Intermediate Band Quantum Dot Solar Cells

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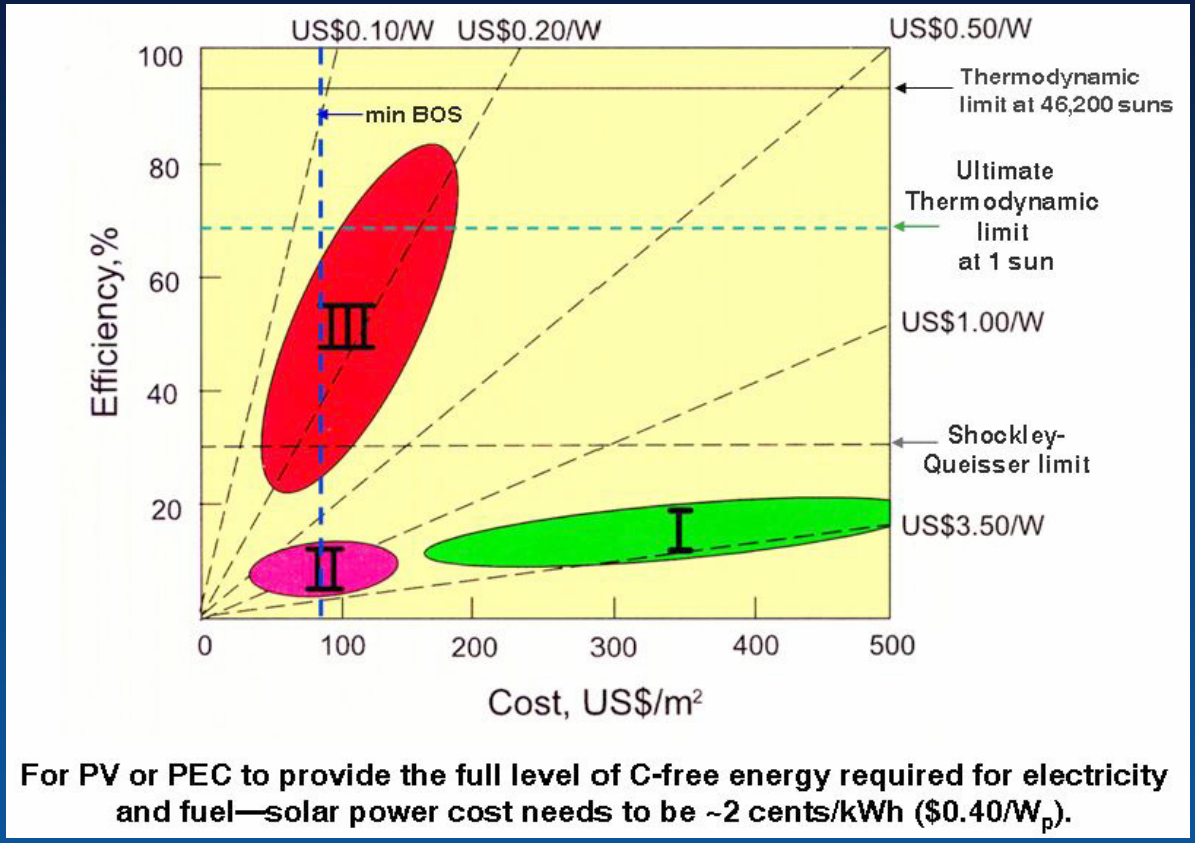
PV power costs ($/Wp) as a function of module efficiency and areal cost (Martin Green, 2004)



For PV or PEC to provide the full level of C-free energy required for electricity and fuel—solar power cost needs to be ~2 cents/kWh ($0.40/$W_p$).

The biggest challenge is dramatically reducing the cost/watt of delivered solar electricity

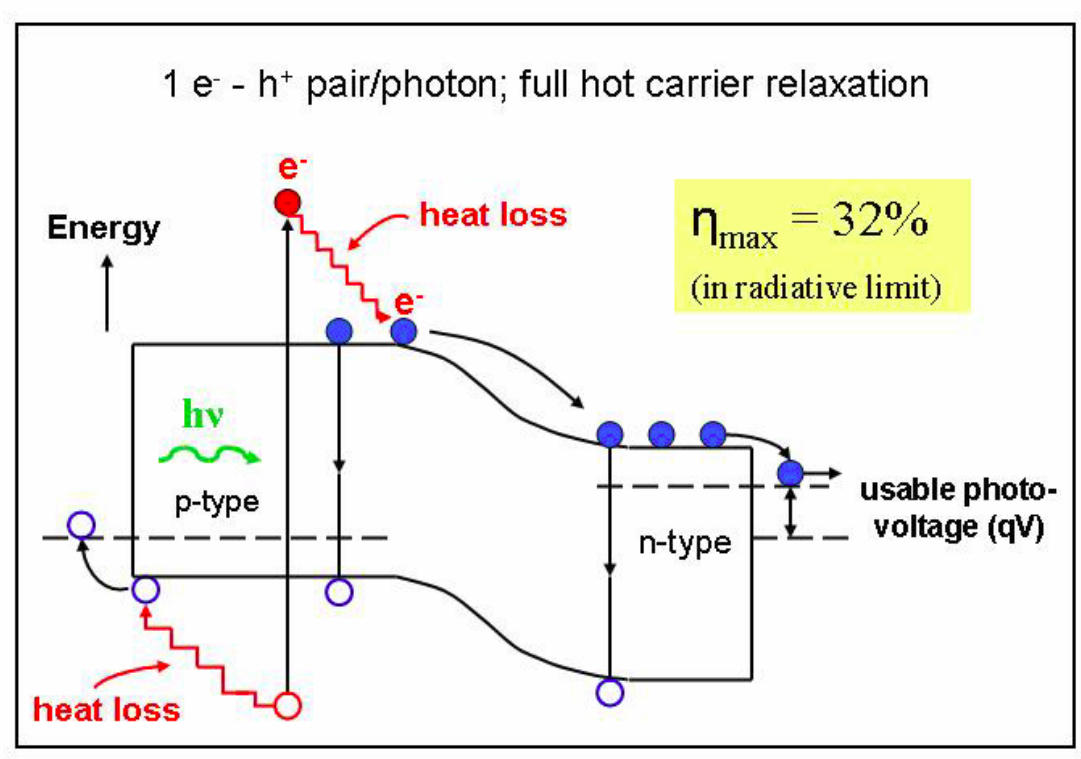
Third-generation PV

- Materials costs and availability are driving the evolution of PV technology towards a “third generation” of low-cost devices operating at efficiencies exceeding single-junction devices
- Possible approaches include:
  - Tandem cells: the only proven technology so far
  - Hot-carrier cells
  - Multiple-exciton-generation cells
  - Multiple-energy-level cells, e.g., intermediate-band cells
  - Thermophotovoltaic and thermophotonic conversion
- See: *Third Generation Photovoltaics: Advanced Solar Energy Conversion*, Prof. Martin A. Green, Springer-Verlag (Berlin, Heidelberg, 2003)

  Next Generation Photovoltaics: High Efficiency through Full Spectrum Utilization, edited by A. Martí and A. Luque, Inst. of Physics (Bristol, 2004)

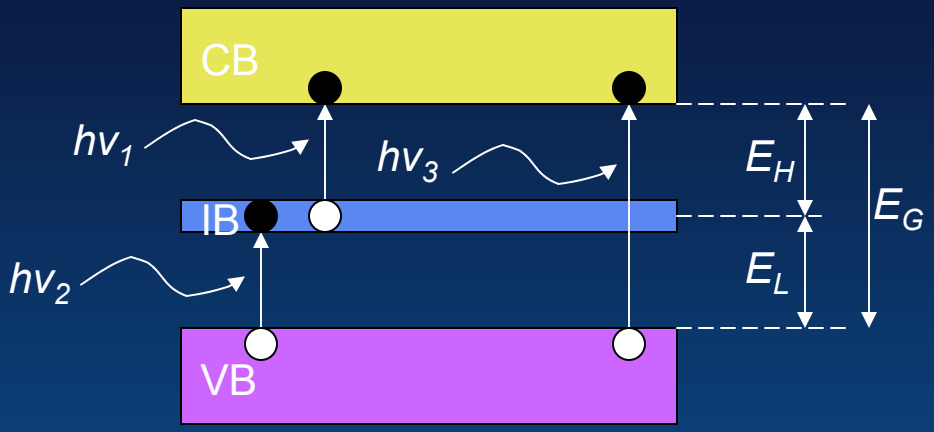
Limiting efficiency of single-junction solar cells

(Detailed balance calculations: Shockley and Queisser J. Appl. Phys. 32 [1961] 510)



- Excess energy of photons absorbed with energies greater than semiconductor bandgap are lost as heat
- Photons with energies less than semiconductor bandgap are not absorbed

Intermediate-band solar cells (IBSC)



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

Optimum gaps for maximum efficiency under maximum concentration conditions at 300 K:

E_L = 0.71 eV

E_H = 1.24 eV

E_G = 1.95 eV

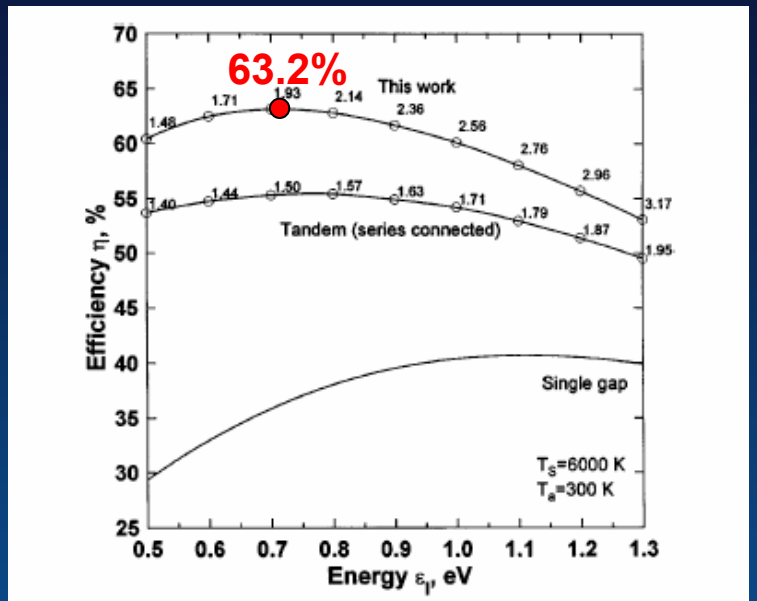


FIG. 2. Efficiency limit for a solar cell with an intermediate band and for a two-terminal ideal tandem cell, in both cases vs the lowest band gap ϵ_l, and for a cell with a single band gap. The corresponding values of the highest band gap in cells with intermediate band (E_G) and in tandem cells (E_C), for maximum efficiency, are also presented.

Maximum theoretical efficiency:

Single-gap solar cell = 40.7%

IBSC = 63.2%

Possible intermediate-band solar cell materials

- **Diluted II-VI oxide semiconductors**

  e.g., $Zn_{1-y}Mn_yO_xTe_{1-x}$ alloys

  Wu et al., Phys. Rev. Lett. **91** (2003) 246403

- **Transition-metal impurities in semiconductors e.g., Ga_4P_3M and Ga_xP_yM alloys, where M is a transition metal such as Ti**

  Wahnon and Tablero, Phys. Rev. B **65** (2002) 165115

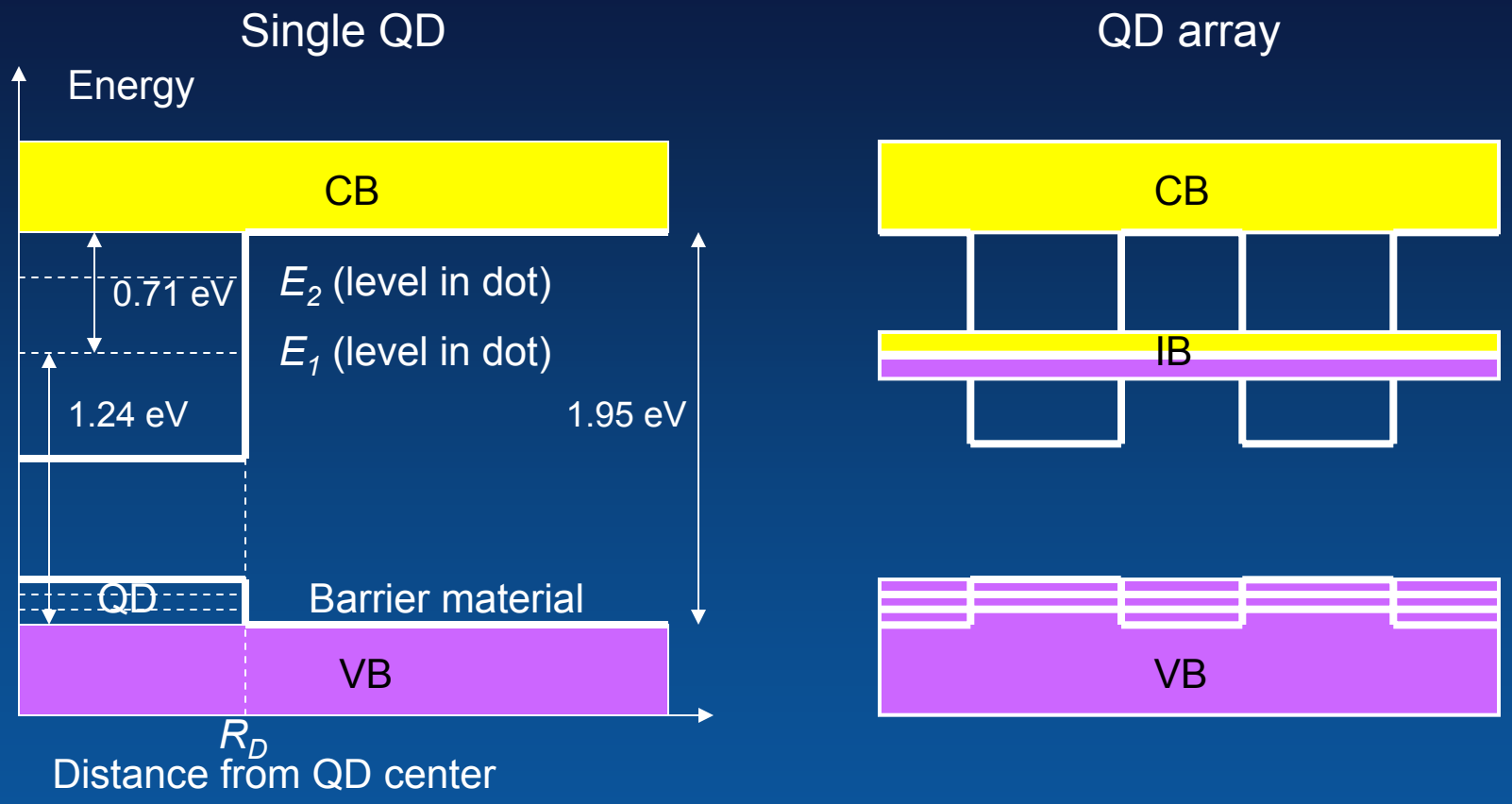
  Tablero, Phys. Rev. B **72** (2005) 035213

- **Quantum dots, e.g., InGaAs/(Al)GaAs**

  Martí et al., Physica E **14** (2002) 150

  Luque et al., J. Appl. Phys. **96** (2004) 903

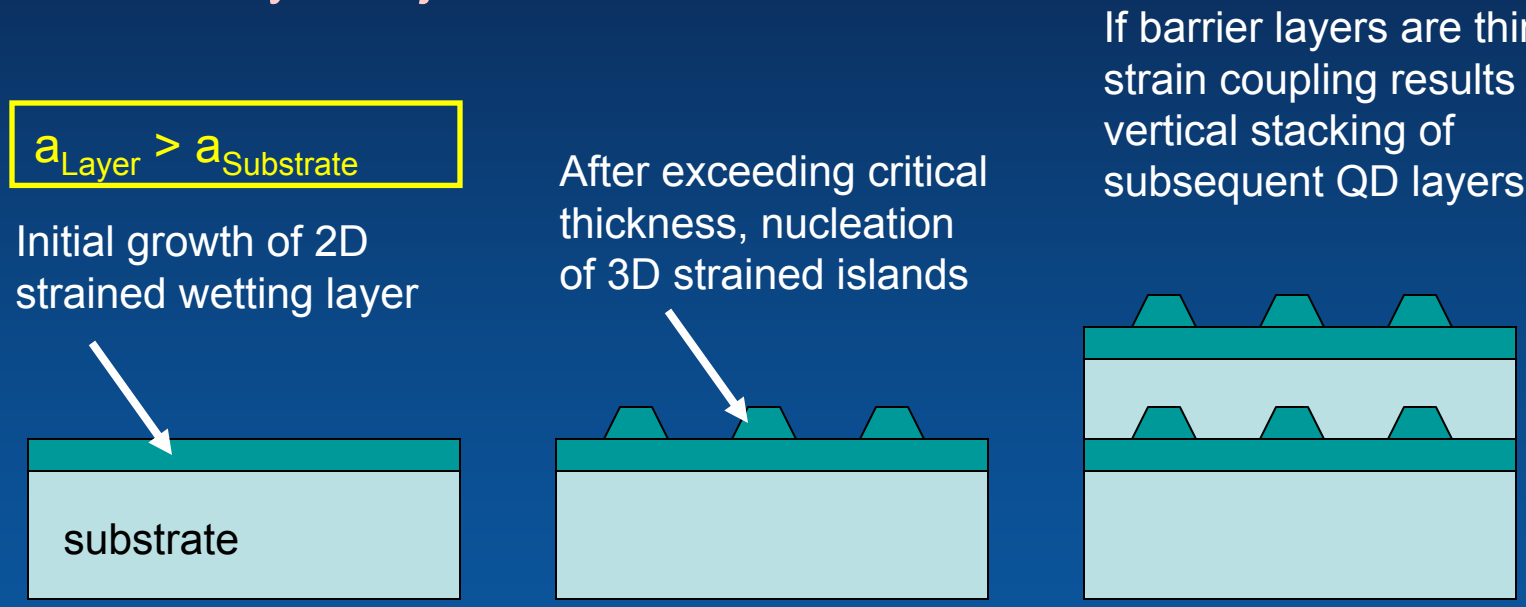
Quantum dot intermediate-band solar cells
(A. Martí et al., 2000)



- Form an intermediate band by growing a close-packed ordered array of quantum dots
- Candidate materials: $Al_{0.4}Ga_{0.6}As$ barriers/InGaAs QDs, but this system has large valence-band offset

Growth of quantum dot superlattices

- Epitaxial growth by MBE or MOCVD using the strain-induced Stranski-Krastanov (SK) process, e.g., InGaAs/GaAs
- MOCVD is currently the preferred growth technique for high-efficiency multijunction solar cells



- 3D island formation is driven by a reduction in strain energy that outweighs the increase in surface energy that occurs

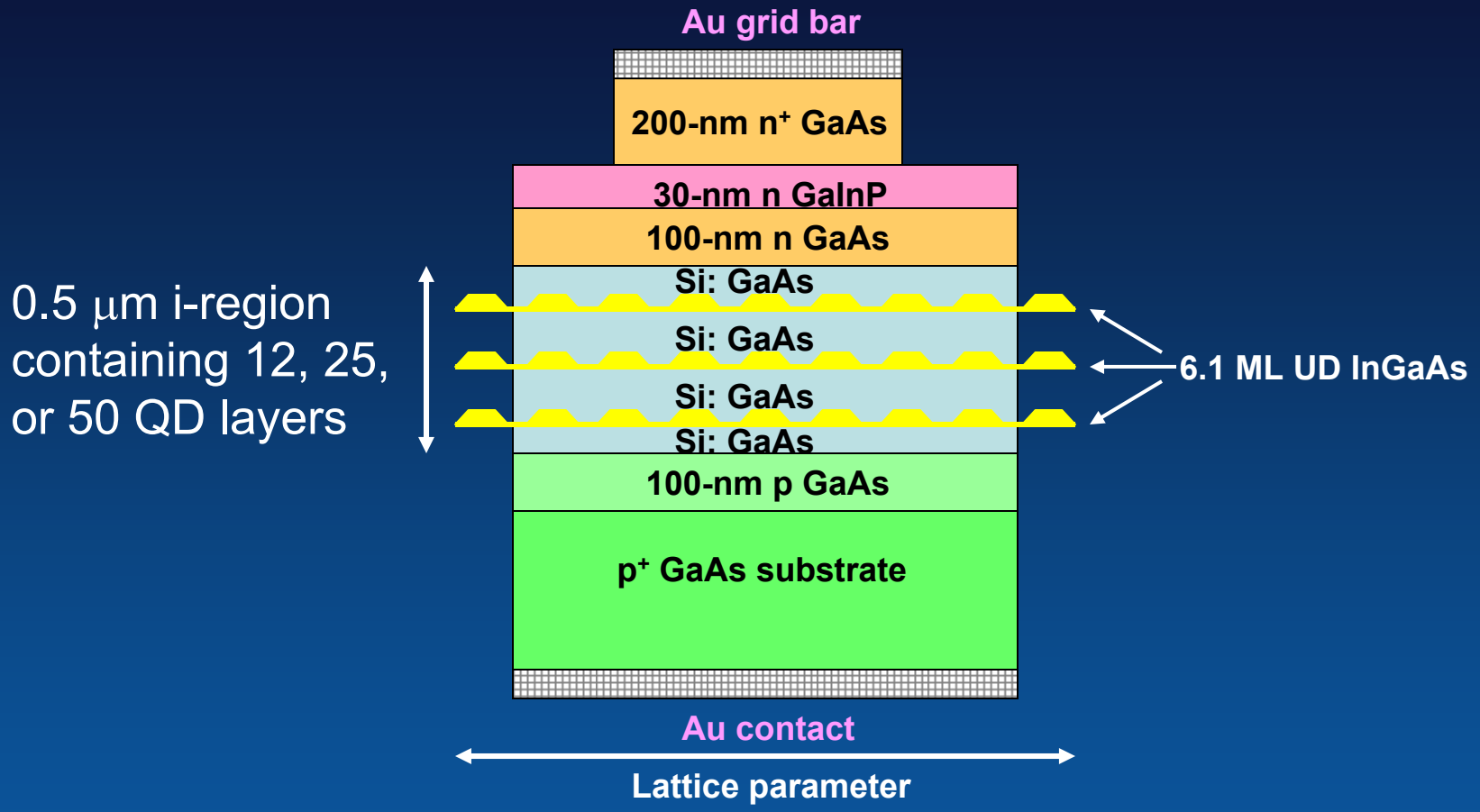
Some important characteristics of QDs for IBSC

- ***Dot size, shape, composition:*** Suitable to obtain confined energy level in optimum position
- ***Dot spacing:*** Ideally require very close-packed 3D array of QDs

  (a) So that wave functions of carriers in individual QDs overlap with each other and discrete energy levels of single QDs broaden into mini-bands

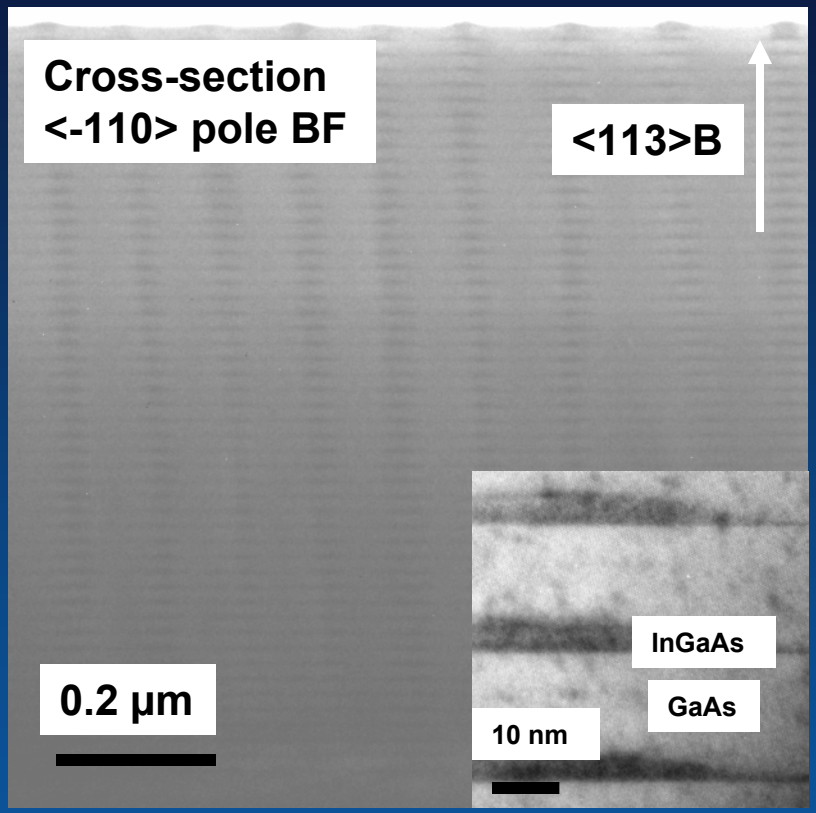
  (b) To obtain a high absorption coefficient
- ***Dot regularity:*** Size dispersion < 10%
- ***Materials:*** QDs and barrier layers with the optimum bandgap values, and good transport properties
- ***Doping:*** The IB needs to be partially-filled with electrons

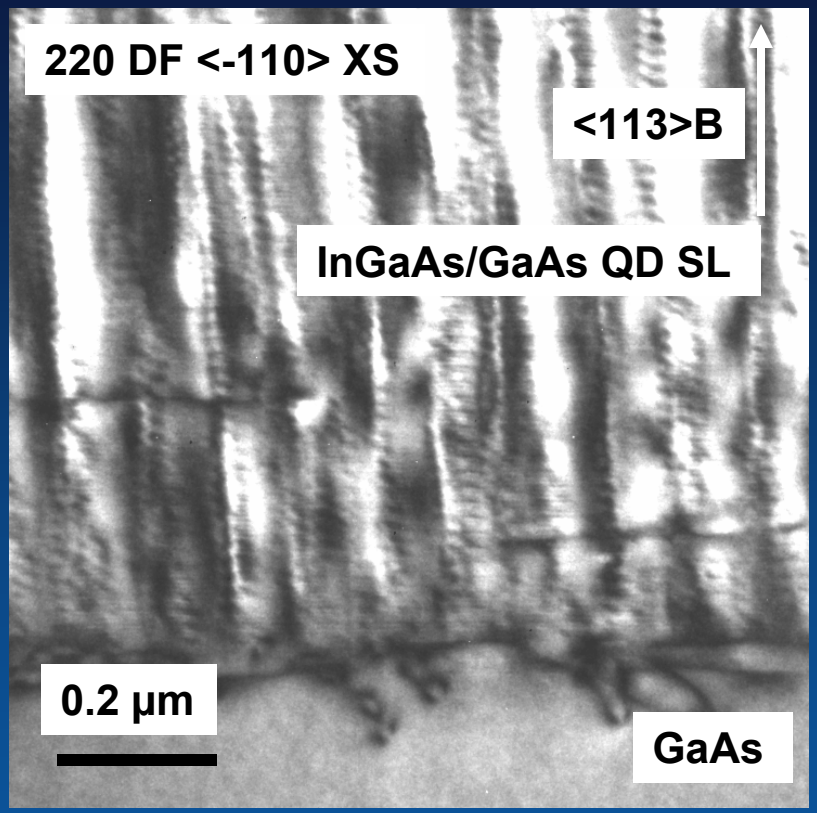
InGaAs/GaAs QD superlattice (SL) *pin* solar cell



- Require QD SL with a high number of periods to maximize absorption and low defect density to minimize non-radiative recombination
- For InGaAs/GaAs QD SL with a large number of periods, the lattice mismatch with the substrate results in the generation of a high density of misfit dislocations that degrades cell performance

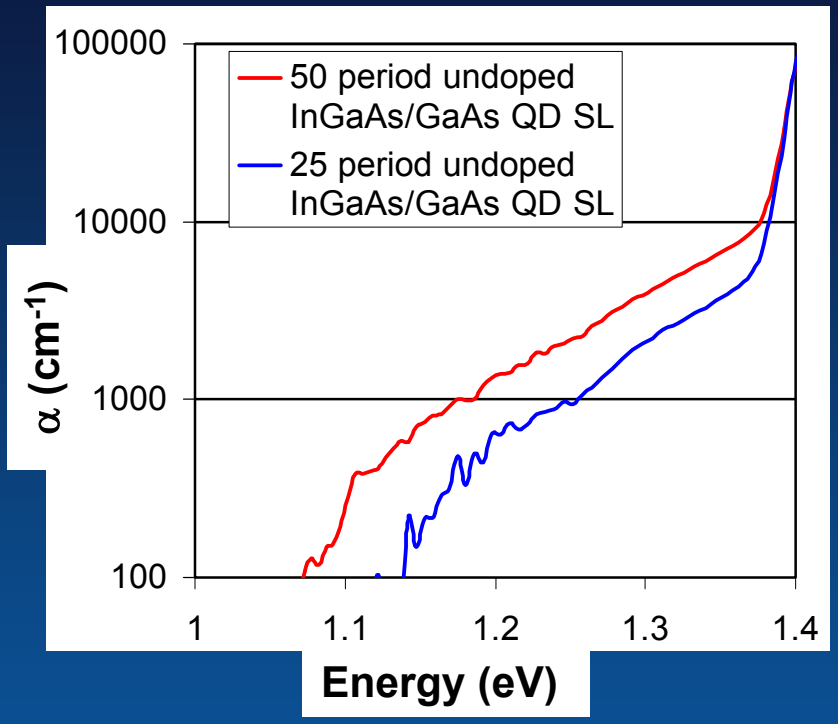
TEM of 50-period undoped MOCVD $In_{0.47}Ga_{0.53}As$ (6.1 ML)/GaAs (20 nm) QD SL on {113}B GaAs





- Vertically stacked quantum dots through whole superlattice thickness along close to <113>B
- High density of harmful dislocations present due to lattice mismatch between QD superlattice and GaAs substrate

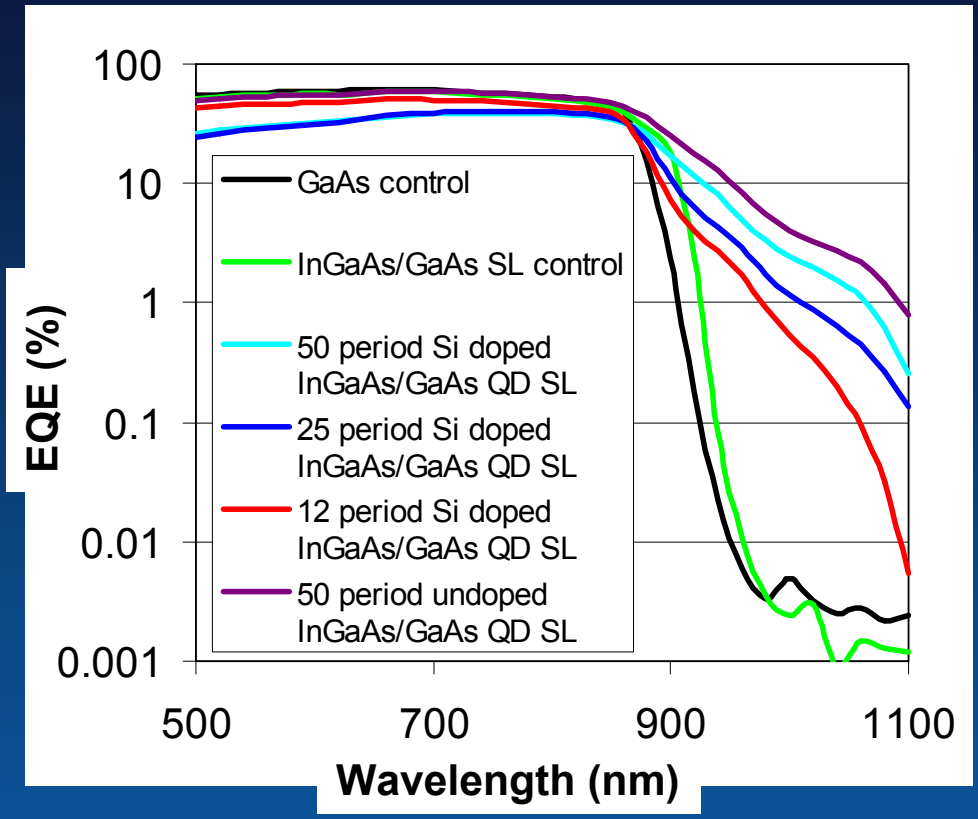
Absorption measurements on undoped $In_{0.47}Ga_{0.53}As/GaAs$ QD SLs



Absorption of sub-bandgap photons associated with VB-to-IB transition in QDs

- Weak absorption from InGaAs QDs starting at energy of ~1.1 eV
- Strength of absorption increases with increasing number of periods in QD SL

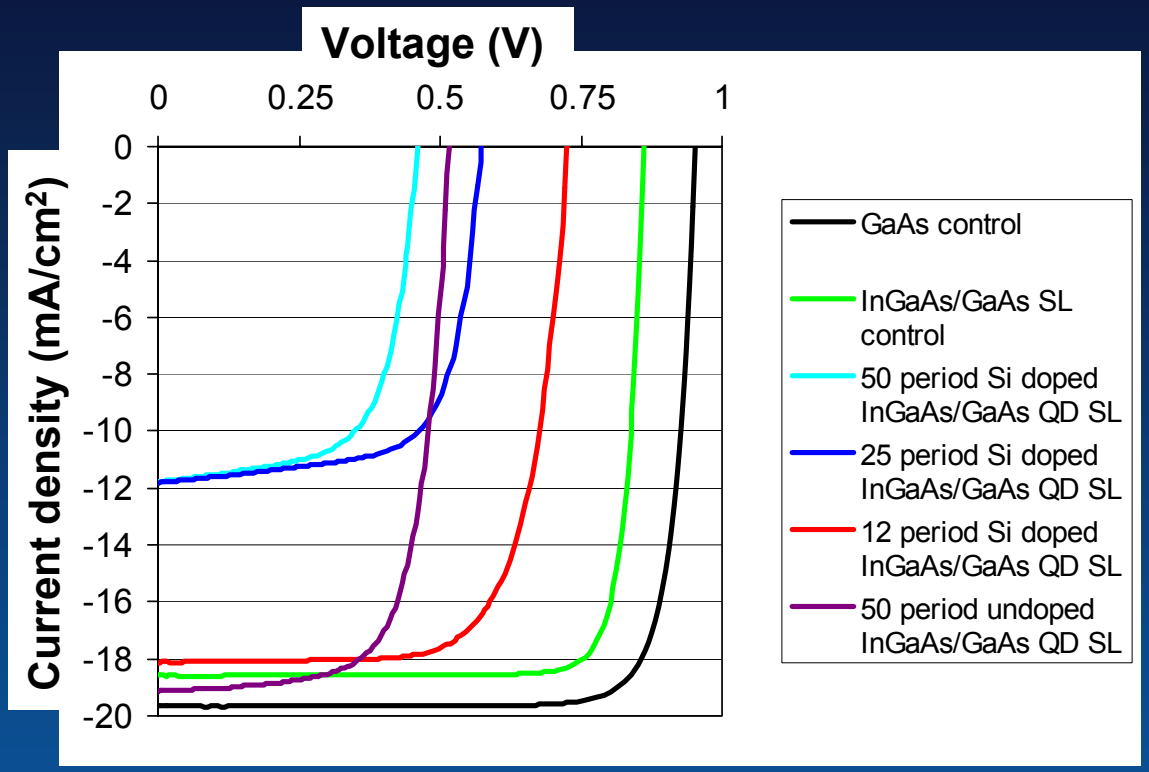
External quantum efficiencies (EQE) measured for cells grown on {113}B GaAs



Current generated by absorption of sub-bandgap photons associated with VB-to-IB transition in QDs

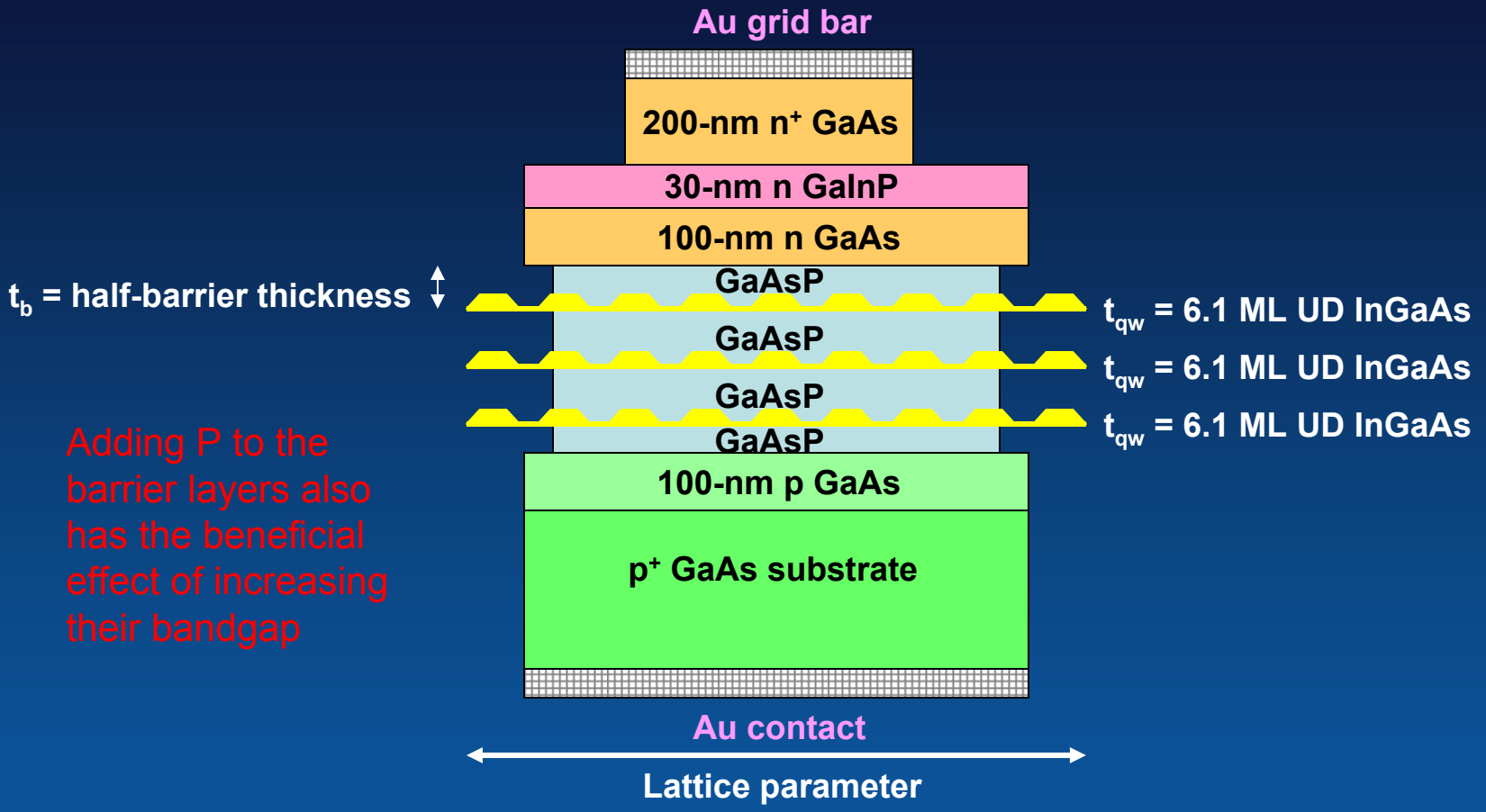
- QD SL devices have photoresponses extended to longer wavelengths than control cells due to absorption of sub-bandgap photons in QDs
- As the number of QD SL periods increases, the EQE increases for Si-doped structures at long wavelengths

Light IV curves measured under one-sun illumination for cells grown on {113}B GaAs



- InGaAs/GaAs SL and QD SL cells show reduced V_{oc} in comparison to GaAs control cell
- V_{oc} decreases as number of periods is increased for Si doped QD SL cells
- 25- and 50-period doped QD SL cells also have much reduced J_{sc} values in comparison to control cells and 12-period doped QD SL cell
- 50-period undoped QD SL cell has J_{sc} comparable to control cells

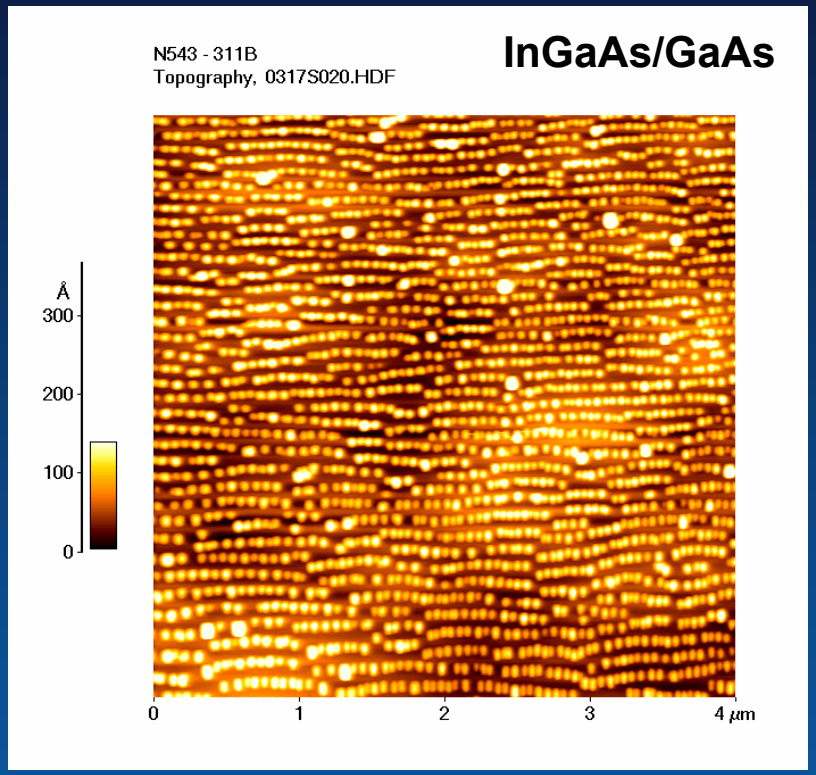
Strain-balanced QD SLs to avoid misfit dislocations

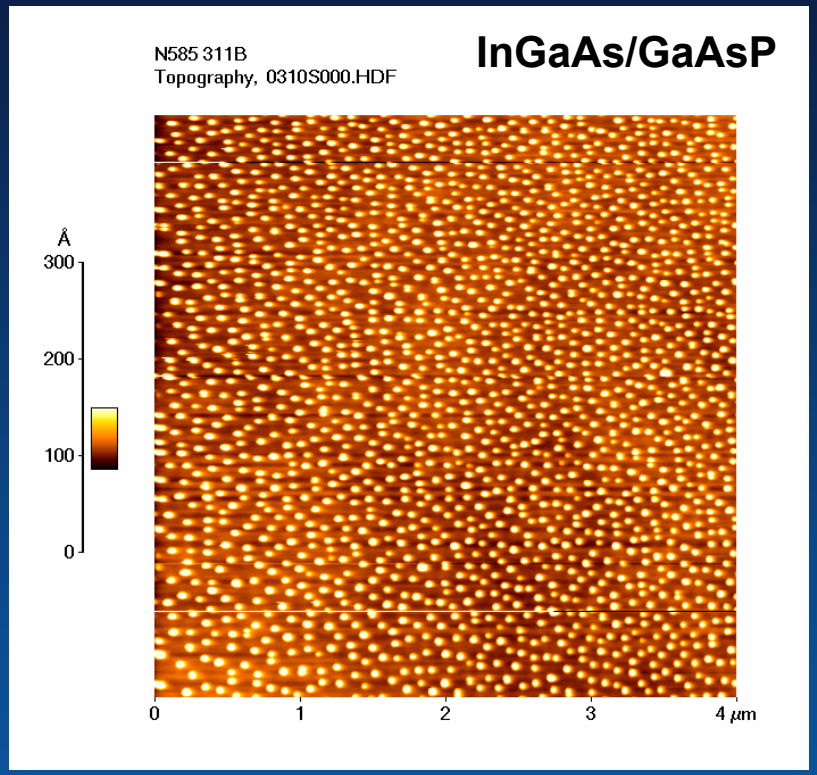


Adding P to the barrier layers also has the beneficial effect of increasing their bandgap

- Compressive strain of InGaAs QD layers is compensated by tensile GaAsP layers such that average lattice parameter of QD SL is equal to GaAs substrate
- $\langle a \rangle = \dfrac{2t_b a_{GaAsP} + t_{qw} a_{InGaAs}}{2t_b + t_{qw}}$ (Ekins-Daukes et al., APL **75** [1999], 4195)

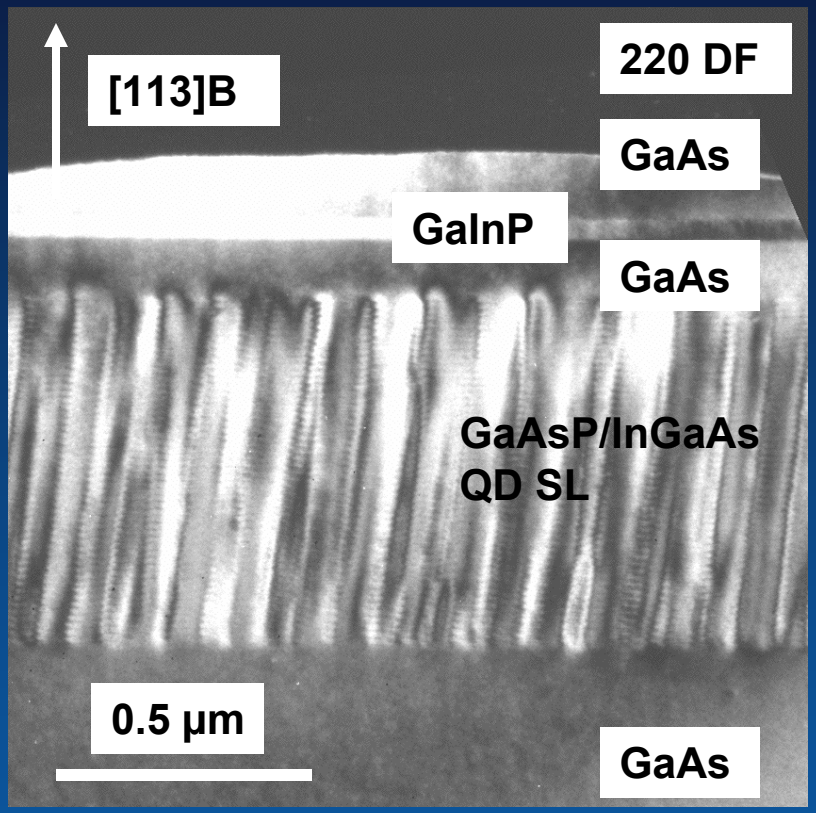
AFM of 50-period InGaAs (6.1 ML)/GaAs (20 nm) and 20-period InGaAs (6.1 ML)/GaAsP (20 nm, 8.3% P) QD SL incorporating 30-second H_2 anneal after each QD layer

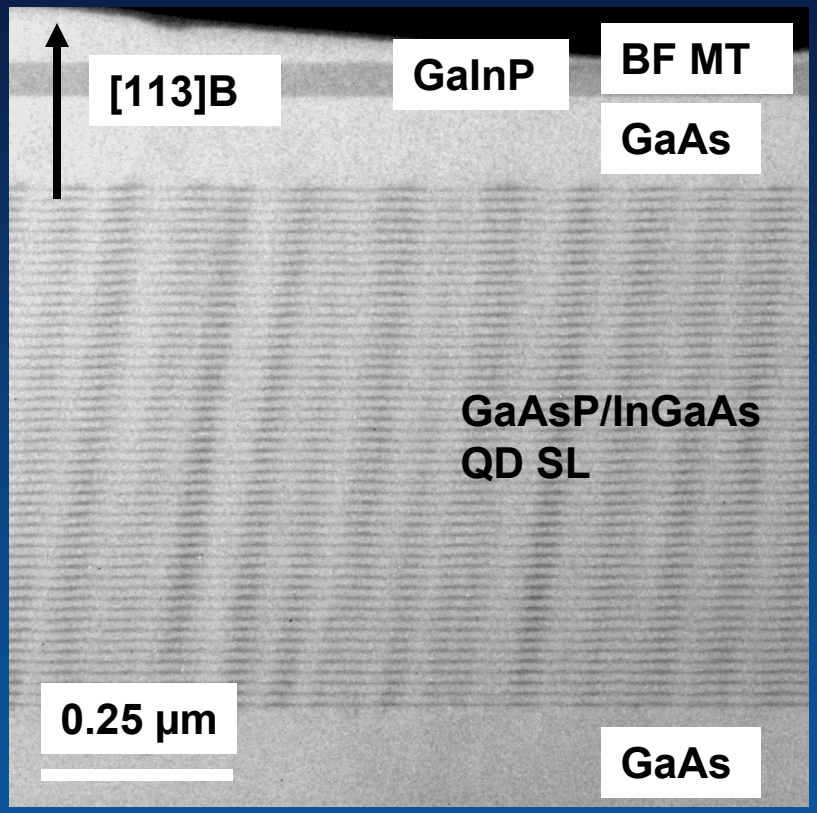




- InGaAs/GaAs: Rows of ordered QDs present aligned along [-110], QD density ~10^{10} cm^{-2}
- InGaAs/GaAsP: No lateral ordering of QDs, QD density ~ 10^{10} cm^{-2}

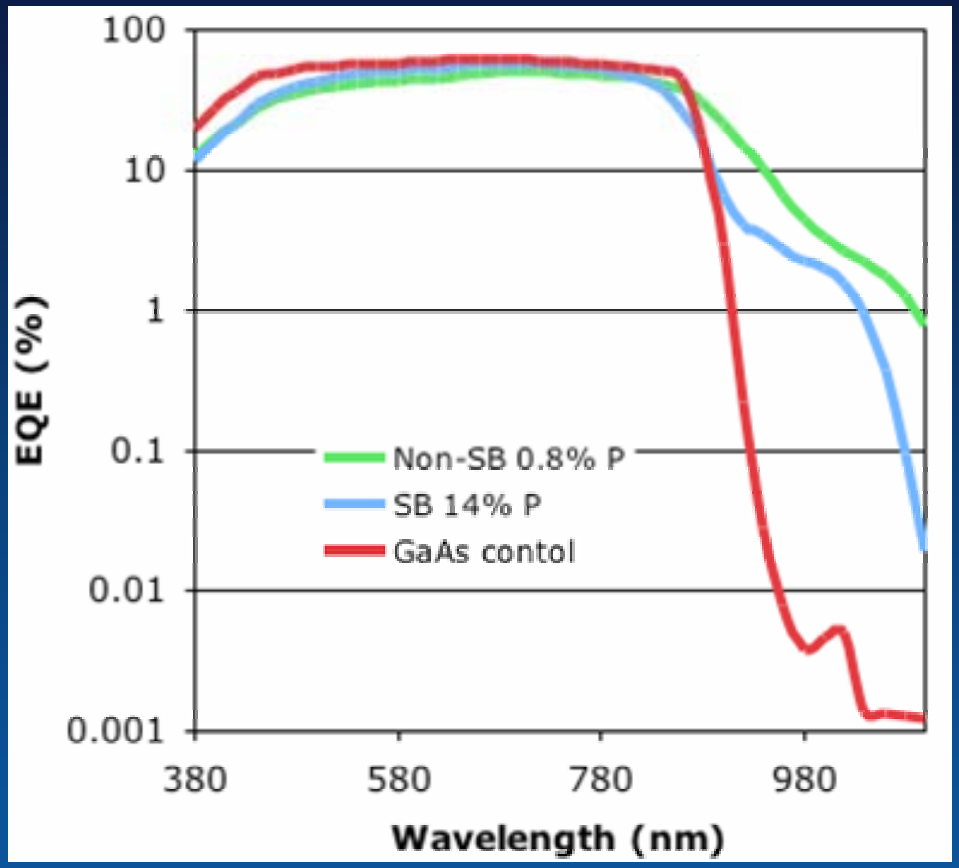
Cross-section TEM of 50-period, undoped SB InGaAs/GaAsP QD SL with 14% P in barrier layers





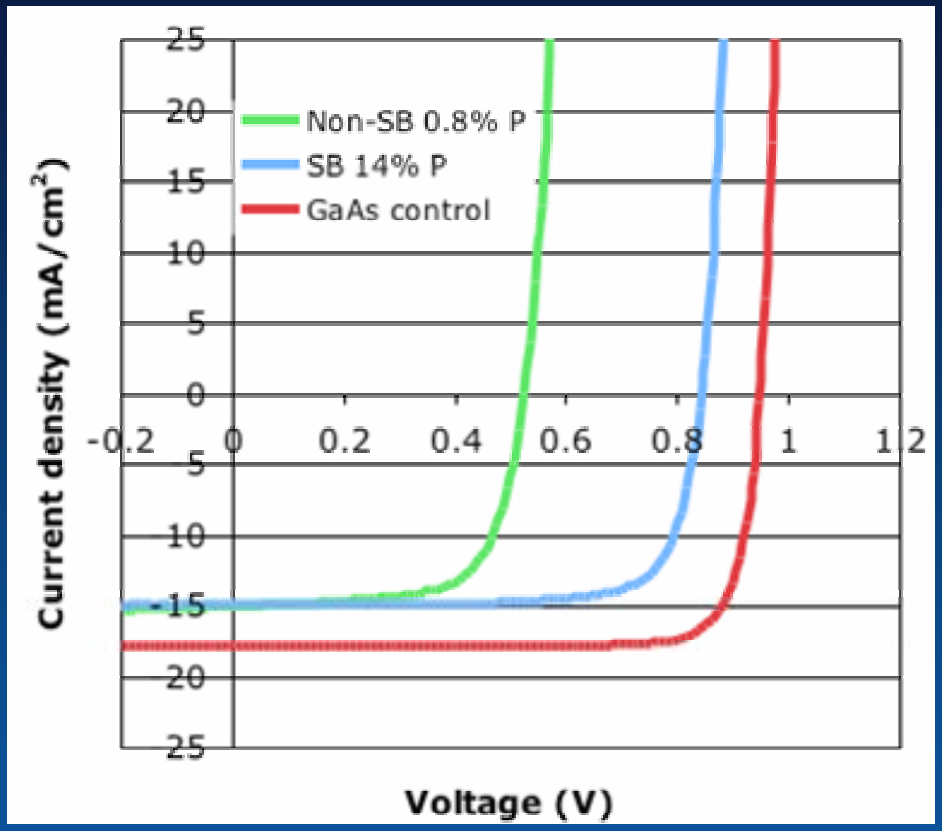
- No misfit or threading dislocations present
- See nearly vertical columns of InGaAs QDs through all 50 periods

External quantum efficiencies (EQE) measured for SB and non-SB InGaAs/GaAsP QD SL cells



- The InGaAs/GaAsP QD SL devices have photoresponses extended to longer wavelengths than GaAs control cells
- Increasing the amount of P in the barrier layers shifts the photoresponse cut-off to shorter wavelengths

Light IV curves: Higher V_{oc} obtained by growth of strain-balanced structures



- Adding P to barrier layers to achieve strain balance leads to a significant increase in V_{OC} (partly due to the increase in bandgap of the barrier layers and partly due to reduction in dislocation density)
- The SB InGaAs/GaAsP QD SL cell still shows reduced J_{SC} and V_{OC} in comparison to GaAs control cell

What limits performance of these QD IBSC?

- **Weak absorption of sub-bandgap photons:** IB-to-CB absorption transition may be weak because of insufficient number of QDs in structures
- **Low open-circuit voltage:** Rapid relaxation and capture of carriers into QDs
- **Low currents:** QDs may be acting as traps for carriers lowering efficiency of carrier collection (will probably need a built-in electric field in intrinsic region of a *pin* device to help separate charge carriers and improve their collection, need to slow down carrier capture and recombination in QDs)
- **Cost:** Epitaxially grown QD structures are very expensive to produce; if concept works, then we may want to move to colloidal QD-based cells to lower cost

Conclusions

- We have achieved MOCVD growth of up to 50-period strain-balanced InGaAs/GaAsP QD SLs with lower defect densities and better optical properties than InGaAs/GaAs QD SLs
- Strain-balanced InGaAs/GaAsP QD SL solar cells show a significant increase in V_{OC} in comparison to InGaAs/GaAs QD SL cells
- QD SL cells show photoresponses extended to longer wavelengths than GaAs control cells, demonstrating current generation from the absorption of sub-bandgap photons

Conclusions

- IBSC theoretically offers a way to significantly increase cell efficiency compared to that of a single-junction solar cell
- Although some of the key operating principles of IBSC have been demonstrated, cell efficiencies have so far not exceeded the Shockley-Queisser limit for a single-junction solar cell
- Much more work needs to be done before IBSC can make a major contribution to the PV market