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Hydrogen in non-crystalline materials: From solar cells to hydrogen Storage

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Hydrogen in Non-Crystalline Materials: from Solar Cells to Hydrogen Storage

For 2009 UNLV RENEWABLE ENERGY SYMPOSIUM, AUGUST 11 & 12, 2009

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**University of Ontario Institute of Technology
(UOIT), Oshawa, ON, Canada**



Supported by:



UOIT- the newest Canadian University (started in 2003)

- At Ontario's first ***laptop-based university*** students and faculty have an opportunity to pioneer innovative educational practices through advanced learning technologies.
- **2009**: Graduate and PhD programs are already offered



Examples of energy related UOIT projects

- Research on **hydrogen production** (23-member team of researchers in Canada and abroad) with a **copper-chlorine cycle that splits water into hydrogen** and oxygen using a heat from nuclear stations. Collaboration with Atomic Energy of Canada Ltd. and Argonne National Laboratory.
- Dr. Peter Berg and Brad Easton (Faculty of Science at UOIT): modelling, simulation and experiment on mass and charge transport in **hydrogen (PEM) fuel cells**. The Canadian team collaborates with members of the newly formed Toyota Research Institute of North America (TRINA), a division of TEMA, in the United States as well as researchers in Japan
- And more, visit <http://www.uoit.ca/>

Solar cells on traffic noise barriers



- Total length of Ontario's highways: ~ 17000 km
- Noise reduction barriers screen living areas
- Could the barriers be combined or *integrated* with other applications?

Sonus/PV (Photo-Voltaic)
Highway Traffic Noise
Barrier Project

If you decide to visit us, this is only 40 min drive from downtown Toronto



Collaborators

- *I. Kupchak, A.V. Sachenko, Yu. Kryuchenko and I. Sokolovskyi.* Institute of Semiconductor Physics, Kiev, Ukraine. **Solar cell optimization, extensive a-Si:H microscopic computer modeling**
- *T. Teatro, L. Henderson and F. Gaspari.* UOIT, Canada. **Molecular dynamics simulation, sample preparation, infrared and Raman spectroscopy**
- *Z. Ibrahim and M.J.G. Lee, N. Kherani.* Department of Physics, University of Toronto, Canada. **Temperature dependent dielectric function calculation, thin film growth and characterization**
- *T. Tiwald, A. Fuchser.* J.A. Woollam Co., Inc., USA. **Infrared ellipsometry for a:Si:H thin film characterization**



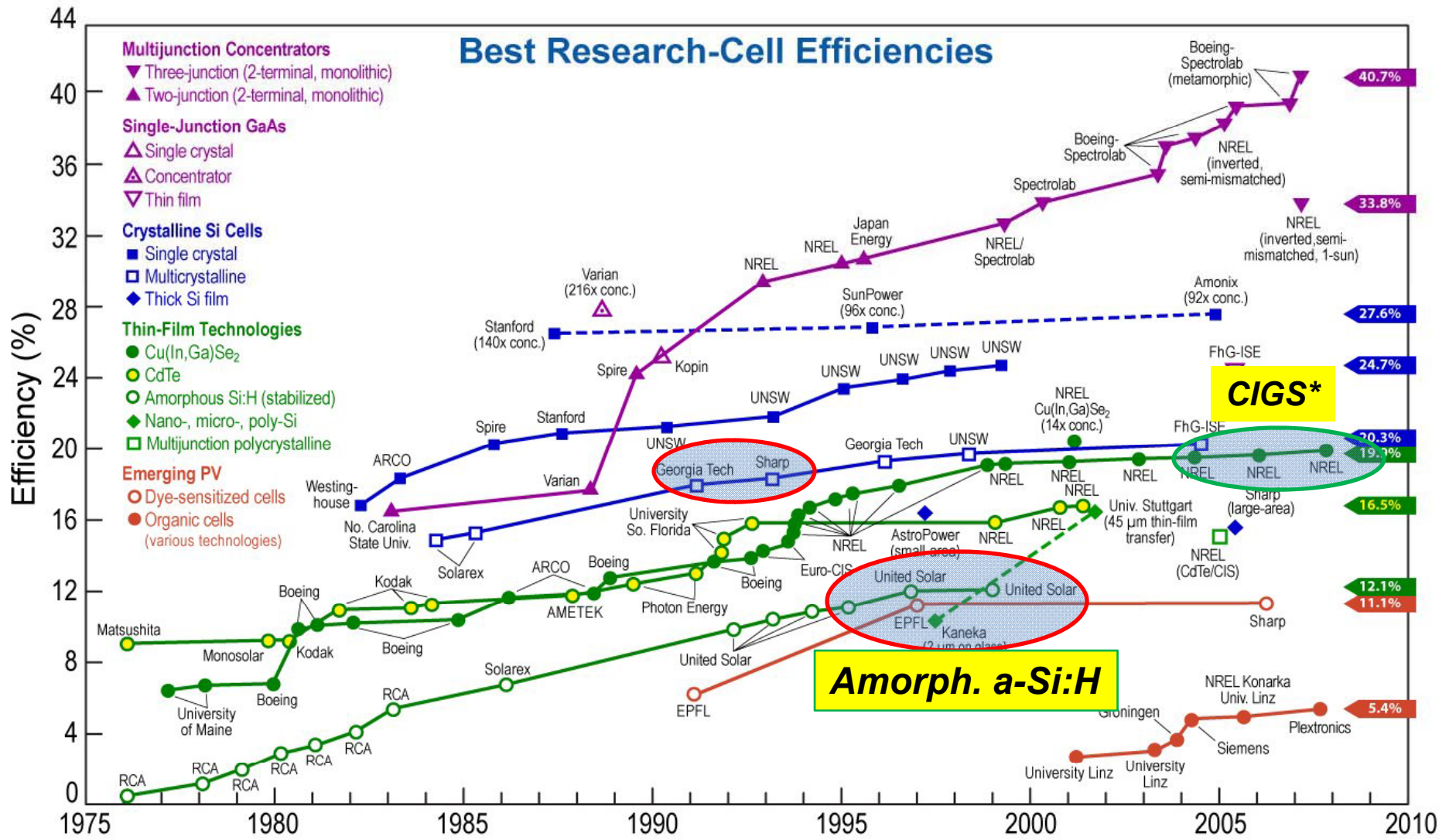
Green: theory (dominates). **Blue:** experiment (more needed)

Application: looking for collaboration with research and industry

Outline

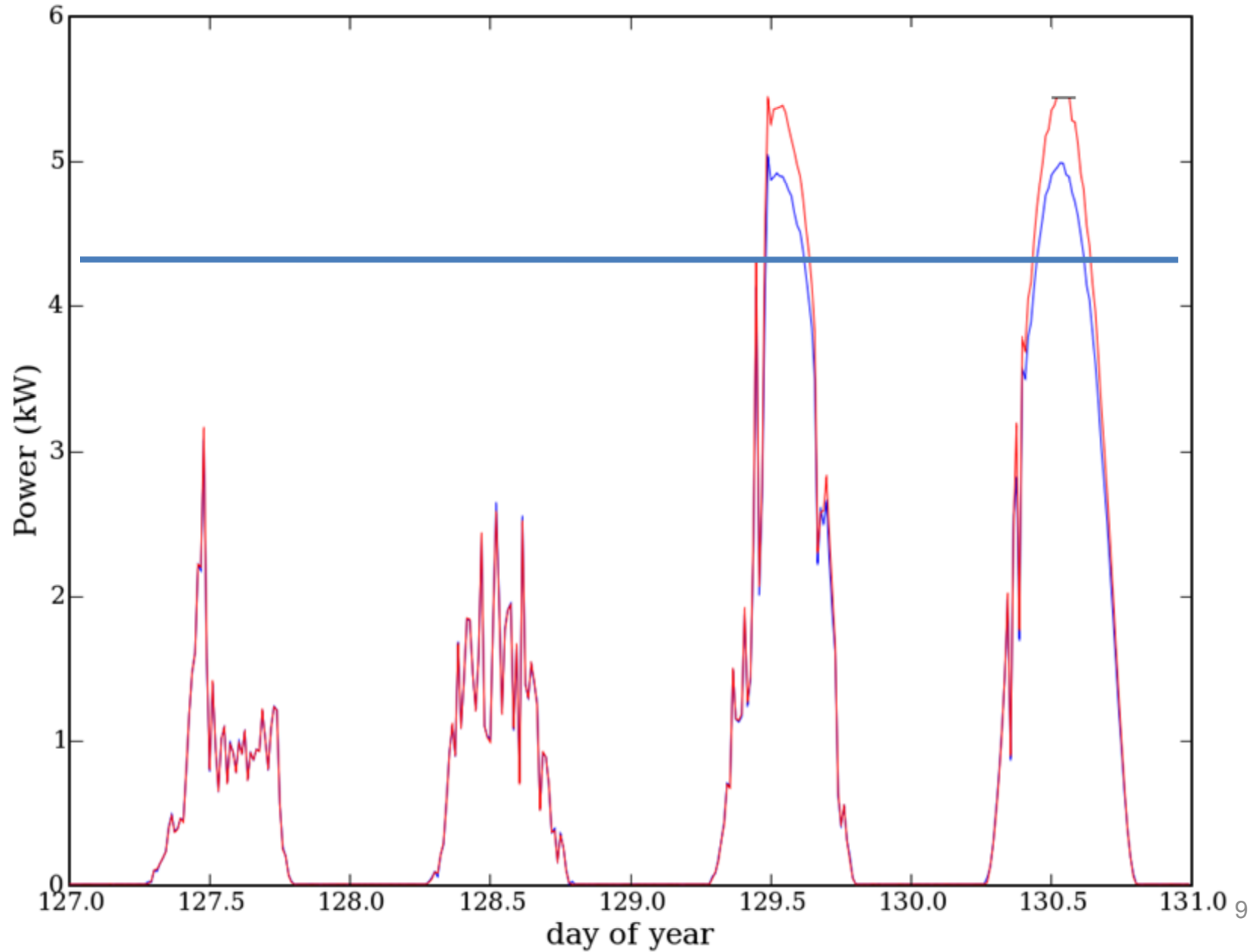
- Amorphous hydrogenated silicon (a-Si:H) based solar cells and hydrogen storage: *what's common*
- *Optimization* of a-Si:H solar cells: comprehensive formalism for *single junction* photovoltaics
- Hydrogen inside a-Si: first principles *numerical simulation* to access H *microscopic* physics
- What's bad for a-Si:H solar cells might be very good for *solid state hydrogen storage*
- Conclusions

www.nrel.gov/solar/ – best research solar cells performance: good for real life?

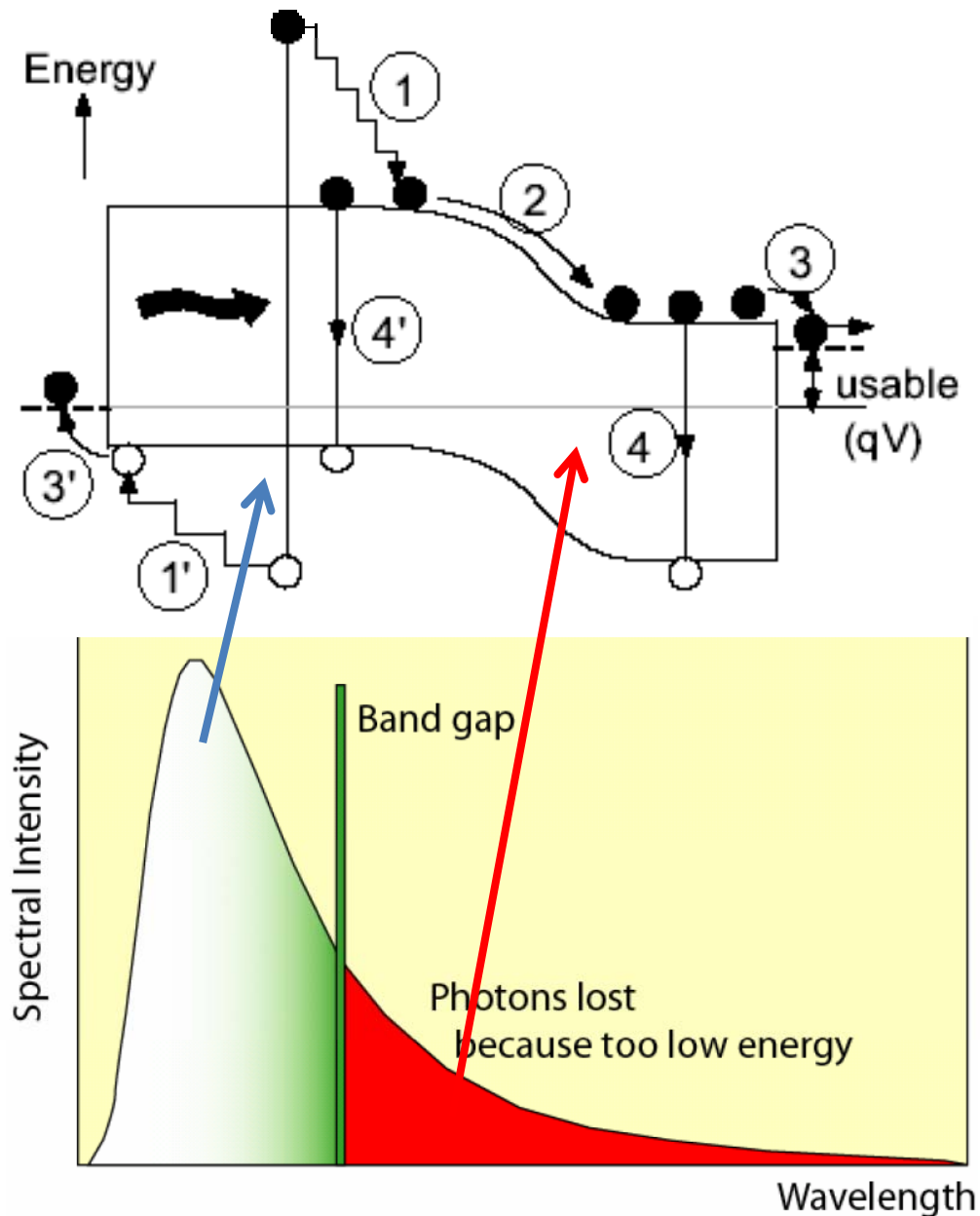


* Copper Indium Gallium Selenide (C.I.G.S.)

Solar Power change: optimization needed



Efficiency Losses in Single Junction Solar Cell

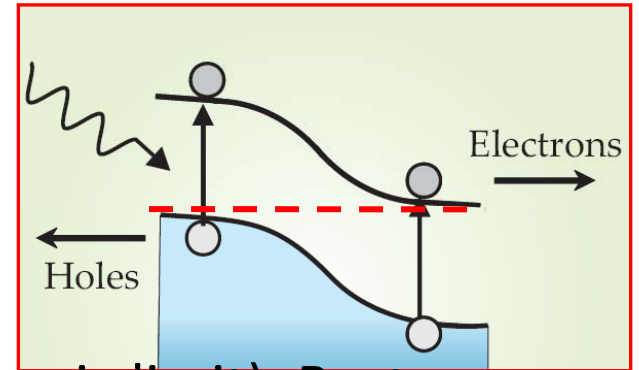


1 → Thermalization loss, or thermodynamic limit (efficiency < 32%)

2 and 3 → Junction and contact voltage loss

4 → Recombination loss

Single junction based solar cells in general



- **Maximum efficiency $\approx 32\%$** (thermodynamic limit). Best research efficiency $\approx 26\%$, too expensive to get higher
- Lower efficiency, but essentially cheaper solar cells are more appropriate for the Earth photovoltaics: **thin solid films** based systems: a-Si:H and Copper Indium Gallium Selenide (CIGS)
- **Indirect sunlight**, panel surface buildup (dirt, grass, dust)
- LOW-LIGHT: Compared to c-Si a-Si:H produces less power but performs better at lower light intensities \rightarrow good for environments where interrupted sunlight is the norm.
- The CIGS panel has better performance than a-Si:H in terms of maximum output, but worse **low light** performance.

Hydrogenated Amorphous Silicon

- Advantages of a-Si:H
 - **Large optical absorption** coefficient (about 0.5 micron will absorb 90% of the incident sunlight)
 - It is plentiful and can be deposited on a variety of substrates (low temperature, large area, flexible)
 - It can be alloyed with other elements (carbon, germanium) to create **multi junction** structures with increased energy conversion efficiency
 - The energy gap can be modulated to allow for near **optimum conversion** efficiency for sunlight: optical gap within 1.6 – 1.8 eV

Deposition method:

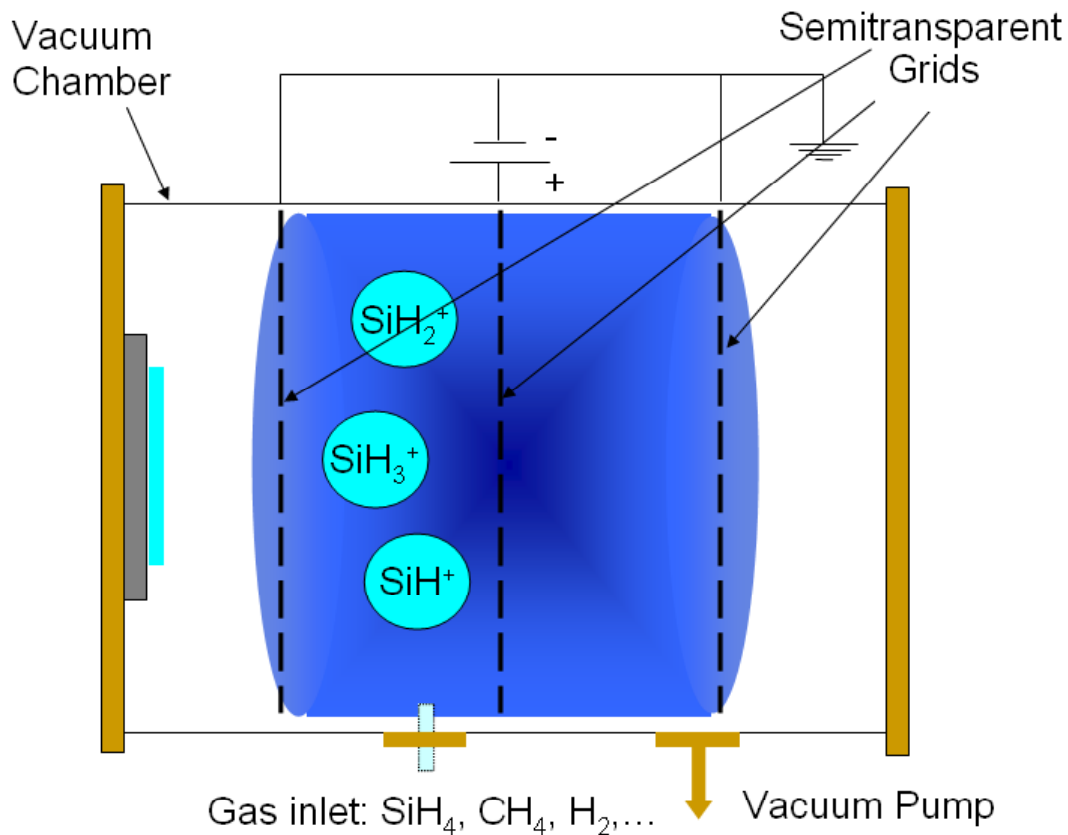
The Saddle Field Glow Discharge

The saddle-field technique is a remote plasma CVD method.

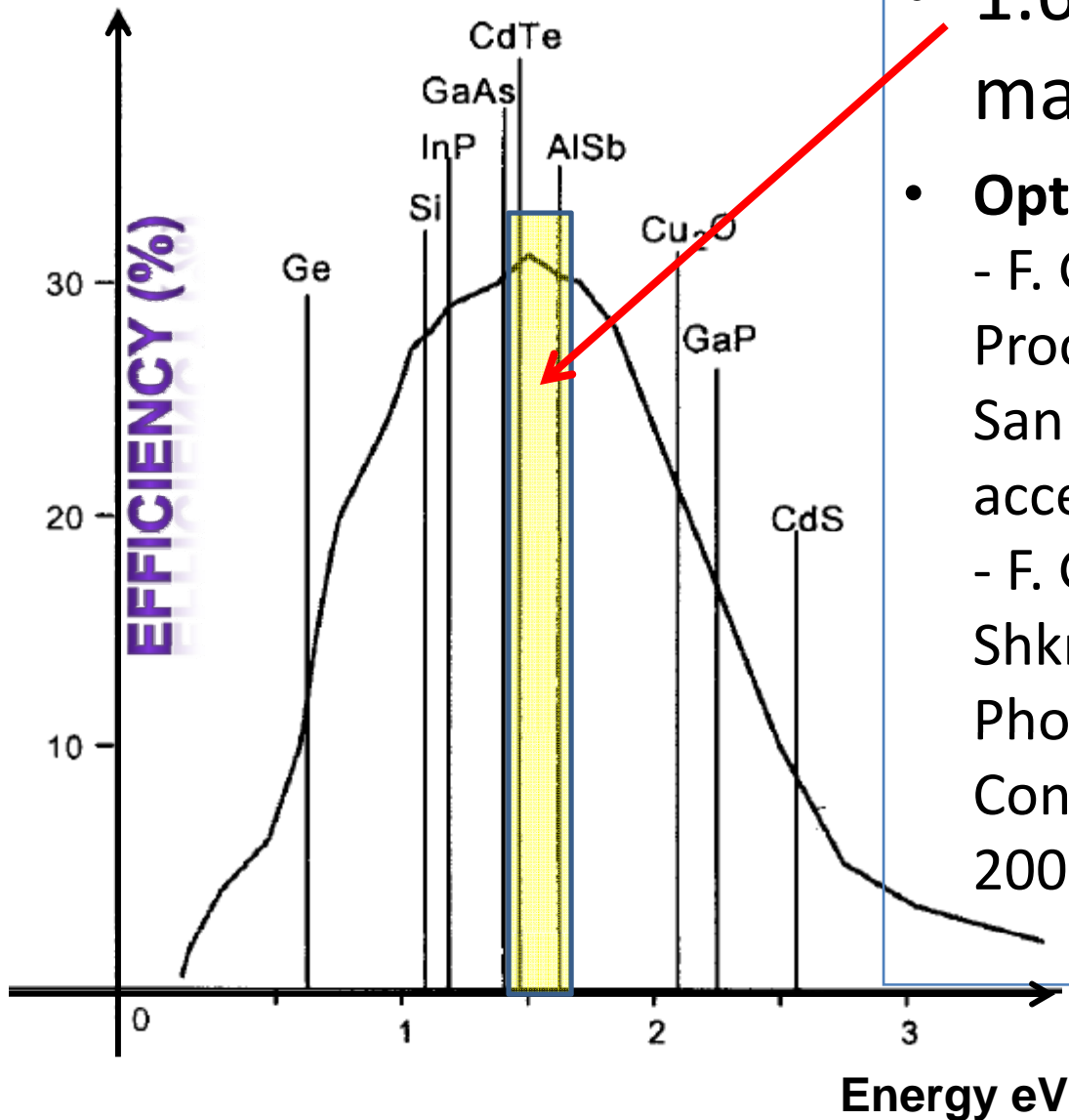
It allows independent control of plasma and deposition parameters.

It is scaleable and more economic to implement than conventional growth techniques

*[Mat. Res. Soc. Proc. 744
(2002) M.5.21]*



Why a-Si:H?

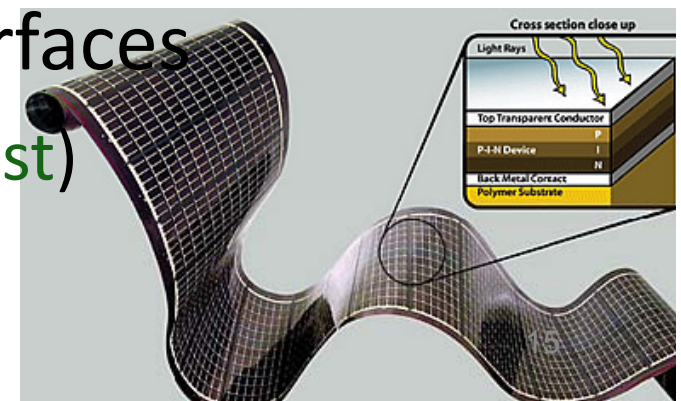
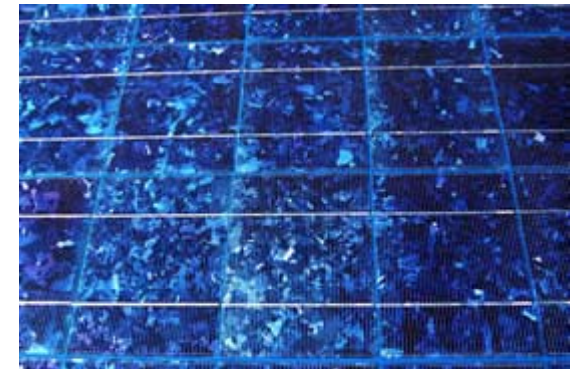


- 1.6 – 1.8 eV gap → maximum SC efficiency
- **Optics of a-Si:H:**
 - F. Gaspari, A.I. Shkrebtii, *et al.* Proc. 2009 MRS Spring Meeting, San Francisco, April, 2009, accepted
 - F. Gaspari, I. M. Kupchak, A. I. Shkrebtii, *et al.* Proc. 33rd IEEE Photovoltaic Specialists Conference, San Diego, May, 2008, p. 206-1

Some numbers ¹⁴ →

Silicon based solar cells (SCs)

- **Crystalline** silicon (c-Si) based
 - typically 15 – 18% efficient (**≈25% best**)
 - expensive (grown as big crystal)
- **Poly-crystalline** silicon
 - 12 – 16% efficient (**≈20% best**)
 - cheaper than c-Si based SCs
- **Amorphous silicon** (non-crystalline) “thin film”, deposited on a wide range of surfaces
 - 6 – 10% effic. (*stabilized*, **≈12% best**)
 - cheapest per Watt

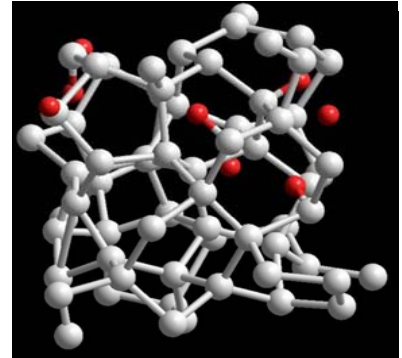


a-Si:H based solar cells

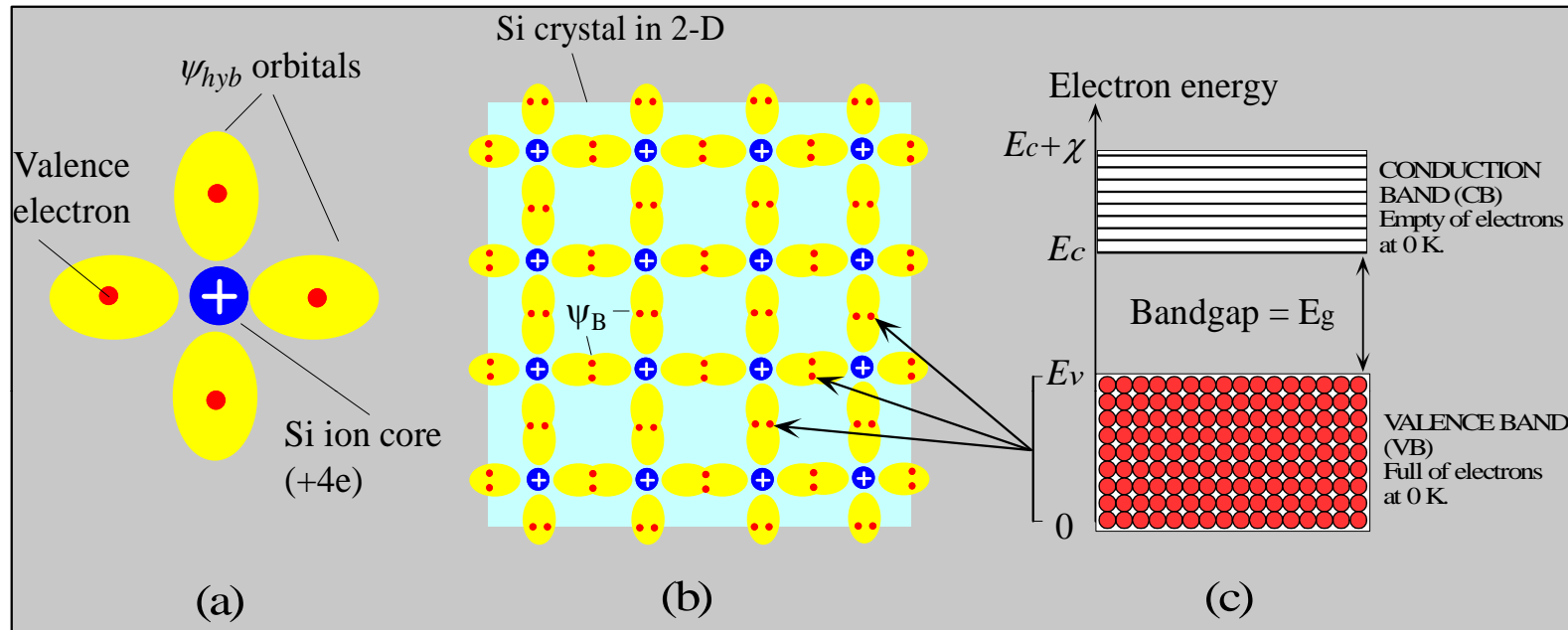
- Thin film *hydrogenated amorphous silicon* (a-Si:H) is widely used in photovoltaics
- **Goal #1**: for the best performance of the a-Si:H based solar cells (SC) it is important:
 - to characterize and optimize a-Si:H films in terms of growth conditions, hydrogen concentration, etc.
 - to optimize the solar cells in terms of mobility gap, *p*-, *i*- and *n*-layer doping levels, electron and hole mobilities μ_n and μ_p and their lifetime, resistance of *p*-, *i*- and *n*-layers
 - to design contact grid and optimize the transparent conducting and antireflecting layers

In addition, hydrogenated Amorphous Si...

- ...is important not only for **solar cells** but for microelectronics applications as well
- Its **stability** is crucial, but there is
 - **Light-induced** degradation, or Staebler-Wronski (SW) effect: [Appl. Appl. Phys. Lett. 31, 292 \(1977\)](#)
- **Very typical example** of disordered materials
- **Goal #2:** (i) Gain **microscopic access** to a-Si:H through **extensive** Molecular Dynamics (MD) simulation and advanced **post-processing**;
(ii) Pave the way for **to monitor and improve** the material's properties
(iii) Apply the formalism developed for different applications: **hydrogen storage**



Physics of Crystalline Silicon

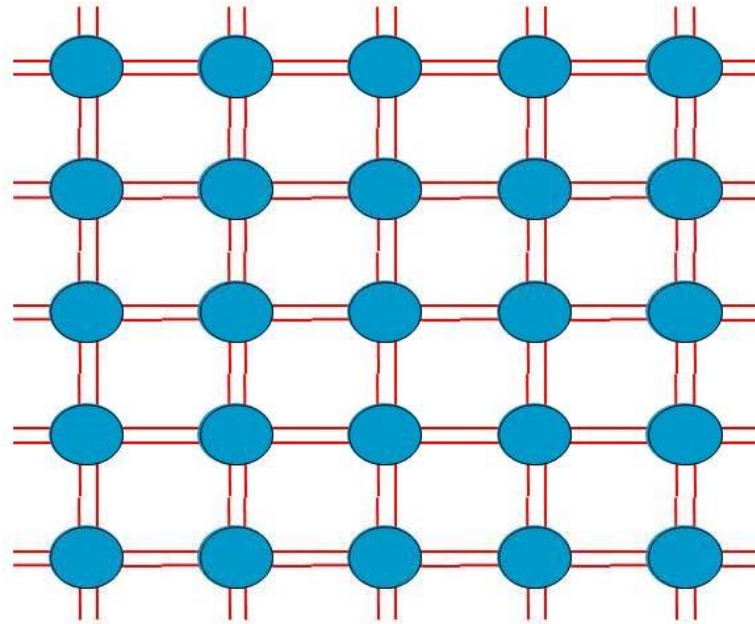


a) Si atom with 4 hybrid orbitals

b) 2-d view of Si crystal showing covalent bonds

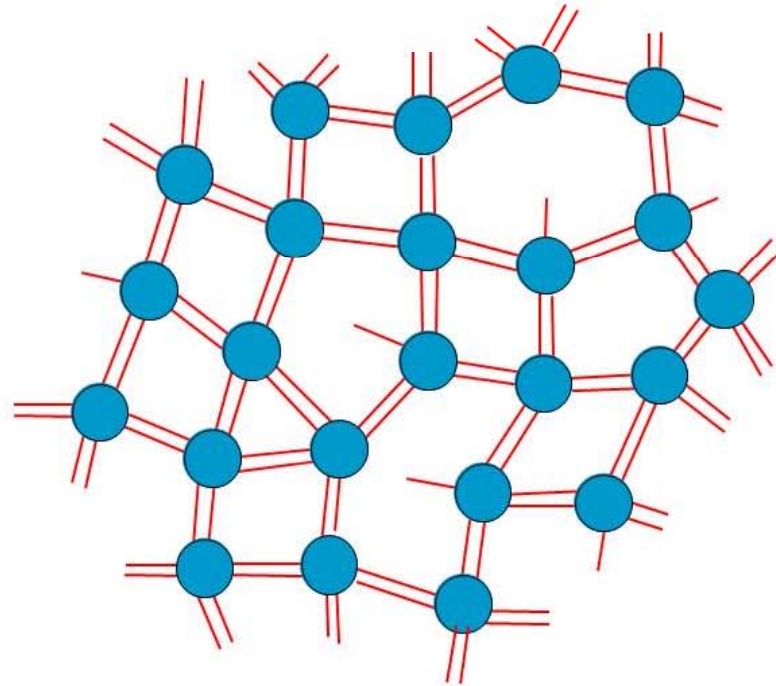
c) Energy Band Diagram at 0 K

Two-dimensional schematic representation of a silicon crystal (3-d – Tetrahedral structure)
bond length 2.33 Å, bond angle 109.5°



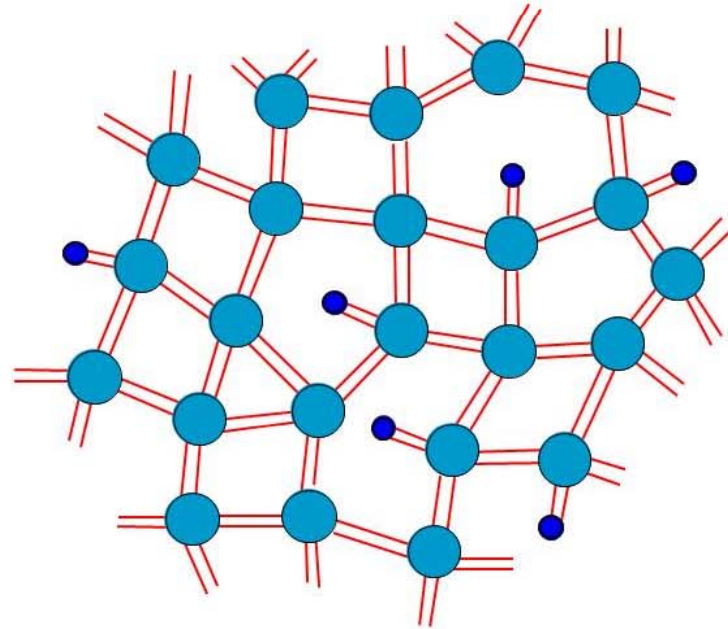
Each line represents an electron in a bond. A full covalent bond has two lines and a broken bond has one line

The structure of amorphous silicon with voids and dangling bonds (DBs) ($\pm 10\%$ deviation from crystalline structure)



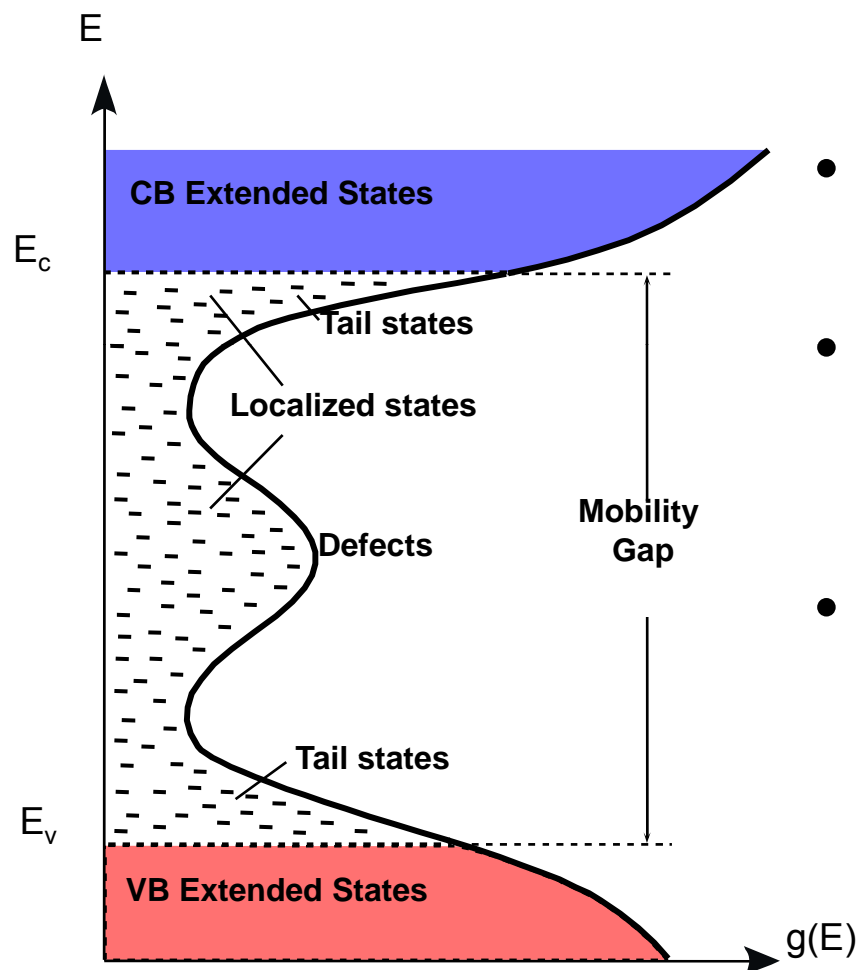
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The structure of amorphous silicon with voids and dangling bonds (DBs) ($\pm 10\%$ deviation from crystalline structure)



Each line represents an electron in a bond. A full covalent bond has two lines and a broken bond has one line

Density of States (DOS) for *a*-Si:H



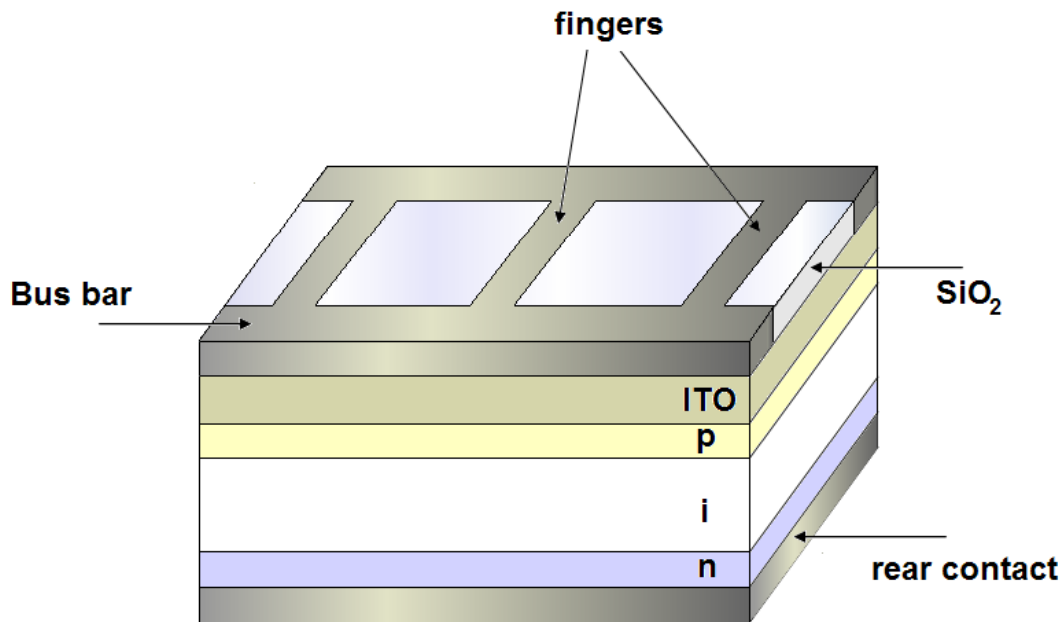
- Electron transport above E_c is due to scattering
- Below E_c we have hopping conduction
- There is a change in electron mobility across E_c , hence we define a *mobility edge*
- The localized states (traps) can be distinguished in tail states (due to disorder). Defect states (under and over coordination, dangling bonds, etc.)

And they are changing!

The Staebler-Wronski Effect

- Exposure to sun light leads to an increase in the density of states in the energy gap of a-Si:H ([Appl. Appl. Phys. Lett. 31, 292 \(1977\)](#))
- This increase in the density of states is linked to the formation of silicon dangling bonds
- Annealing at elevated temperatures reduces the density of states back to the original value

Optimization of the collecting grid, reflection, ITO layer, and more



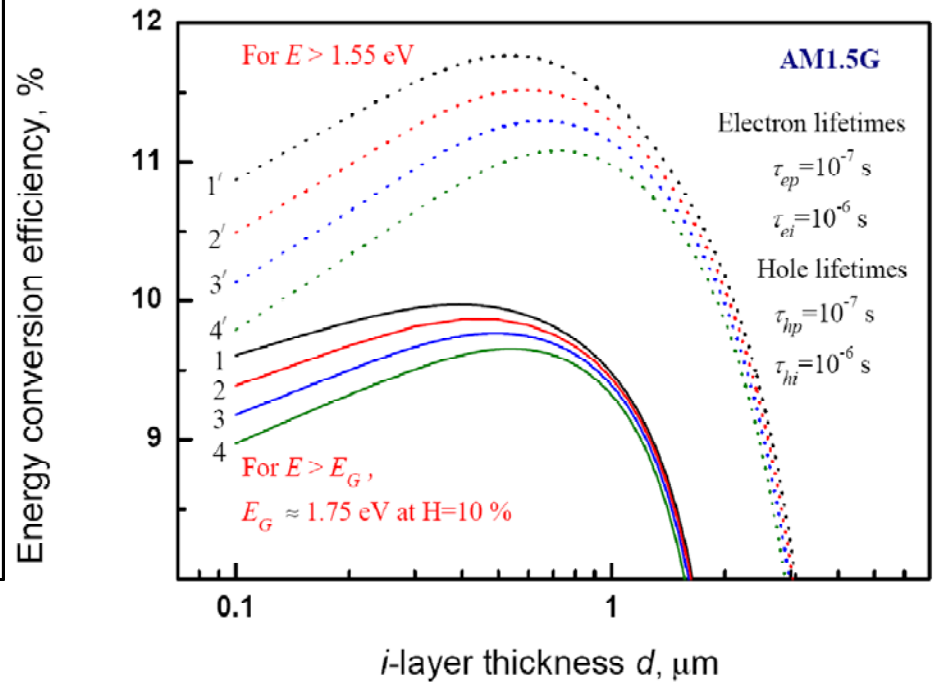
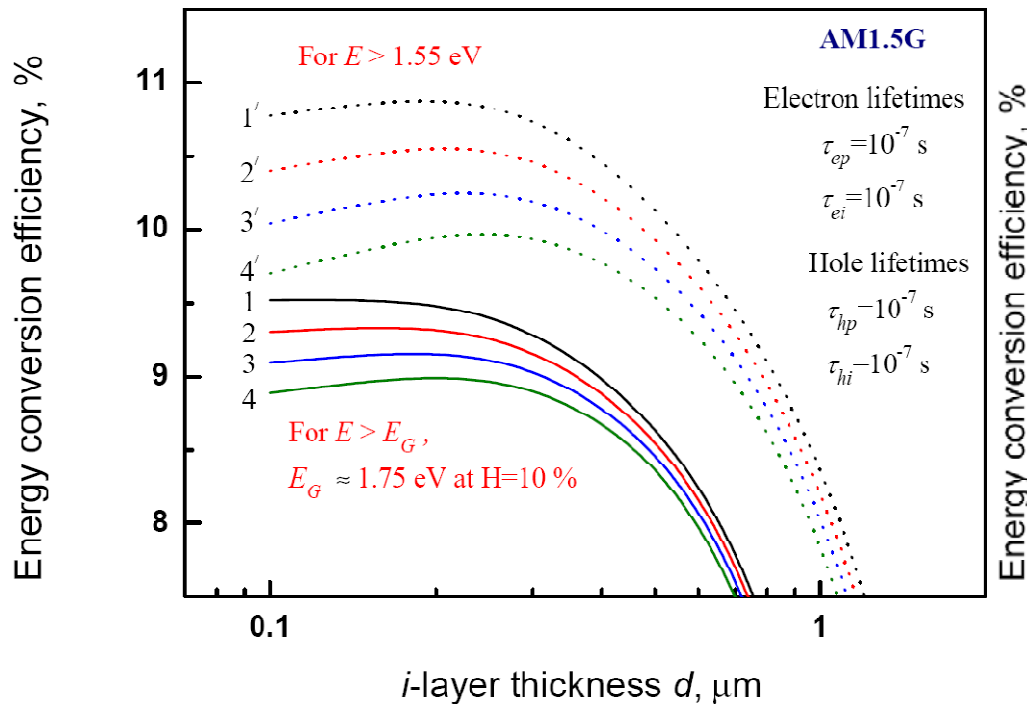
The frontal collecting grid electrode with parallel metal fingers connected to each other through two bus bars. The frontal grid is placed on a top of transparent conducting ITO/SnO₂ layer.

How to orient the metal finger?

The numerical optimization model includes...

- Space charge region of $p-i-n$ junction has been considered **self-consistently** (in particular, adjustment of current densities and excess electron-hole densities due to band bending)
- **Multiple light** reflection in active layers and multiple reflection from metallic finger electrodes (for oblique light incidence) have been considered, including multiple reflection from rear contact and front surface sublayers
- **Local orientation** of SC in a definite geographical point, changes in the angles of light incidence during a year and daytime have been taken into account, as well as possible changes in the orientation of finger electrodes in the plane of SC; it allows calculating and optimizing mean SC efficiency during the long-term period (e.g., year)
- **Experimental solar cell spectra** at the Earth's surface as well as AM0 as the numerical program input
- **Executable** file will be available on request

Energy conversion efficiencies, examples



- Energy conversion efficiencies versus thickness d of i -layer before Stabler-Wronski effect. In the left panel electron lifetime $\tau_{ei} = \tau_{hi} = 10^{-6}$ s, while for the right panel $\tau_{ei} = 10^{-7}$ s and $\tau_{hi} = 10^{-7}$ s.

Can we extend the model to other single junction solar cell systems?

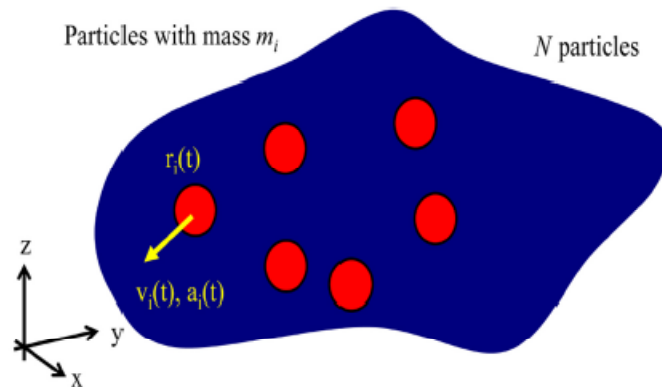
- The model that calculates band bending *selfconsistently* is very general and valuable especially when a semiconductor consists of a lot of imperfections inside the gap.
- CIGS technology, e.g., is improving: CIGS based thin film solar cells approaching laboratory efficiencies of up to 20%. However, the semiconductor contains a lot of defect states that have to be properly accounted for

Staebler-Wronski effect...

- has prompted us to access a microscopic hydrogen behaviour through the extensive computer simulation and post processing
- There are many other microscopic properties that require immediate computational (Molecular Dynamics) attention and detailed analysis

Molecular Dynamics (MD) solves...

- System of coupled 2-nd order diff. equations ...
- by discretizing in time (spatial discretization given by “atom size”), forces from the **first principles**



$$F = ma$$

$$m \frac{d^2 r_j}{dt^2} = -\nabla_{r_j} U(r_j) \quad j = 1..N$$

Total energy of system

$$E = K + U$$

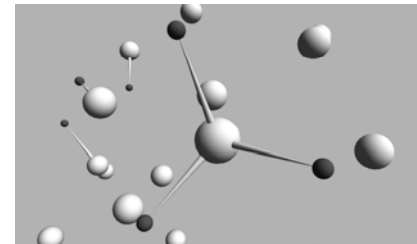
$$K = \frac{1}{2} m \sum_{j=1}^N v_j^2$$

$$U = U(r_j)$$

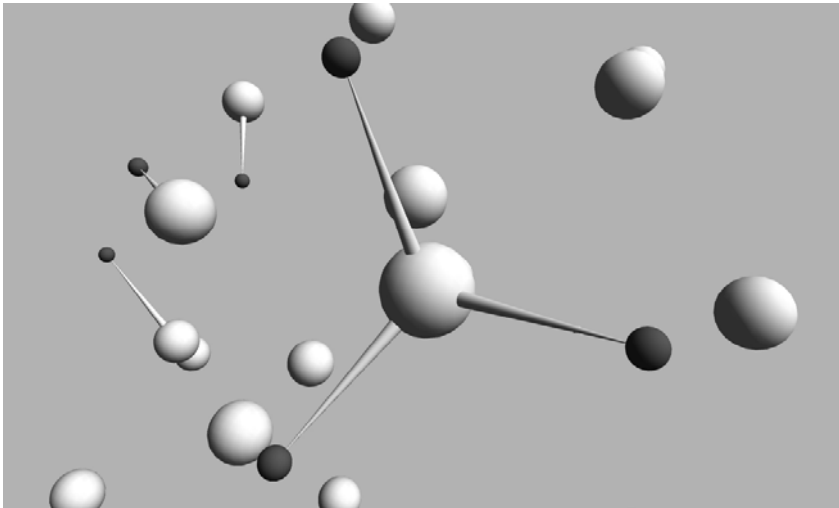
Coupled system N-body problem, no exact solution for $N > 2$

Tools and Technical details for α -Si:H

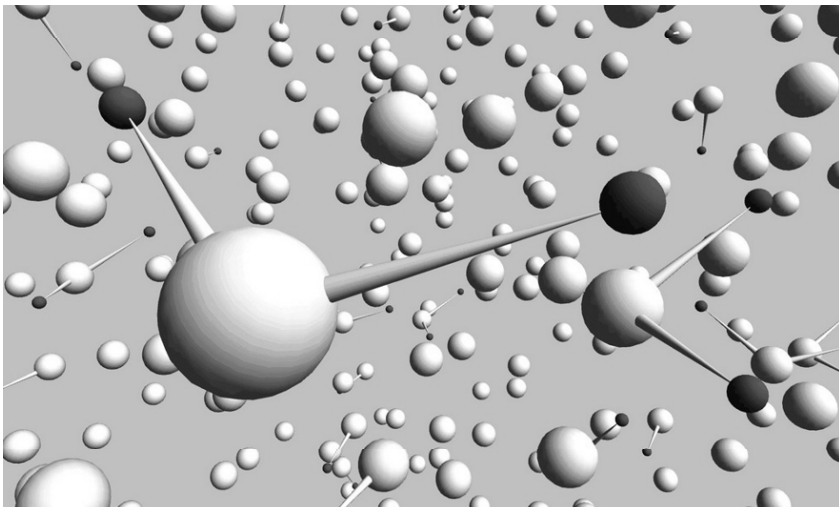
- *Ab-initio* Molecular Dynamics (AIMD) + **improved signal processing technique** + computer visualization
- Numerous **64 Si atom** supercells (“samples”) in wide range of Hydrogen concentration: from **0** to **20 at. %**
- “Melted” at **3000K**, equilibrated for 5 + ps, slowly “cooled down” to 0 K and relaxed to ground state
- **MD at Room Temperature** ($\sim 300\text{K}$) to collect statistics
- **Annealing** at 500 ÷ 700K, then **MD at RT** repeated
- Dynamics was computer visualized
- *Details are in:* I. Kupchak, F. Gaspari, A.I. Shkrebtii, and J. M. Perz, J. Appl. Phys. **103**, 123525, 2008



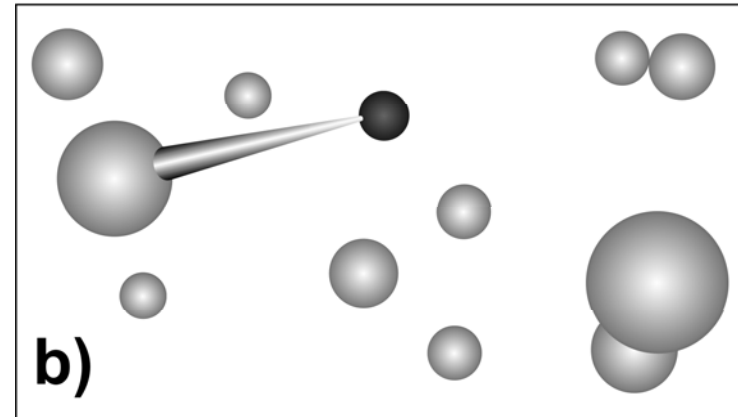
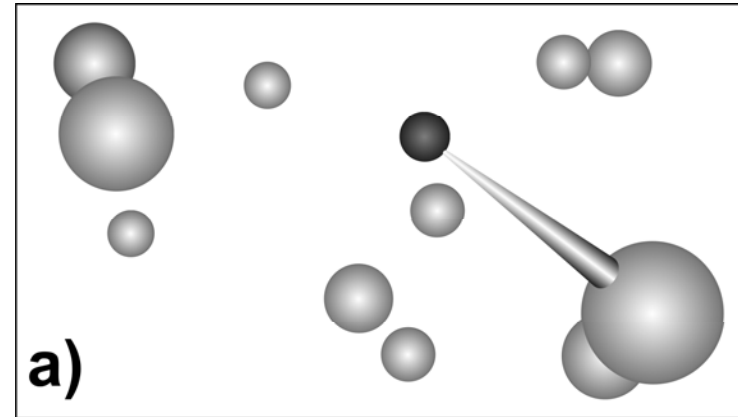
Many “samples”— all possible complexes



1. $\text{Si} - \text{H}_3$ and $\text{Si} - \text{H}$ (monohydride)



2. Two dihydride $\text{Si} - \text{H}_2$ and $\text{Si} - \text{H}$



3. Hydrogen rebonding/diffusion (two frames are shown above),

as well as interstitial H atoms and H_2 molecule (shown next)

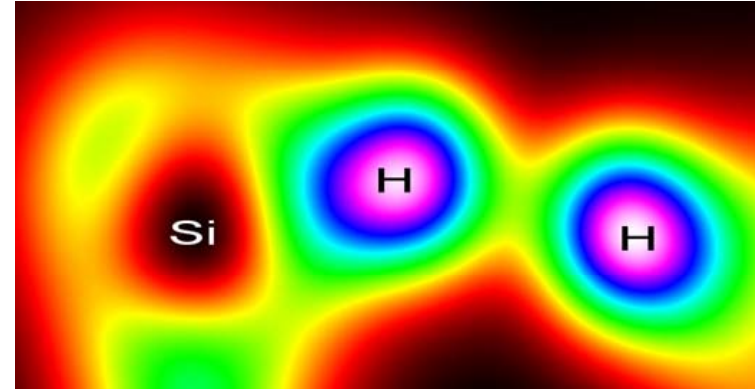
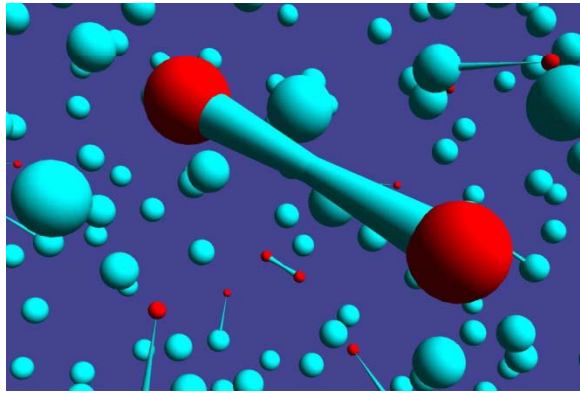
**Various Si-H complexes, obtained theoretically
using $Si_{64}H_4 - Si_{64}H_{12}$**

H amount (%)	SiH	SiH ₂	SiH ₃	H ₂	Si ₂ H
Si ₆₄ H ₄ (6%)	X	-	-	-	-
Si ₆₄ H ₆ (9%)	X	-	X		X
Si ₆₄ H ₈ (11%)	X	-	-	X	-
Si ₆₄ H ₁₀ (14%)	X	X	X	X	-
Si ₆₄ H ₁₂ (16%)	X	-	-	-	X

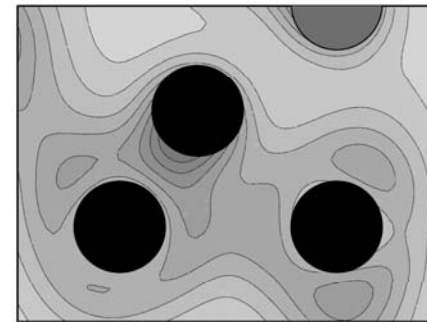
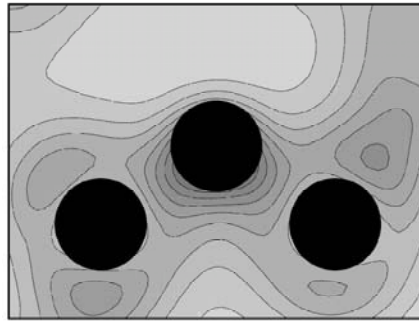
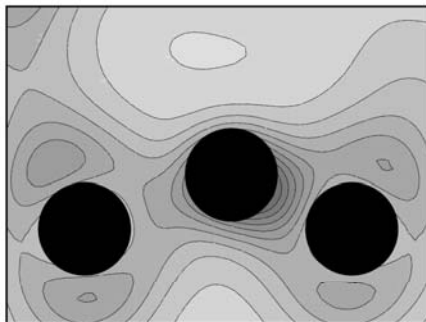
Si₂H complex, the so-called **“jumping atom”** – a hydrogen atom that is shared between two neighboring silicon atoms. Si-H-Si was proposed earlier (see, e.g., R. A. Street “Hydrogenated Amorphous Silicon”), and such complexes have been found for the first time **numerically** in two different numerical samples.

Examples of hydrogen bonding and bond instability

- Formation of H_2 “molecule” inside a-Si:H

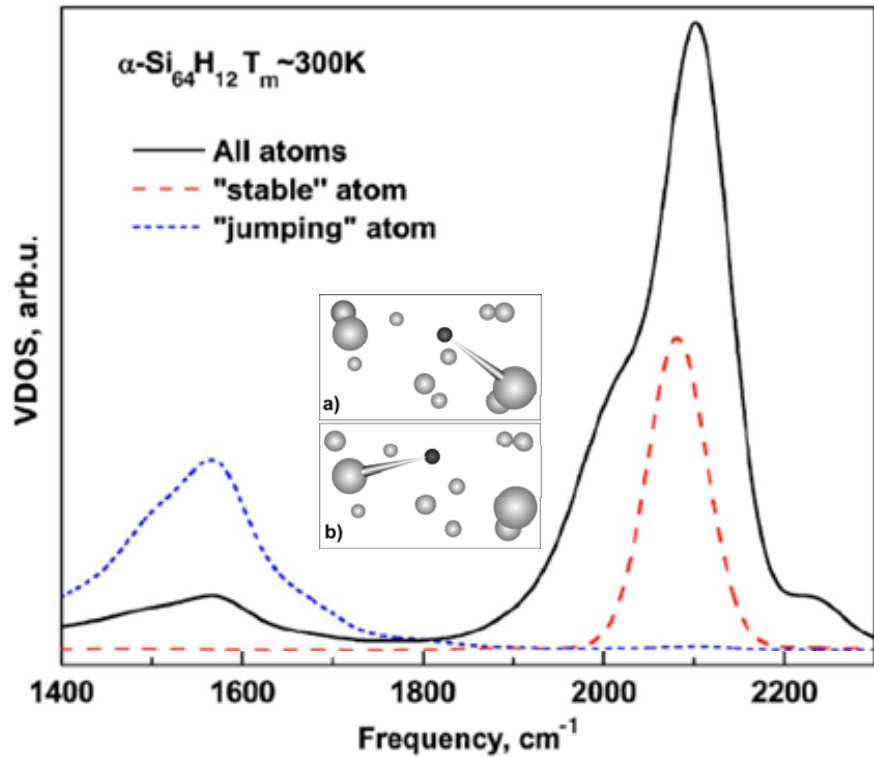
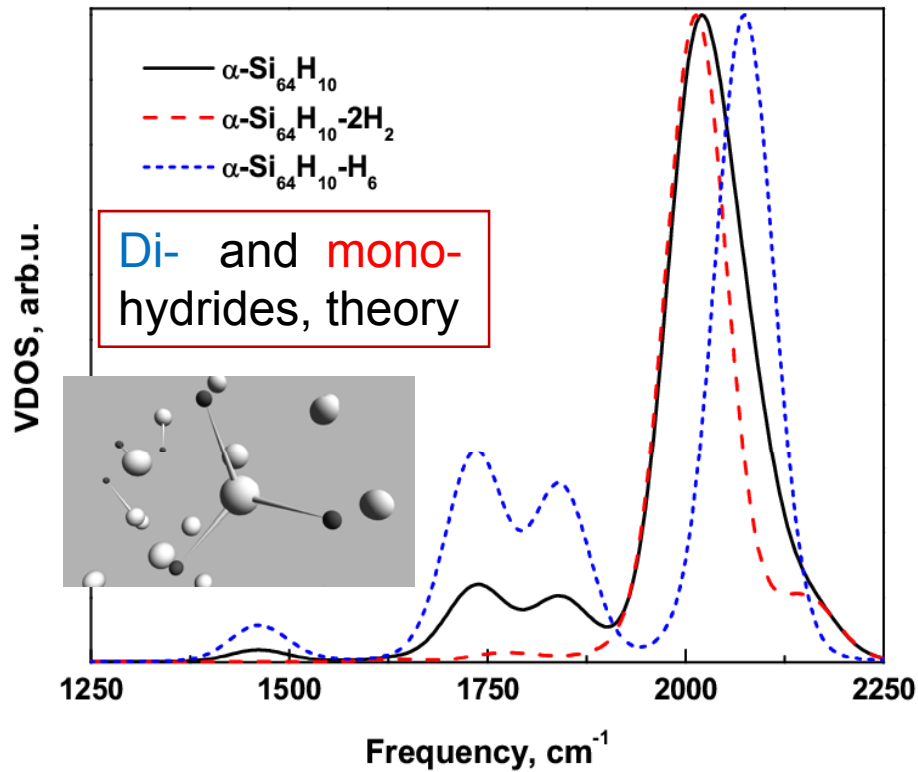


- And charge density of jumping H atom



- **How can we verify this experimentally?**

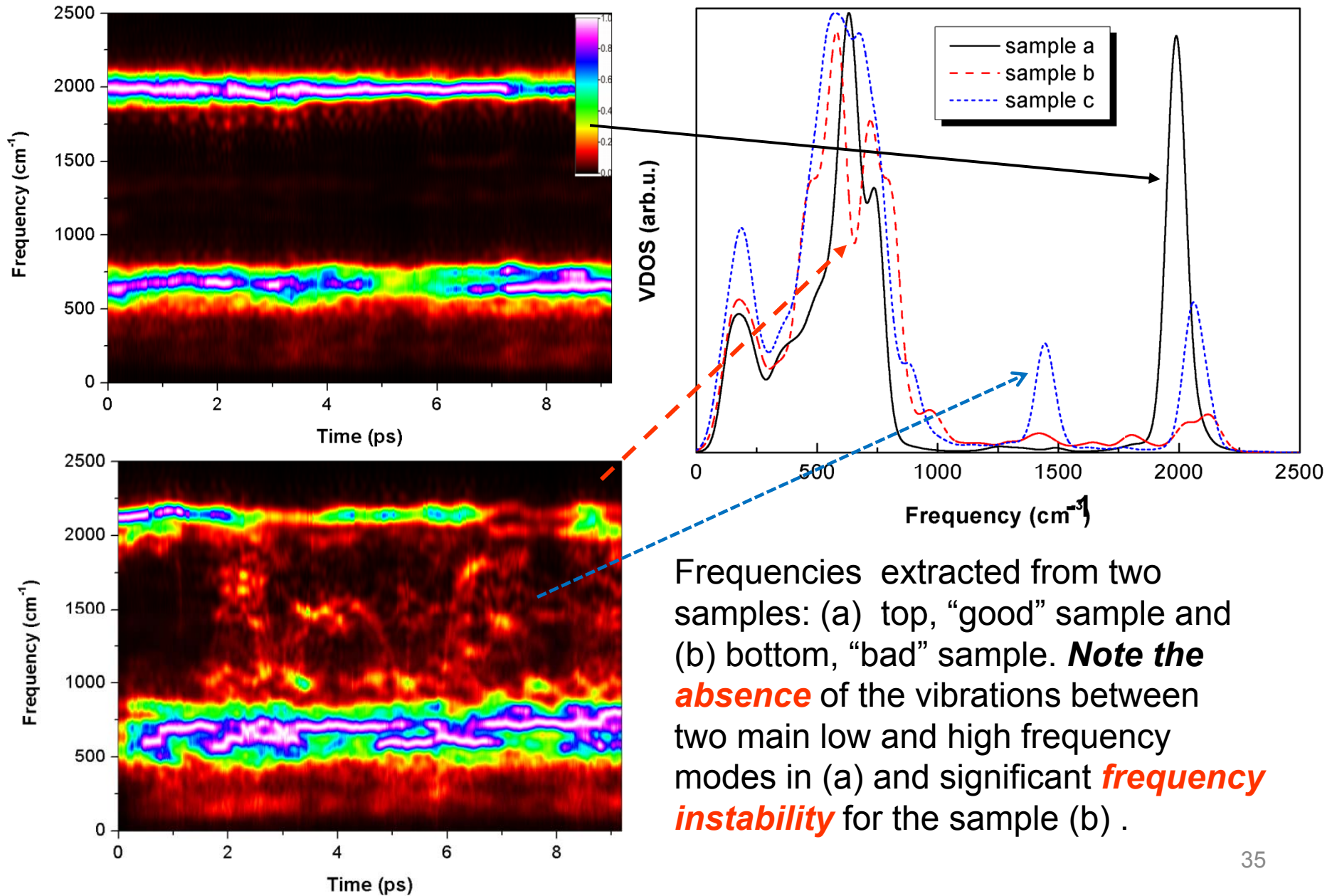
Calculated vibrational spectra: a-Si:H signature



H - stretch vibrations for a-Si₆₄-H₁₀ system at high frequency. Black line: all H-associated stretching vibrations, dihydride modes (blue, short dash) & monohydride modes (red, long dash). Note very close agreement with expt. by Lucovsky, *et al.*

H - stretch vibrations for a-Si₆₄_H₁₂ system. Black line: all H vibrations, red long dash: stable monohydrides. Blue, short dash: bond-switching H-atom, consistent with three centre Si—H—Si bond (**T_{CB}**) - Darwich *et al.*, infrared transmission spectroscopy (IRT) for SW effect (light soaking experiment).

Real time frequencies: *a*-Si:H stability



Frequencies extracted from two samples: (a) top, “good” sample and (b) bottom, “bad” sample. **Note the absence** of the vibrations between two main low and high frequency modes in (a) and significant **frequency instability** for the sample (b).

My hydrogen “strong bonding” theory that was always accompanied by experiment

- Si(100)2x1:H - PRL **70** (1993) 2645
- GaAs(110):H - J. El. Spec. **64/65** (1993) 697
- Si(111)7x7:H - PRL **76** (1996) 4923
- Si(110):H - PRB **57** RC12709 (1998)
- ***Recent combined with Molecular Dynamics results***
- a-Si:H: dynamics, electronic structure, H diffusion, bonding dynamics, temperature dependent optical response, main results are in: PRB **79** (2009) 224203, PRB **77** (2008) 125218, J. Ap. Phys. **103** (2008)123525
- Diamond C(111)2x1 clean and H covered. Dynamics (including ***quantum zero point vibrations***), surface bands, temperature dependent optical response (in preparation)

But for the hydrogen storage we need...

- ***Low decomposition temperature*** is the most desirable case, which allows simple thermodynamic control of hydrogen release.
- Weak Van der Waals bonding (physical rather than chemical adsorption) is preferable
- In the theoretical approaches quantum mechanical considerations for very light hydrogen atoms behavior has to be included

What about hydrogen solid state storage?

- We have proven numerically that H can be added, removed, annealed, *etc.* numerically
→ very accurate ***computational experiment***.
- For a-Si:H we prefer as strong hydrogen bonding as possible to avoid H instability.
- Not for hydrogen storage systems!
- Infrared spectroscopy is extremely sensitive tool to characterize the hydrogen bonding, absorption, or release and ***can*** be accurately modeled to predict H behaviour

More hydrogen storage

- No perfect (solid state) storage for hydrogen has been discovered yet.
- However, only a few light elements, such as Li, B, **C**, Na, Mg, Al, P and **Si**, and (better) their compounds can make a suitable lightweight hydrogen storage
- Systems with essentially developed surface are the best candidates: porous materials or/and, nanomaterials

Conclusions

- *Comprehensive optimization formalism* for a single-junction solar cells (a-Si:H based) had been developed using the experimental diffusion, mobilities, *p-i-n* parameter, defect distribution inside the gap, *etc.*
- *Comprehensive parameter-free approach* to access micro structure, dynamics, bonding, and diffusion of hydrogen inside ***α-Si:H***. Applicable to other systems!
- *Vibrational* spectra have been extracted and compared with the experiment to characterize the systems
- The model *can be extended* to structural, dynamical and electronic properties of ***non-crystalline materials*** in general. *Particular interest is in solid state storage.*

Theoretical assumptions

- **Diffusion theory** of photo-conversion was used for the amorphous Si based cells
- **Comprehensive model** has been developed and solved numerically. **For limiting cases analytical expressions** we have derived for the conversion efficiency: A.V. Sachenko, *et al.*, Semiconductor Physics, Quantum Electronics & Optoelectronics, 10 p. 60 (2007)
- **Bulk** recombination dominates
- Optimization of the **top contact grid** was performed using a concept of effective collection length [A.V. Sachenko, A.P. Gorban Semiconductor Physics, Quantum Electronics & Optoelectronics, 2 P. 42 (1999), http://www.journal-spqeo.org.ua/n2_99/42_299.htm]