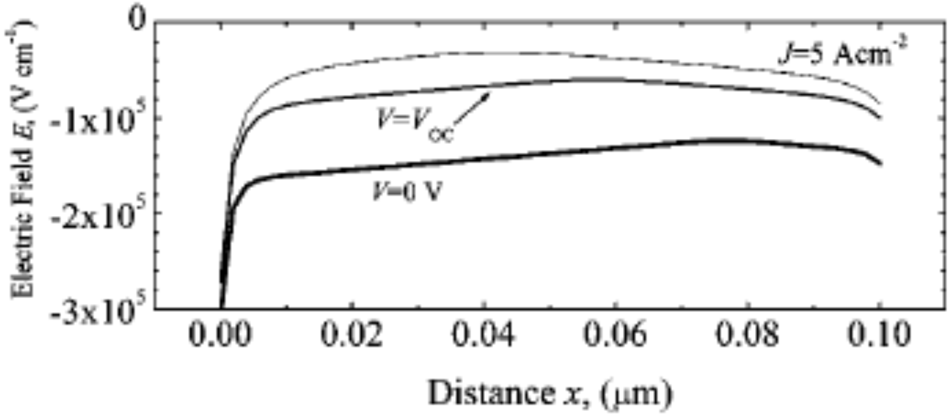


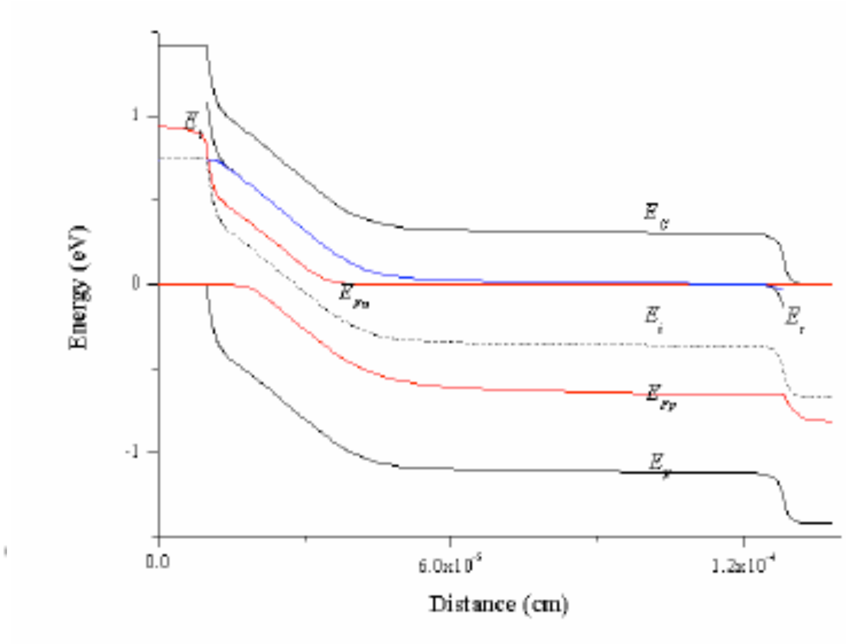
$$e\,V_{OC} < E_G$$

E. Antolín, A. Martí, P. G. Linares, I. Ramiro, E. Hernández, C. D. Farmer, C. R. Stanley, and A. Luque, in Proc.25 Photovoltaic Specialists Conference (IEEE, Honolulu, 2010).

Electric field in IB cell





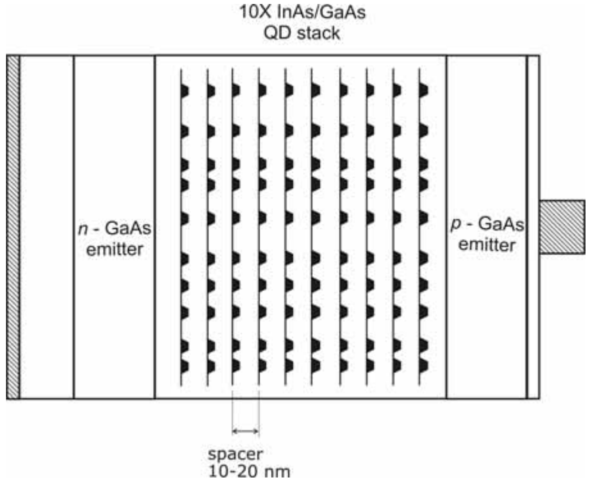


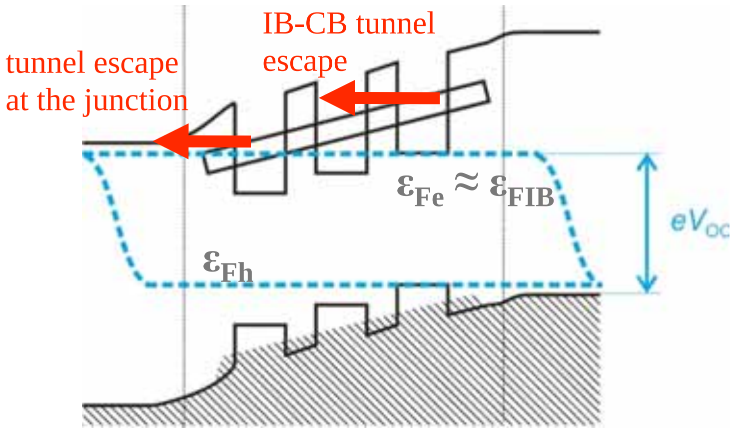
I. Tobías et al. ***Semiconductor Science and Technology,issue in honor Nobel Laur. Z I Alferov; in the press.***

A. Luque, and A. Marti, IEEE Transactions on Electron Devices **57, 1201 (2010).**

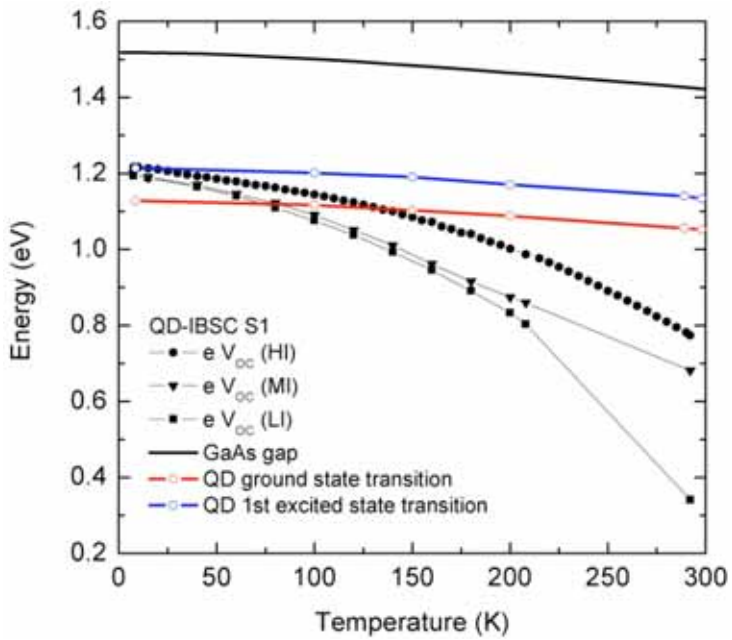
A. Luque *et al., Journal of Applied Physics* ***99, 094503 (2006).***

Test of voltage preservation





QD-IBSC 1

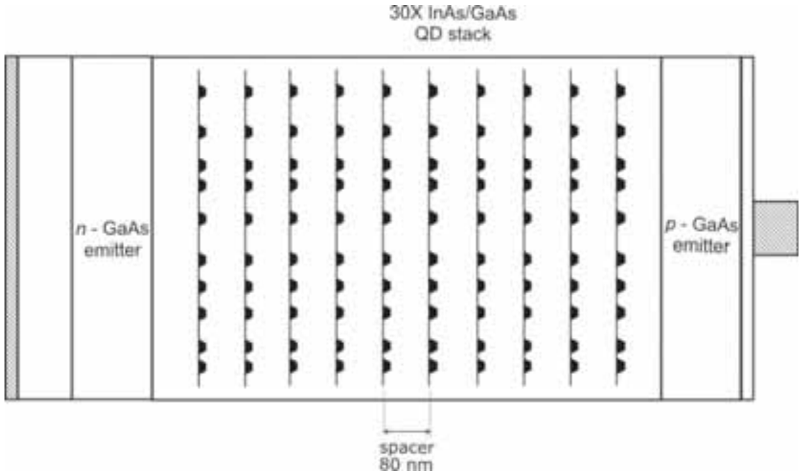


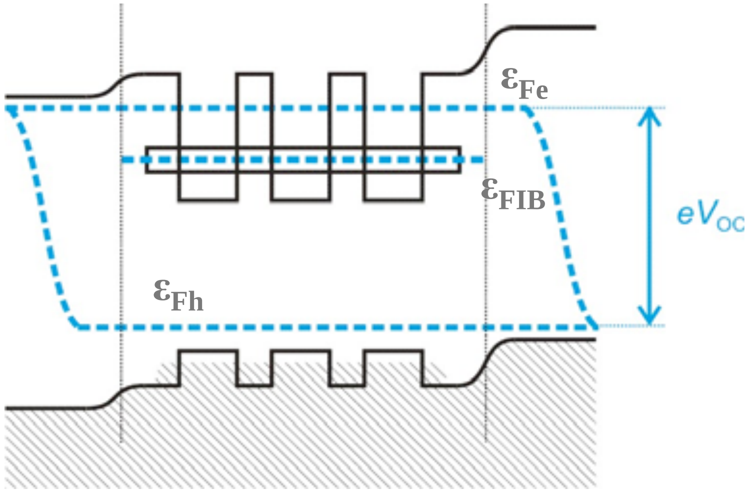
$$e\,V_{OC} \leq 1.2 \text{ eV}$$

✕ tunnel escape short-circuits IB - CB

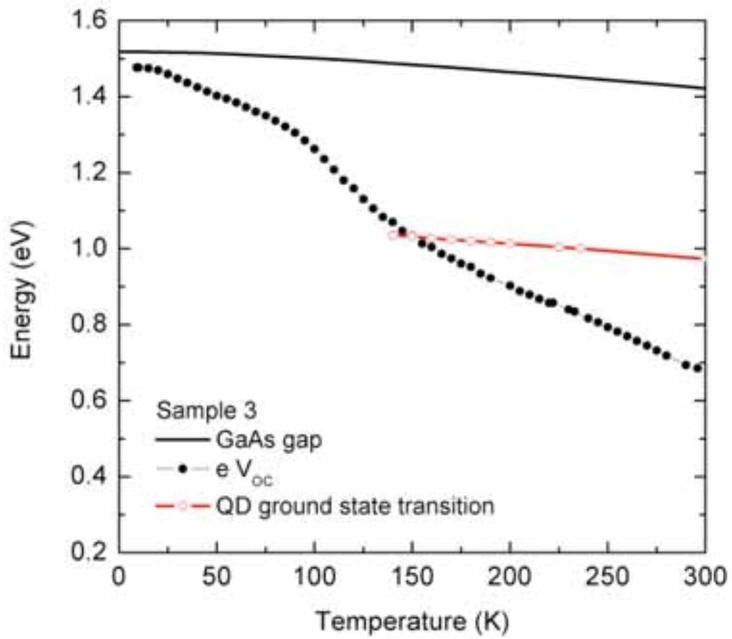
E. Antolín, A. Martí, P. G. Linares, I. Ramiro, E. Hernández, C. D. Farmer, C. R. Stanley, and A. Luque, in Proc.25 Photovoltaic Specialists Conference (IEEE, Honolulu, 2010).

Test of voltage preservation





QD-IBSC 3
(with InAlGaAs capping)



$E_H < e\,V_{OC} < E_G$

✓ voltage preservation

E. Antolín, A. Martí, P. G. Linares, I. Ramiro, E. Hernández, C. D. Farmer, C. R. Stanley, and A. Luque, in Proc.25 Photovoltaic Specialists Conference (IEEE, Honolulu, 2010).

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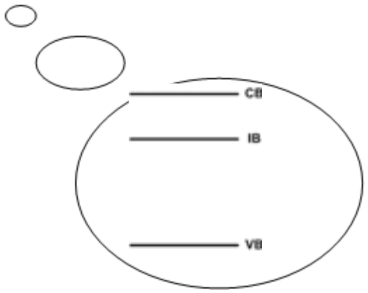
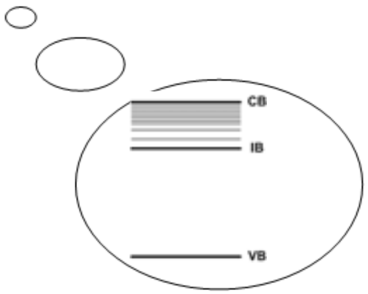
IB-CB strong thermal contact

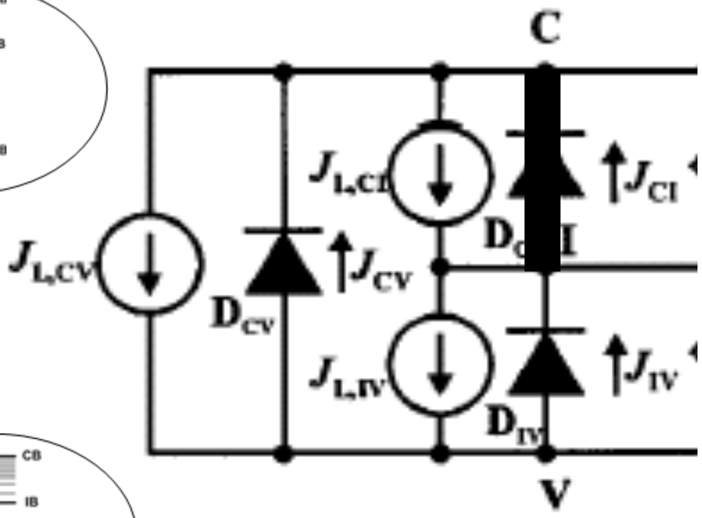
Disconnected:
$\sigma_e \sim 10^{-18}$ [cm^2]

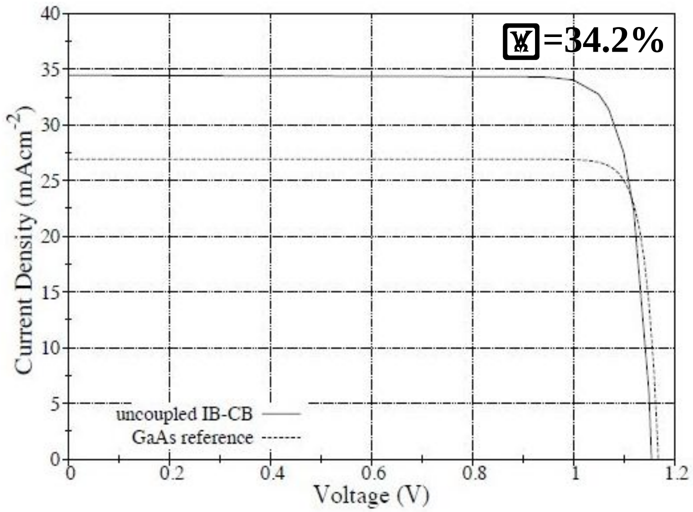


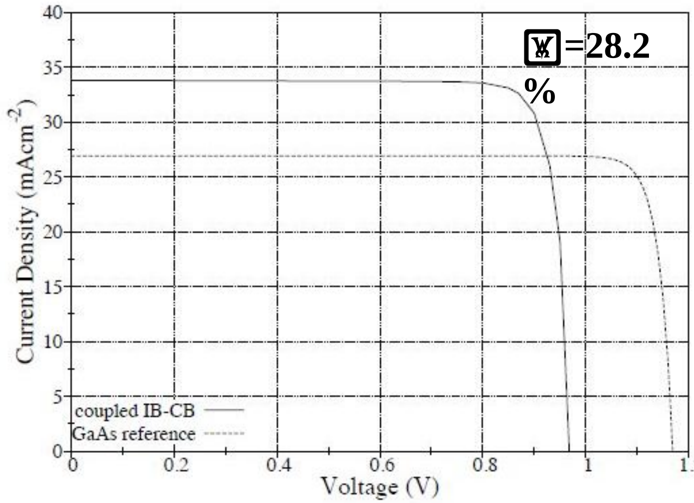
Connected:
$\sigma_e \sim 10^{-13}$ [cm^2]



Capture cross section







A. Luque and A. Martí, IEEE (2010)

Low absorption in IB→CB transitions in QDs

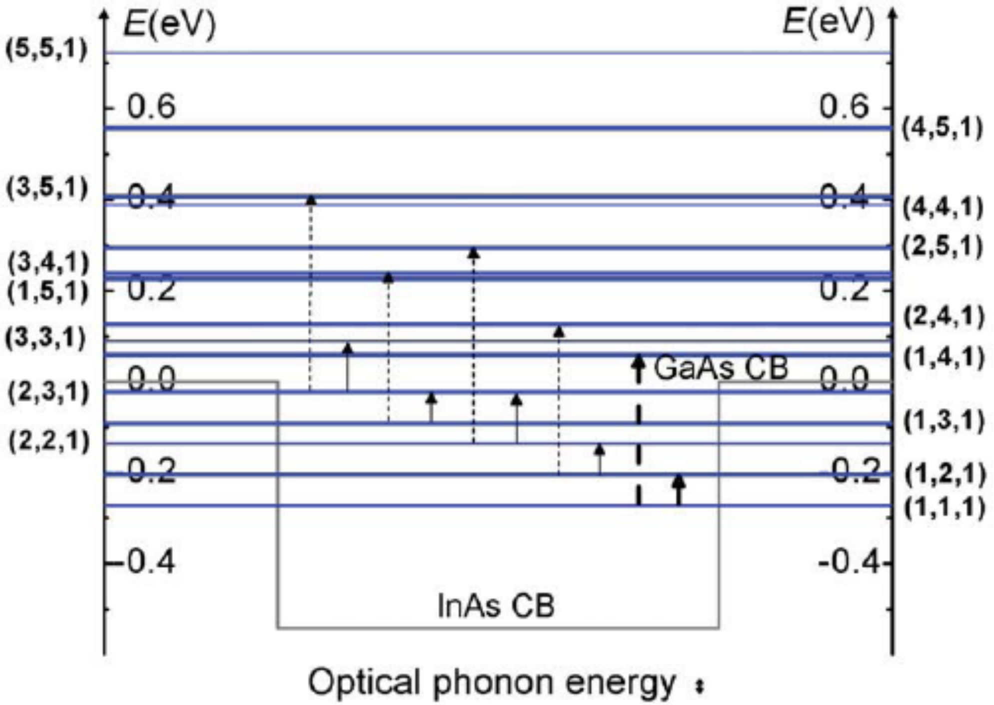
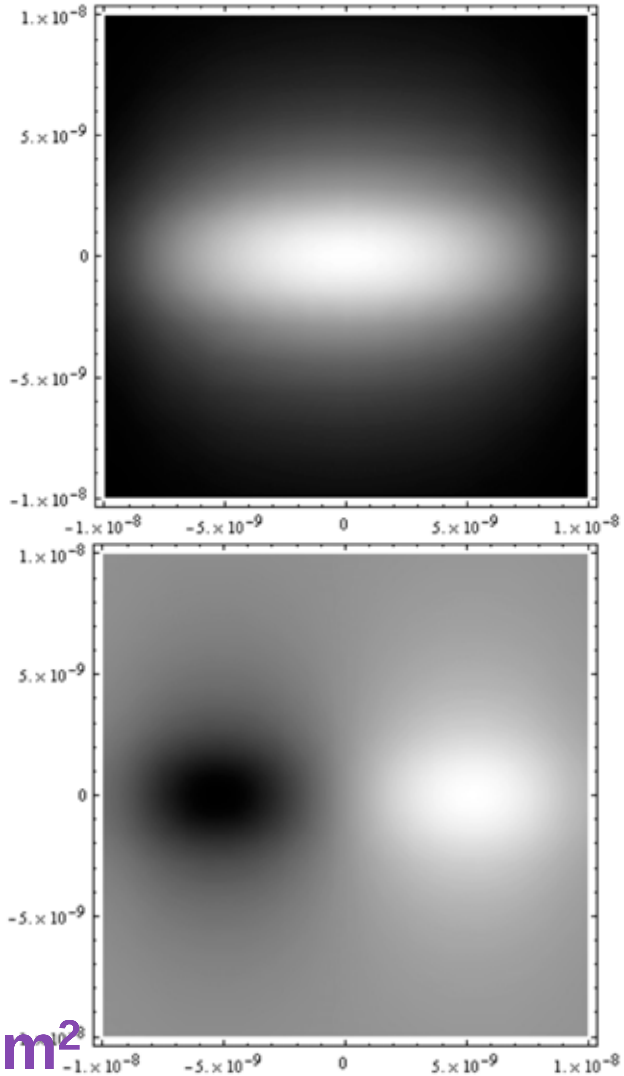


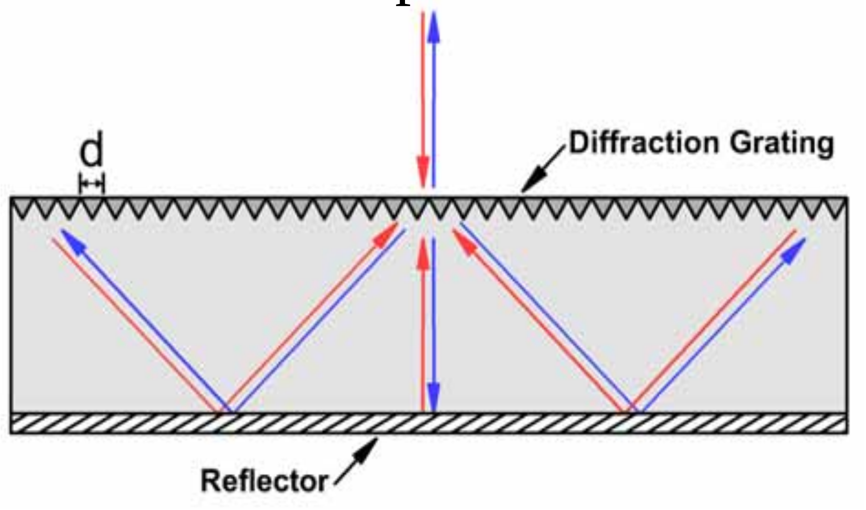
Fig. 2. Horizontal lines: confined state energy levels in an InAs QD in GaAs; thick lines are double degenerated (besides spin degeneracy). Solid/dashed vertical arrows: strong/weak permitted optical absorptions departing from negative energy levels. Thick arrows for absorptions departing from the fundamental state. The energy of an optical phonon is drawn for comparison.

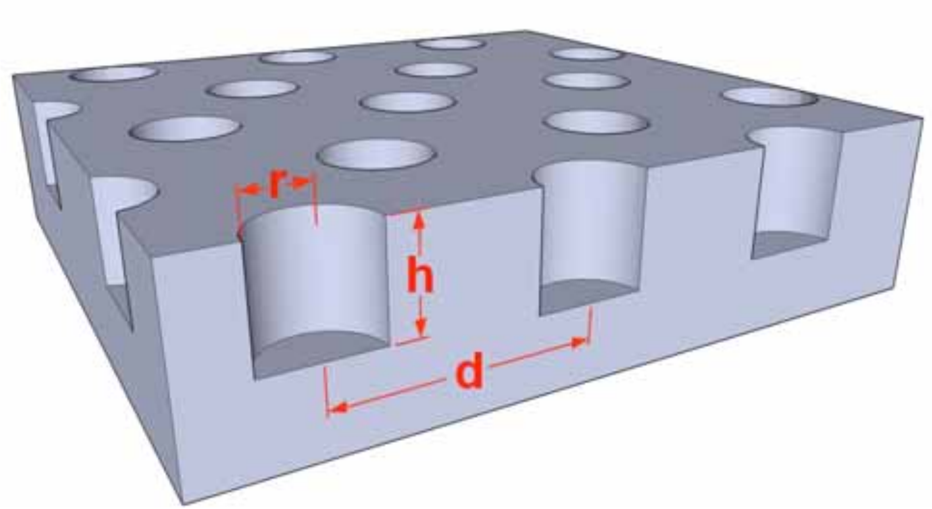


Solution: to change the size form present 3.5X16X16 nm^2 to 6X7.3X7.3 nm^2

A. Luque, A. Marti, E. Antolin, and P. Garcia-Linares, Intraband Absorption for Normal Illumination in Quantum Dot Intermediate Band Solar Cells. Solar Energy Materials & Solar Cells 94 (2010) 2032–2035.

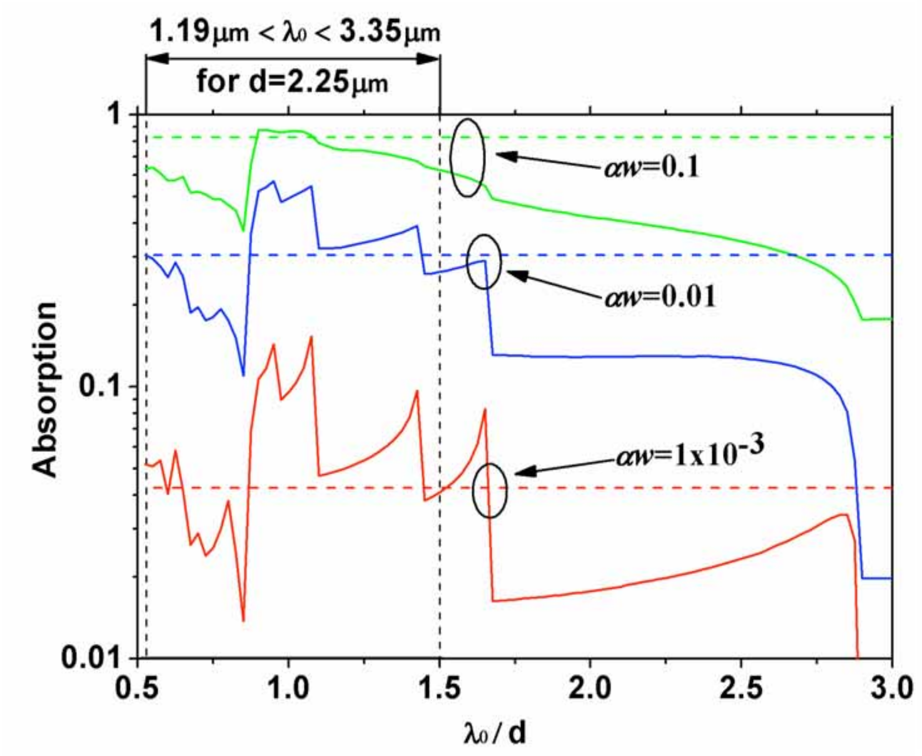
Simulated cell structure and grating profile

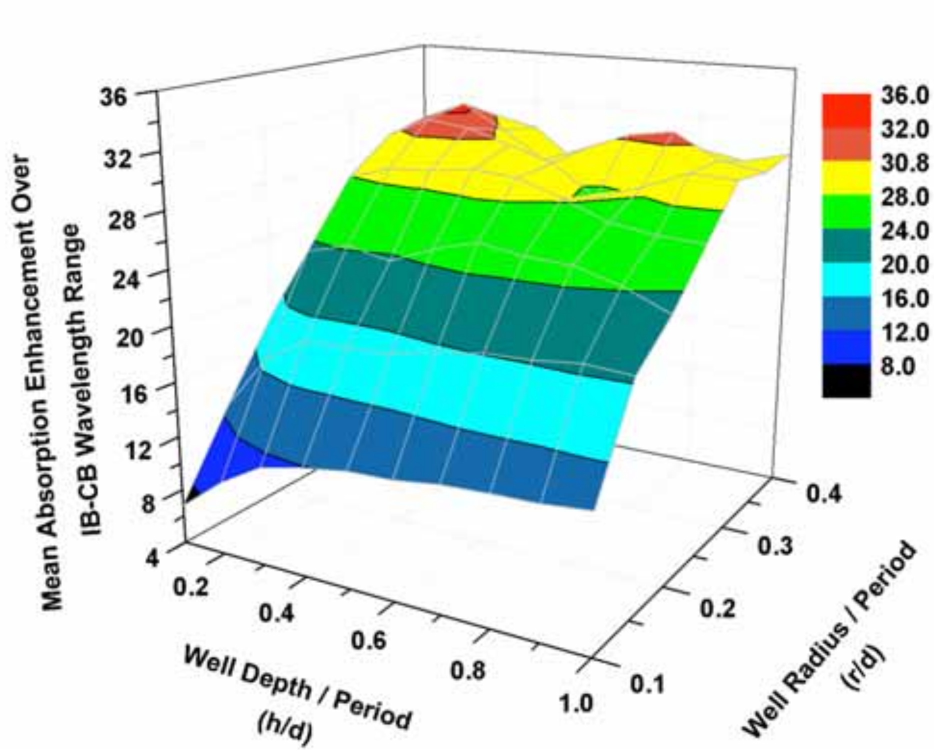




Mellor A. Tobías I. Martí A. Luque A., "Light Trapping Properties of Cylindrical Well Diffraction Gratings in Solar Cells: Computational Calculations", 25th PVSEC Proceedings, Valencia (2010)

Light management (far field)

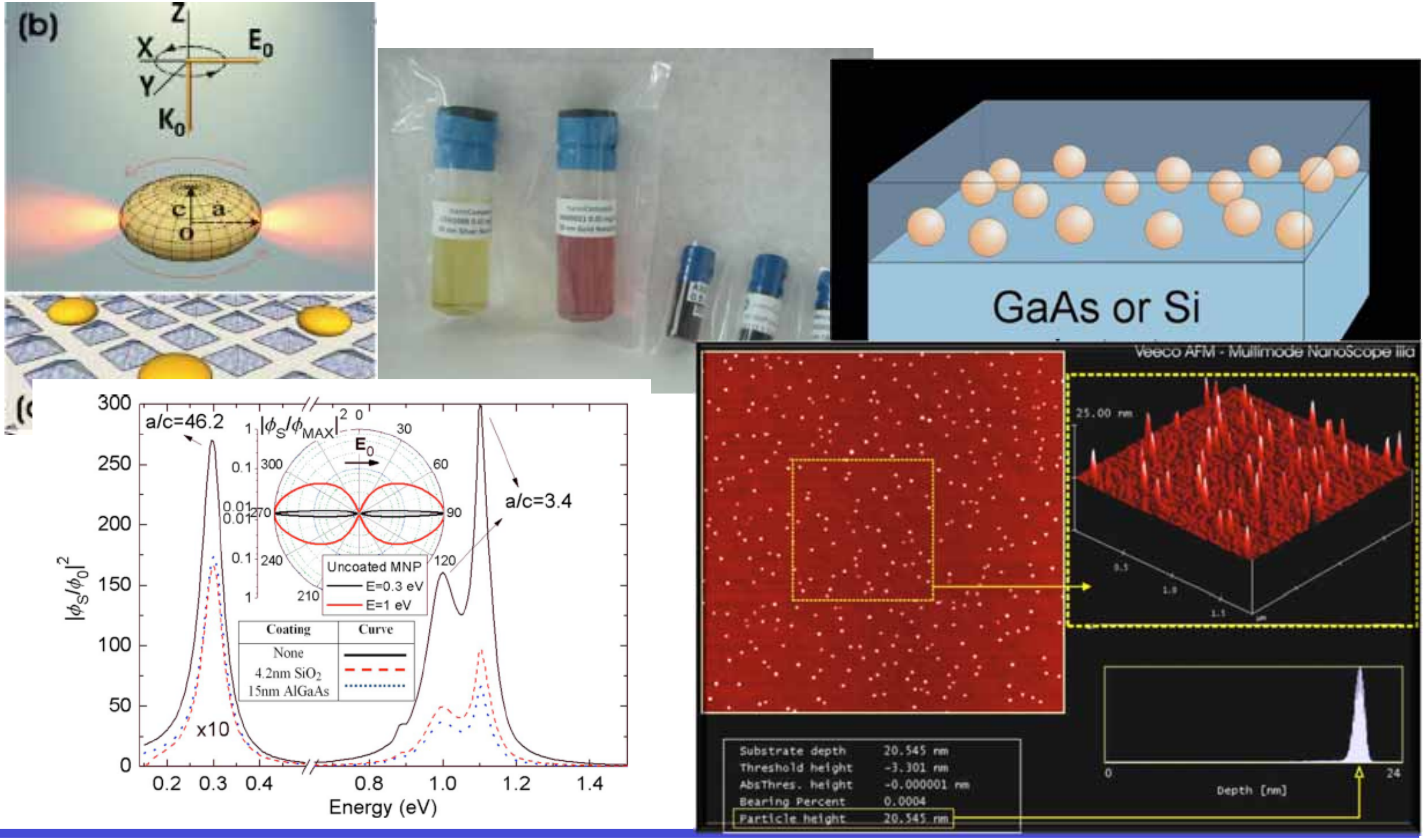




Mask designed and ordered. Soon experimental !!

Mellor A. Tobías I. Martí A. Luque A., "Light Trapping Properties of Cylindrical Well Diffraction Gratings in Solar Cells: Computational Calculations", 25th PVSEC Proceedings, Valencia (2010)

Light management approaches: Surf. Plasmons



A. Luque, A. Marti, M. J. Mendes, and I. Tobias, Journal of Applied Physics 104, 113118 (2008).
M. J. Mendes, A. Luque, I. Tobías and A. Marti, Applied Physics Letters 95, 071105 (2009).

Contents

- Introduction
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  - IB and SRH recombination
  - Proven bulk IB materials and cells
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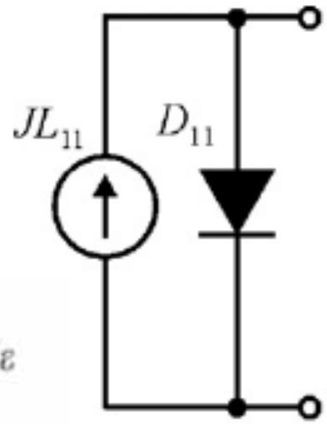
DB modeling; the effect of concentration

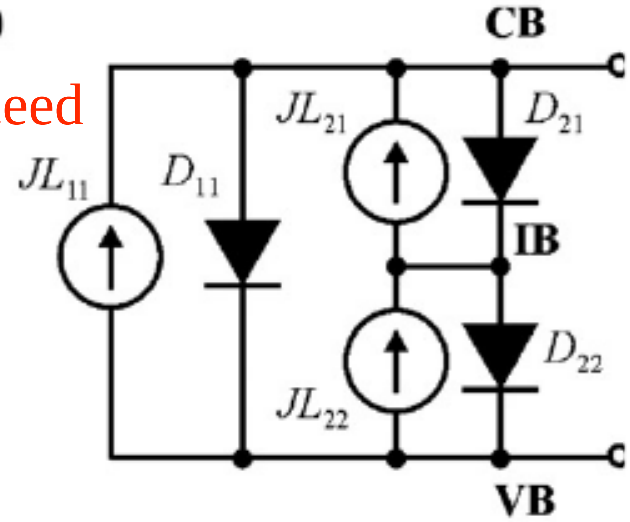
(a)

$$J_{XY} \approx J_{0,XY}\left(\exp\frac{eV_{XY}}{mkT} - 1\right)$$

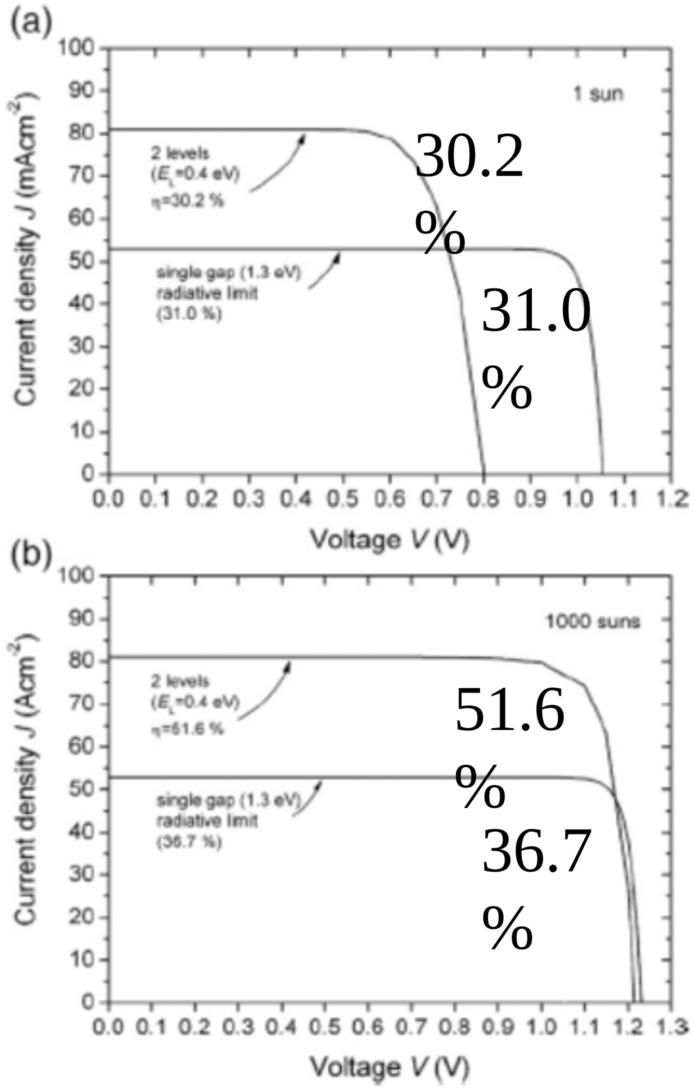
$$J_{0,XY} = \frac{2\pi}{h^3c^2}\int_{E_{XY}}^{\infty} \varepsilon^2 \exp\left(\frac{-\varepsilon}{kT_C}\right) d\varepsilon$$



(b)

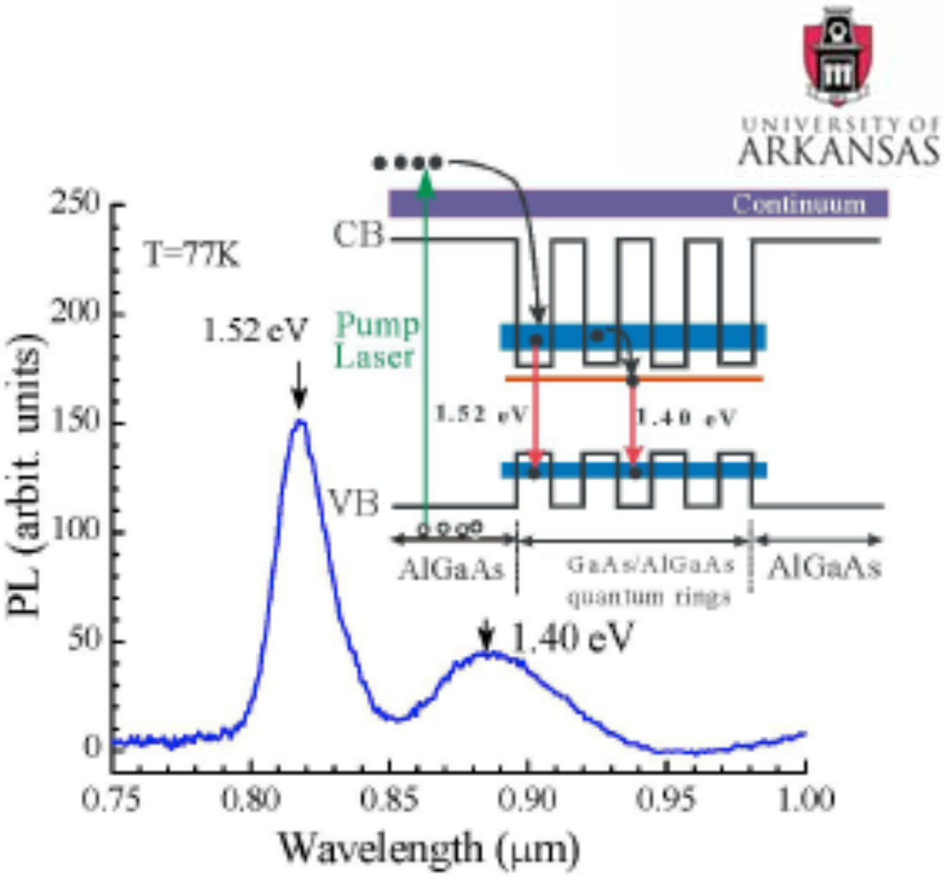


Impossible to exceed ordinary cells!!! (at one sun with GaAs/InAs)



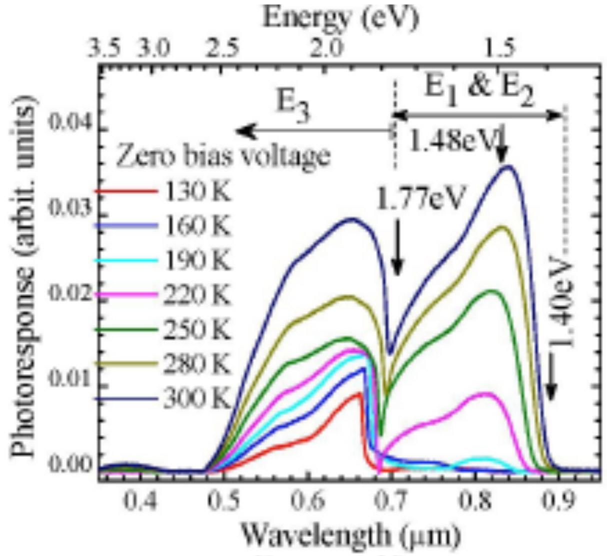
A. Marti *et al.*, *Thin Solid Films* ***516*****, *****6716 (2008).***

A QD material with better shape & gaps

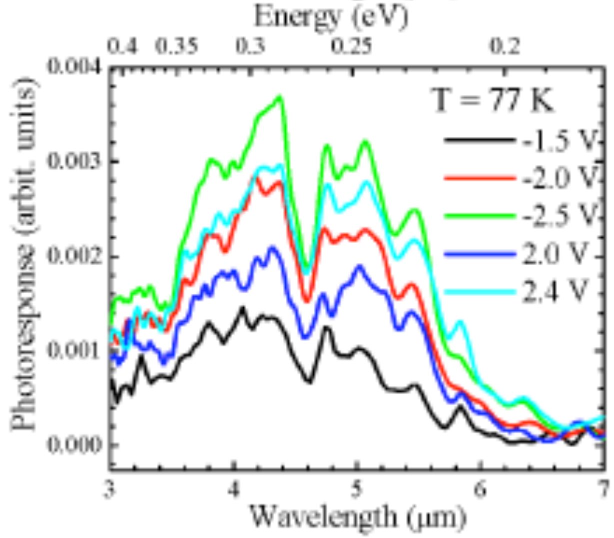


VB→CB

VB→IB



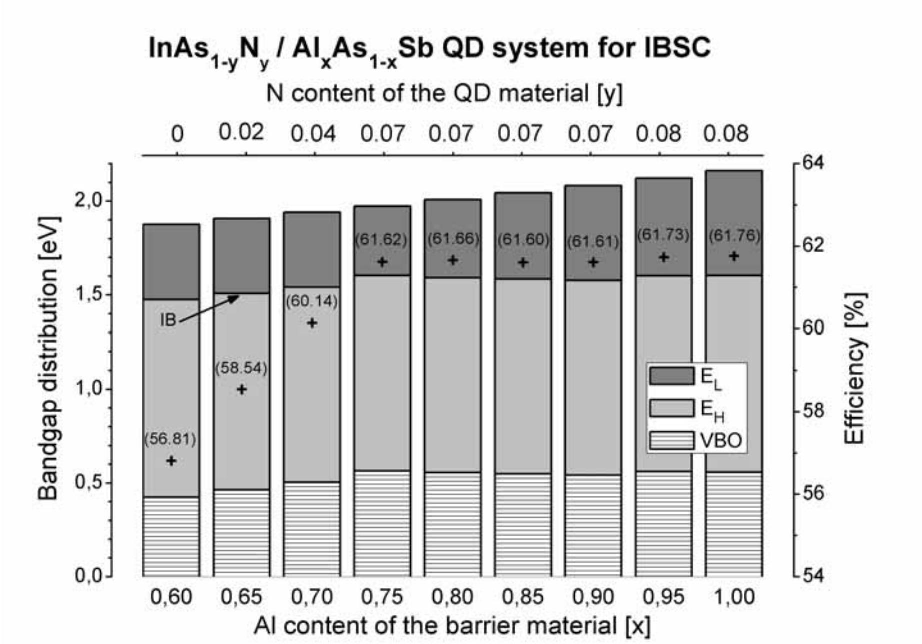
IB→CV



Quantum Ring Infrared Photodetector

[1] J. Wu, D. L. Shao, Z. H. Li, M. O. Manasreh, V. P. Kunets, Z. M. Wang, G. J. Salamo, Applied Physics Letters 95 (2009) 071908

Search for QD-IB material candidates



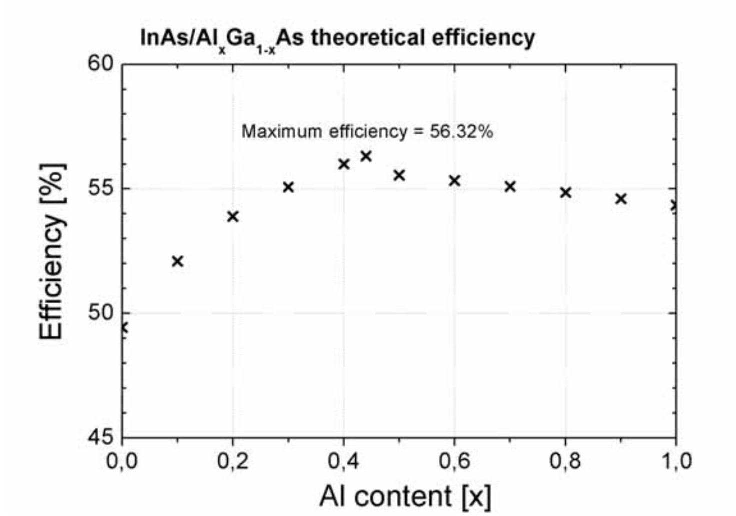


Table II: High efficiency $In_zAs_{1-z}N/Al_x[Ga_yIn_{1-y}]_{1-x}P$ data

x	y	z	E_G^* $[meV]$	E_L $[meV]$	Nature	Efficiency
0.42	0.05	0.06	1662.4	595.8	direct	61.65
0.02	0.68	0.08	1685.2	595.7	indirect	62.35
0.03	0.74	0.09	1683.3	606.1	indirect	61.68
0.04	0.72	0.09	1680	606.4	indirect	61.5

P. G. Linares, A. Martí et al., "III-V Compound Semiconductor Screening for Implementing Quantum Dot Intermediate Band Solar Cells, (submitted)

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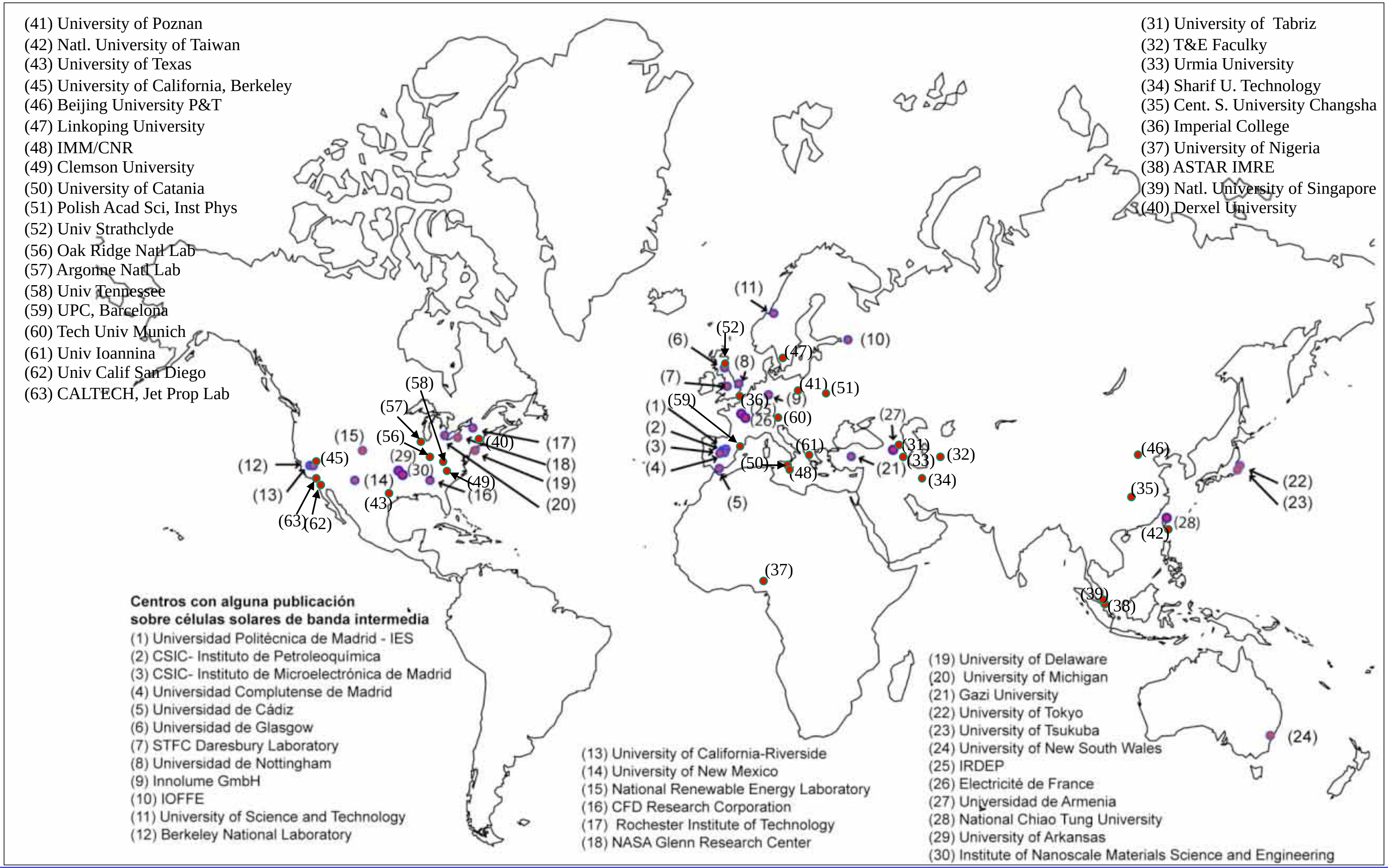
Centres having published referenced papers on IBCS



Conclusions

- IB Alloys for sub bandgap light absorption have been found
  - Theoretical and experimental arguments show that SRH Recombination decreases at high impurity concentration by electron delocalization
  - IB solar cells have been produced in ZnTe:O, Efficiency still low
- Physical principles have been established and experimentally proven
  - Two photon operation
  - Three quasi Fermi level splitting
  - Preservation (increase) of voltage
- IB solar cells have been made with InAs QD's in GaAs
  - Efficiency is low mainly because of:
    - Photogeneration not fully collected
    - IB-CB thermally connected
  - But DB modelling tells that no advantage is to be expected with InAs/GaAs QD unless
    - QD shape is changed and cells operate in concentration
    - Materials are changed
- First attempts of GaAs QRs in AlGaAs matrix promising
- **Topic highly attractive**