A Green Campus and PV Research

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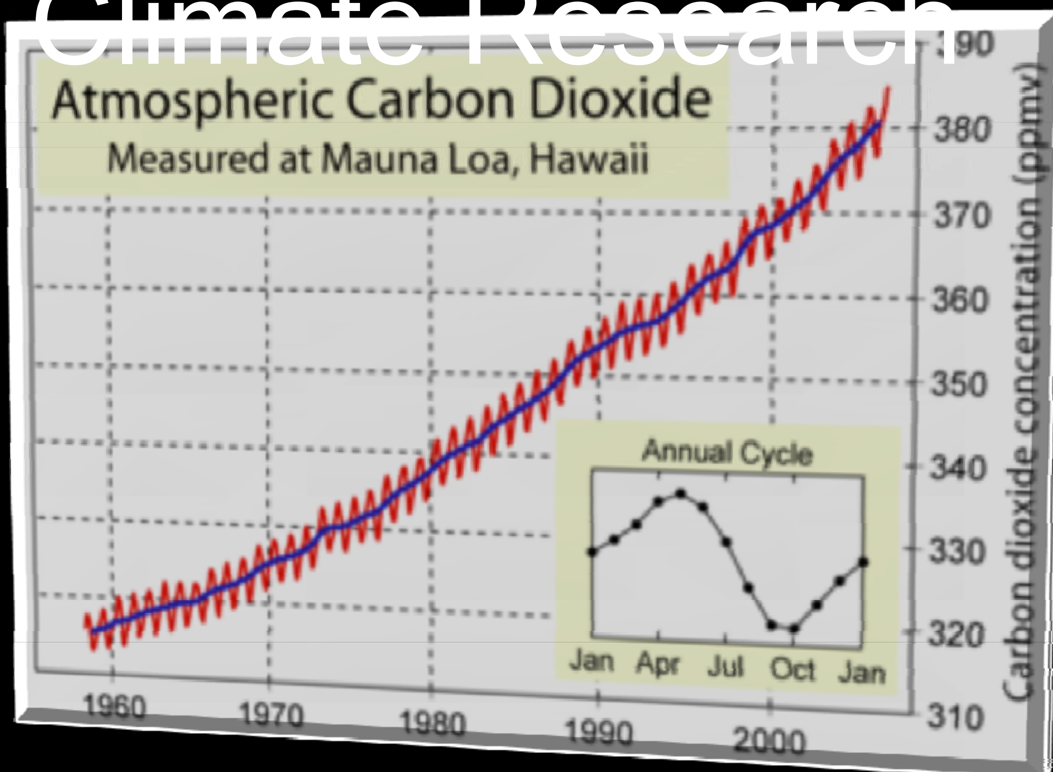
- *Introduction : A Green Campus*
- *QWSC with nanoscatters*
- *NW solar cells*
- *Branched NW photoelectrochemical cells*
- *Summary*

A History in Climate Research

UC San Diego and its Scripps Institution of Oceanography has long been internationally recognized for ***pioneering research*** in global climate change.

We feel it is imperative to have commensurate leadership in the sustainability of UC San Diego's ***operations***.

As a ***living laboratory*** for climate solutions, UC San Diego will be an early adopter for real-world tools and leading-edge technologies for California and global marketplace.



Campus Quick Facts

With a daily population of over 45,000, UC San Diego is the size and complexity of a small city.

As a research and medical institution, we have two times the energy density of commercial buildings

13 million sq. ft. of buildings, $250M/yr of building growth

Self generate 87% of annual demand

- 30 MW natural gas Cogen plant
- 2.8 MW of Fuel Cells contracted
- 3.2 MW of Solar PV installed,

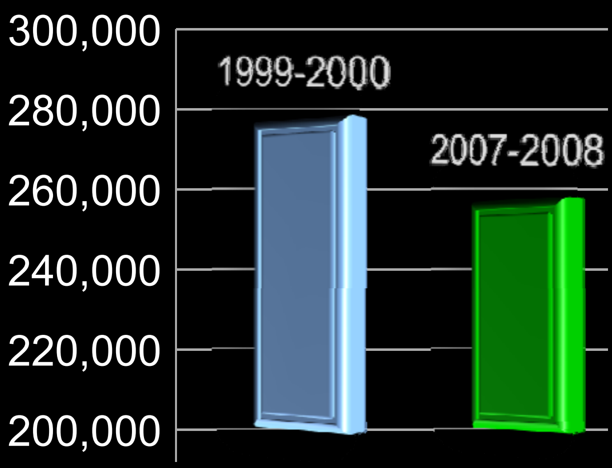
UC San Diego Operates a 42 MW_{peak} Microgrid

New Technology in Old Buildings

Continue to be a Leader in Carbon Reduction and Energy Efficiency

Completed $60M in energy retrofits reducing energy use by 20% or 50M kWh/yr, saving UCSD $12M / year

Even with increased energy intensive activities and growth, facility retrofits have decreased energy consumption per sq. ft.



Alternative Transportation

Maximize Use of Alternative Transportation & Alternative Fuels

Replace UCSD vehicle fleet with hybrid, bio-diesel, and electric vehicles

56% of commuters use alternative transportation to get to campus

Deploying Solar Power

Become one of the Leading University Sites in the World for Solar Energy

We have used Soitec incentives to develop 1.2MW of PV energy

- Introduction
- QWSC with nanoscatters
- NW solar cells
- Branched NW photoelectrochemical cells
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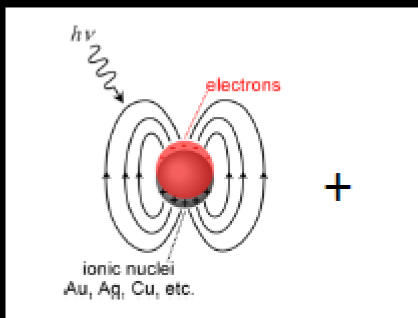
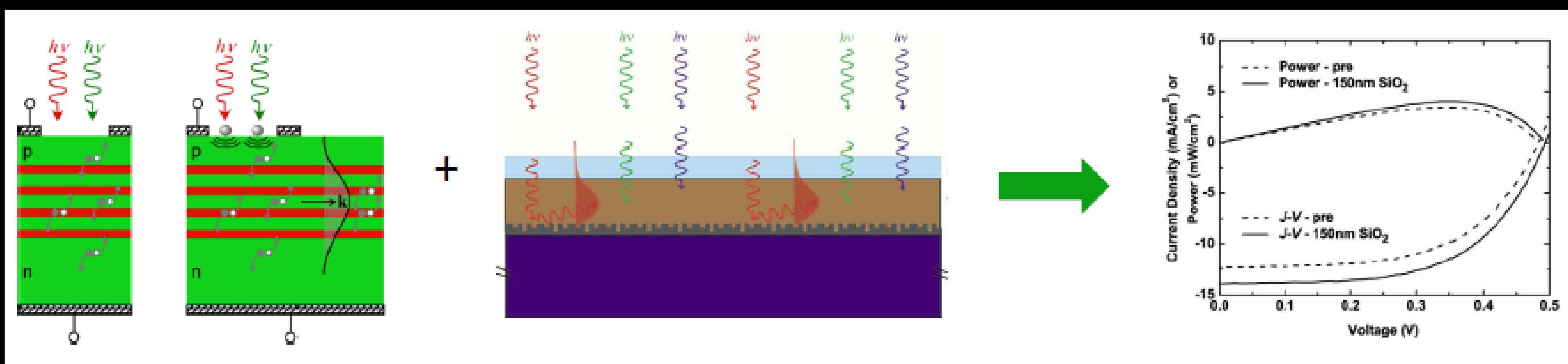
Exploiting Nanostructure-based scattering Effects in high-efficiency photovoltaic devices

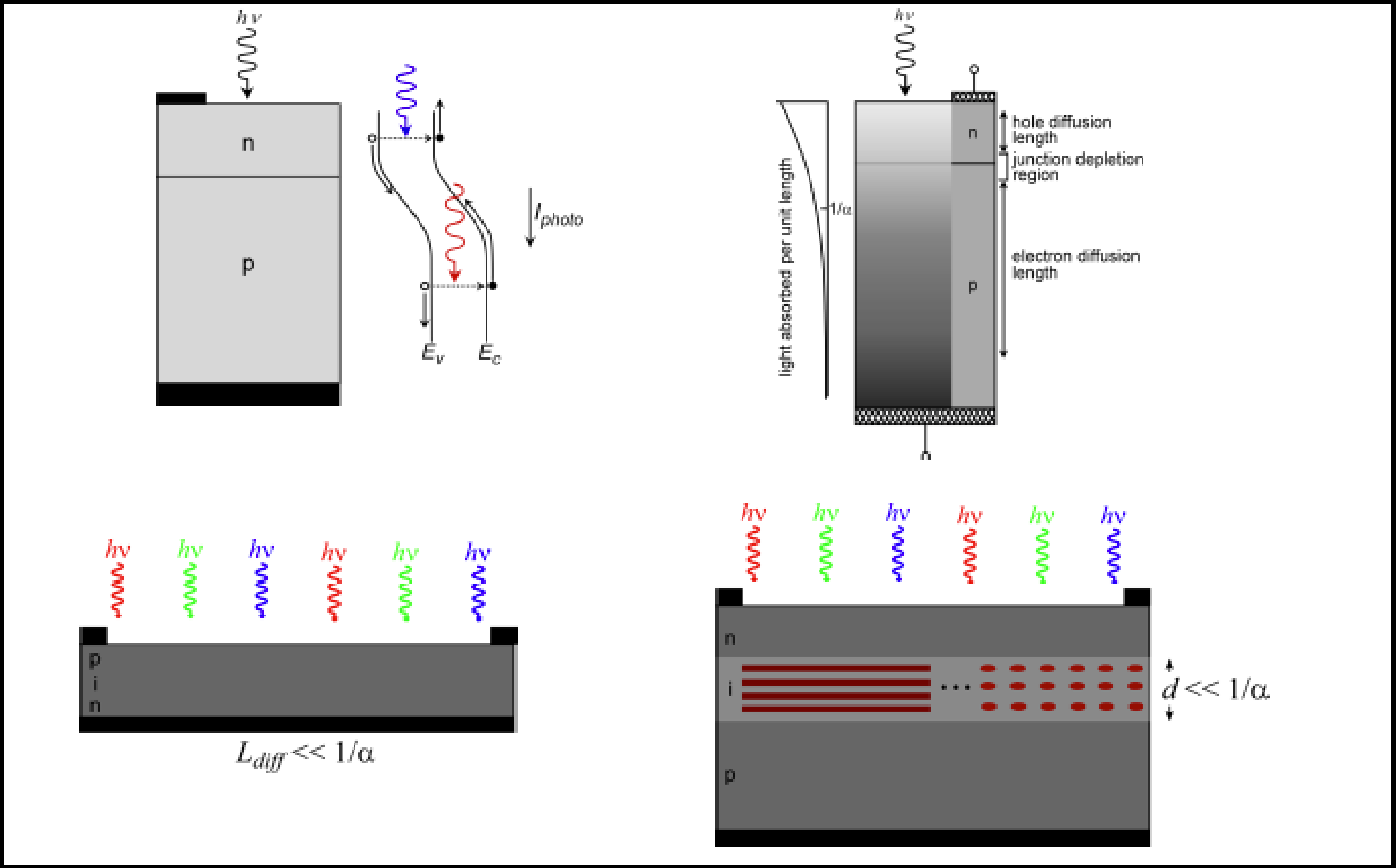
project led by Prof. Edward Yu, Univ. of Texas, Austin





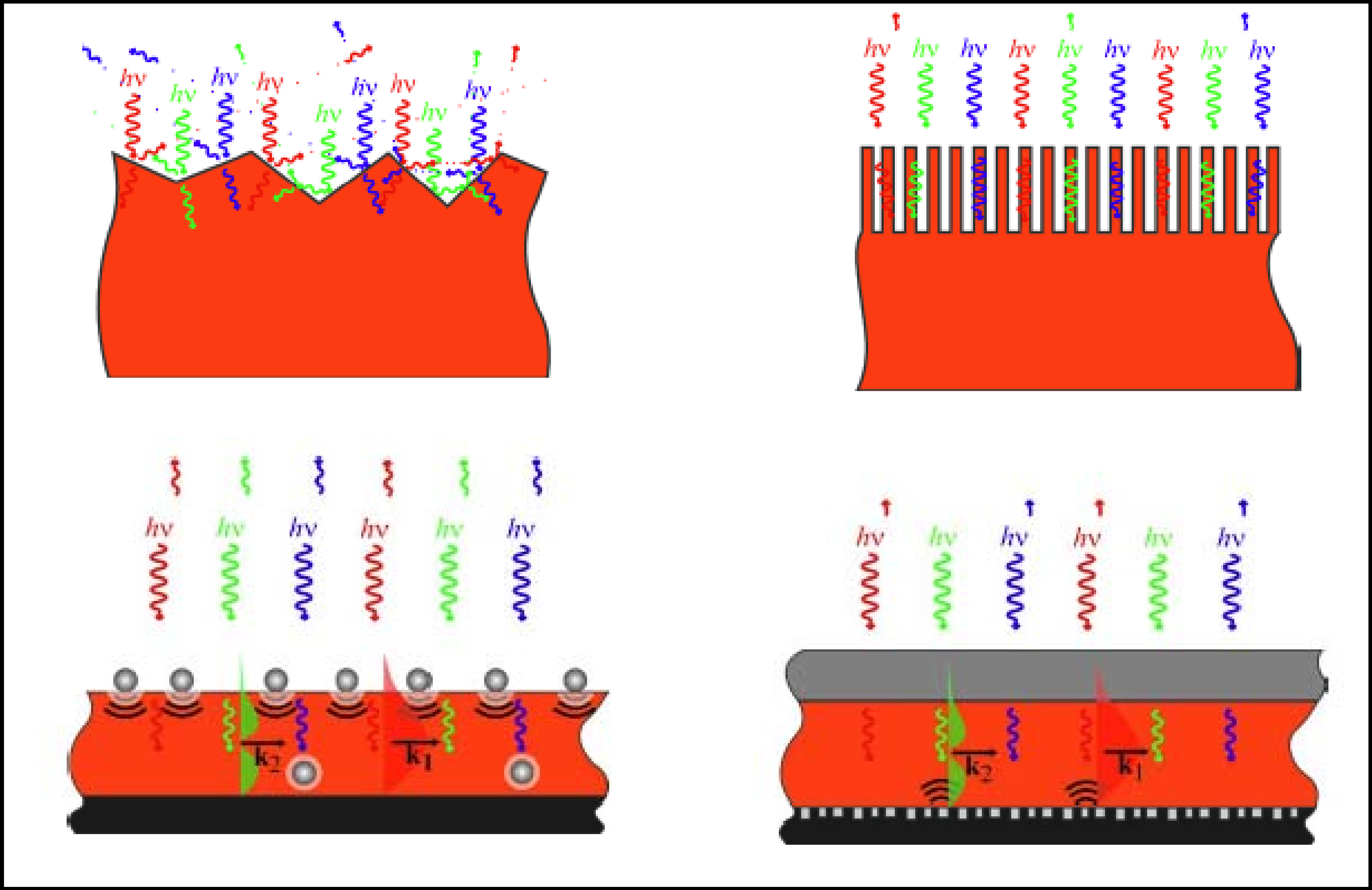
Optical absorption vs. carrier collection

- Optical absorption efficiency and carrier collection efficiency can impose conflicting requirements on solar cell dimensions:



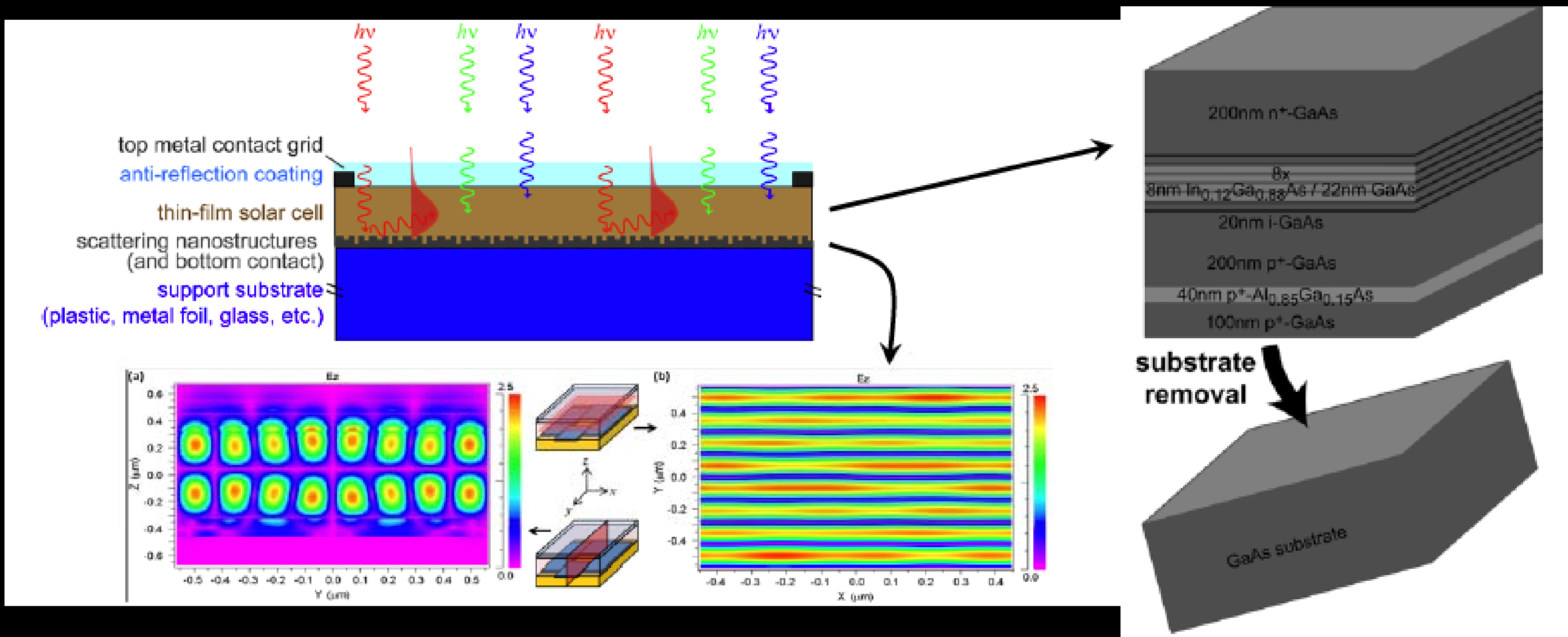
Increasing optical absorption in fixed volumes

- "Light trapping" and related approaches can improve optical absorption efficiency in thin layers:

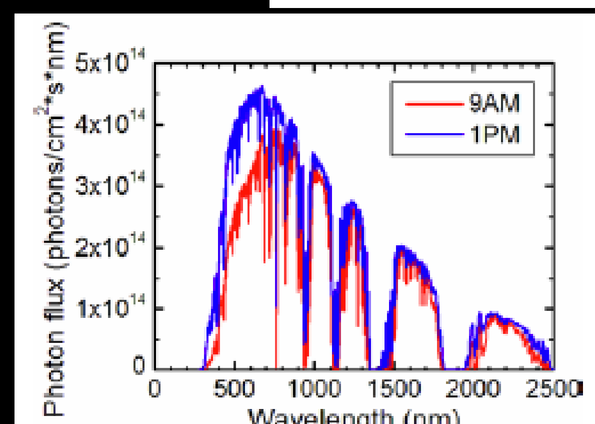


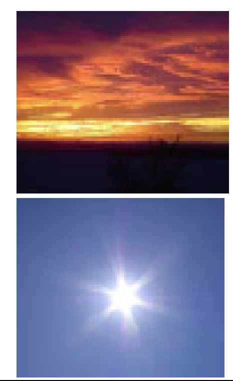
Quantum-well solar cells with light trapping

- Light trapping and substrate removal can provide quantum-well solar cells and related devices with increased long-wavelength absorption

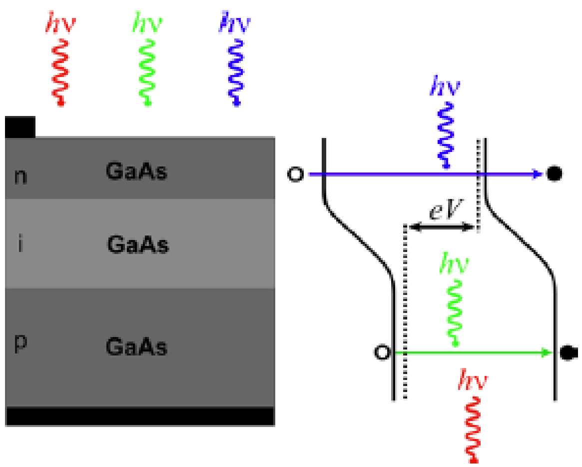


- Quantum-well solar cells and related devices can offer high efficiency over a broad range of spectral conditions due to absence of current-matching constraint

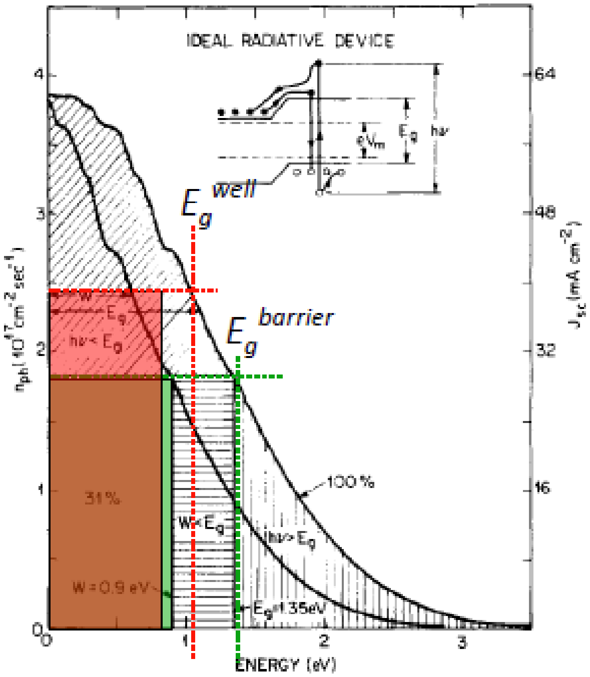


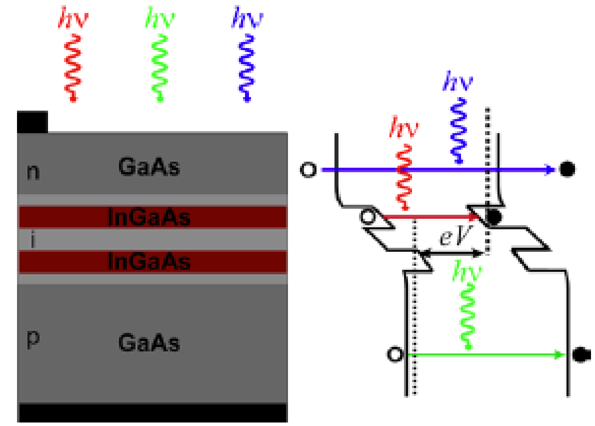


Quantum-well solar cells for high efficiency



[C.H. Henry, *J. Appl. Phys.* 51, 4494 (1980).]





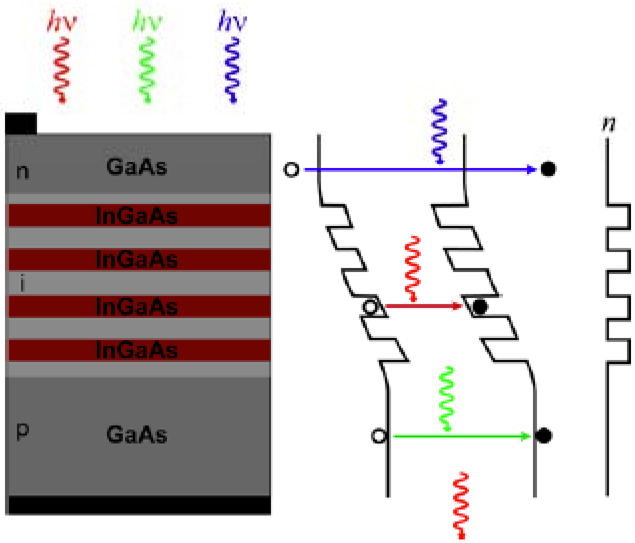
[cf. K. Barnham, G. Duggan, *J. Appl. Phys.* 67, 3490 (1990).]

- Predicted maximum power conversion efficiencies for quantum-well solar cells are ~45% up to >60% (vs. ~31% to ~37% for "conventional" solar cell)

  [G. Wei, K.T. Shiu, N.C. Giebink, S.R. Forrest, *Appl. Phys. Lett.* 91, 223507 (2007);
  S.P. Bremner, R. Corkish, C.B. Honsberg, *IEEE Trans. Electron Devices* 46, 1932 (1999).]

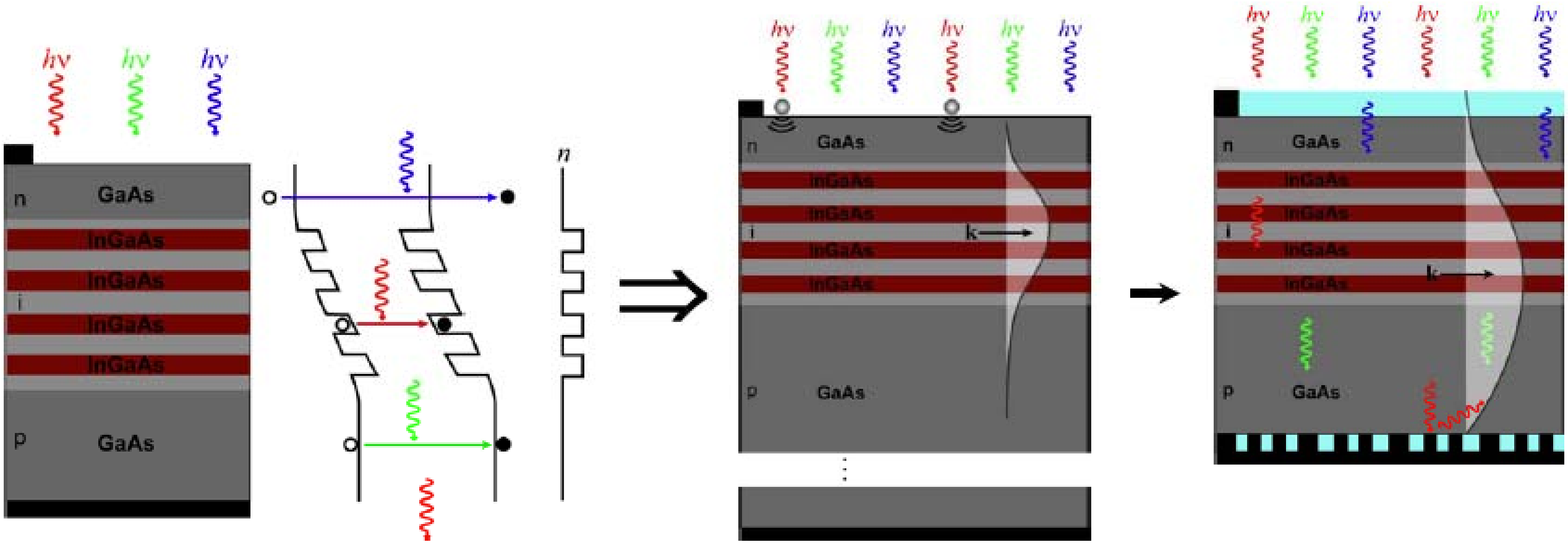
- Robust performance under spectrally varying (terrestrial) illumination by avoiding current-matching constraint present in multijunction solar cells
- Numerous challenges exist in realization of high QWSC efficiency
  - Multiple-quantum-well materials issues, e.g., critical thickness
  - High quantum efficiency in long-wavelength absorption
  - Efficient carrier extraction from quantum wells

Quantum-well solar cells for high efficiency



- Multiple-quantum-well layers enable absorption at energies below band gap of barrier, electrode layers
- Thickness of multiple-quantum-well layers subject to conflicting requirements
  - Thick (~1μm or more) layer required for full absorption
  - Lattice mismatch will limit multiple-quantum-well layer thickness
  - Thinner multiple-quantum-well layer (~0.2-0.3 μm) improves field-assisted carrier extraction
- Can efficient absorption be achieved in thin multiple-quantum-well layer?

Quantum-well solar cells for high efficiency

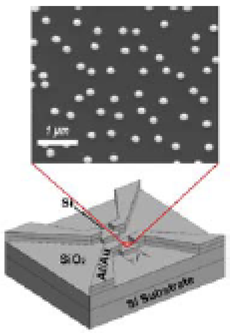


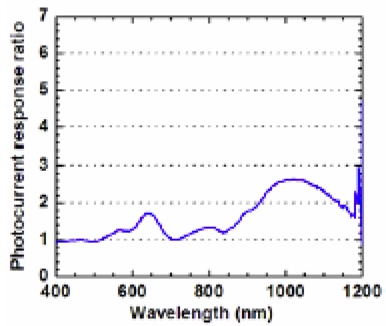
[D. Derkacs, W. V. Chen, P. Matheu, S. H. Lim, P. K. L. Yu, E. T. Yu, *Appl. Phys. Lett.* 93, 091107 (2008).]

- Index contrast leads to optical confinement in multiple-quantum-well region
  - Optically confined, lateral photon propagation paths supported
  - Metal or dielectric nanoparticles can scatter light into lateral propagation paths
  - Poor confinement due to low index contrast with bulk substrate
- Substrate removal allows thin (~1μm) device layer to act as waveguide
  - Metal/dielectric subwavelength structures on back of device to scatter long-wavelength photons into guided modes
  - Allows incorporation of antireflection coating on top surface
  - Device structures can be transferred to variety of mechanical support substrates

Design of metal/dielectric scattering structures

- Metal/dielectric subwavelength structures can enable efficient coupling to thin-film waveguide modes
  - Random vs. periodic vs. multiply periodic structures
  - Simultaneous optimization of scattering structure and absorption vs. wavelength
  - Large enhancement in absorption vs. high absolute absorption efficiency





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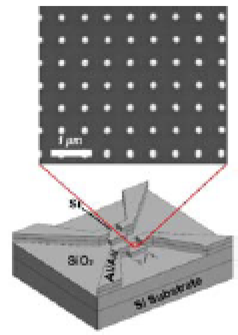
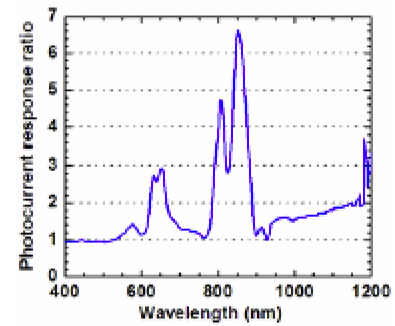
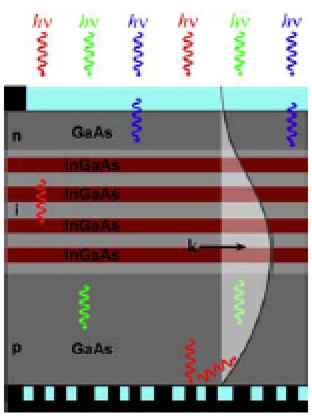
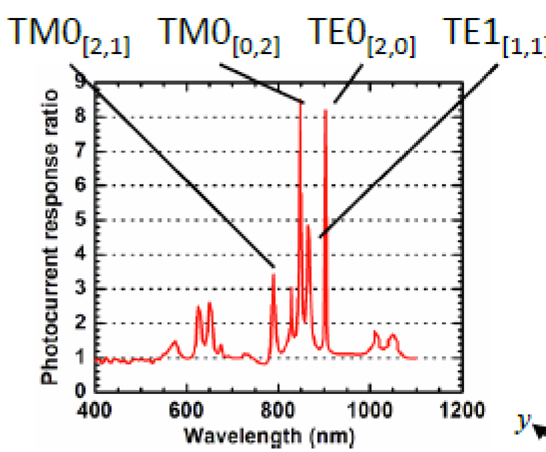
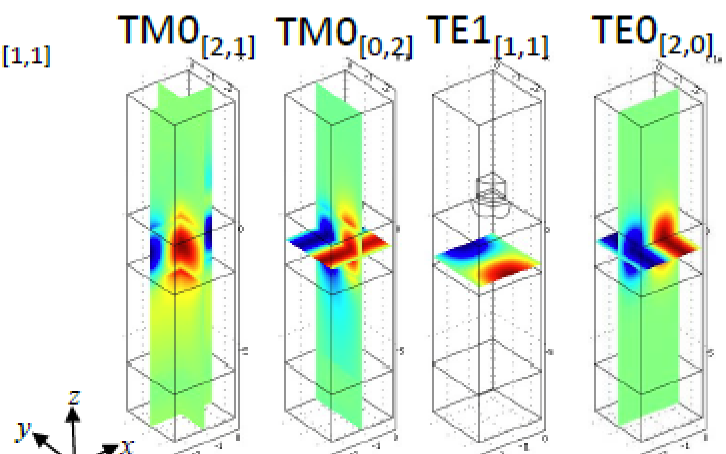




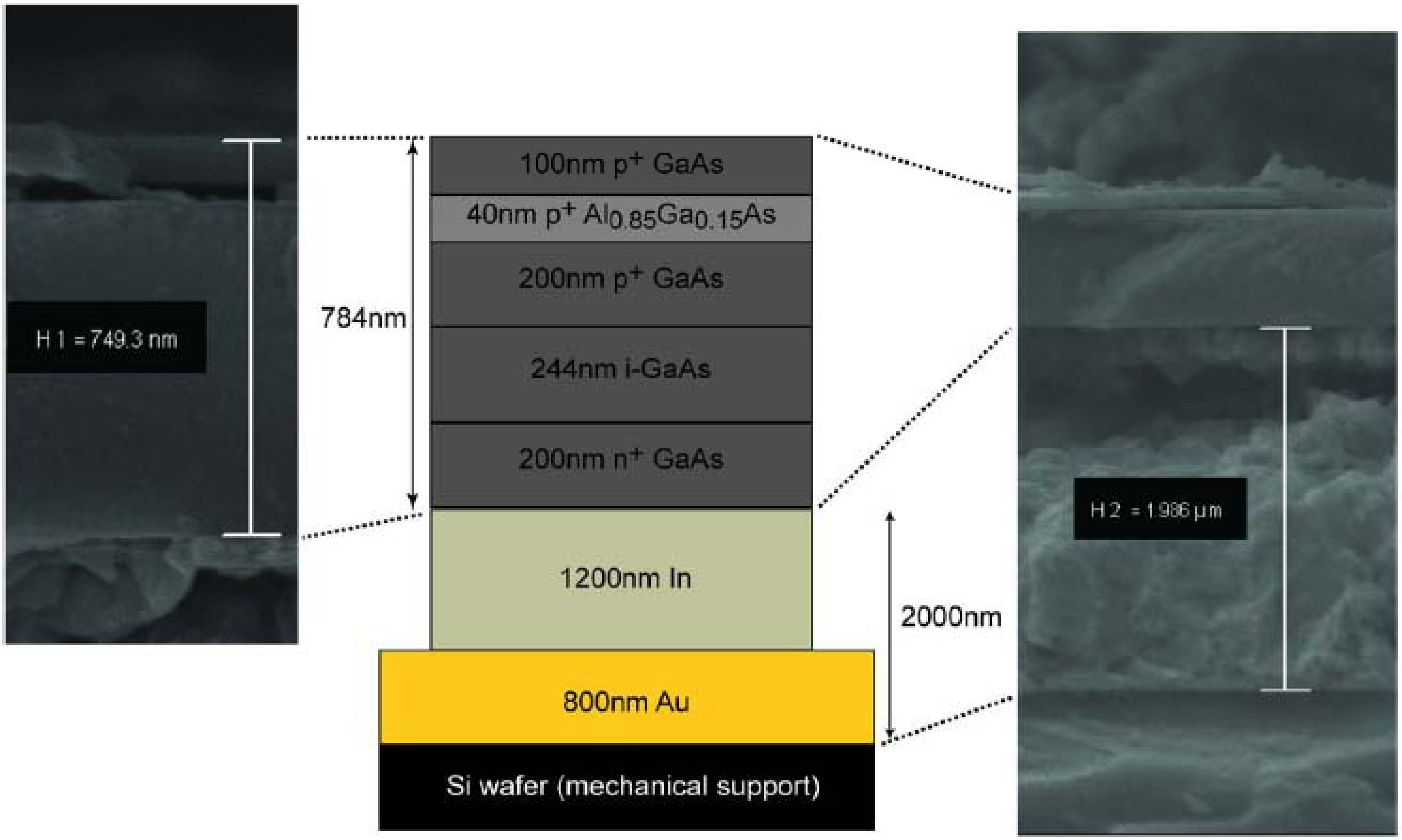






[S. H. Lim, D. Derkacs, and E. T. Yu, *J. Appl. Phys.* 105, 073101 (2009).]

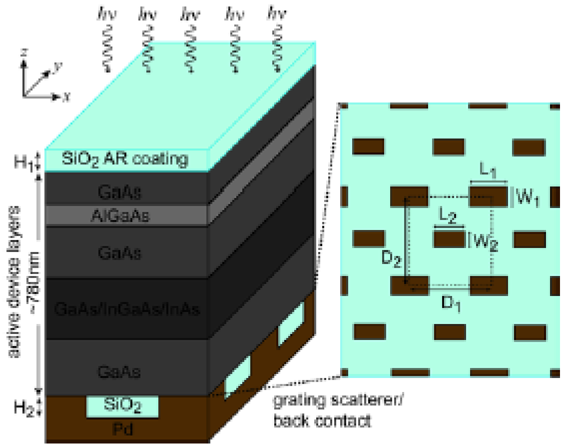
Structures after bonding and substrate removal



- Bonding of epitaxial layers to mechanical support wafer and mechanical/chemical removal of growth substrate results in ultrathin device structure with mechanical support provided by alternate substrate

Simulation results

- Wavelength-dependent optical absorption computed relative to absorption in identical structure with planar metal back contact
  - <550nm: unity absorption ratio due to high absorption coefficient
  - 550-850nm: oscillations due to effect of ~140nm SiO_2 on Fabry-Perot oscillations
  - >850nm: large increases in absorption via scattering into specific waveguide modes



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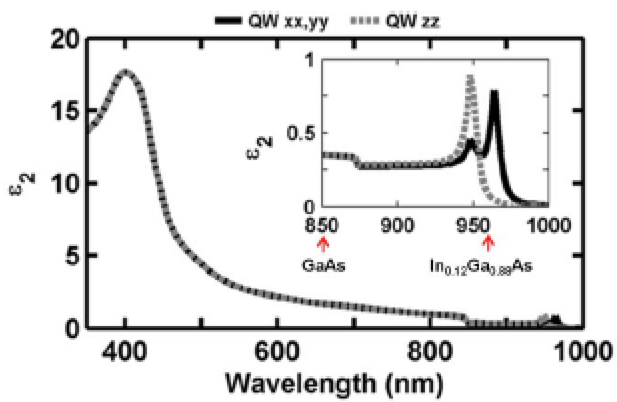
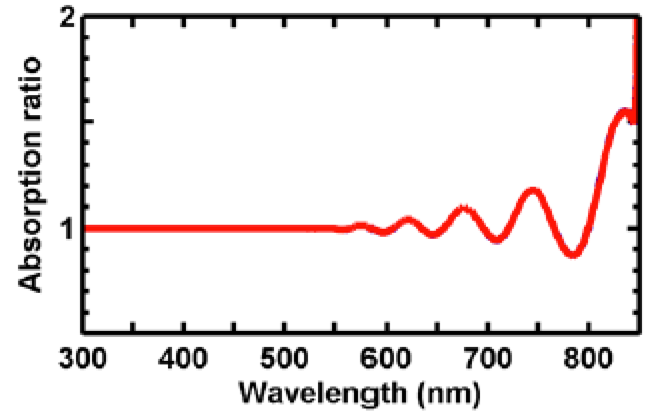
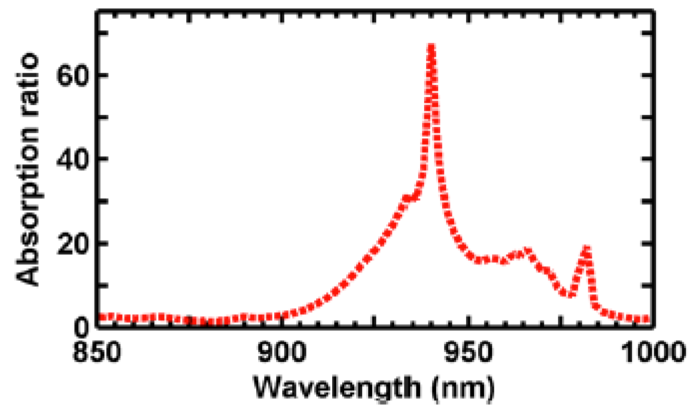
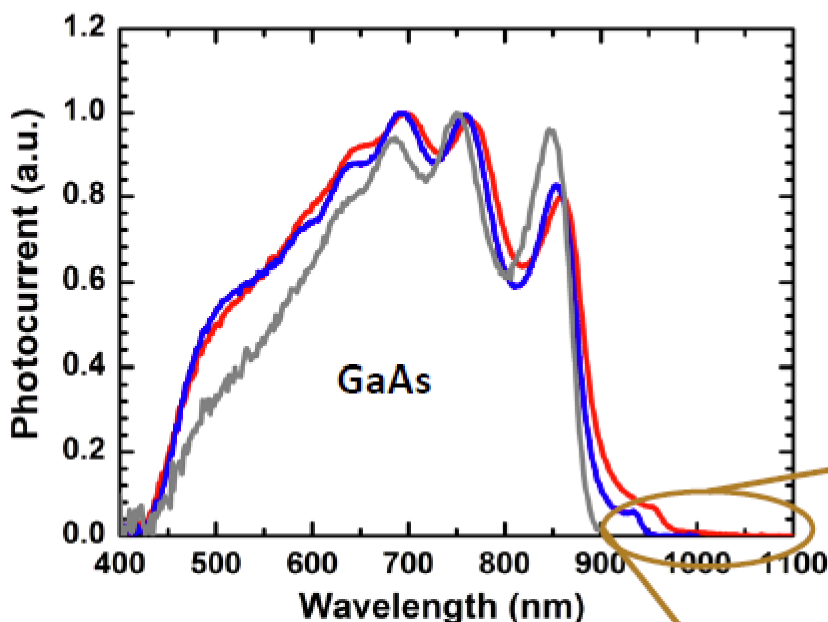
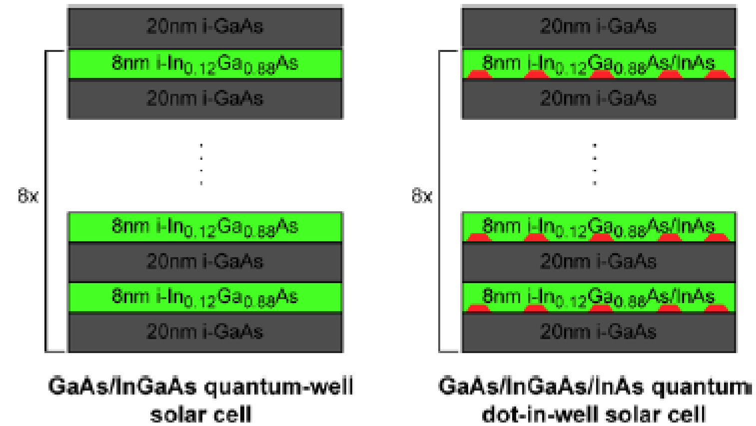


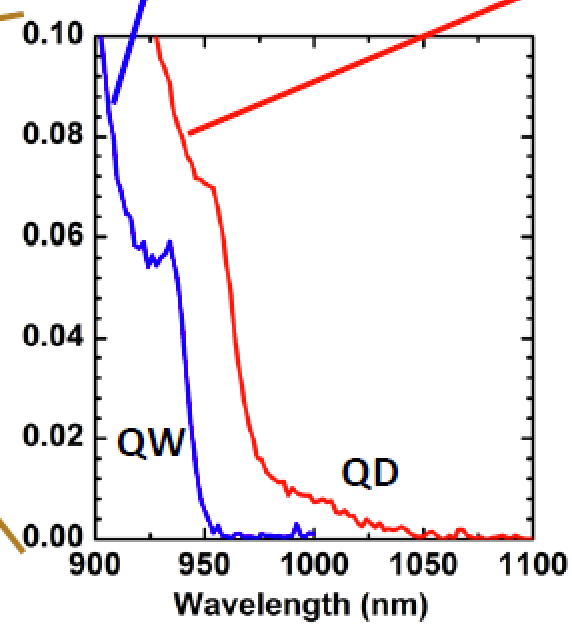




Device characteristics after substrate removal



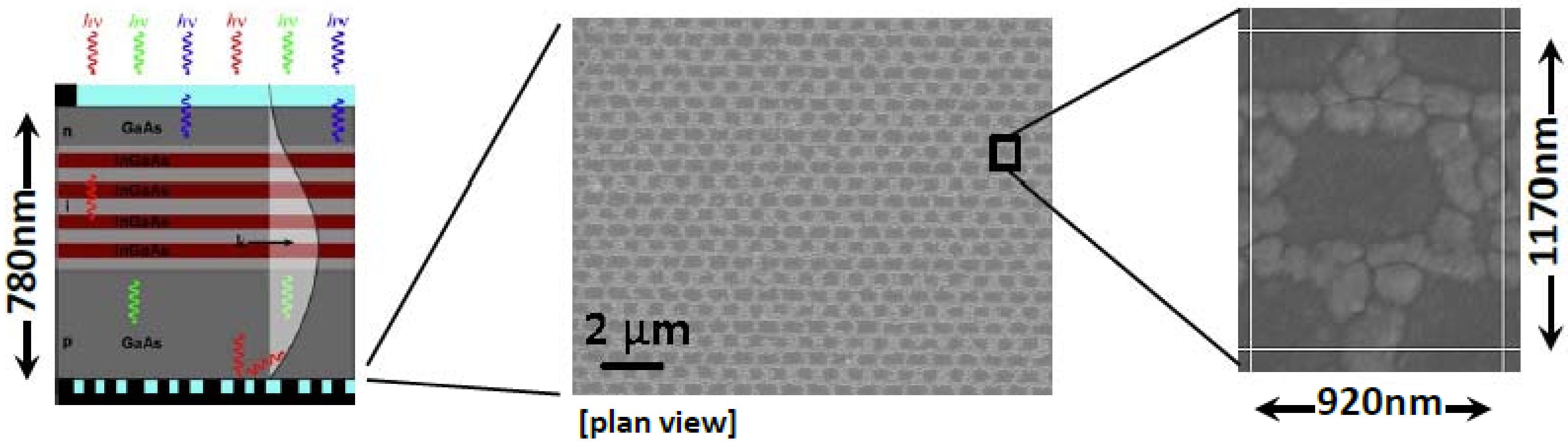


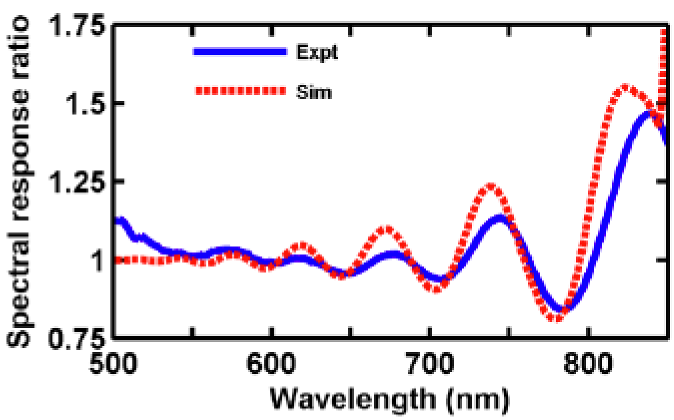


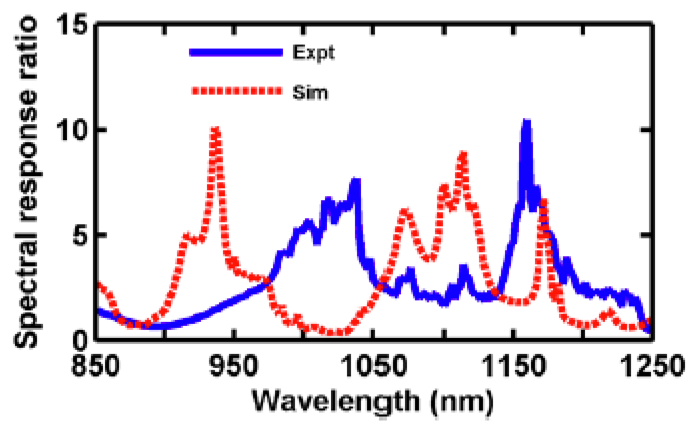
- Photocurrent response spectra confirm absorption and carrier collection from InGaAs quantum-well and InAs quantum-dot regions
- Nanostructured scatterers should enable increased photocurrent response from quantum-well/dot regions and potentially high absolute efficiencies

Devices with nanostructured back contacts

- Devices with nanostructured back contacts show anticipated changes in optical absorption relative to devices with planar metal back contacts
  - Constant or oscillatory absorption ratios for $\lambda < 850$nm
  - Large increases in optical absorption over relatively narrow wavelength ranges for $\lambda > 850$nm



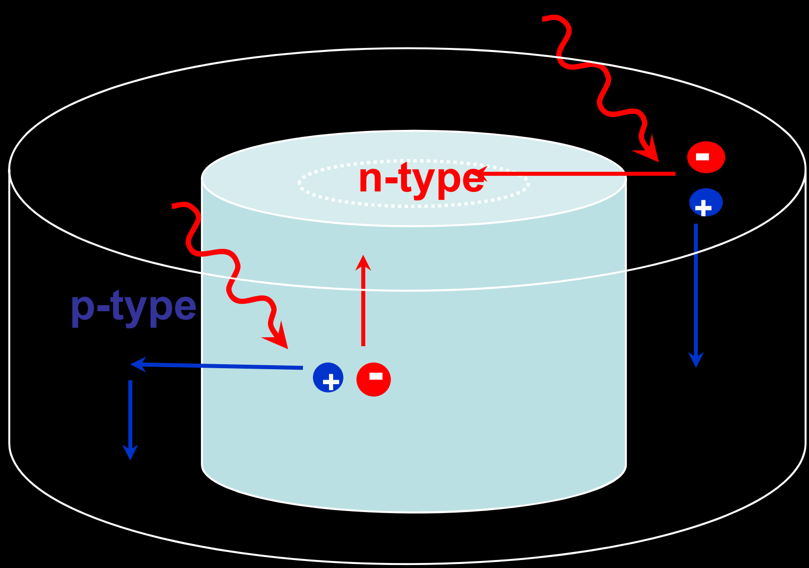


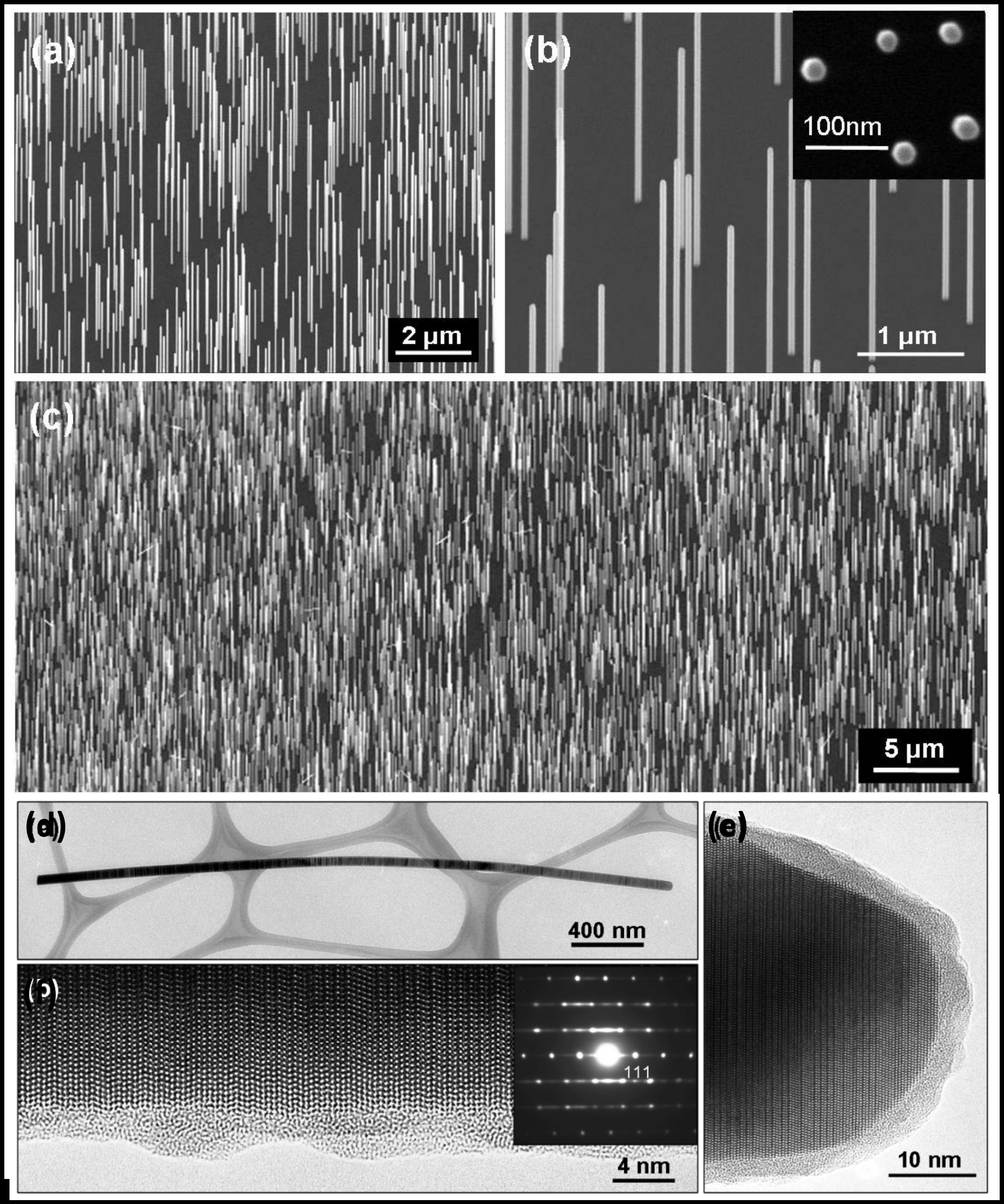


- *Introduction*
- *QWSC with nanoscatters*
- *NW solar cells – effort led by Prof. D. Wang*
- *Branched NW photoelectrochemical cells*
- *Summary*

Nanowire Solar Cells

- Vertical NW arrays enhance light absorption → improve light harvesting
- Vertical NW arrays reduce angular dependence → improve light harvesting
- NW device engineering/multi-junction architectures allow tandem stacking → improve solar harvesting & photon conversion
- Carrier collection at short diffusion length → improve carrier collection
- Yielding much enhanced solar absorption and conversion to electricity
- Large area, less materials, cheap substrates, flexible, etc.



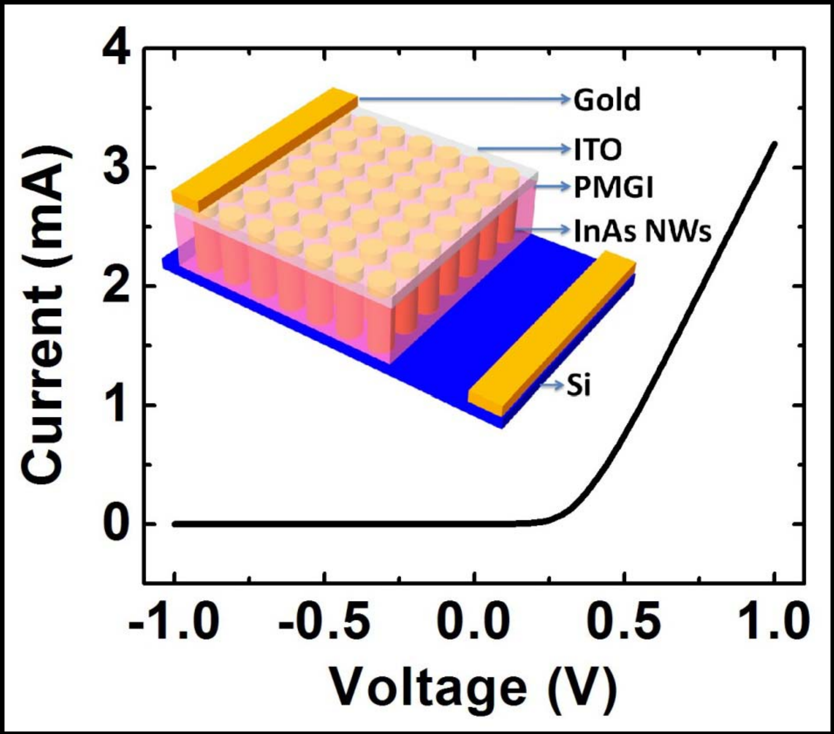


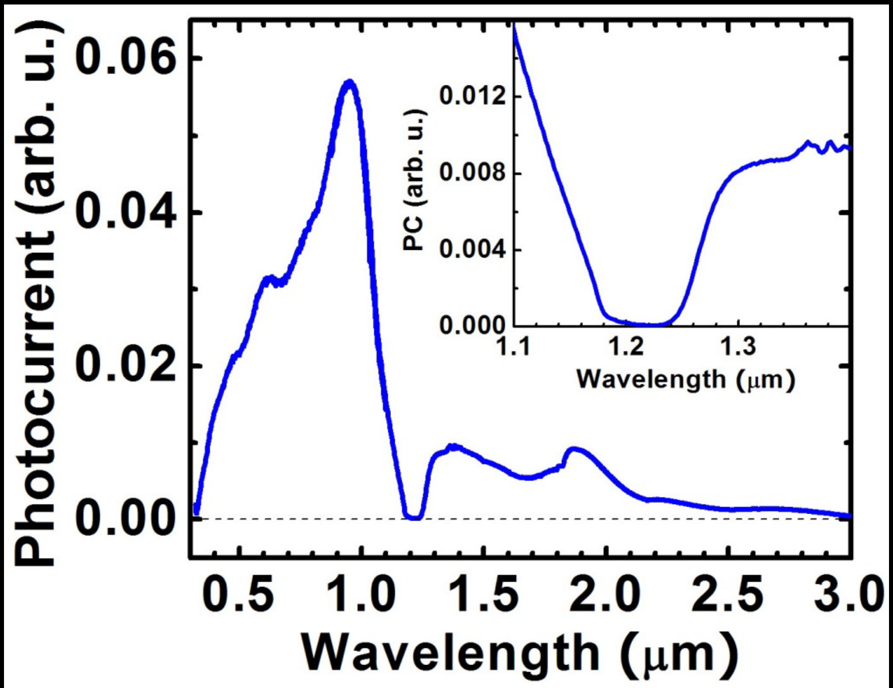
Direct integration vertical III/V NWs arrays on Si – InAs NWS/Si PDs and PVs

- ❖Direct growth of InAs on Si(111)
- ❖Vertical heteroepitaxy
- ❖Simple one step etching of native SiO2
- ❖Uniform nanowire morphology
- ❖Single crystal Wurzite
- ❖Wafer scale (2” Si)

Wei, Soci, et al. Nano Lett 2009

n-InAs NW on p-Si heterojunction devices

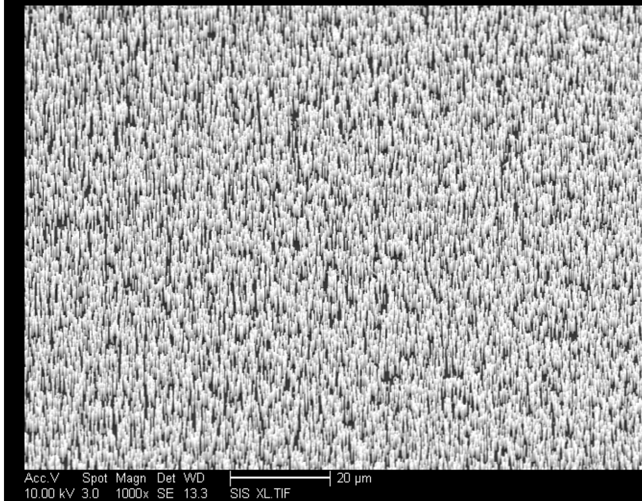


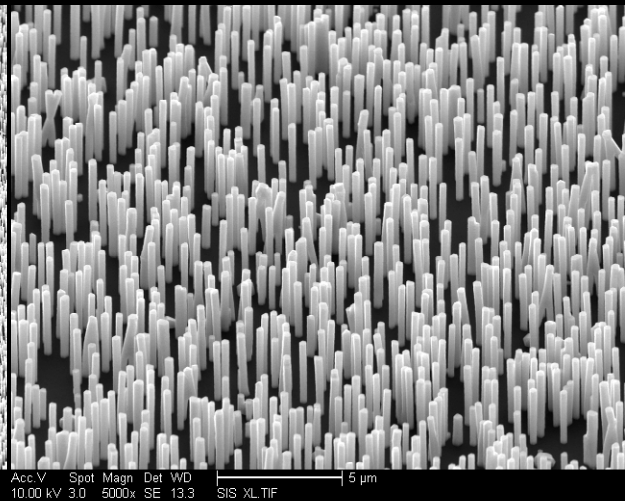


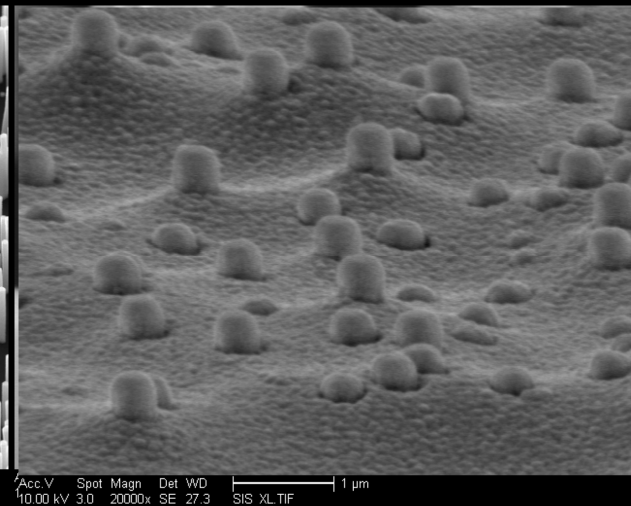
- *III/V compound semiconductor on Si*
- *Heterojunction p/n photodiode*
- *Broadband photoresponse - both visible and infrared ranges*

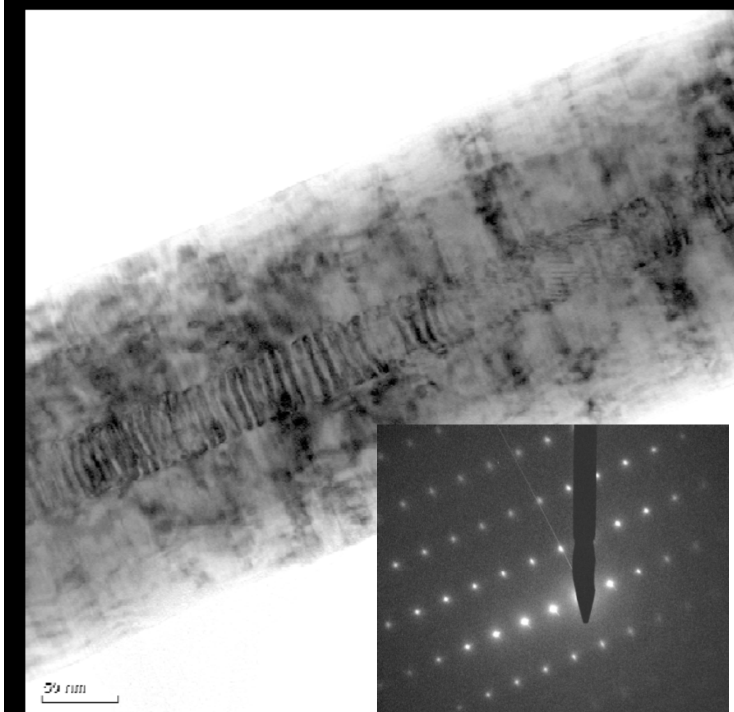
Wei, et al. Nano Lett 2009

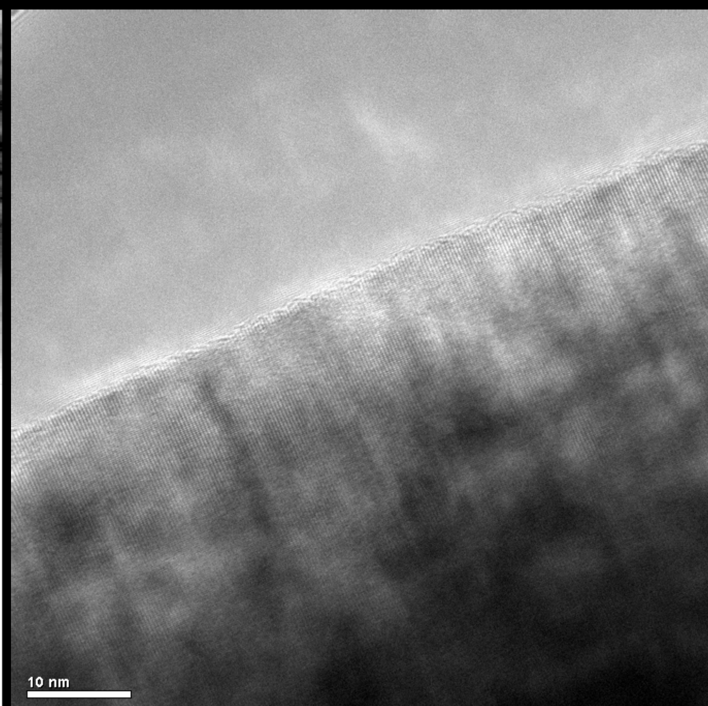
Core/shell NWs on Si ---- InAs(n)/InGaAs/GaAs/InGaP(p)











- ❖**Uniform core/mutlti-shell NWs**
- ❖**Solar cell show very low energy conversion efficiency (<0.5%)**

YJ, KS, KK (SFU, CA), et al. To be submitted to *Nanoscale (feature article)*.

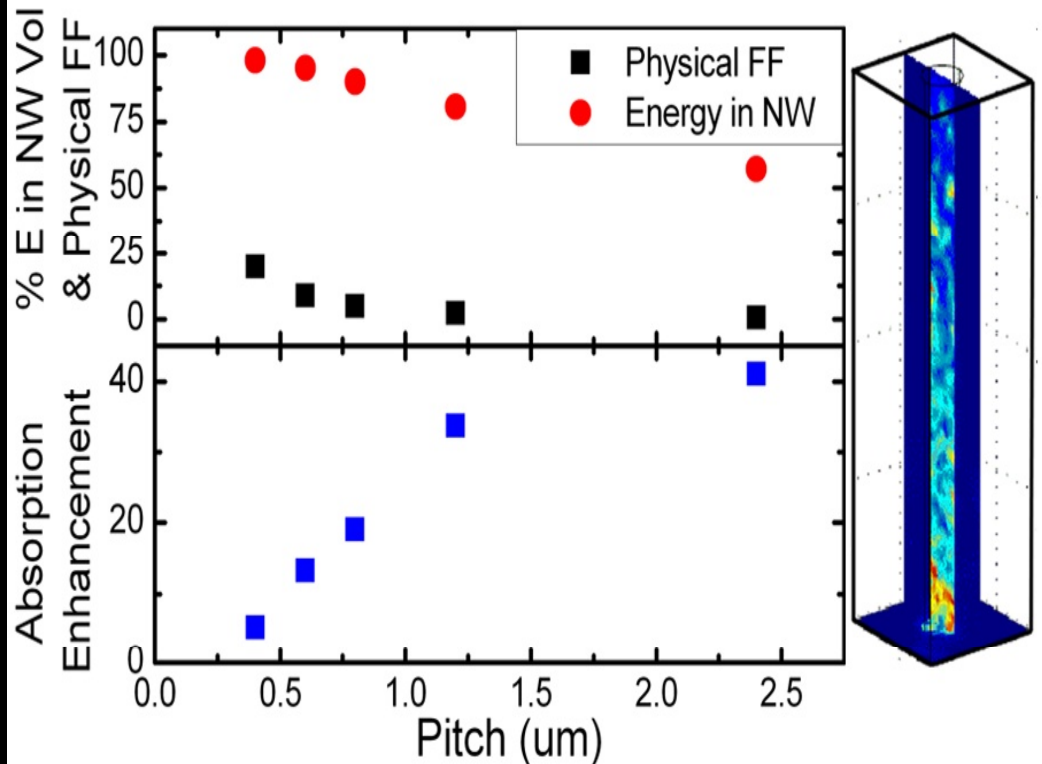
Model System –

Radial *pn* Junction Si NW Solar Cells

Enhanced Light Coupling

Vertical NW geometry can couple light into nanowires due to high index contrast

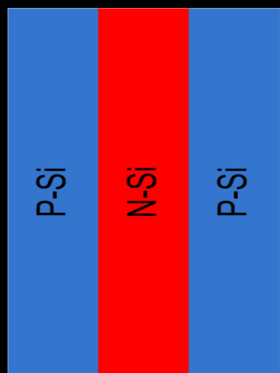
- **<u>Comsol Multiphysics Simulation</u>**
- 2μm length, 200nm diameter wire, varying pitch
- n_{si}=5.43, $n_{polymer}$=1.6
- Light input from top (λ=350nm)
- Periodic boundary conditions, simulations performed with and without NWs
- **Difference in index of diffraction funnels light into nanowires, increasing the coupling efficiency > 40x**



A. Zhang, C. Soci, et.al. APL 2008.

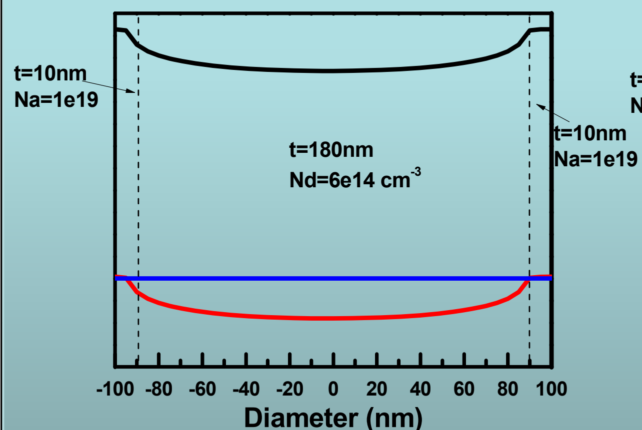
Effect of NW core Doping

1 D Poisson Simulation
Slab Structure

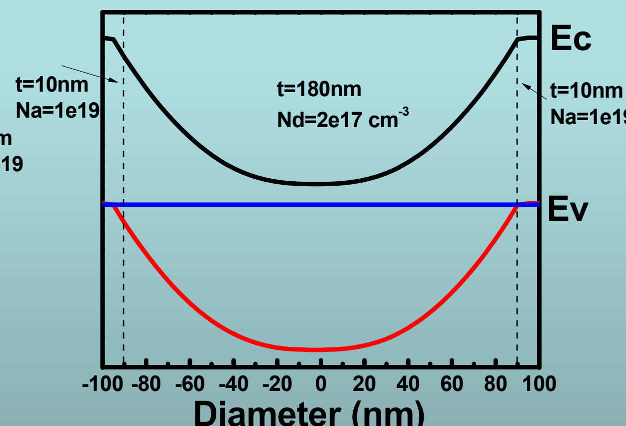


- **Lightly doped core cause fully depletion.**
- **NW core, i.e. substrate should be heavily doped.**
- **Small diameter NWs require higher core doping level to avoid fully depletion.**

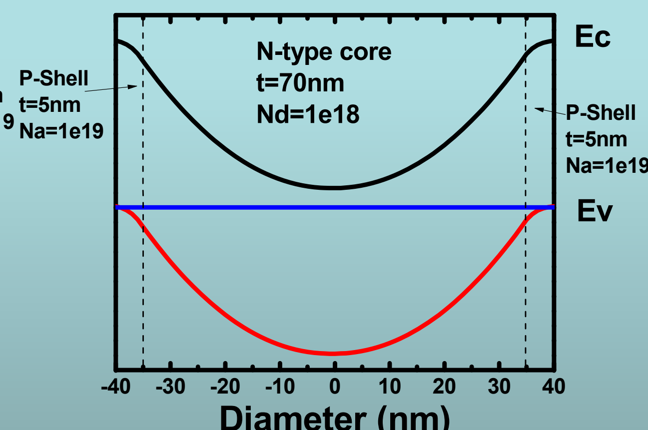
Total Thickness=200nm



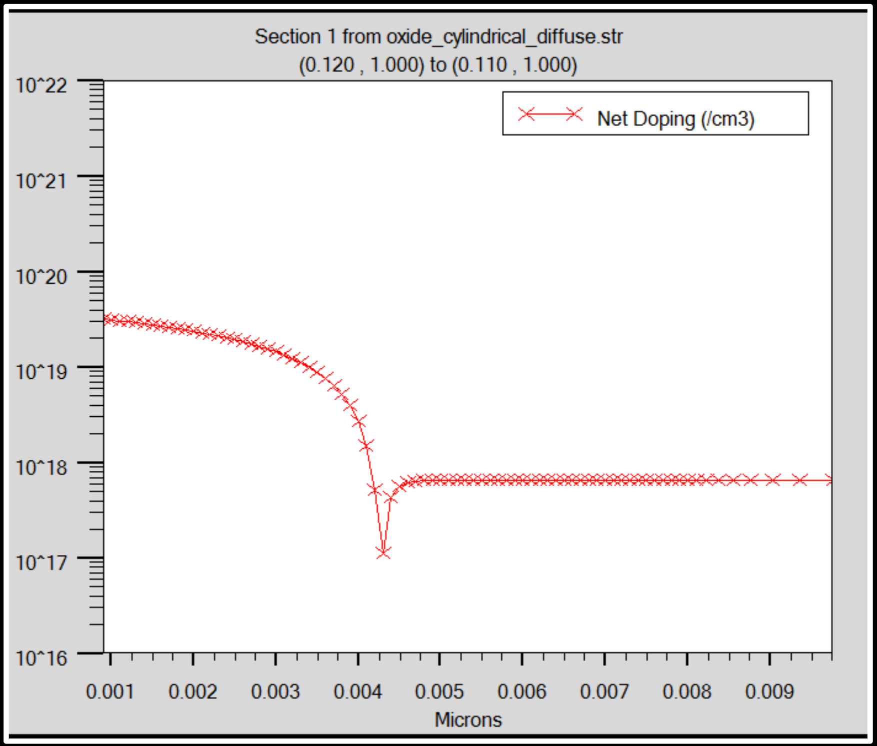
Total Thickness=200nm



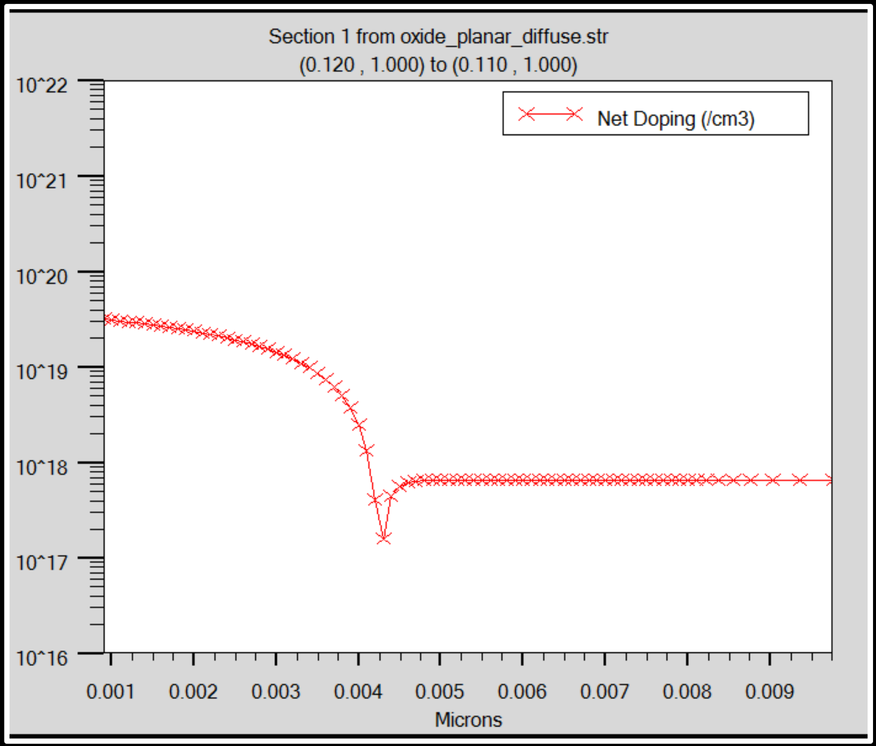
Total Thickness=80nm



Doping Profile vs NW Geometry



Cylindrical geometry

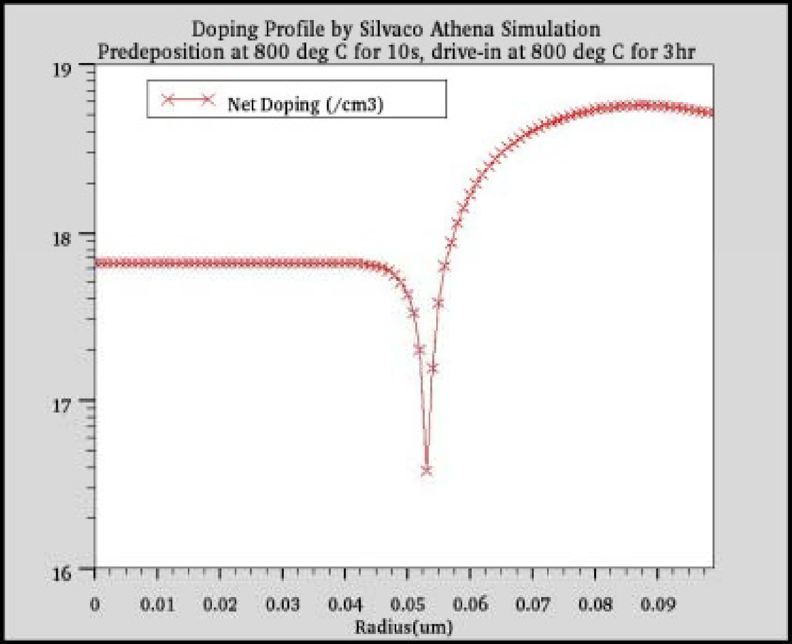


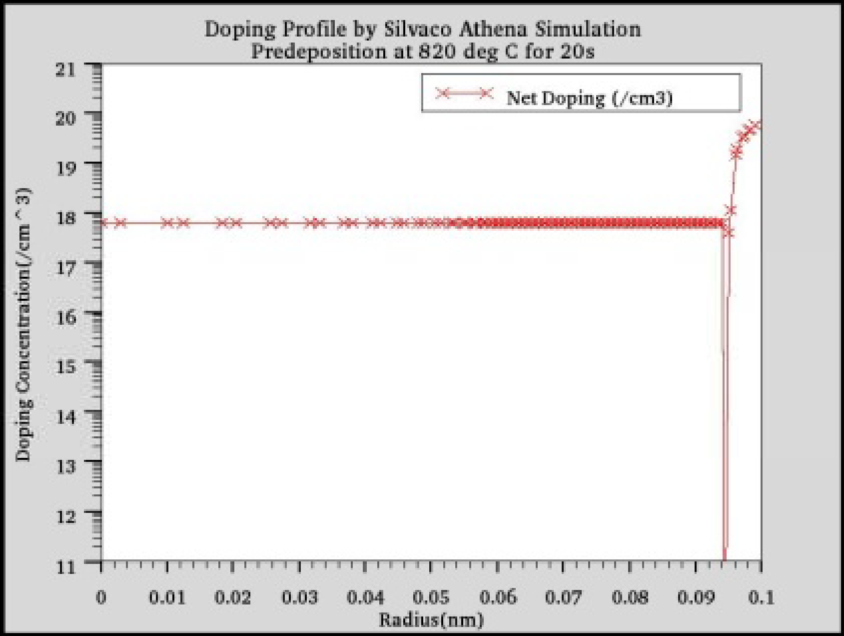
Planar geometry

- *Junction depth identical*
- *Doping profile slightly different (cylindrical higher)*

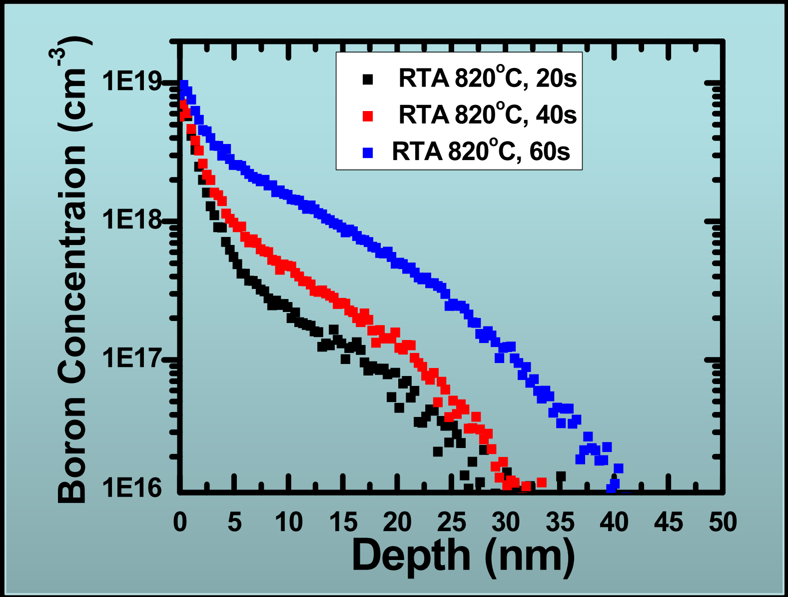
S. Vishniakou 2011.

NW Shell Doping

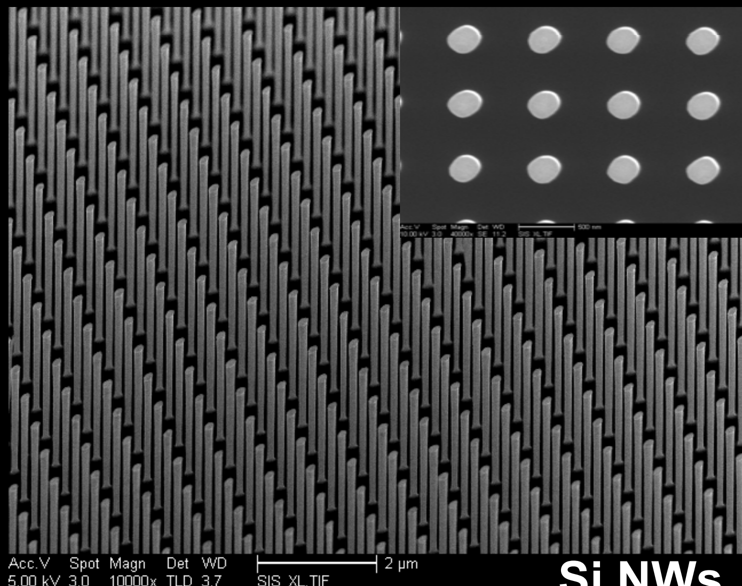




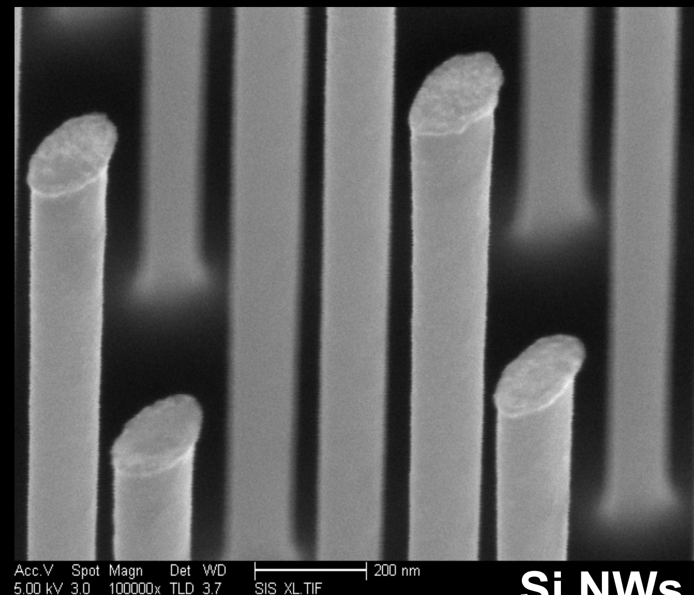
- Junction depth can be well controlled by tuning annealing temperature and time
- Junction depth as shallow as 5nm can be achieved.



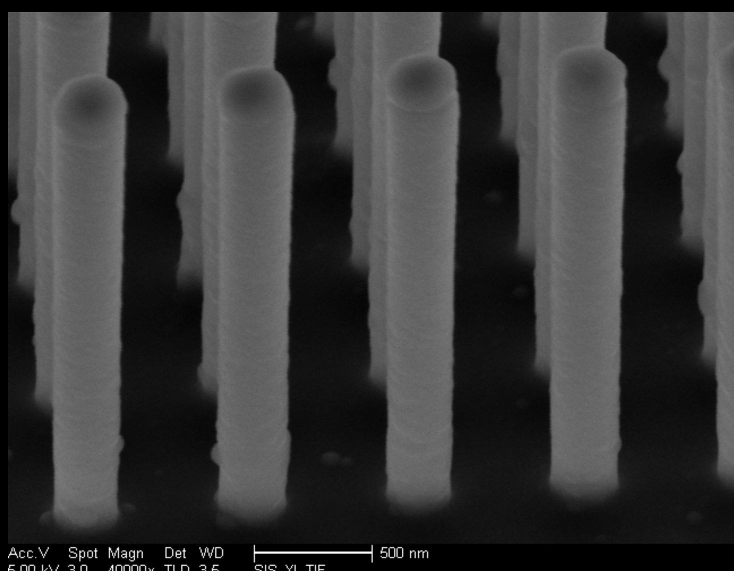
SiNWs by ICP-RIE



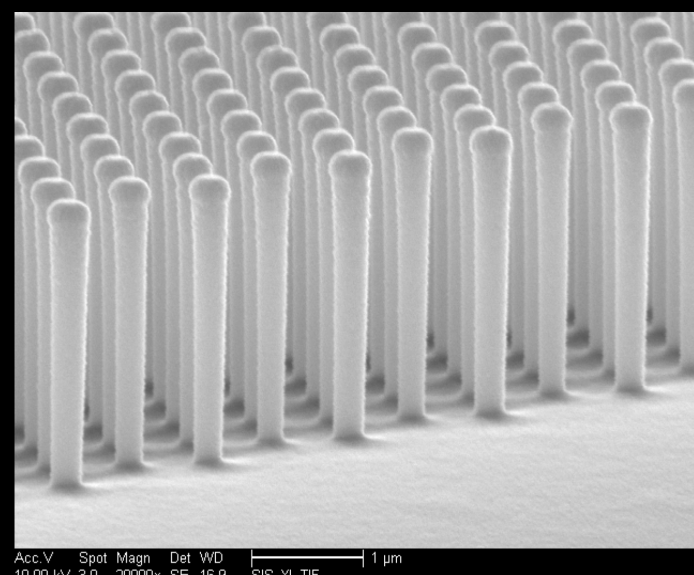
Si NWs



Si NWs

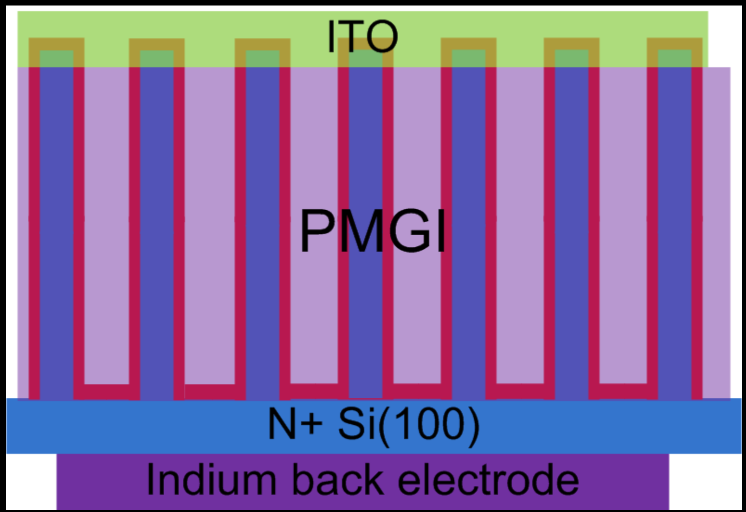


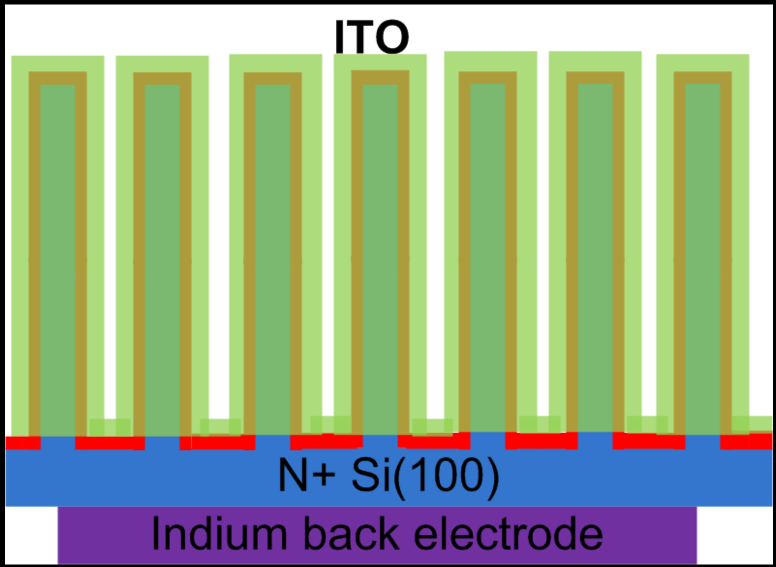
Si NWs with SiNx coating



Si NWs with ITO coating

With PMGI vs. Conformal ITO coating





- ❖SiNW core doping, 6.5e17cm^{-3}.
- ❖Dope P type shell at 820°C for 20s
- ❖Spin coat PMGI insulating layer.
- ❖Remove excess PMGI using O_2 RIE.
- ❖Sputtering ITO top contact.

- ❖SiNW core doping, 6.5e17cm^{-3}.
- ❖Dope P type shell at 820°C for 20s
- ❖Without PMGI
- ❖Sputtering ITO top contact directly on NW shell.

Y. Jing, et. al. submitted (2011).

Results of Core/Shell NW Solar Cell

Sample	Core doping (cm^{-3})	SOD condition	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE(%)
#1:No shell coating	1e15	820°C,20s	0.33	0.26	0.18	0.015
#2: No shell coating	6.5e17	820°C,20s	0.13	5.52	0.27	0.194
#3: 60nm PECVD Si_3N_4 shell coating	6.5e17	820°C,20s	0.15	12.2	0.269	0.49
#4: 60nm ITO shell coating	6.5e17	820°C,20s	0.235	13.4	0.285	0.90
#5: 60nm ITO shell coating	6.5e17	Predeposition: 800°C,10s; Drive-in: 800°C,3hr	0.314	26.6	0.296	2.38

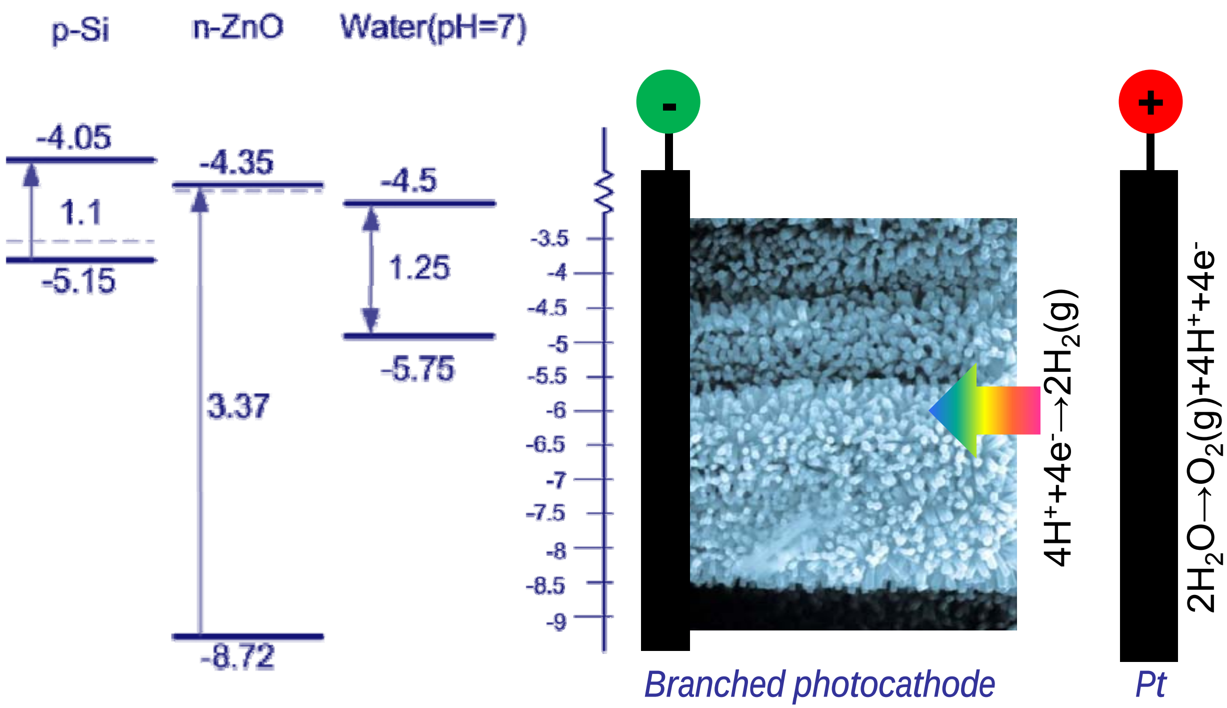
Y. Jing, et. al. submitted (2011).

Summary

- Well controlled nanoscale doping was achieved; junction depth and doping profile can be tuned by changing anneal temperature and time.
- Si NW radial P-N junction solar cells were demonstrated.
- To avoid fully depleted NW core, high doping concentration of NW core is required.
- Devices with conformal top contact show better performance.
- Charge collection was enhanced by using conformal ITO top contact.
- Energy conversion efficiency was increased to 2.4%.
- By using Ag grid contact, charge collection can be further improved
- Fill factor is low, indicating a large series resistance and small shunt resistance. More work needed on contact to improve the efficiency.

- *Introduction*
- *QWSC with nanoscatters*
- *NW solar cells*
- *Branched NW photoelectrochemical cells*
- *Summary*

3D Branched Nanowire Heterojunction Photoelectrodes for High-Efficiency Solar Water-Splitting and H_2 Generation

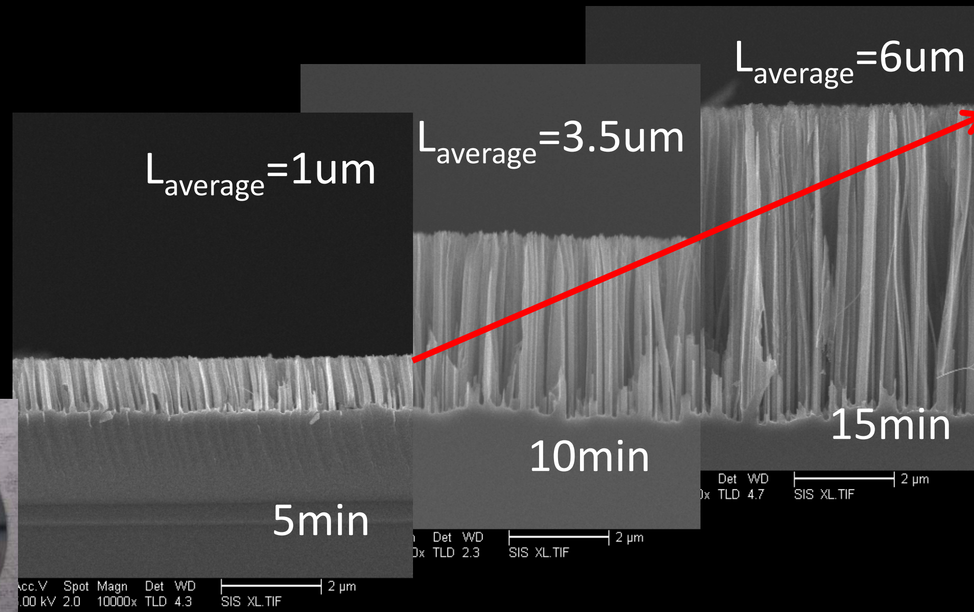


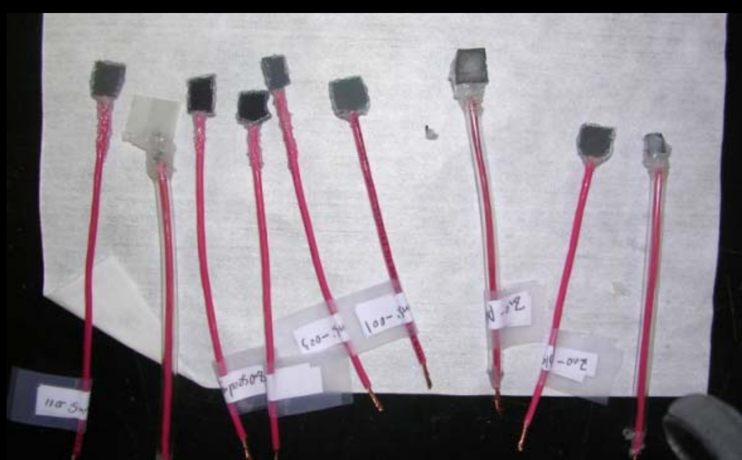
- ❖**Vertical NW arrays enhance light absorption**
- ❖**Large junction area enhances the minority carrier generation, separation, and transport**
- ❖**Much enlarged surface area for chemical reaction**
- ❖**Large surface curvature increase gas evolution**

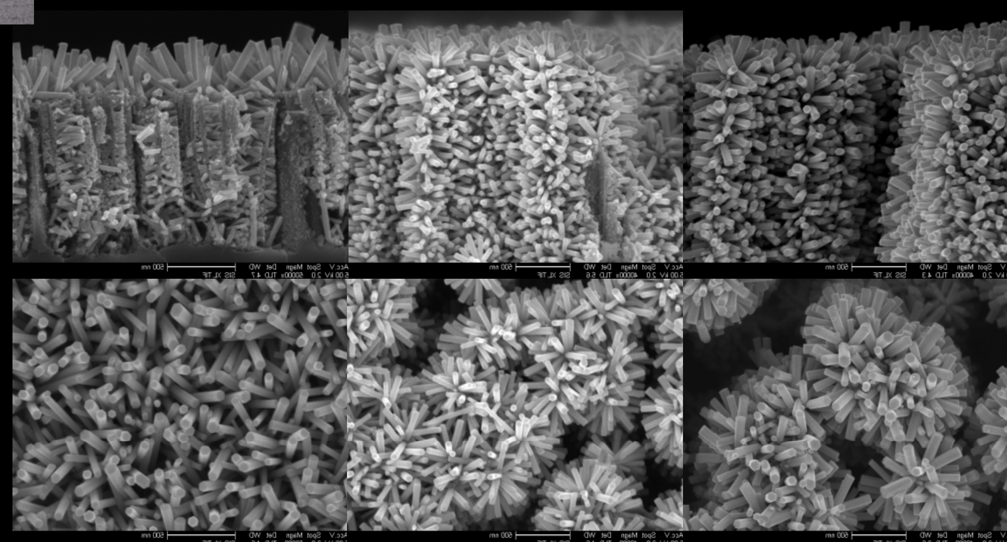
K. Sun, et al., submitted, 2011.

Branched NW Photoelectrode Fabrication

- **Si etching and cleaning**
- **ZnO seeding**
- **ZnO growth**
- **Back contact and wiring**
- **Epoxy sealing**



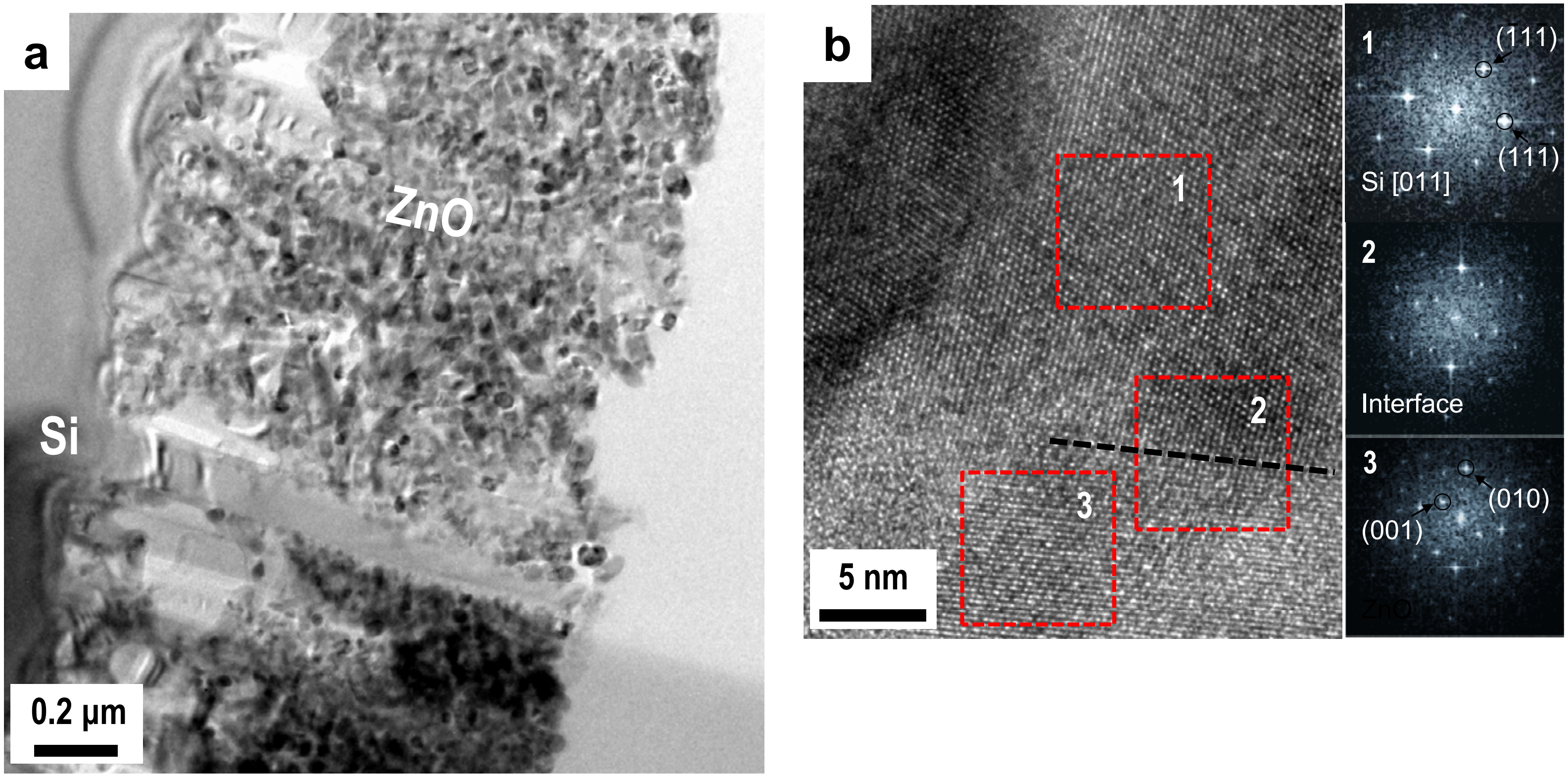




5min etched SiNW **10 min etched SiNW** **15 min etched SiNW**

K. Sun, et al. ***Nanoscale (accepted*****).**

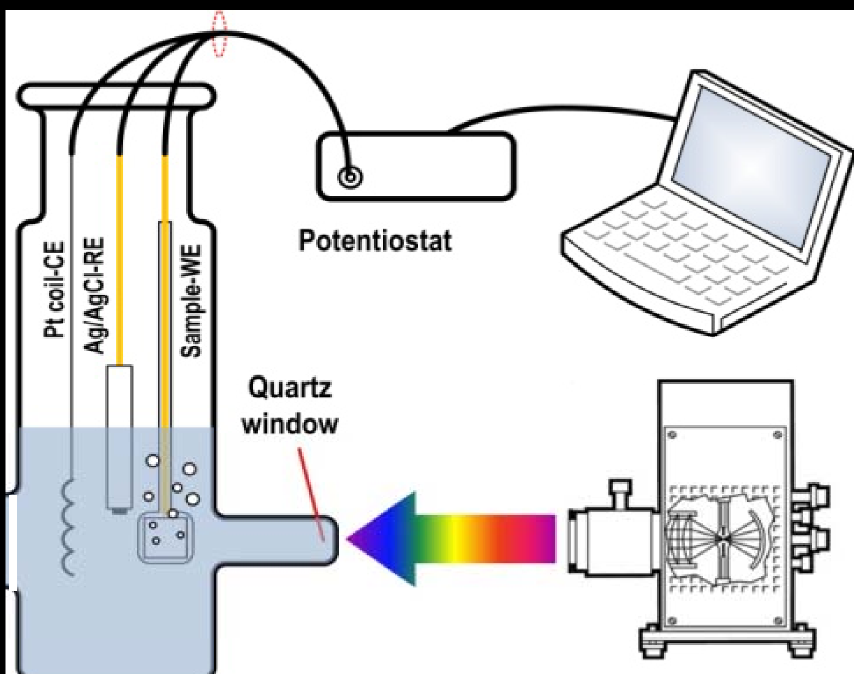
Branched NW Photoelectrode Characterization

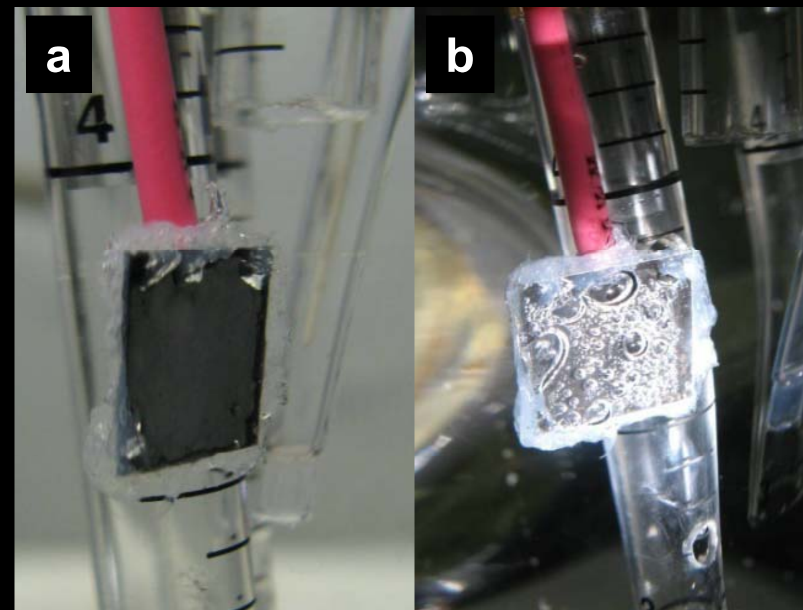


❖**Clean, sharp ZnO/Si interface**
❖**Enhanced light absorption**
❖**Longer ZnO NWs scatters light and reduce light absorption**

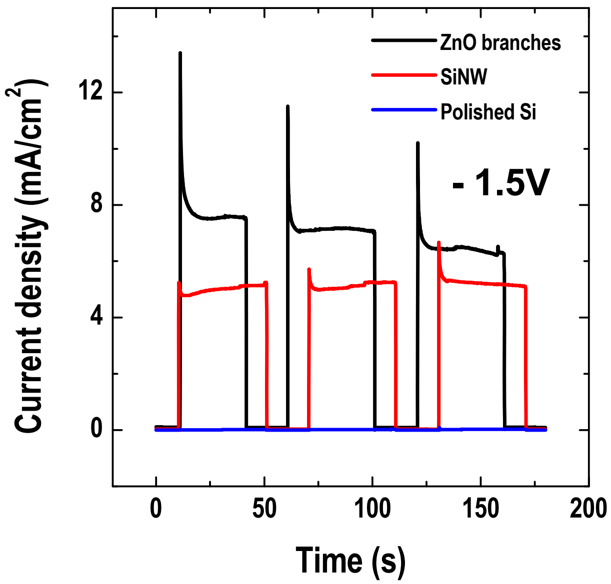
K. Sun, et al., *Nanoscale* (accepted).

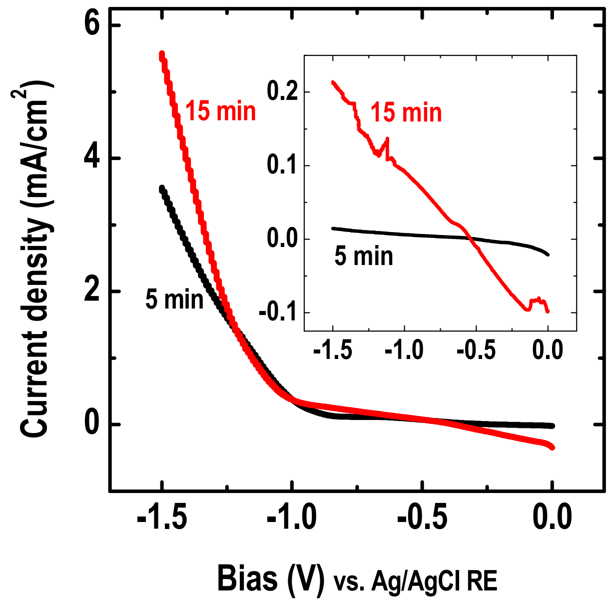
PEC Measurement & Hydrogen Generation

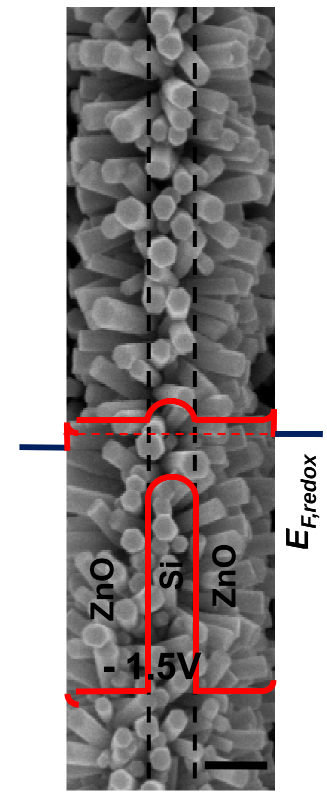




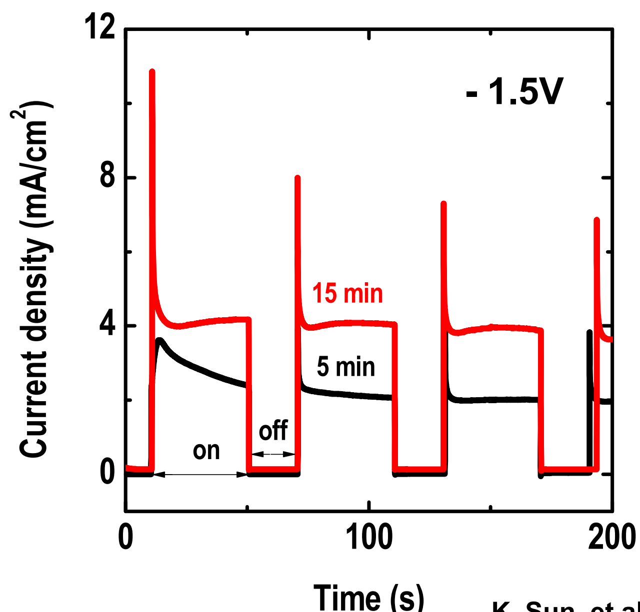
Branched ZnO /Si NW PEC





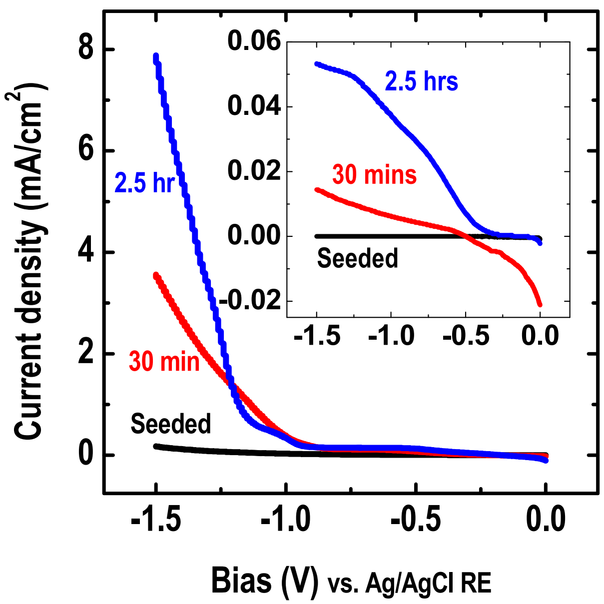


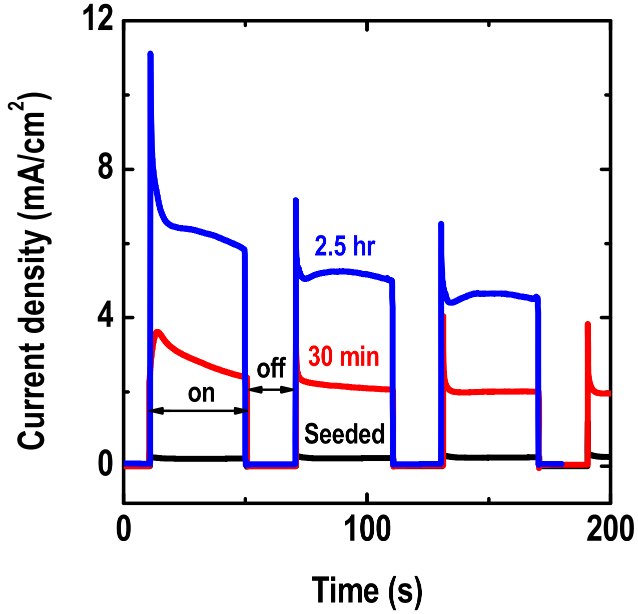
❖Branched NW heterostructure array photocathodes
❖Much enhanced current density compared to bare SI NWs
❖Longer Si NWs show increased cathodic photocurrent and dark current (light absorption and surface area)
❖Longer Si NWs also show larger anodic dark and photo currents (larger surface area)



K. Sun, et al. Nanoscale (Accepted),

Branched ZnO /Si NW PEC





❖Branched NW heterostructure array photocathodes
❖Much enhanced current density compared to bare Si/ZnO core/shell NWs
❖Longer ZnO NWs show increased cathodic photocurrent and dark current (light absorption and surface area)
❖Longer and wider ZnO NWs also decrease anodic dark current (larger diameter, less surface band bending and charge separation)

K. Sun, et al., To be submitted, 2011.
C. Soci, et.al. "Nanowire photodetector", Journal of Nanoscience and Nanotechnology 10, 1430 2010.

Summary

❖**Vertical NW array photovoltaics promise high energy conversion efficiency (solar cell and photoelectrochemical cells)**

❖***Vertical NW arrays enhance light absorption***

❖***Heterojunction improves light absorption and charge generation***

❖***NW structures (radial and branched heterostructures) increase device junction area, and gas evolution efficiency (PECs)***

❖**Wafer scale, low cost synthesis of branched SiNW photoelectrode demonstrated**

❖**Branched SiNW photocathode shows improved photocurrent and enhanced spectrum response comparing to bare SiNWs**

❖**Orders-of-magnitude improvement of photocathodic/photoanodic currents - branched NW heterostructures compared to single materials NW arrays**

❖**Selective photoelectrochemical production of H_2 or O_2 by tailoring doping in Si core NWs**

❖ **These unique 3D branched NW heterostructures are promising photoelectrodes for high efficient photoelectrochemical H_2 generation**

Thank You