Strongly Correlated Electron Systems Functionalized for Solar Cells and Memristors

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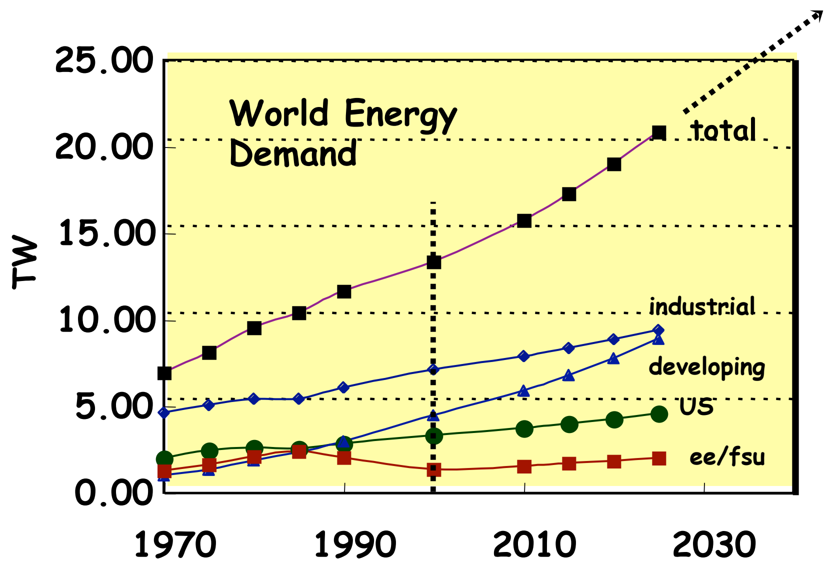
"The energy challenge is one of the greatest moral and intellectual imperatives of our age"

Grand Energy Challenge

Gap between production and demand: ~14TW by 2050

Install one 1GW new power plant/day for the next 40 yrs!

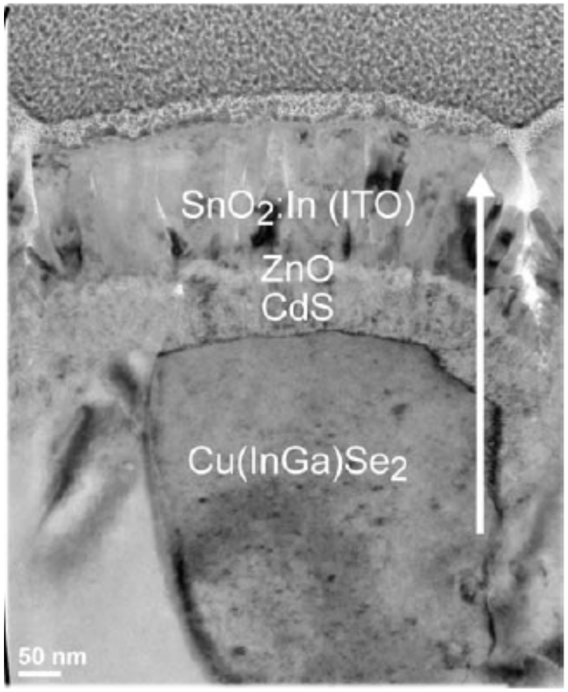


Energy source	World Capacity
Solar	36,000 TW
Geothermal	10 TW
Biomass	7 TW
Hydro	5 TW
Wind	4 TW
Tide	2 TW

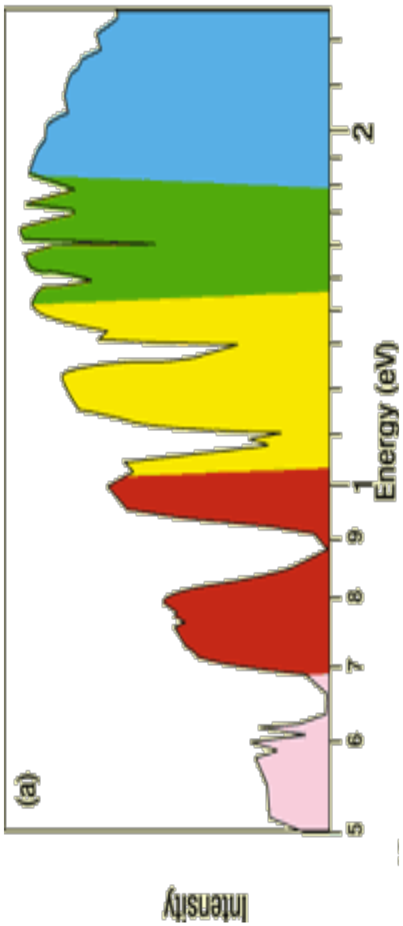
Strongly Correlated Physics in Solar Cells

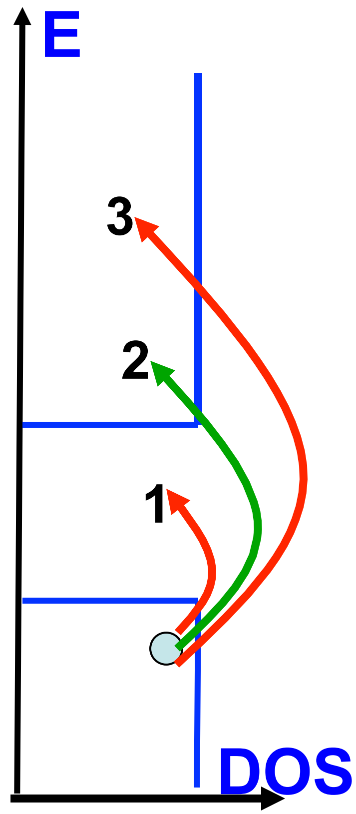
"Progress largely driven empirically,
understanding of even existing cells is lacking" – DOE report, 2010

1. Correlated impurities + Coulomb interaction
2. Multiple scattering theory
3. Plasmon-enhanced solar cells
4. Avalanches on driven Bethe-lattices
5. Designing path-breaking PV architectures
6. <u>Strong Coulomb interaction in nanoparticles</u>



Solar Cells Are Extremely Wasteful





1. No absorption below gap:
   photon wasted

2. Absorption to bottom of
   conduction band: efficient

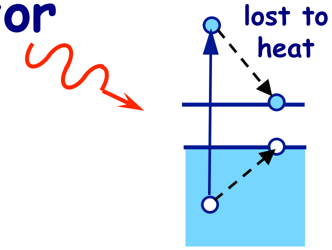
3. Absorption high into band:
   excess energy heats cell

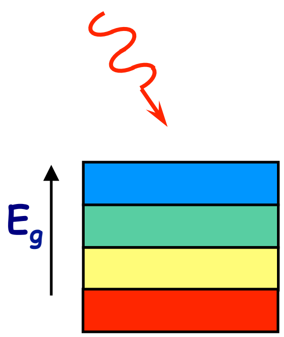
Optimization of gap:
   max efficiency: **31%**
   (Shockley Queisser 1961)

In real PV cells 80-85% of incident solar energy is lost!

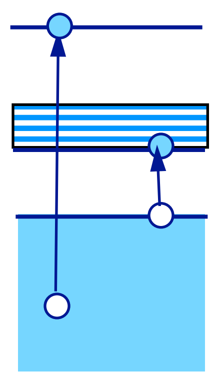
5. Path-breaking PV Designs

Present technology: 31% limit for
- single junction
- one exciton per photon
- relaxation to band edge

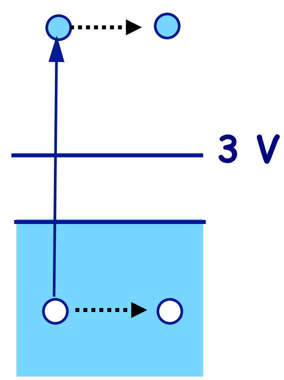




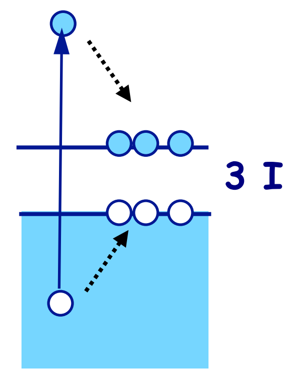
multiple junctions



multiple gaps



extract hot carriers



multiple electrons per photon

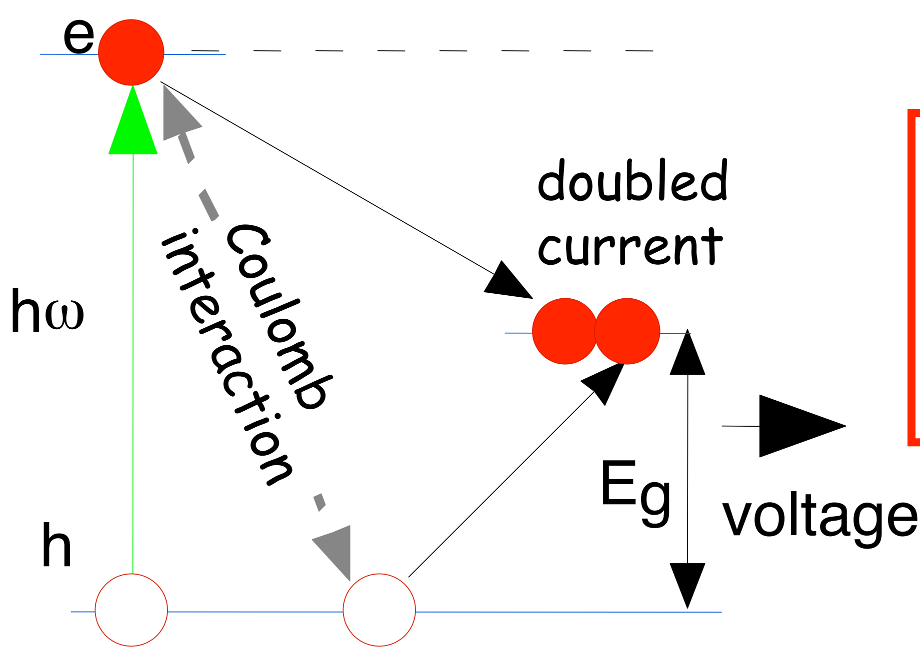
6. Strong Coulomb Interaction in Nanoparticle Solar Cells

1. Generate multiple electrons by each photons! How?

2. Increase strength of Coulomb interaction so that $\tau_{x \to xx} < \tau_{e-ph}$

3. Maximize Coulomb interaction by using nanoparticles with radius less than screening length - Nozik (2001)

4. Use Mott insulators – Manousakis (2010)

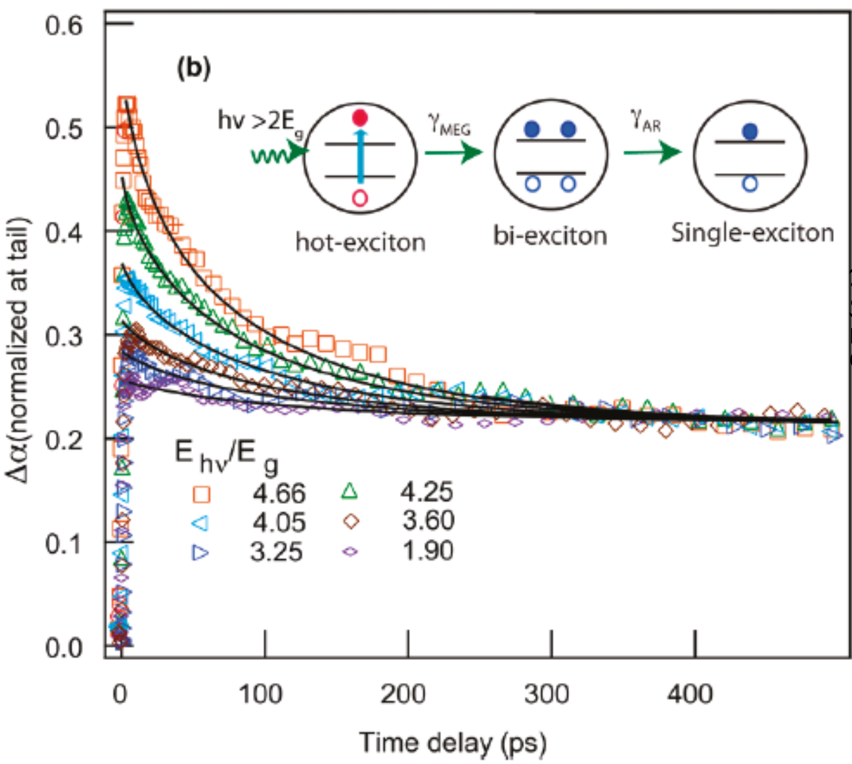


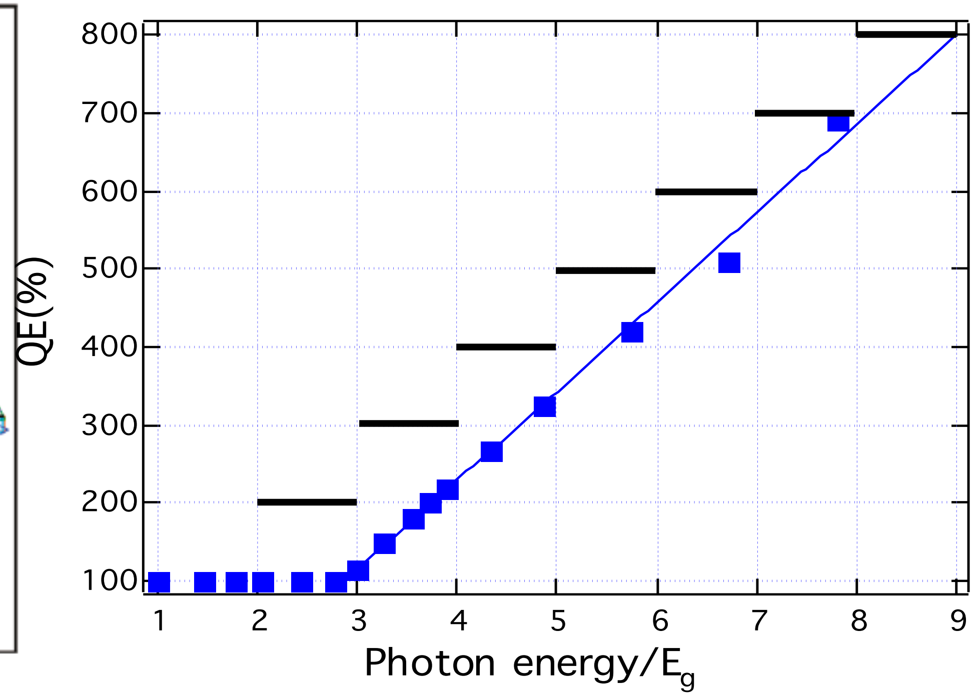
Max efficiency for Solar Cells with Multiple Exciton Generation (MEG):
44%

MEG in Nanoparticle Solar Cells: Basics

Klimov(2004) pump & probe:

- found new class of excited states, shorter lived than excitons
- identified them as Multi-Exciton states
- reported Quantum Yield (QY=#(electrons)/photon) upto 700%

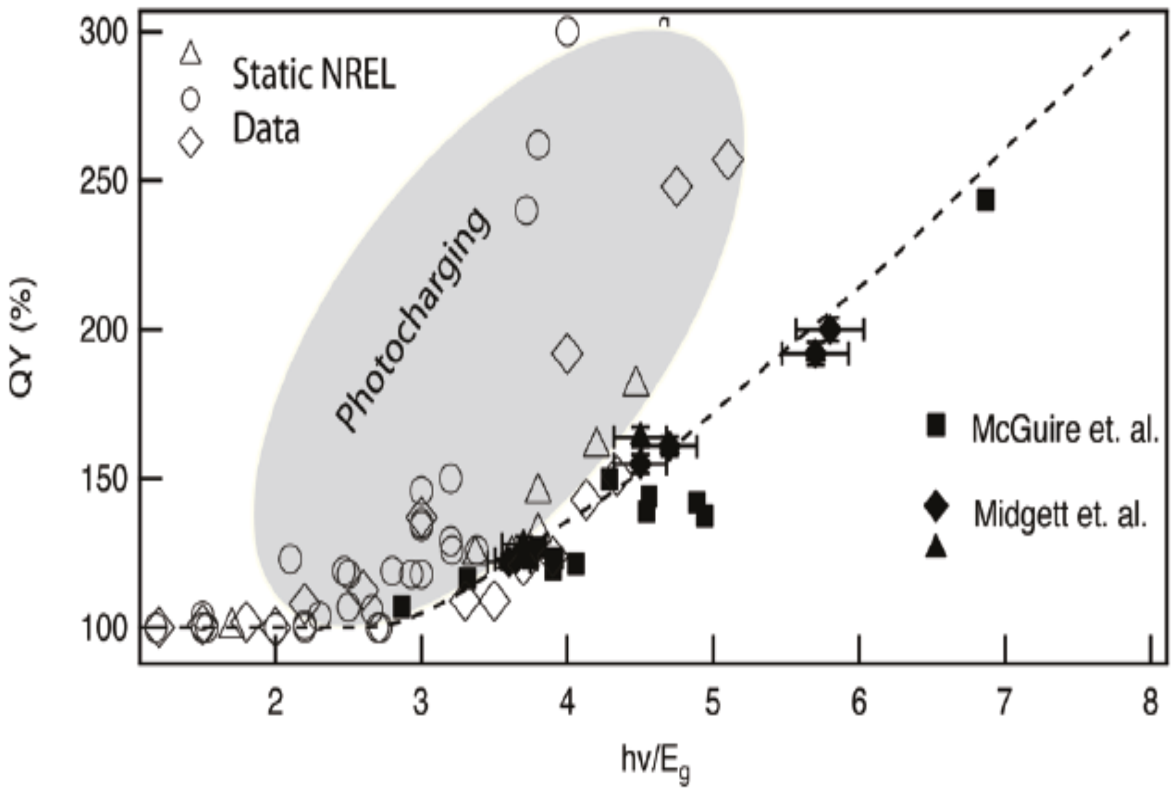




MEG: Consensus Status

Bawendi (2008): charging effects can be misinterpreted as MEG

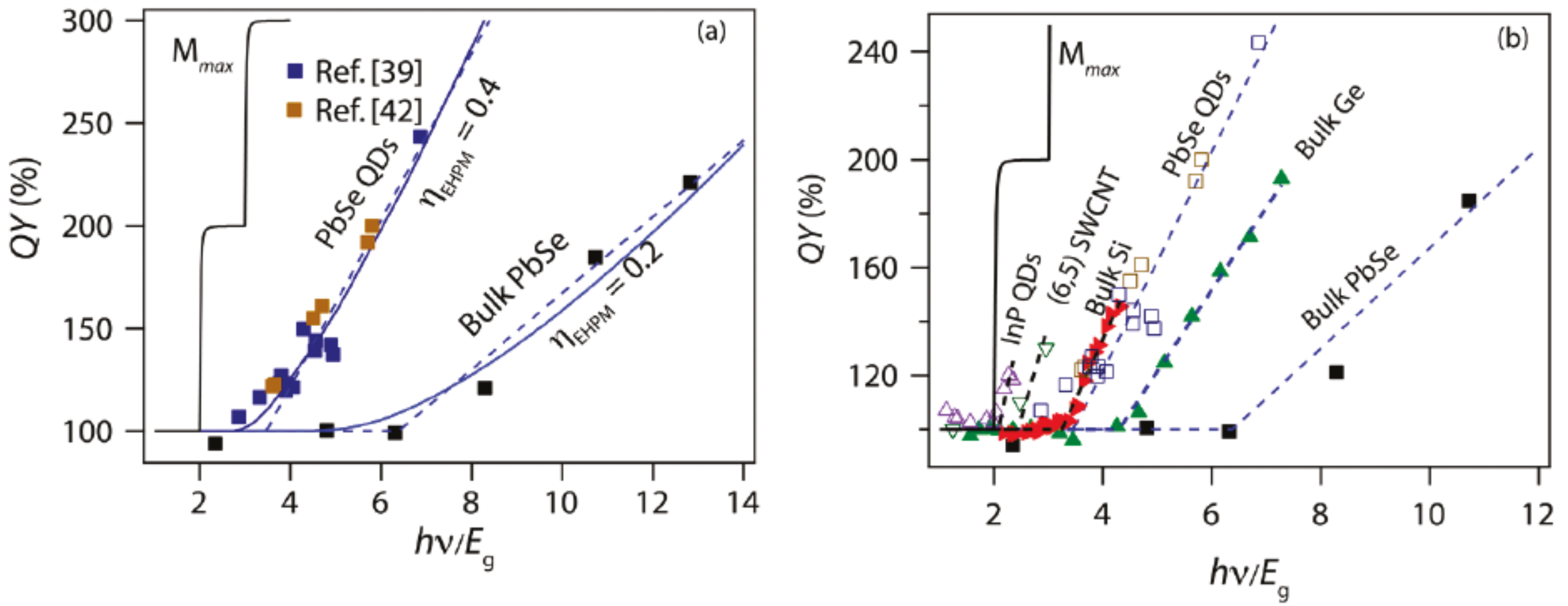
Beard (2011): MEG is present in NPs after charging is suppressed



MEG: Consensus Status

* Conversion efficiency good: MEG more efficient in NPs than in bulk, as slope on relative energy scale hν/Eg is closer to theoretical max.

* Threshold energy bad: But Eg is larger in NPs, so on absolute energy scale NP solar cells absorb smaller fraction of solar spectrum



The Solar Collaborative at UC Davis

1. Reduce gap to maximize benefit of high energy conversion efficiency of MEG-based NP solar cells

2. Explore MEG in non-toxic materials

   MEG primarily demonstrated with toxic materials:

   environmental regulations discourage their use:

   concentrate instead on Si, Ge

3. Optimize quantum confinement

   Competing demands on Quantum Confinement in NPs:

   increase confinement to enhance Coulomb and thus MEG

   decrease confinement to extract the photo-electrons:

The Solar Collaborative at UC Davis/UCSC

Experiment:

S.Kauzlarich – synthesize NPs

D.Larsen – photoluminescence (PL/TA) characterization of NPs

S.Carter – assemble NPs into working solar cells

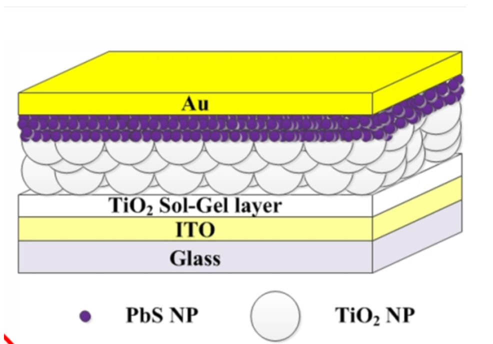
Theory:

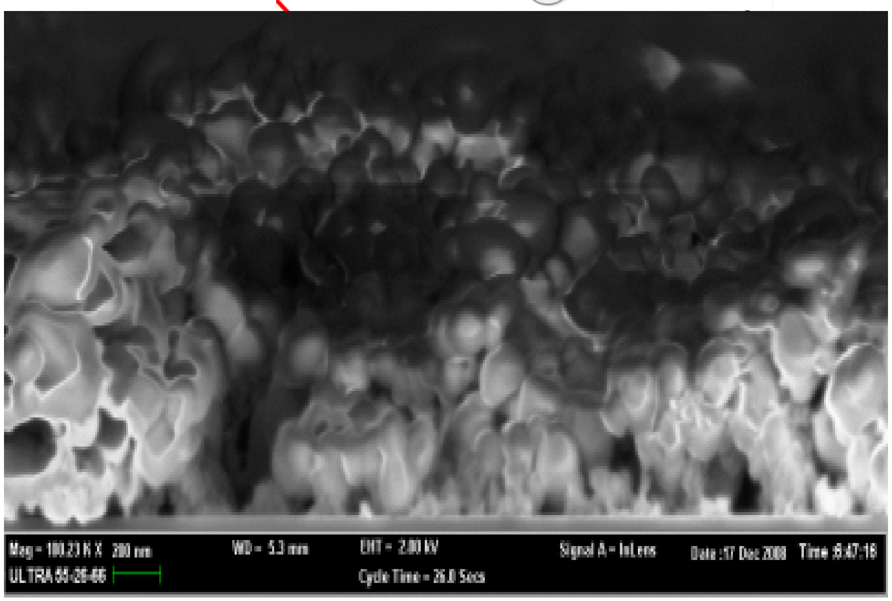
G.Galli, A.Gali, G.Zimanyi – gap reduction by manipulating NP shape,
M. Voros reconstruction, embedding

Z.Bai, D.Rocca – code development for Bethe-Salpeter

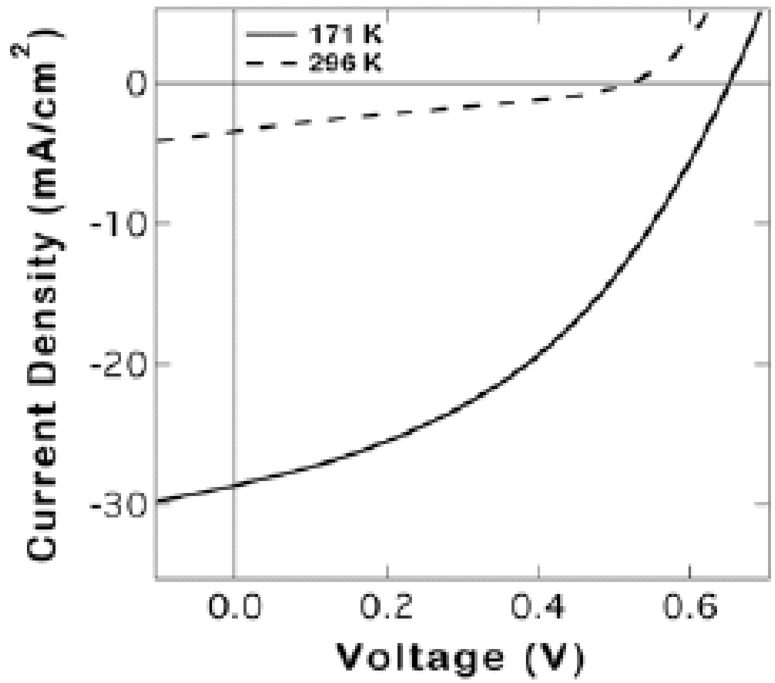
D.Paul – multivariate analysis of PL/TA data

Characterizing Nanoparticle Solar Cells





TEM image of ALD of Cu_2S onto TiO_x with radius<1nm



I-V of PbS NP solar cell:

Large current enhancement at low T!

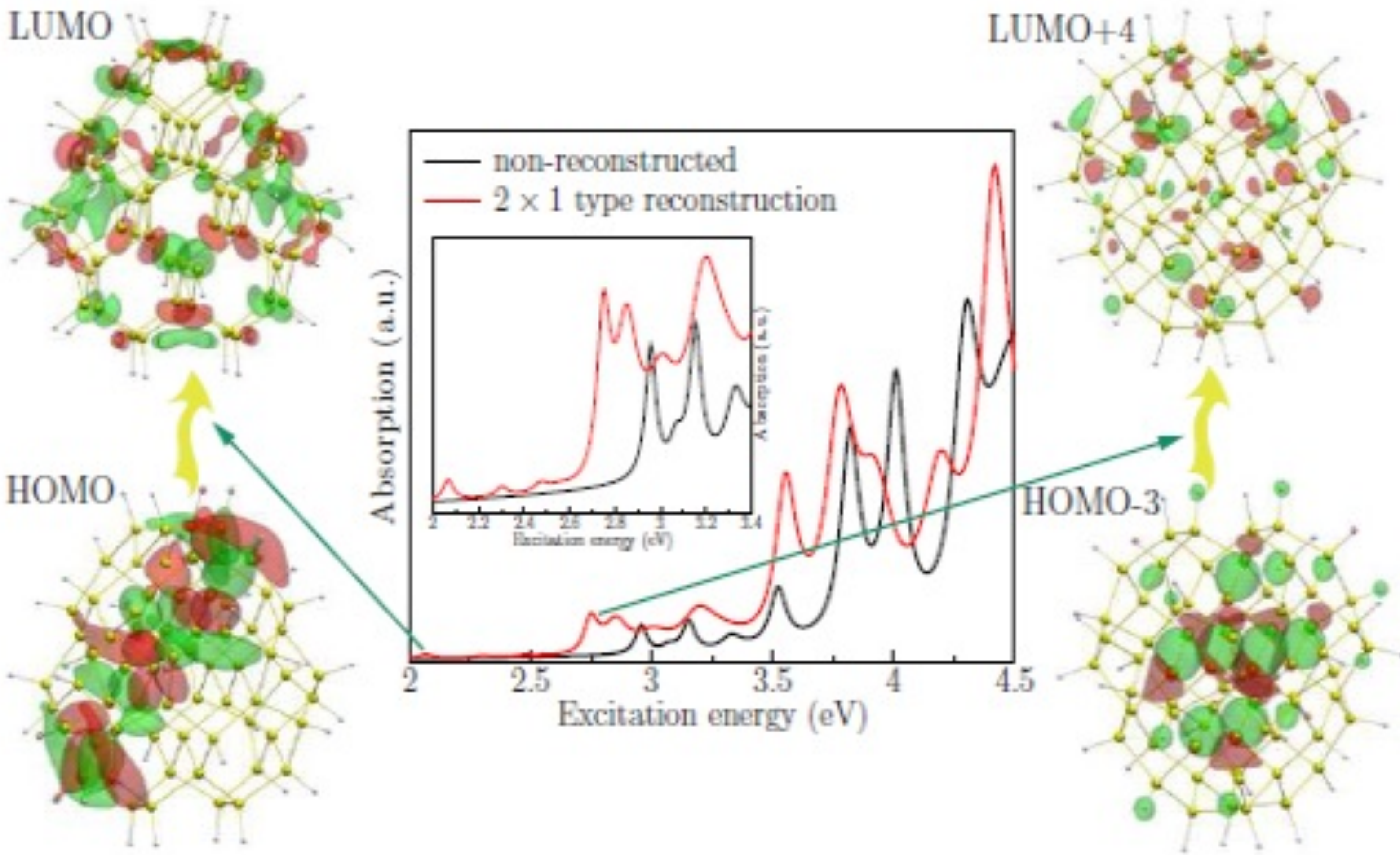
Efficiency: 8%

Role of NP-NP distance?

Theory: Turbo-charged Time-Dependent Density Functional Analysis

1. NP Spectrum – How to decrease gap
    1.1. Effect of surface reconstruction
    1.2. Effect of shape
    1.3. Effect of NP-NP distance
2. Multi-Exciton Generation
    2.1. Screening of interactions
    2.2. Effect of surface reconstruction
3. Code development for Bethe-Salpeter Equation (BSE)
    3.1. Liouvillian super-operator matrix formalism
    3.2. Projecting out unoccupied states
    3.3. Lanczos continued fraction solution of BSE
    3.4. Self-consistent treatment of self-energy ImΣ

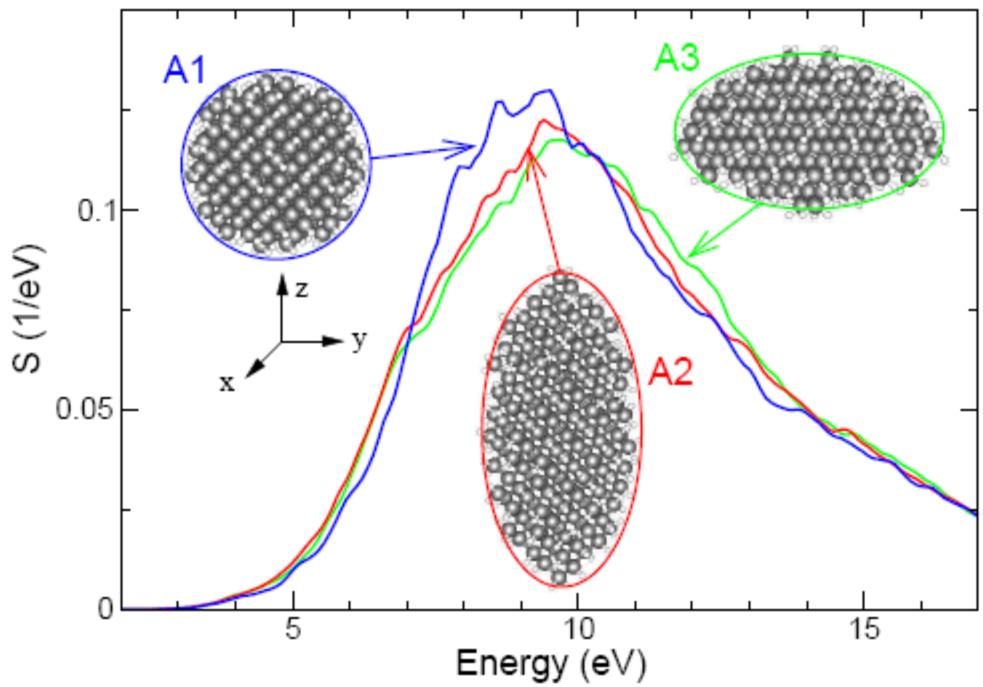
1. NP Spectrum:
1.1. Effect of Surface Reconstruction

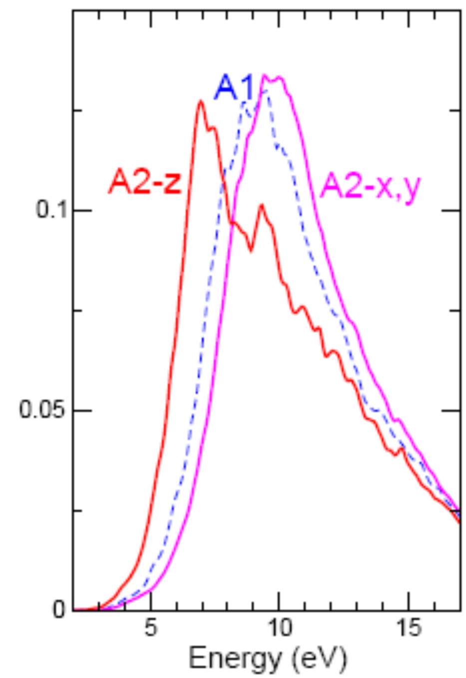


Surface reconstruction reduces gap by ~10% and creates intra-gap states

Gali, Zimanyi et al, NanoLetters (2009)

1. NP Spectrum:
1.2. Effect of Shape Symmetry

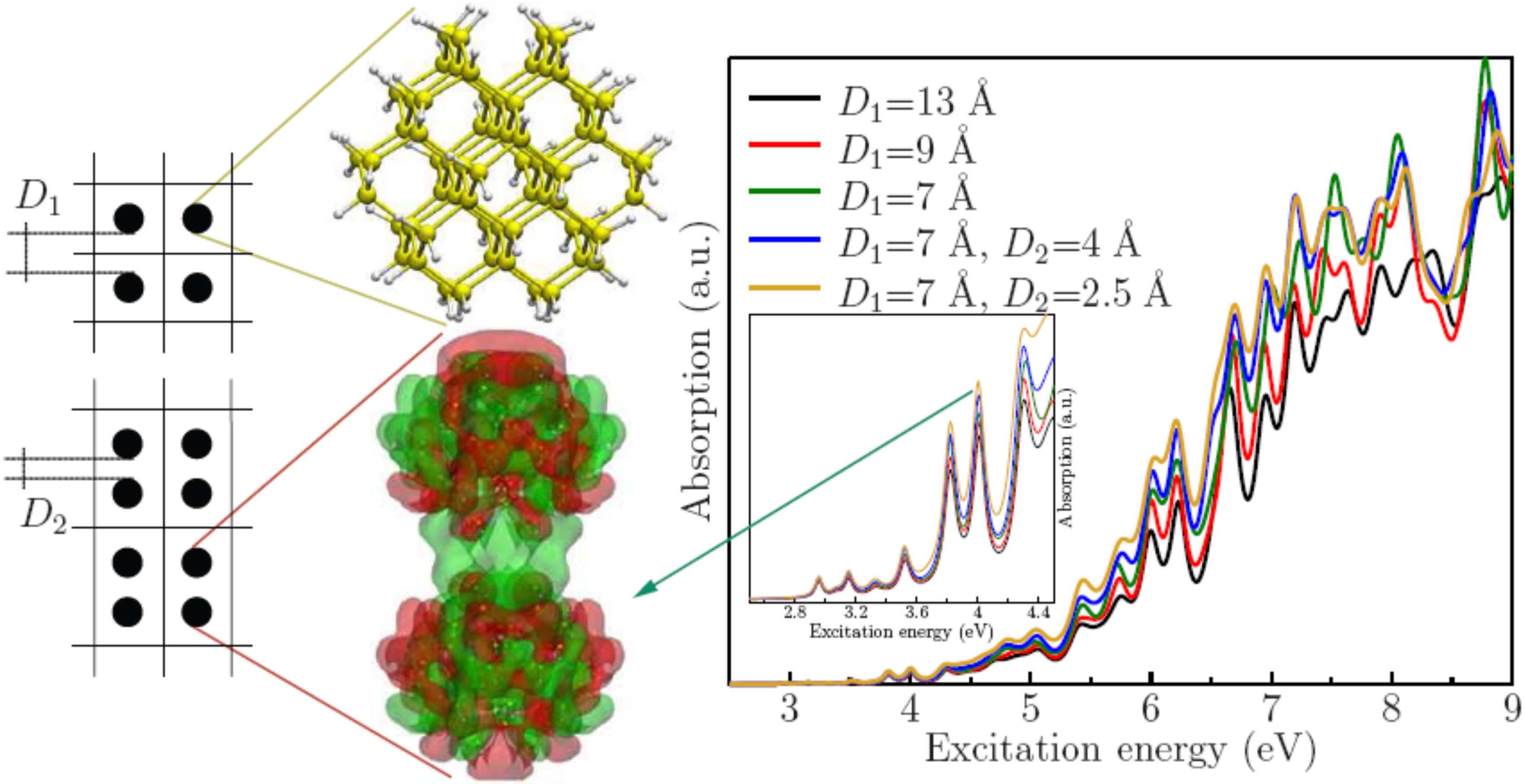




Reducing symmetry of shape reduces gap because a lot of transitions which were forbidden by selection rules become allowed

Gali, Kaxiras, Zimanyi, Meng, PRB (2011)

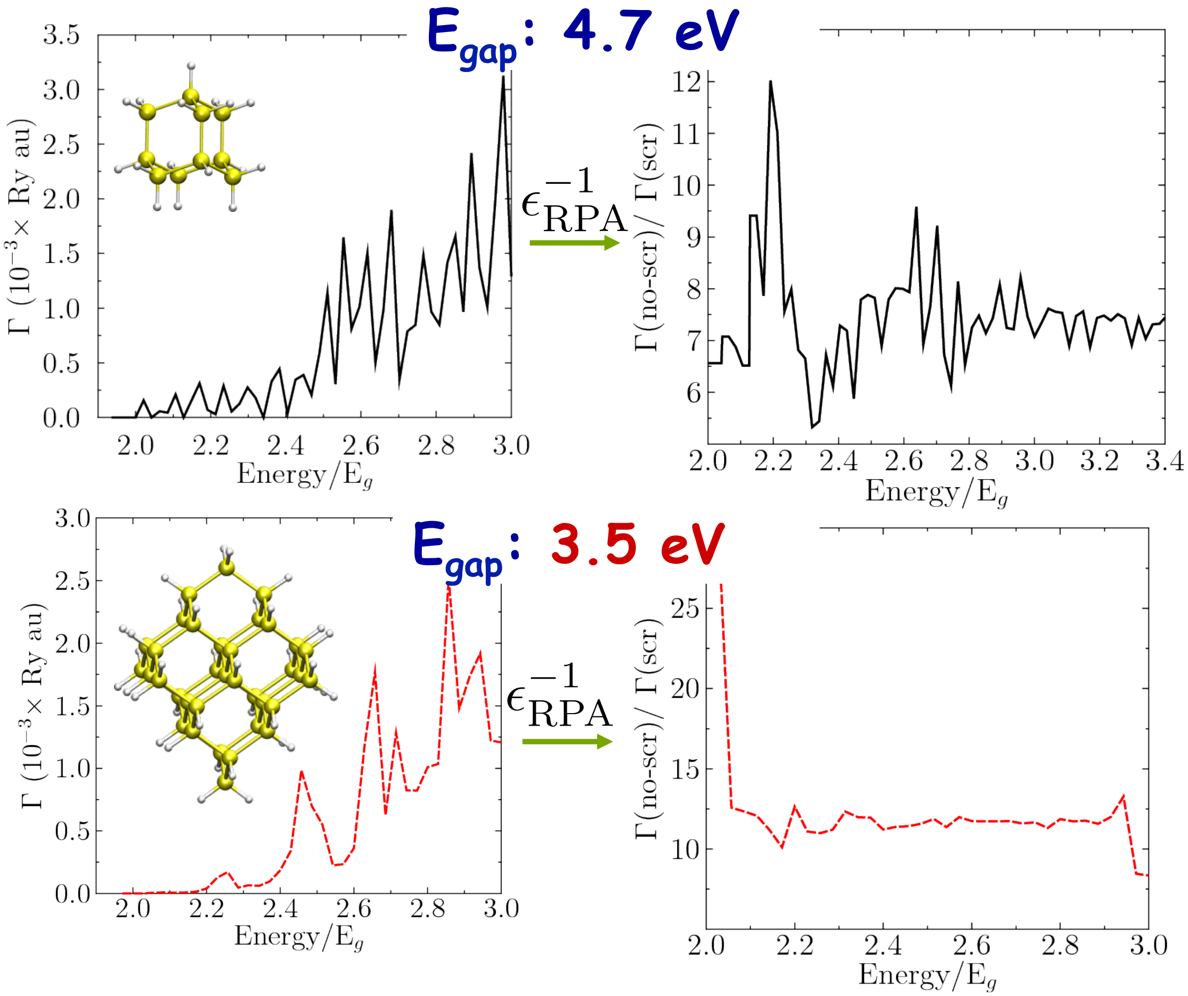
1. NP Spectrum:
1.3. Effect of NP-NP separation



NP spectrum is impacted at surprisingly large NP-NP separations – QY enhancement at low T?

2. Multi-Exciton Generation:
2.1. Screening of interactions

- static screening approximation
- hydrogenated surface



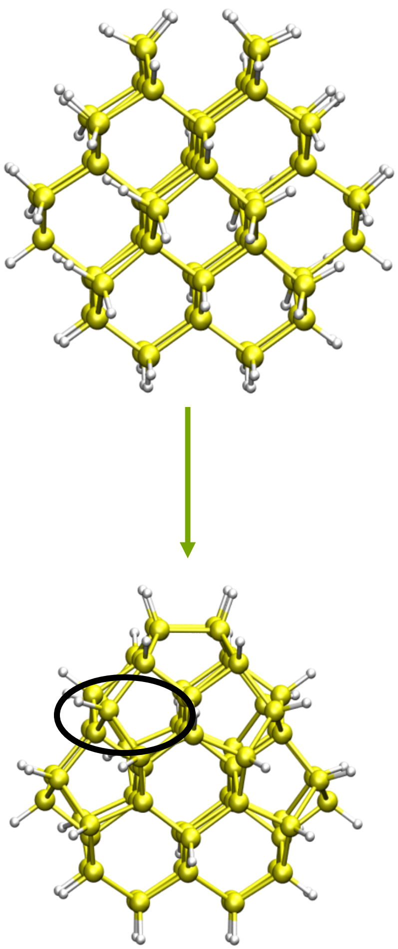
Screening is surprisingly strong even for smallest NPs

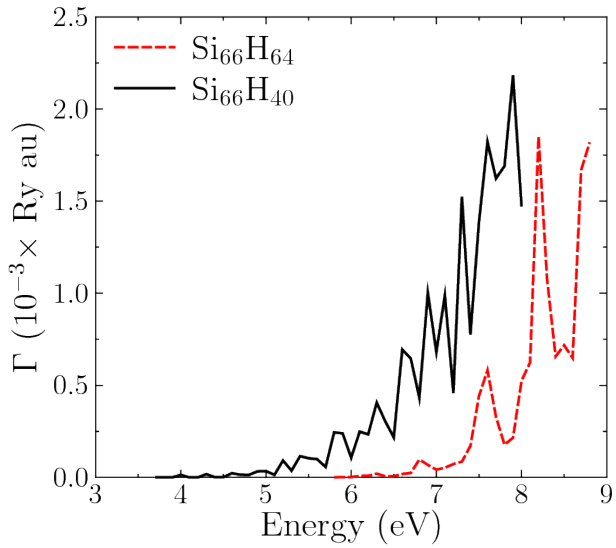
- screening is smaller for the smaller NP (~7.5 vs. 12)

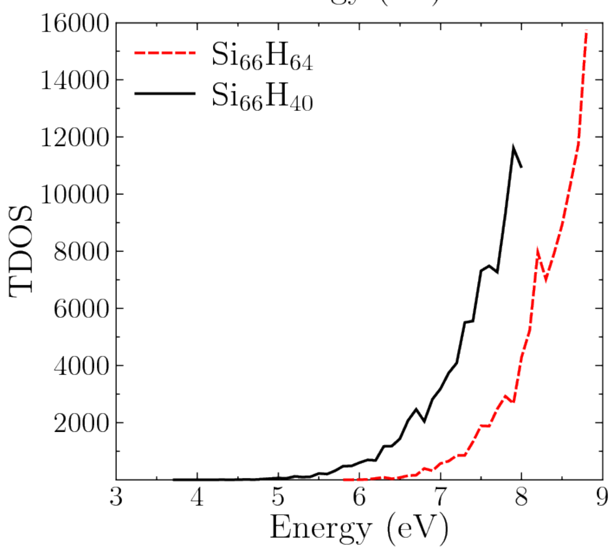
- energy dependence of screening is minimal: static approximation is self-consistent

static dielectric constant of bulk Si ~12

2. Multi-Exciton Generation:
2.2. Effect of Surface Reconstruction







1. **Reconstruction (H64 -> H40):**

   MEG creation starts at 30% lower energies because gap reduction

2. **Gap reduction:**

   Driven by increased density of continuum states, not isolated defect states

3. Code Development for Bethe-Salpeter Equation

3.1. Self-consistent treatment of self energy Σ

3.2. Liouvillian super-operator formalism:

eigenvalues of L give excitation energies

3.3. Coulomb Hole + Screened Exchange

3.4. Summation over conduction states avoided by

projecting to valence states

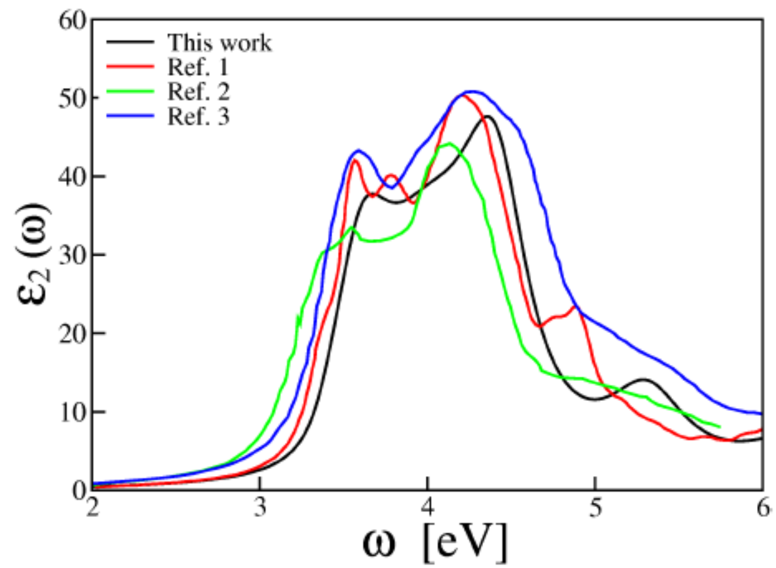
3.5. Bethe-Salpeter equation for interactions

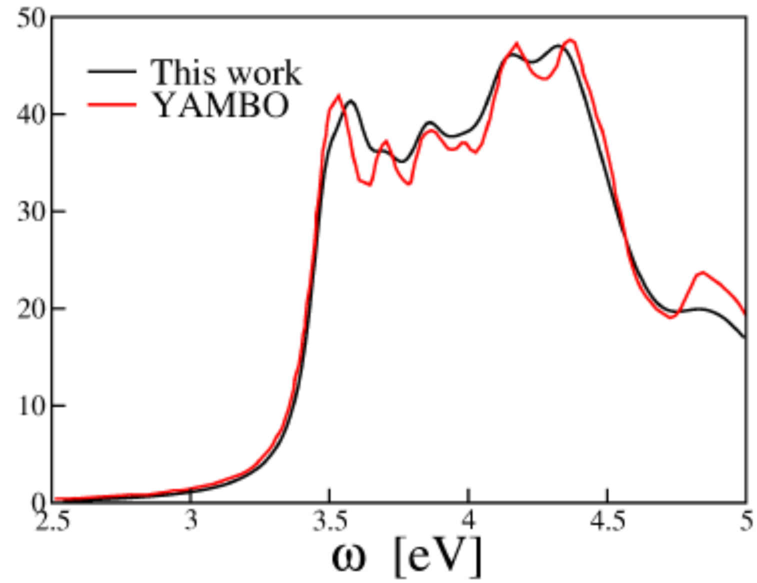
3.6. Polarizability determined by Lanczos continued

fractions

3.7. Turbocharging by vectorising (~ GPUs for video games)

3. Code Development for Bethe-Salpeter Equation
Comparison to Literature: Si





CPC 180, 1392 (2009)

This work: $12 \times 12 \times 12$+shift k-point mesh

[1] S. Albrecht, L. Reining, R. Del Sole, and G. Onida, PRL (1998)
[2] L. X. Benedict, E. L. Shirley, and R. B. Bohn, PRB (1998)
[3] M. Rohlfing and S. G. Louie, PRB (2000)

SUMMARY

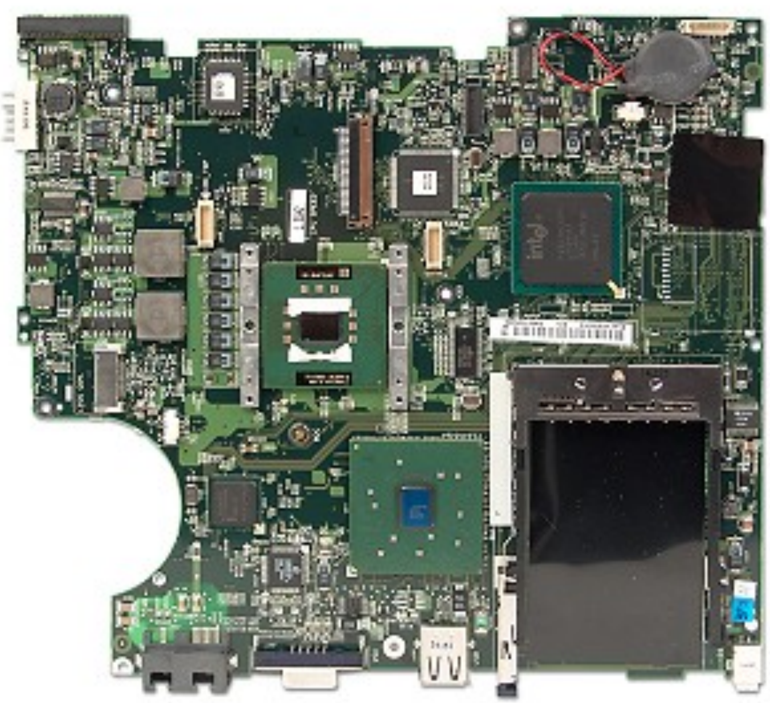
1. Solar energy problem is intellectually complex and morally honorable
2. Multiple Exciton Generation by strong Coulomb interactions is one of the most promising pathways to increase the solar cell efficiency
3. Energy conversion efficiency by MEG in NPs is better than in bulk
4. NP Gap needs to be reduced: optimizing shape, surface reconstruction, NP-NP distance & surface chemistry are promising
5. Advanced many-body methods (Liouville operators, BSE, SC ImΣ, Lanczos continued fractions) are adapted
6. Optimizing quantum confinement for maximizing MEG vs. extracting photo-electrons efficiently remains central challenge

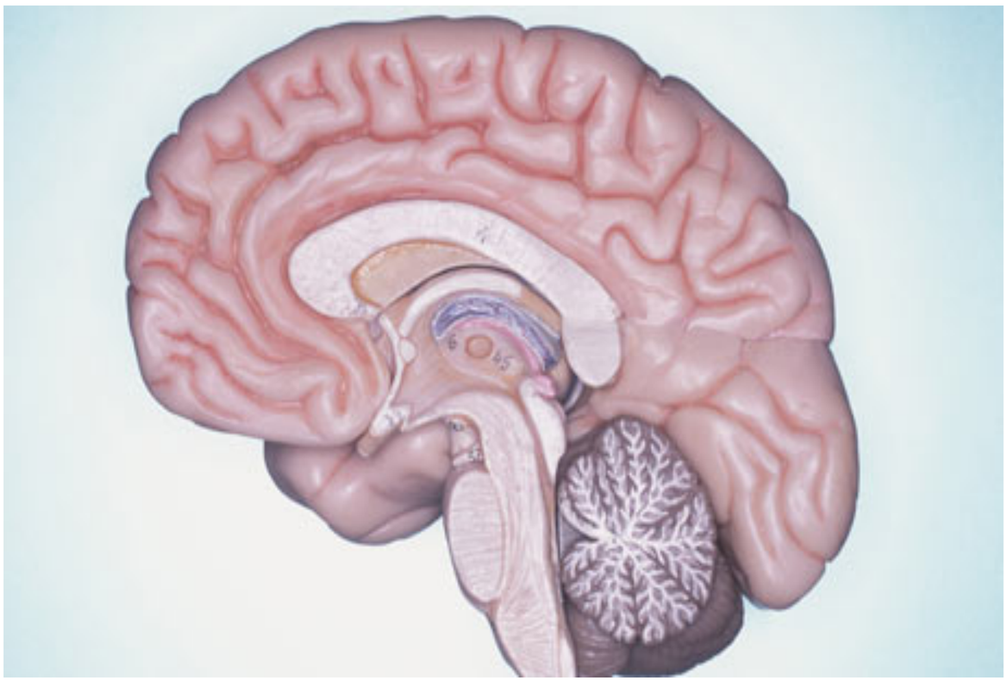
Memristors – A Revolution on the Horizon

Olle Heinonen (Argonne)
Duk Shin (UC Davis)
GTZ (UC Davis)

Memristors – The excitement

There are two really good computers on Earth: CPUs & Brains





CPUs vs. Brains

	CPU	Brain
Similarity: both are based on switching elements	**Transistor**	**Neuron**
Difference: memory	**No**	**Yes**
Difference: number of terminals of switching element	**3** Emitter, collector, gate	**2** Axon, dendrite

CPUs vs. Brains

	CPU	Brain	Memristors
Similarity: both are based on switching elements	Transistor	Neuron	Memristor
Difference: memory	No	Yes	Yes
Difference: number of terminals of switching element	3 Emitter, collector, gate	2 Axon, dendrite	2 In & out terminal

Memristor Manifesto

Until now, a key justification for doing condensed matter physics was to accept the existing design of CPUs, and only to make its elements smaller and faster.

If we can make a switch with a memory, we can give a completely new building block into the hands of computer scientists, forcing them to completely reorganize CPU architecture

Memristor Manifesto II.

1. 70-80% of CPU cycles used for shuffling data between processor and memory. Transistors with memory allow in-situ processing, integrating logic and storage: no need to shuffle data

2. In-situ processing allows hierarchically distributed processing by millions of cores in parallel: a revolution in CPU design

3. In-situ processing can accelerate computation time dramatically

Secondary:

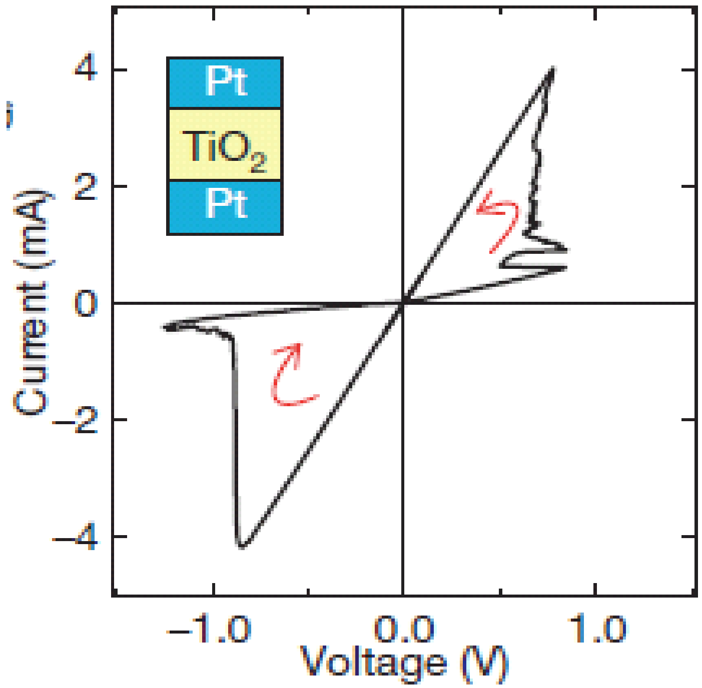
1. Memristors are a non-volatile memory: flash-beater, much faster access time

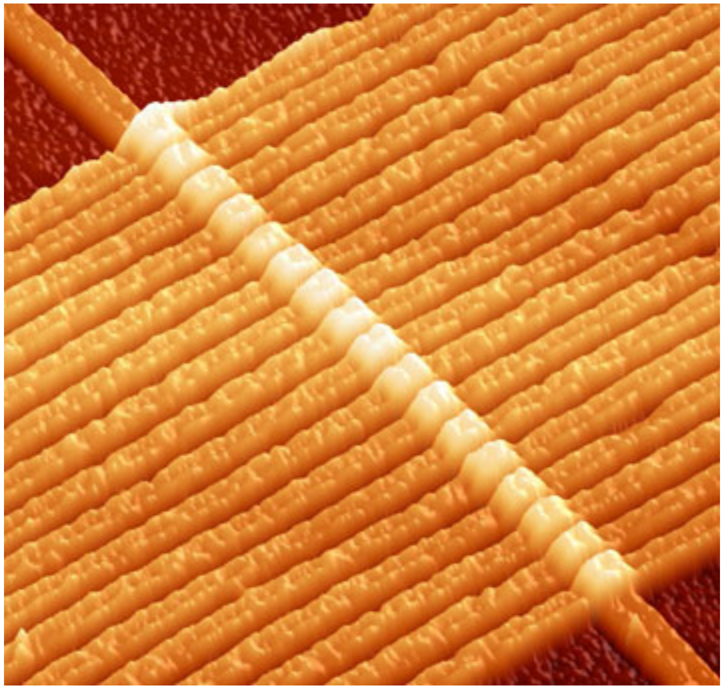
2. Two terminals: qualitatively simpler wiring topologies

3. A single memristor can perform logical function equivalent to the 6 transistors of an SR latch: much higher element density

Memristors – The Explosion

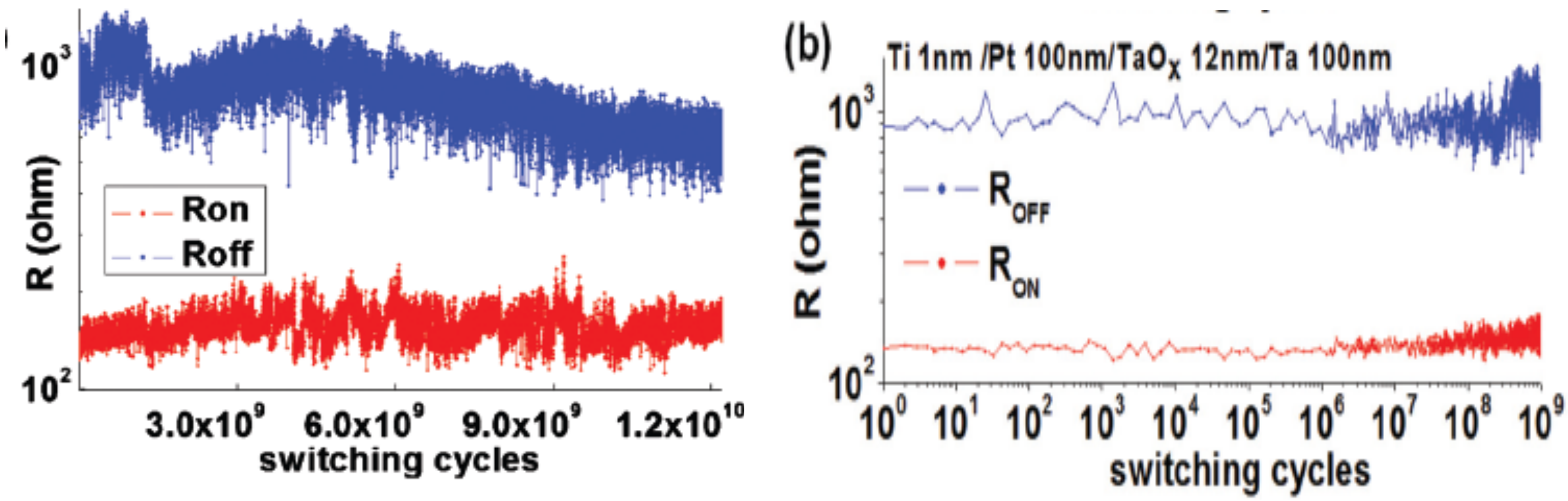
HP group of Stan Williams reported hysteretic/switching behavior in Pt/TiO/Pt structures: Nature 2008 May.
As of midnight: 401 citations





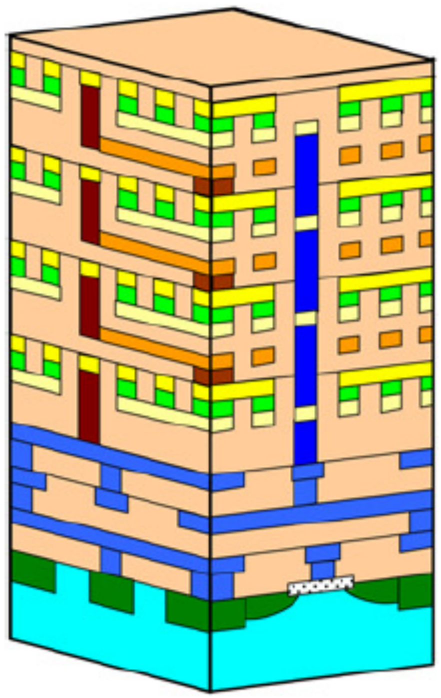
Performance: HP at the Sweet Spot

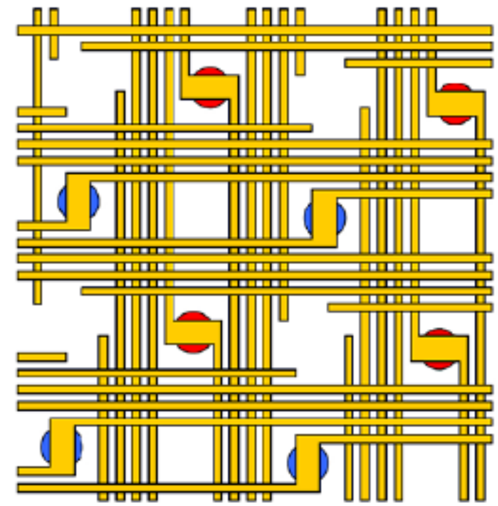
1. High endurance:
   10^9 is enough for DRAM replacement
   10^{15} is needed for processor applications

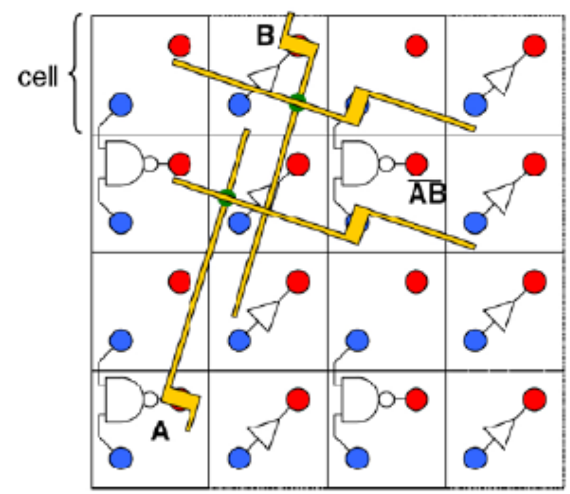


2. Fast write time:<10 nsec
   beats flash by several orders of magnitude
3. Low energy consumption: 1 pJ/operation Energy!
4. Long retention: > 10 years

"4D Scaling" – Crossbar Design

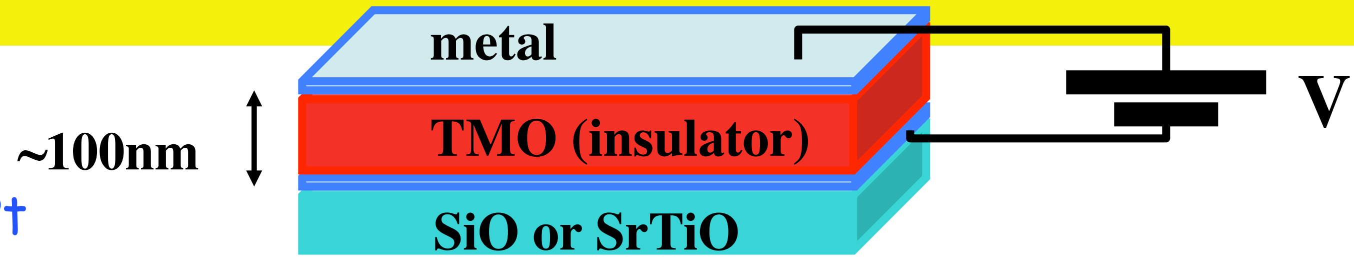






- Simple crossbar: 1 ON memristor shorts row
- Rotate crossbar
- 2D CMOS array used to address blue vias,
  2D CMOS array to address red vias = "4D"
- 3D possible because of 1pJ/operation

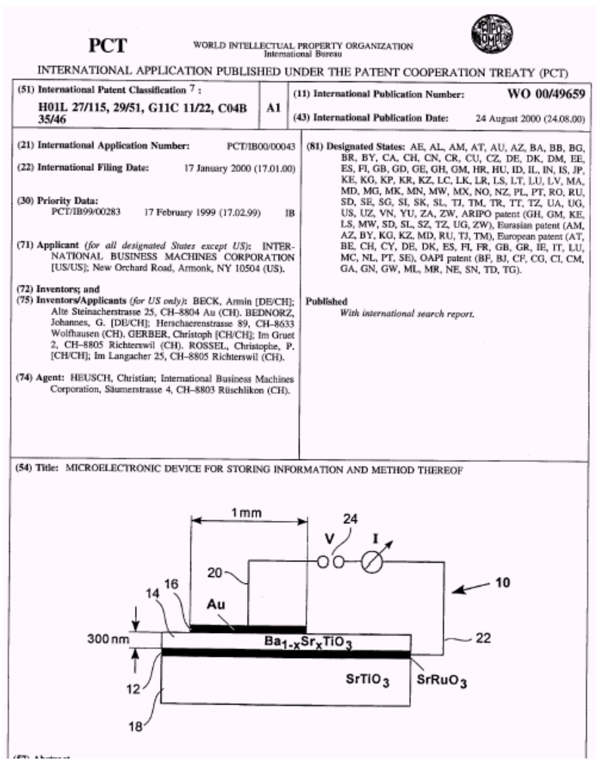
Transition Metal Oxides Make Great Memristors



Electrode: Au, Pt

TMO: PrCaMnO, (Ba,Sr)TiO, SrZrO, CeO, NiO, TiO, TaO

IBM-Zurich patent



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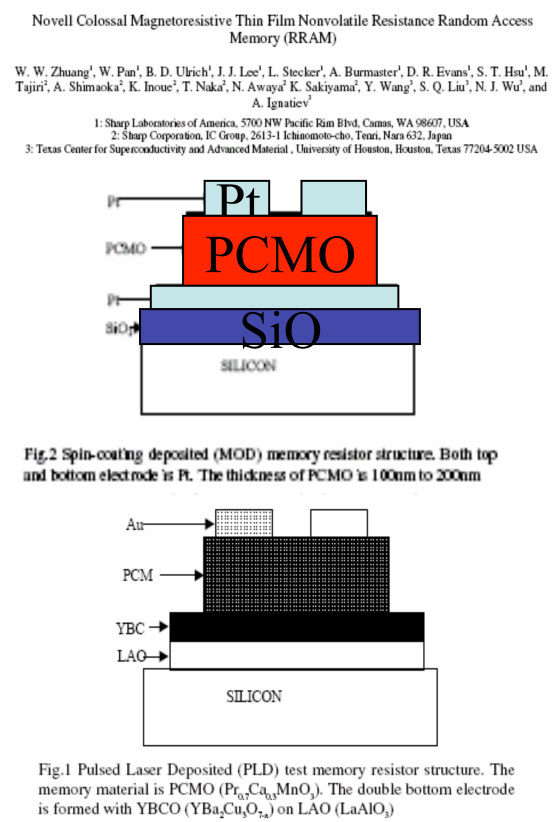
Published

With international search report.

(54) Title: MICROELECTRONIC DEVICE FOR STORING INFORMATION AND METHOD THEREOF

UT Houston, Sharp group



Novell Colossal Magnetoresistive Thin Film Nonvolatile Resistance Random Access Memory (RRAM)

W. W. Zhuang[1], W. Pan[1], B. D. Ulrich[1], J. J. Lee[1], L. Stecker[1], A. Burmaster[1], D. R. Evans[1], S. T. Hsu[1], M. Tajiri[2], A. Shimaoka[2], K. Inoue[2], T. Naka[2], N. Awaya[2] K. Sakiyama[2], Y. Wang[3], S. Q. Liu[3], N. J. Wu[3], and A. Ignatiev[3]

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2: Sharp Corporation, IC Group, 2613-1 Ichinomoto-cho, Tenri, Nara 632, Japan
3: Texas Center for Superconductivity and Advanced Material, University of Houston, Houston, Texas 77204-5002 USA

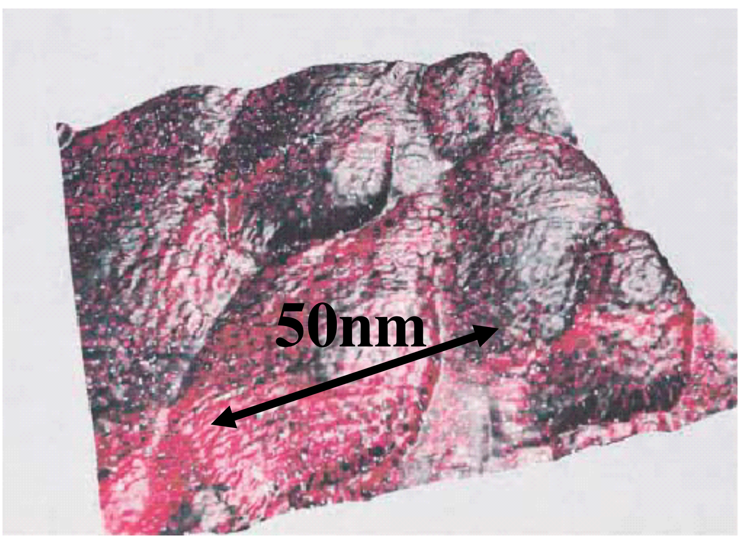
Fig.2 Spin-coating deposited (MOD) memory resistor structure. Both top and bottom electrode is Pt. The thickness of PCMO is 100nm to 200nm

Fig.1 Pulsed Laser Deposited (PLD) test memory resistor structure. The memory material is PCMO ($Pr_{0.7}Ca_{0.3}MnO_3$). The double bottom electrode is formed with YBCO ($YBa_2Cu_3O_{7-x}$) on LAO ($LaAlO_3$)

Mechanism? – Electrons!

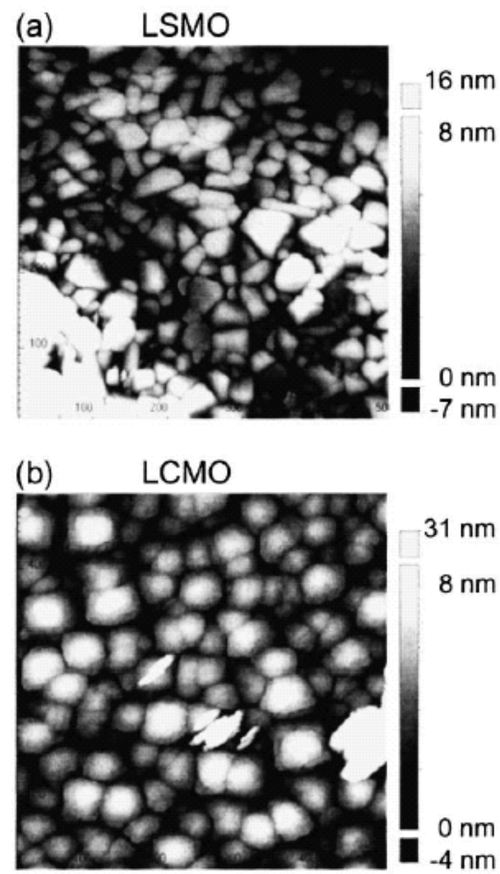
Rozenberg 2006-2010

- Inhomogeneities are ubiquitous in TMOs: conduction channels are formed during switching
- Switching: high field drives insulating TMO through Mott transition to become metallic



LCMO

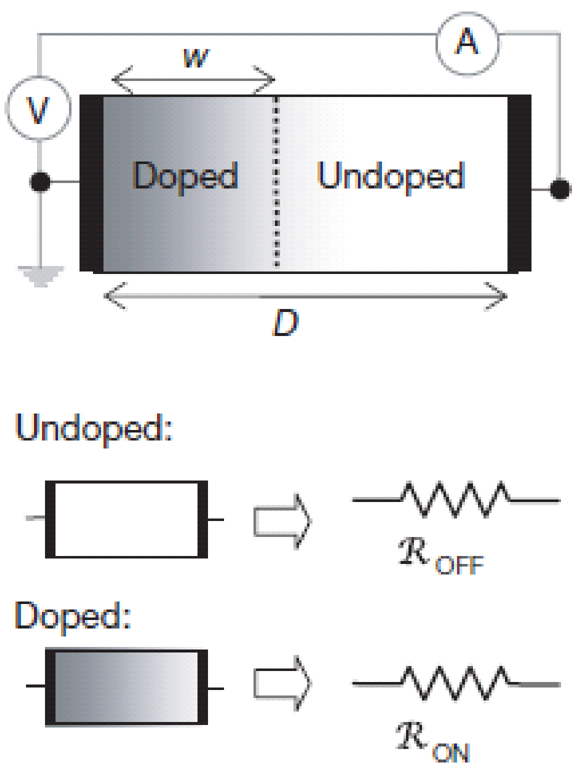
Becker et al PRL '02



100nm

Mechanism? – Vacancies!

Switching = Movement of Oxygen vacancies (HP)



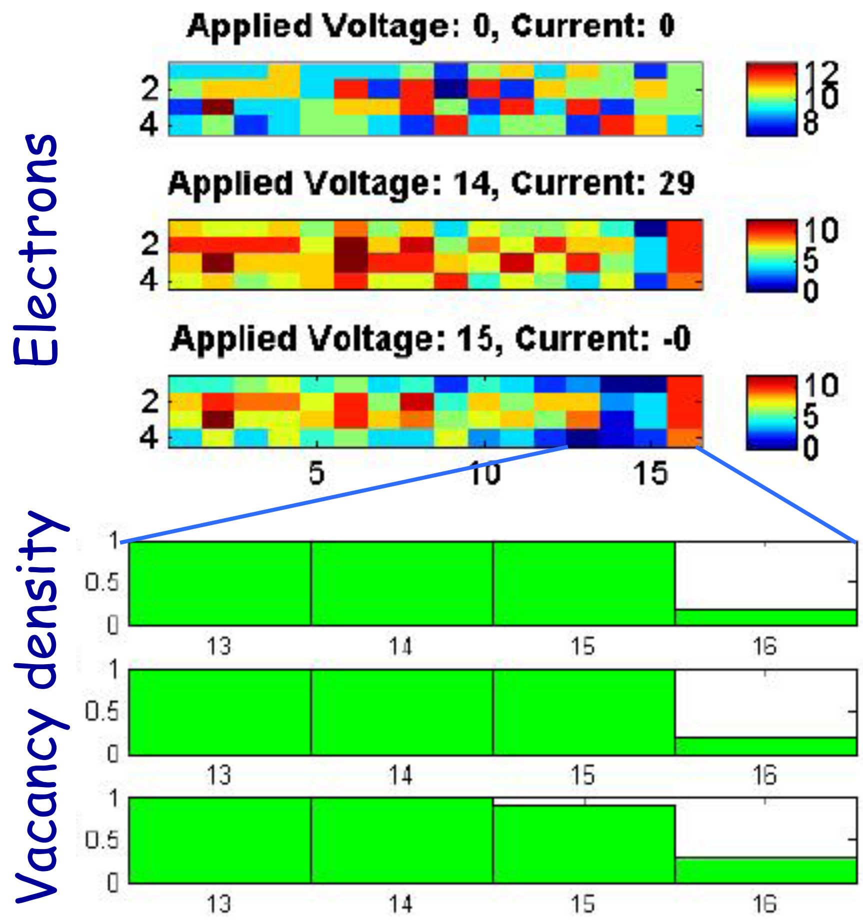
- Cause of switching is ion movement: explains long memory
- Domain wall between high R and low R region moves
- True nano-phenomenon: effect scales with 1/size, absent in macroscopic limit.

Our Simulations

Model:

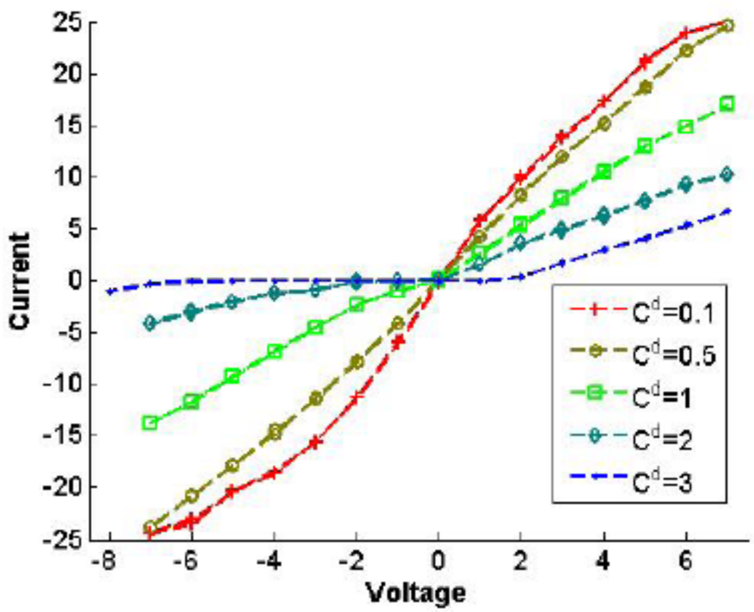
Electrons:
- Coulomb interaction
- grain charging energy
- disorder
- move driven by electric
  field to lower energy
- mobility~vacancy density

Vacancies:
- move driven by electric
  field generated by electrons
- mobility~exponential in field



No hysteresis without vacancy movement

No vacancy movement



No hysteresis

Vacancy movement

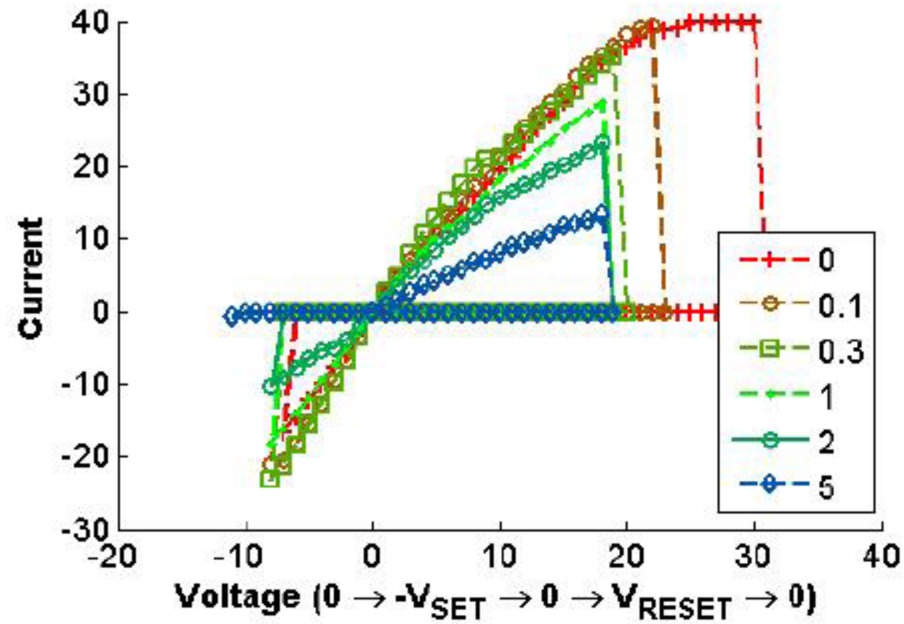


FIG. 6. IV curves with varying disorders

Hysteresis

Simulation vs. Experiment

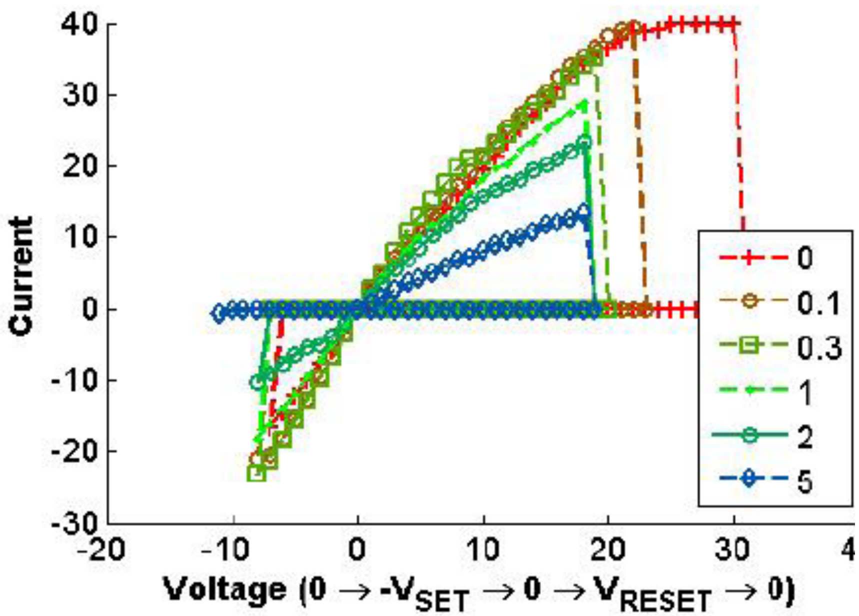
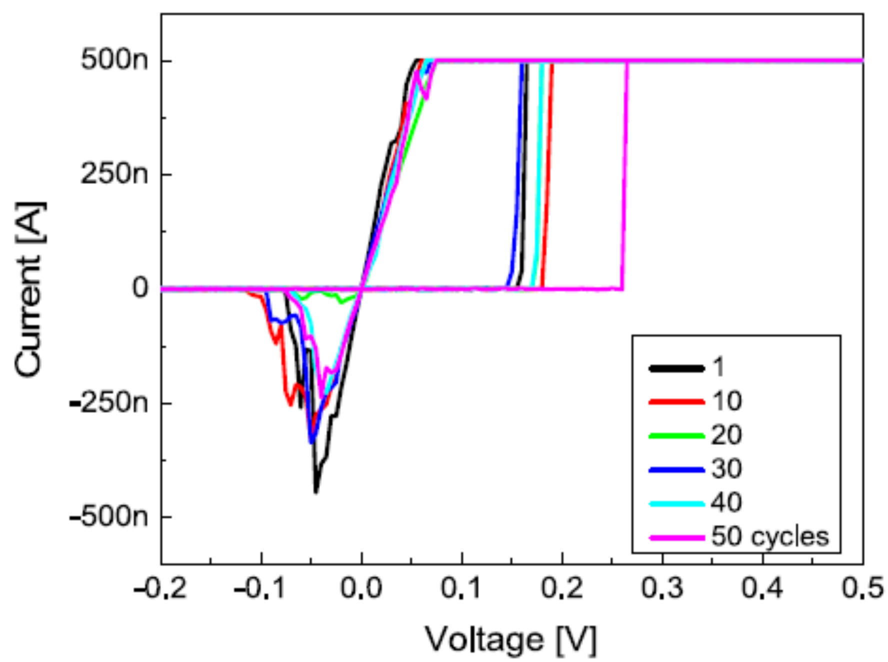


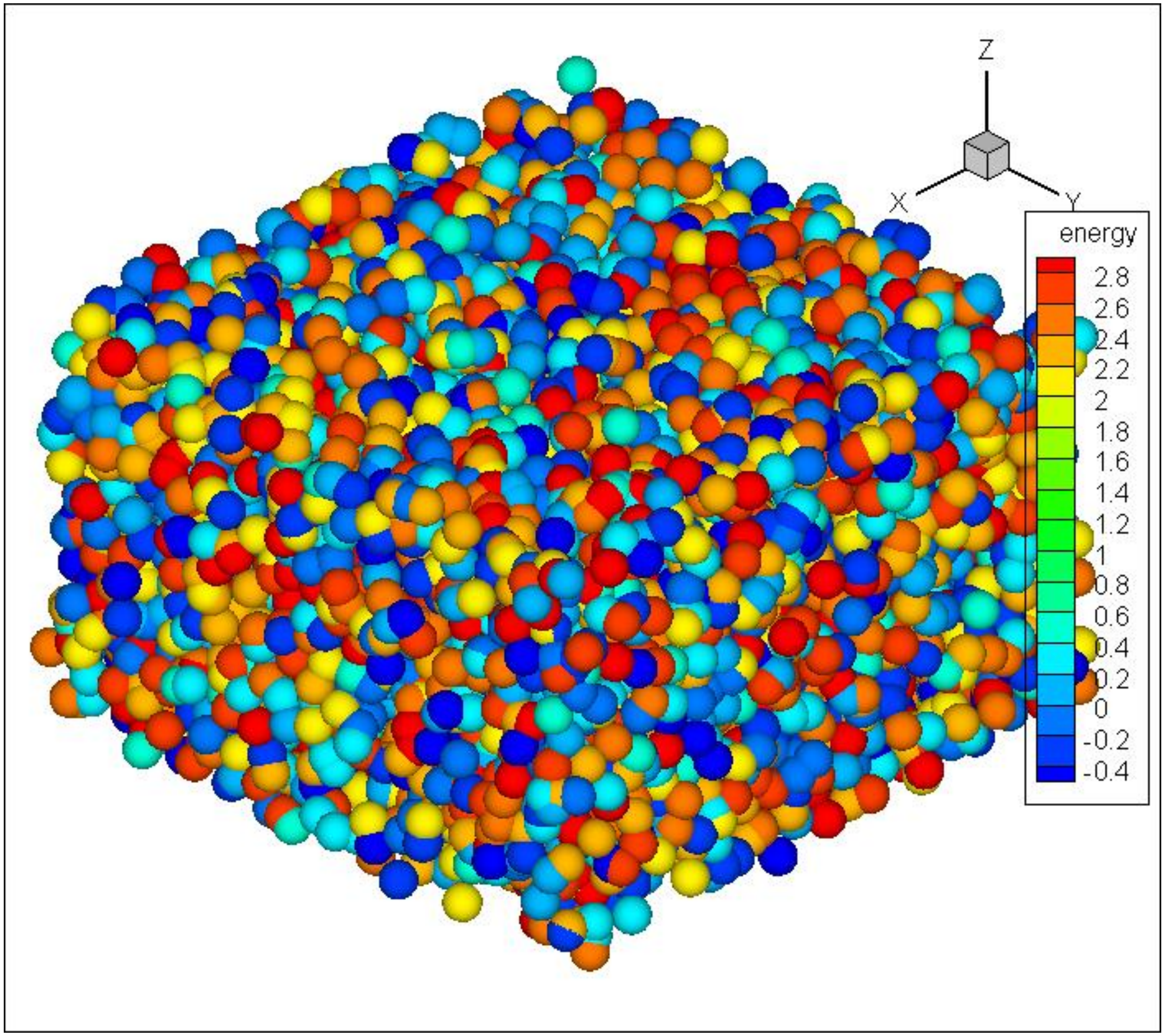
FIG. 6. IV curves with varying disorders



Simulation

Cu/WO3/PT cell

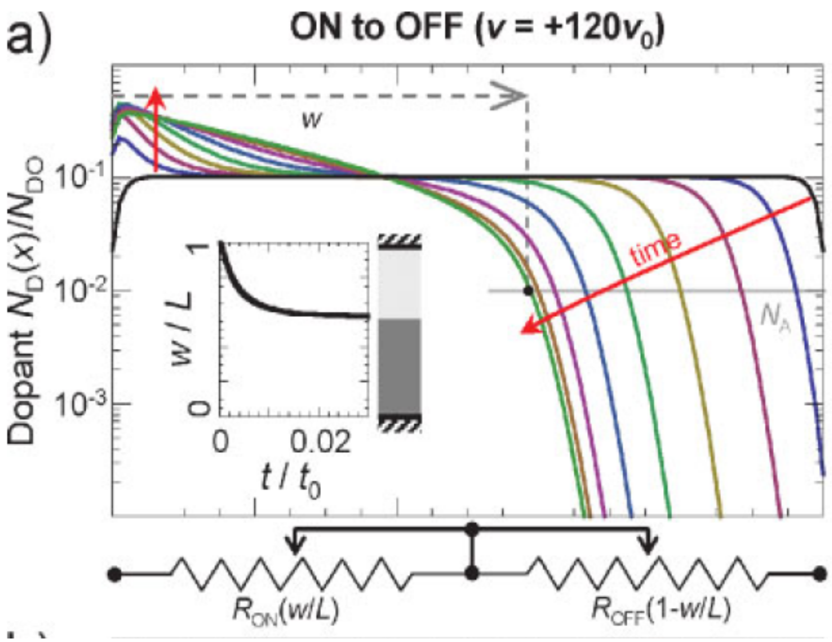
Our Model – Next Generation



- 3000 atoms
- Random energies
- Coulomb interaction (100,000 grid point)
- Electrons jump by master eq.

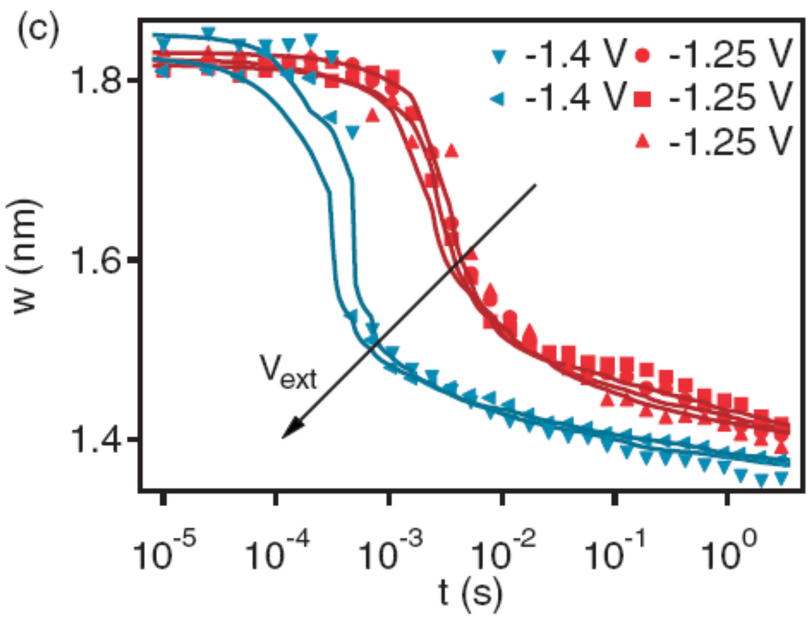
HP Phenomenological Simulations

HP simulations (Strukov)



Simulation: w(ON)=0

ON/OFF width measured



Expt: w(ON)=1.4nm

Outstanding Problems

Switching is still ill-understood:

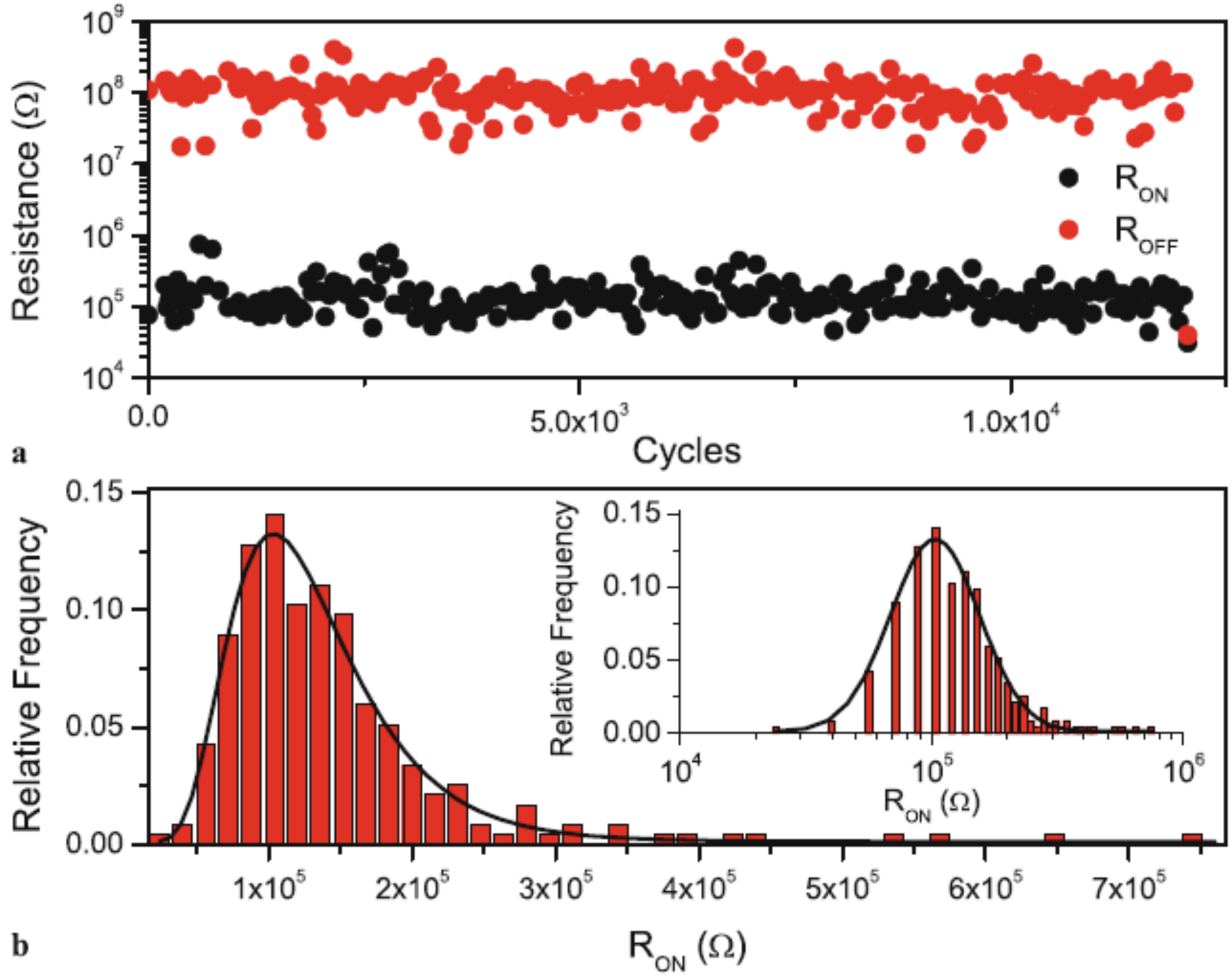
1. Debatable phenomenological assumptions

$$\dot{w} = f_{\text{off}} \sinh\left(\frac{i}{i_{\text{off}}}\right) \exp\left[-\exp\left(\frac{w - a_{\text{off}}}{w_c} - \frac{|i|}{b}\right) - \frac{w}{w_c}\right]$$

2. Simulation: w(ON)=0 vs. Expt: w(ON)=1.4nm

3. Presently: large V(ON) device-to-device fluctuations
   Uniformity is needed for scaling
   Presently: control/select circuitry is added, losing several advantages

Broad Distribution of Switching Parameters



Summary

1. Memristors are switches with non-volatile memory

2. Distributed processing integrated with memory possible

3. High endurance, fast switching, low power

4. Two-terminals: crossbar architecture

5. Low power: 3(4)D scaling of crossbar layers

6. Synaptic circuitry/neural networks for learning, self-programming