

Growth Chemistry and Its Relationship to Amorphous Si Devices for Photovoltaic Energy Conversion

Vikram L. Dalal

Iowa State University

Dept. of Elec. And Comp. Engr.

© 2002 Iowa State University. All rights reserved.

Outline of Talk

- Introduction to Photovoltaics
- Amorphous Silicon, its properties
- Growth chemistry of semiconductors
- Relationship of growth to properties
- Some recent results at Iowa State
- Future research perspectives

Solar Energy

- **Plentiful in most areas of the world**
- **On the average, about 1 kw/m² during daytime**
- **In sunny areas, almost 3000 kWh/(m²- year)**
- **A distributed, and reliable energy source where the climate is right**

- **(Southwestern US, Mexico, Western India, China, Arabian peninsula, southern Africa etc.)**

Solar Energy cont..

- **Distributed nature important for economic development**
 - **Provide rural lighting using simple battery chargers and fluorescent lights**
 - » (**Solar lantern, cost about \$50**)
 - **Clean drinking water from tube wells**
 - **Power for irrigation**
 - » **Make 3 crops a year possible in tropical countries**

How do we convert solar energy into electricity?

- **Solar thermal – focus sunlight with a field of mirrors, produce steam
(A large plant was built in Barstow, CA)**
- **Photovoltaic conversion**
- **Solar fuel production – produce chemicals**
- **Biowaste – a form of indirect solar**

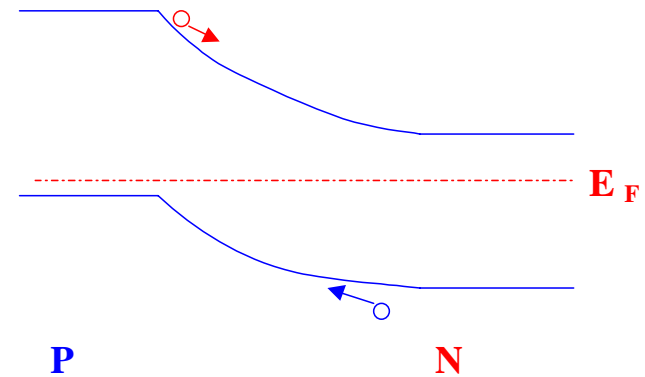
- **Photovoltaic Conversion is the most developed technology**

- Major industry
- About 400 MW production/year
- \$ 2.5 billion+/year, and growing at 25-30%

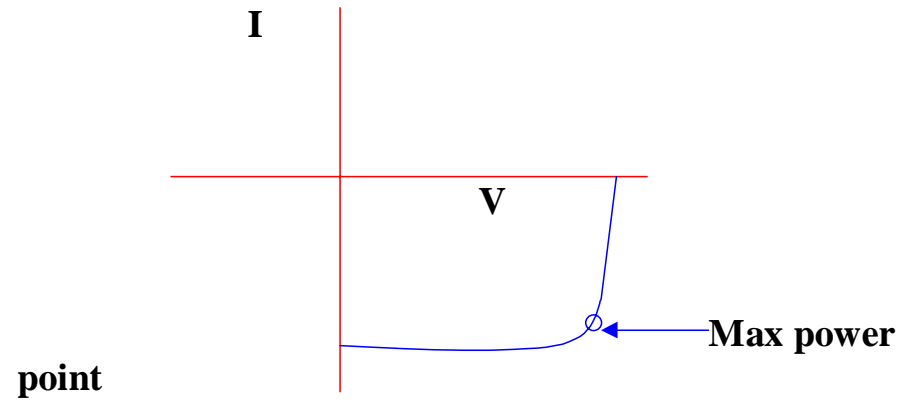
- * The major issue is COST.
 - If installed system cost \$ 2000/kW, will produce at ~ 8 c/kWh
- (Current cost, more like \$ 4000-6000/kW)

Introduction to Photovoltaic Technology

- **Photovoltaic (PV) Technology** relies on semiconductors
- Using a p-n junction, directly convert photons into electrons and holes, and then separate them



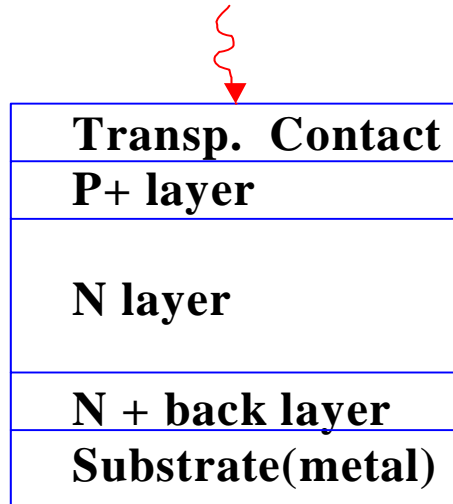
- Short circuit- Only current
- Open circuit – Only voltage



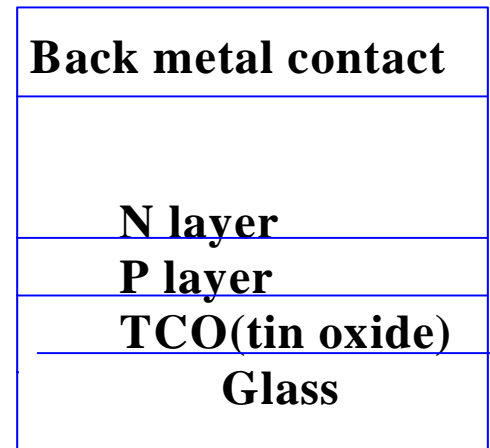
- Current density is a function of bandgap – smaller the gap, higher the current density (More photons absorbed)
- Voltage is a function of bandgap (Higher the gap, higher the voltage)
- We need (I x V) – There is an optimum bandgap for PV conversion
- For solar photons, between 1.3 to 1.7 eV
- (GaAs is almost a perfect material!)
 - Each individual cell only produces a small voltage (Si ~ 0.6 V)
 - Need to series-interconnect many identical cells to get reasonable voltage (12 V and above)
 - Voltages add, current remains the same as for a single cell

- **A solar cell consists of:**
 - **Substrate – can be Si wafer**
 - **Back contact (metal)**
 - **N layer**
 - **P layer**
 - **A transparent top contact**

Substrate type cells:



Superstrate type cells



Problem is:

- Si wafers are expensive
- Si is not a good material for PV conversion
- A poor absorber of light – a consequence of its band structure
- Processing is not continuous- cannot make monolithic, integrated panels to get high voltages without cutting and soldering

Properties of a good PV material:

- **A good absorber of light- have the right energy band structure (A direct gap material)**
- **(CdTe, GaAs, a-Si, CuInSe₂)**
- **Then, we can use only ~ 1 micrometer thick film**
- **Ability to make p-n homo or hetero-junctions**
- **Be able to deposit inexpensively**
- **Be non-toxic (e.g. CdTe – problem with Cd)**
- **Japan recently stopped all work on CdTe.**

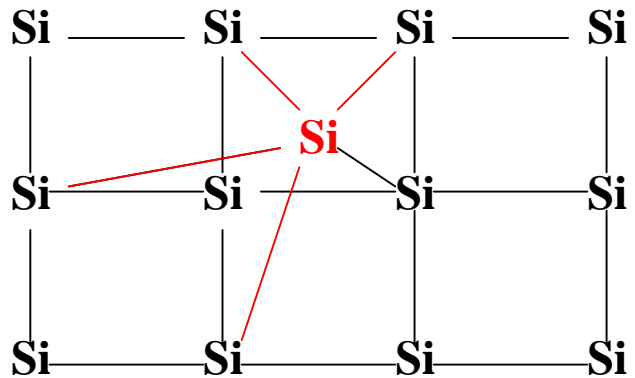
Amorphous and crystalline Si

- **Si based technology is the best from all viewpoints, except absorption!**
 - **Non-toxic**
 - **Plentiful**
 - **Very good technology base**
 - **Easy to deposit**
 - **P-n junctions easy to make**
- **So, make it absorbing!**
- - **Amorphous Si and Ge**

Amorphous Si and Alloys

A. Crystalline Si

Perfect bonding angles and lengths – Tetrahedral bonding



**Produces perfectly periodic potential energy diagram
Excellent electronic properties, but poor optical
properties**

a-Si- partially disordered lattice

Distorts the bond angles and lengths

Some Si-Si bonds will break- defects!

Leads to variation in periodic potential within the lattice

Leads to electron “confinement” within narrow potential wells- changes band structure \Rightarrow optical properties

Also leads to a great number of defects within the material – degrades electronic properties

How do we get good optical properties and acceptable electronic properties?

By using something to bond with broken Si bonds

Si is tetravalent- 4 electrons in outer shell

It bonds covalently with 4 other Si atoms

To form a covalent bond, use H!

Si-H is a covalent bond, with a bond strength ~ 2.4 eV, slightly higher than bond strength of Si

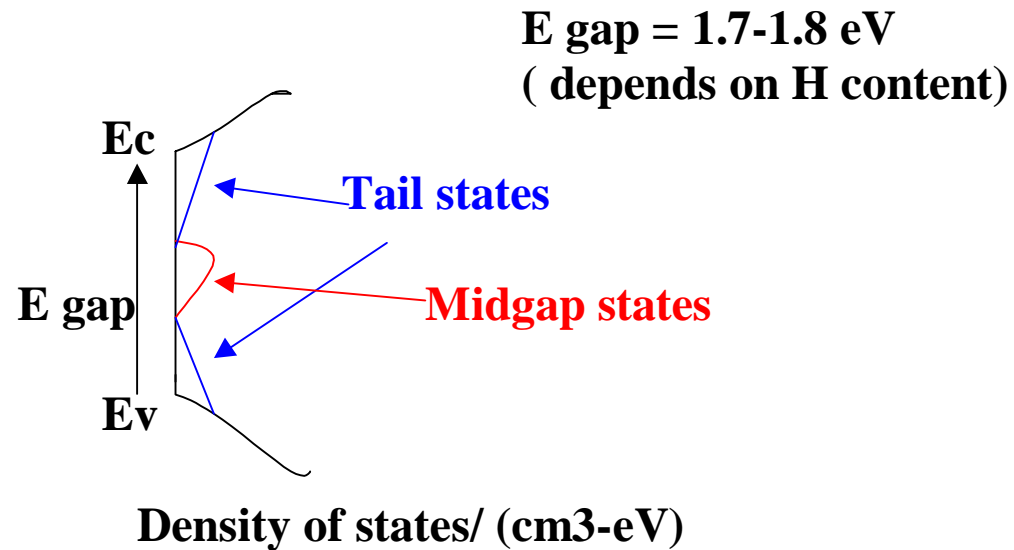
So, really, useful a-Si is a-Si:H, an alloy of Si and H

Defect density decreases from $1\text{E}20/\text{cm}^3$ to $5\text{E}15/\text{cm}^3$

$5\text{E}15/\text{cm}^3$ is an acceptable defect density in semiconductors- $1\text{E}20$ is not.

Properties of a-Si:

1. Energy Band structure



- **Material has absorption at ~1.7 eV**
- **Conduction takes place in conduction and valence bands**
- **The tail states and midgap states act as defects**

Tail states control movement of Fermi level

Midgap states control recombination

Within the conduction and valence bands, the material acts

As a polycrystalline, multi-small-grain semiconductor with grain boundaries passivated by H.

So, mobilities are low ($\sim 10\text{-}20 \text{ cm}^2/\text{V}\text{-sec}$)

Minority carrier Lifetimes are relatively high ($1\text{E}\text{-}7 \text{ sec}$ for electrons, $1\text{E}\text{-}8 \text{ sec}$ for holes)

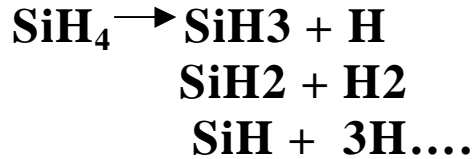
(Compared to c-Si of $> 1\text{E}\text{-}6 \text{ sec}$.)

The material is limited by hole transport! (Solar cell is a minority carrier device)

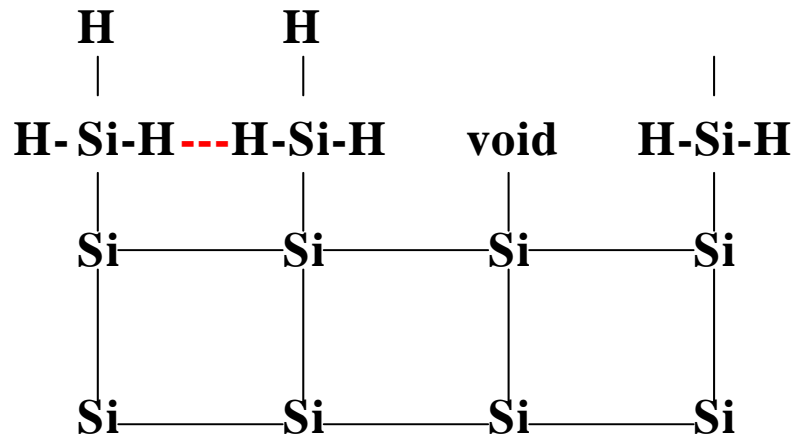
Fabrication technology for a-Si:H

1. Plasma deposition

Plasma breaks down Silane into its radicals



The radicals are unstable- they deposit on any substrate and form Si, with H being driven away if temperature is high enough



When insertion takes place, we get not only a new layer of Si, but also upto 3 additional H atoms

Also, because the temperatures must be kept low, the radicals have a limited mobility on the surface – some sites do not get a radical \Rightarrow VOIDS!

If more than one radical present (SiH_3 and SiH_2), some surface atoms are passivated and some are open for another bonding round.

Non-homogeneity!

Critical question of growth chemistry is:

How is the excess H eliminated (upto 3 atoms for every Si atom)?

In crystalline Si growth, not a problem \Rightarrow High temperatures (>900 C)

H elimination:

Standard model (Matsuda, Gallagher, Perrin)

Spontaneous adjacent neighbor H-H recombination

Problem (Dalal): Kinetics:

The surface SiH₃ radical is almost like a free SiH₄ molecule Therefore bond energy high > 1 eV.

$$\nu = \nu_0 \exp (-E_A /kT)$$

ν is attempt to break bond frequency at the given temperature T, E_A is the activation energy (bond strength)

ν_0 is ~ 1E11/sec

estimate of E_A from crystalline Si epitaxial growth.

There, growth takes place readily for $T > 550-600$ C

**Putting this into the equation, we get E_A of ~ 1.47
eV**

**Then, at 300 C, the attempt to escape frequency
would be ~ 0.012 /sec.**

**No spontaneous H elimination from neighboring
atoms in any reasonable time frame.**

Other mechanisms for H elimination

1. H abstraction (high H flux in the plasma)



2. Ion bombardment by H or other elements (He)

Ions have significant energy $> 10 \text{ eV}$

He should break more efficiently than H -It does!

Conclusion

Standard model is wrong!

H elimination is not by spontaneous recombination,
but by H abstraction or ion bombardment.

**If we do it right, we should be able to grow films at
> 10 Å/sec, and have ~ 0.5-1% H**

(Corresponding to 1E20 bonding defects/cm³)

But, really, get 5-10% H.

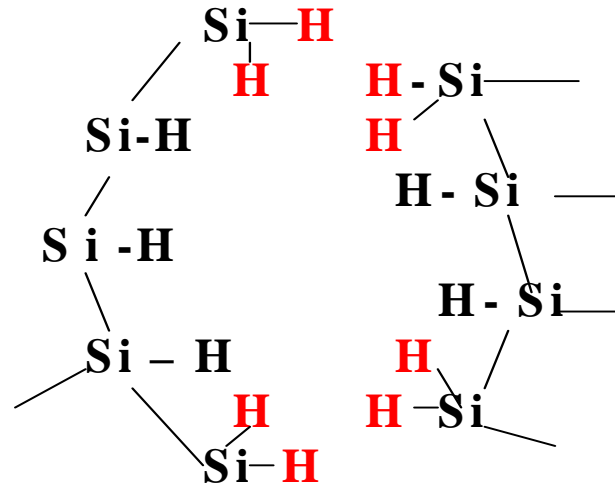
What is the excess H doing, and where is it?

**There are two kinds of Silicon-Hydrogen bonds
(from NMR data)**

- 1. Random Si-H bonds**
- 2. Clustered Silicon-H- may be SiH₂ and higher hydrides**

Why **clustered** bonds?

VOIDS – Internal surfaces



Voids lead to dihydride, AND close proximity of H
Both are problems!

- **Dihydride bonds weaker than mono H**
- **Proximity of H in cage-like structure can lead to rearrangement and breaking of Si-H bonds**
- * **Breaking of bonds is creation of defects (Called Staebler- Wronski effect)**

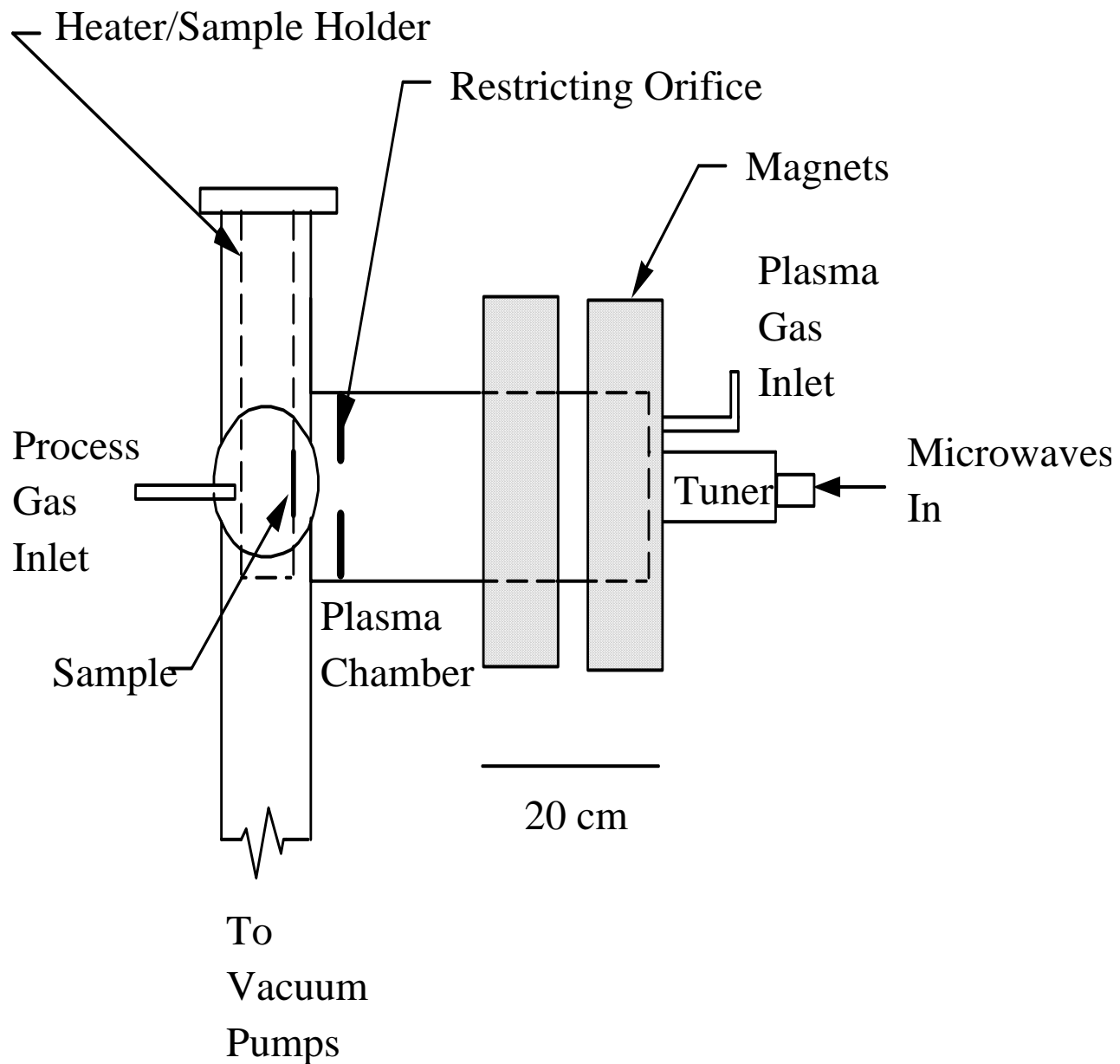
So, to reduce SW effect , change growth chemistry

HOW?

- 1. Reduce void density**
- 2. Reduce deleterious Si-H bonds- SiH₂ bonds**

By using clever plasma deposition, where effective ion bombardment takes place

ECR deposition



Controlled plasma chemistry- Electron cyclotron resonance plasma

A beam of H and/or He ions impinges on the substrate

Silane introduced near substrate

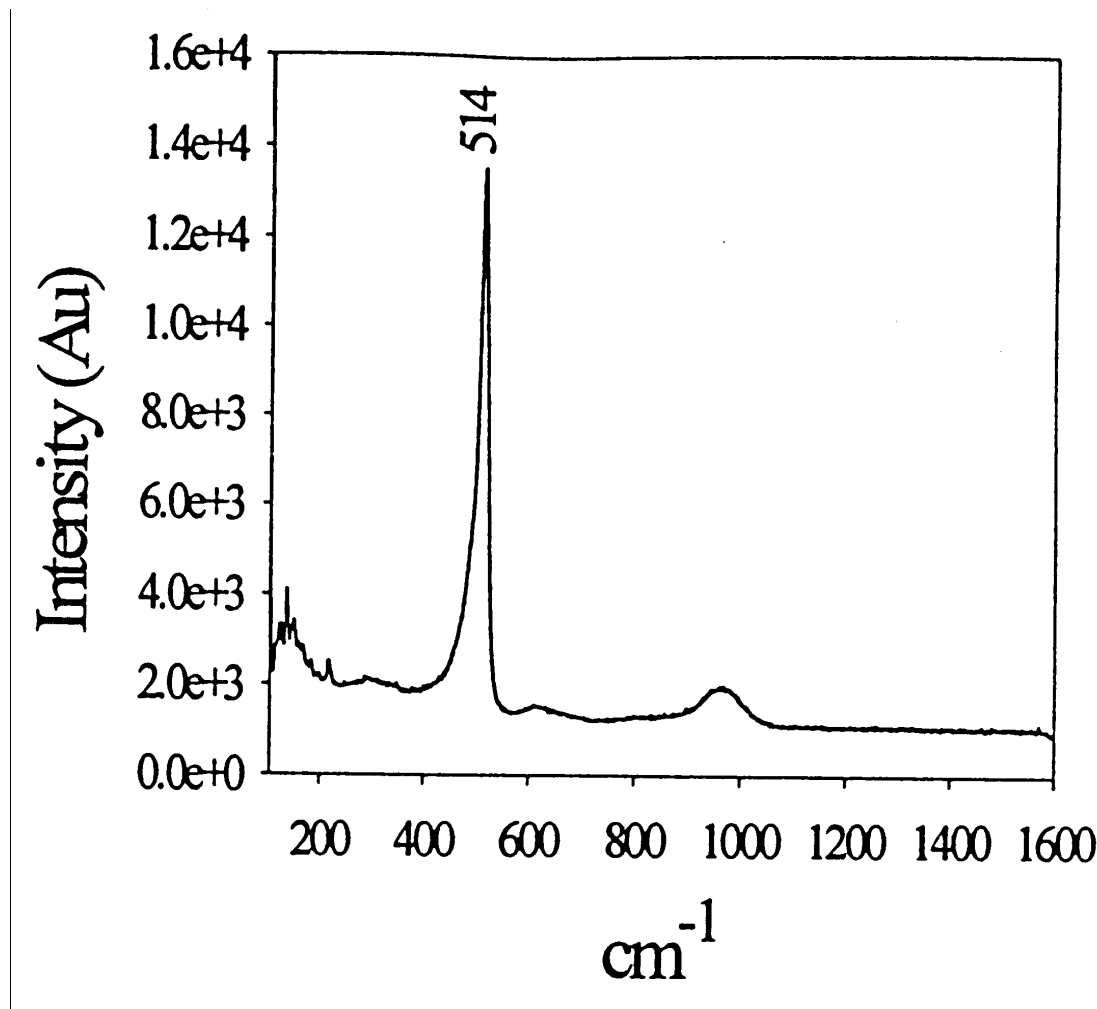
H ions or He ions do chemistry during growth

H: _ Etches weak bonds, eliminates H

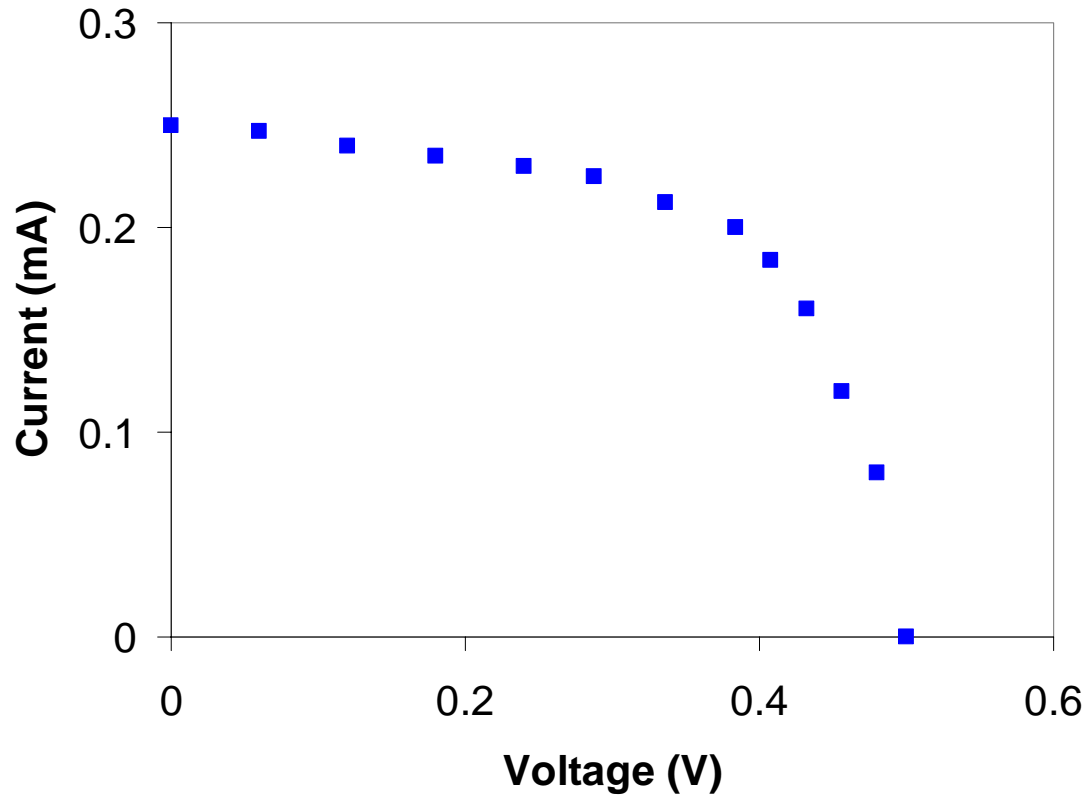
Etching during growth- can promote microcrystallinity by removing the weakest (amorphous bonds)

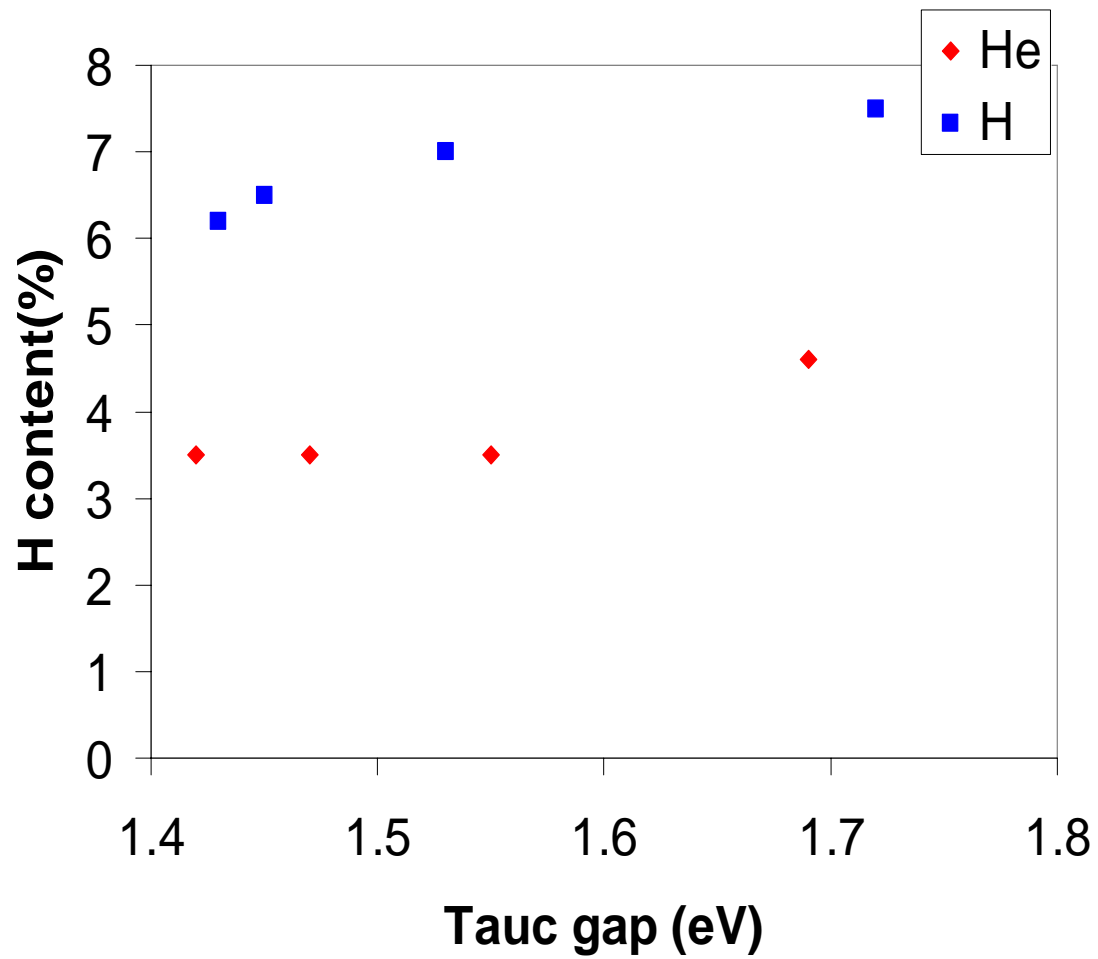
REVOLUTIONARY [SEE NEXT SLIDE]

Microcrystalline Si on Plastic



Microcrystalline Si solar cell on plastic substrate (Dalal et al)





Alloys of Silicon:

a-(Si,Ge):H

Why?

In a single gap cell, power conversion efficiency low (maximum ~30%) because we need a moderate gap, not too low and not too high.

High energy photons generate high energy electrons, and they collide with the lattice, and thermalize into lower energy electrons

Thermodynamic loss

To minimize this loss:

Use Multiple gap, series connected cells

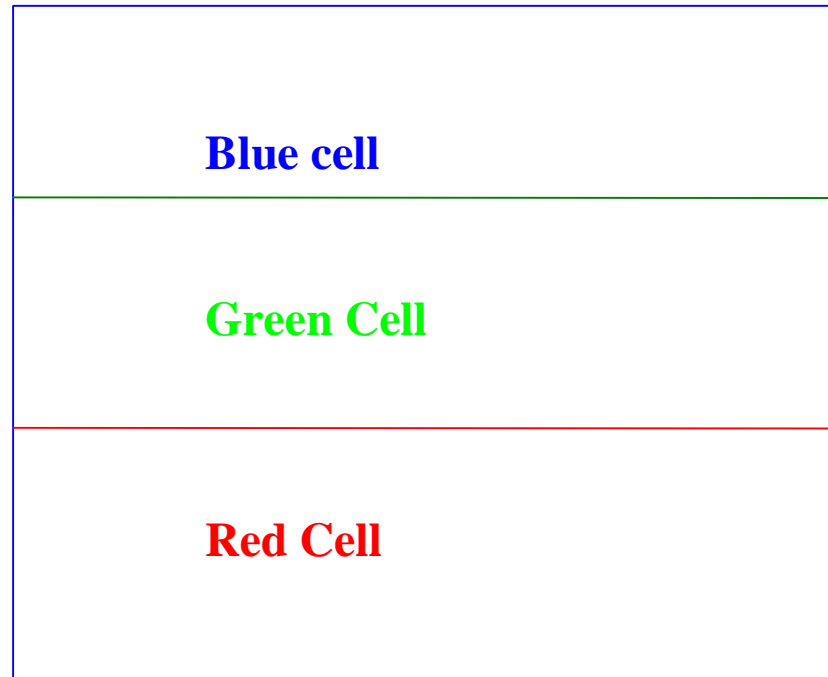
Use high gap for high photon energy

Low gap for low photon energy

Thereby minimize thermodynamic loss

**a-(Si,Ge):H system, with varying ratios of Ge to Si,
offers the flexibility of bandgap**

a-Si:H 1.7- 1.8 eV ; a-(Si,Ge):H 1.1-1.7 eV



High energy photons in the top cell

Mid energy photons in the middle cell

Low energy photons in the bottom cell

Problems with a-(Si,Ge):H

Two different materials, two different precursors

Silane and Germane (GeH₄)

Many radicals being produced:

Silane : SiH₃, SiH₂, SiH

Germane: GeH₃, GeH₂, GeH

Silyl (SiH₃) and Germyl (GeH₃) radicals have very different mass

Therefore, diffusion of radicals on the surface during growth will be different

Germyl (heavier radical) will not diffuse rapidly to find an open site

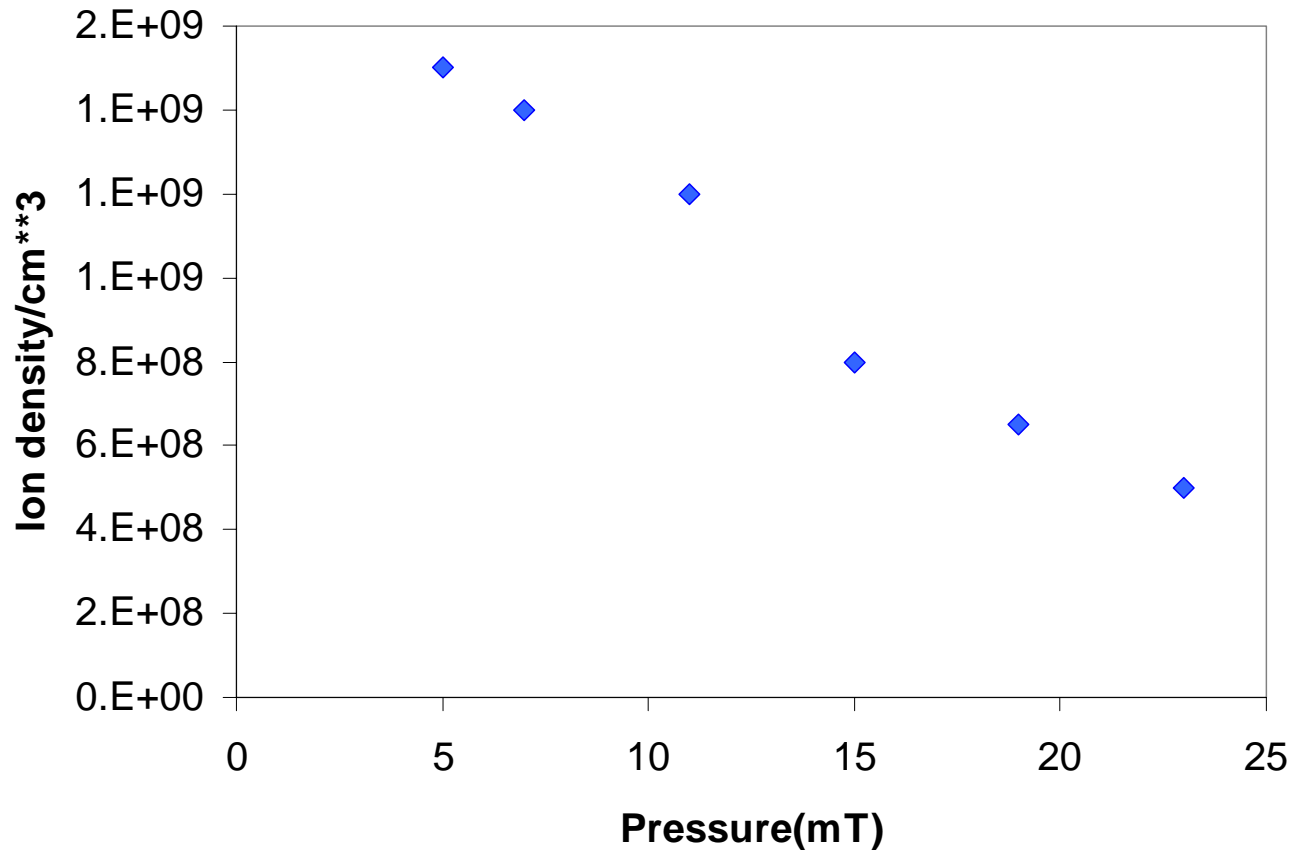
Therefore, **there may be localized clustering** – instead of a homogeneous Si-Ge alloy, we will get localized excess Si-Si or Ge-Ge bonds

Non-homogeneity means more voids, more defects, poorer electronic properties

A **structural Signature** would be: H bonding would be affected- **more SiH₂ bonds**

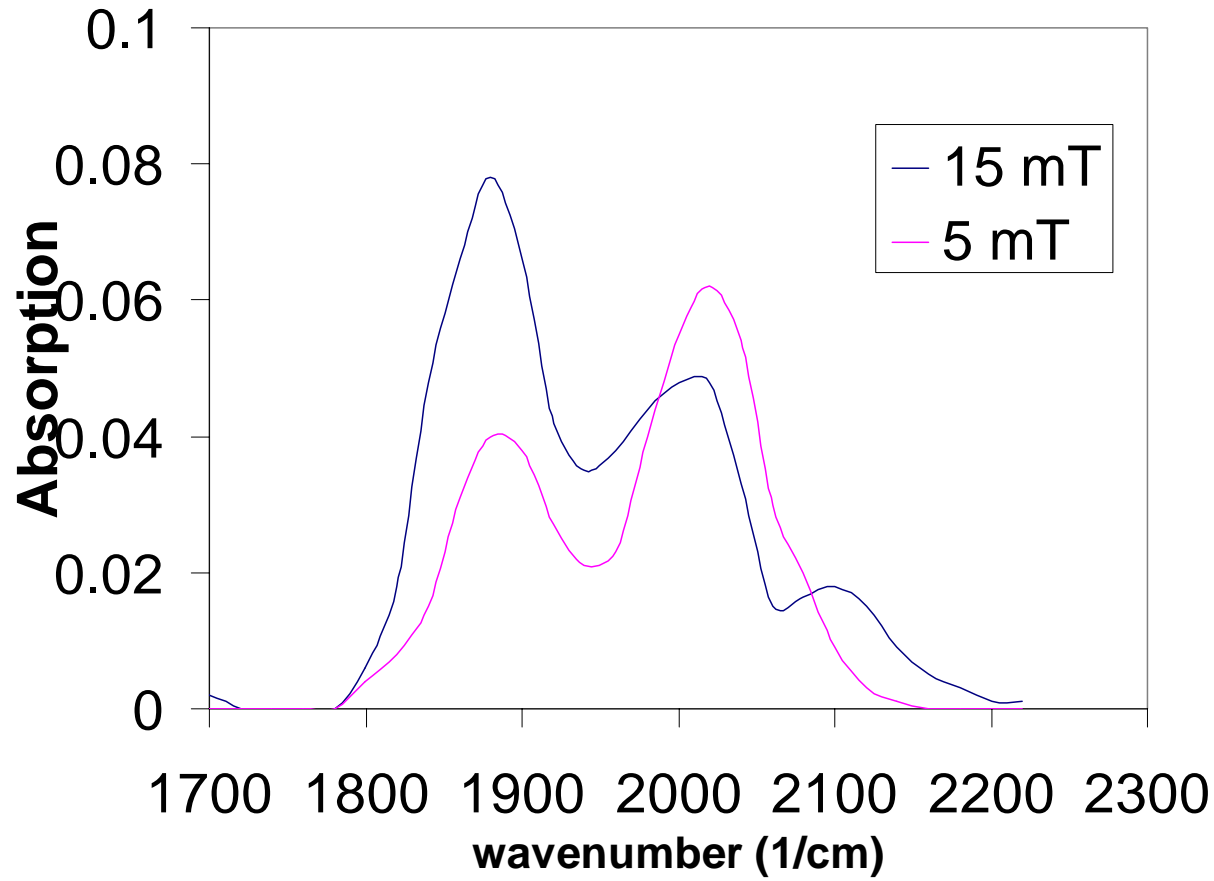
Always found (until our work)

Use ion bombardment – low pressure leads to a higher ion flux at the substrate

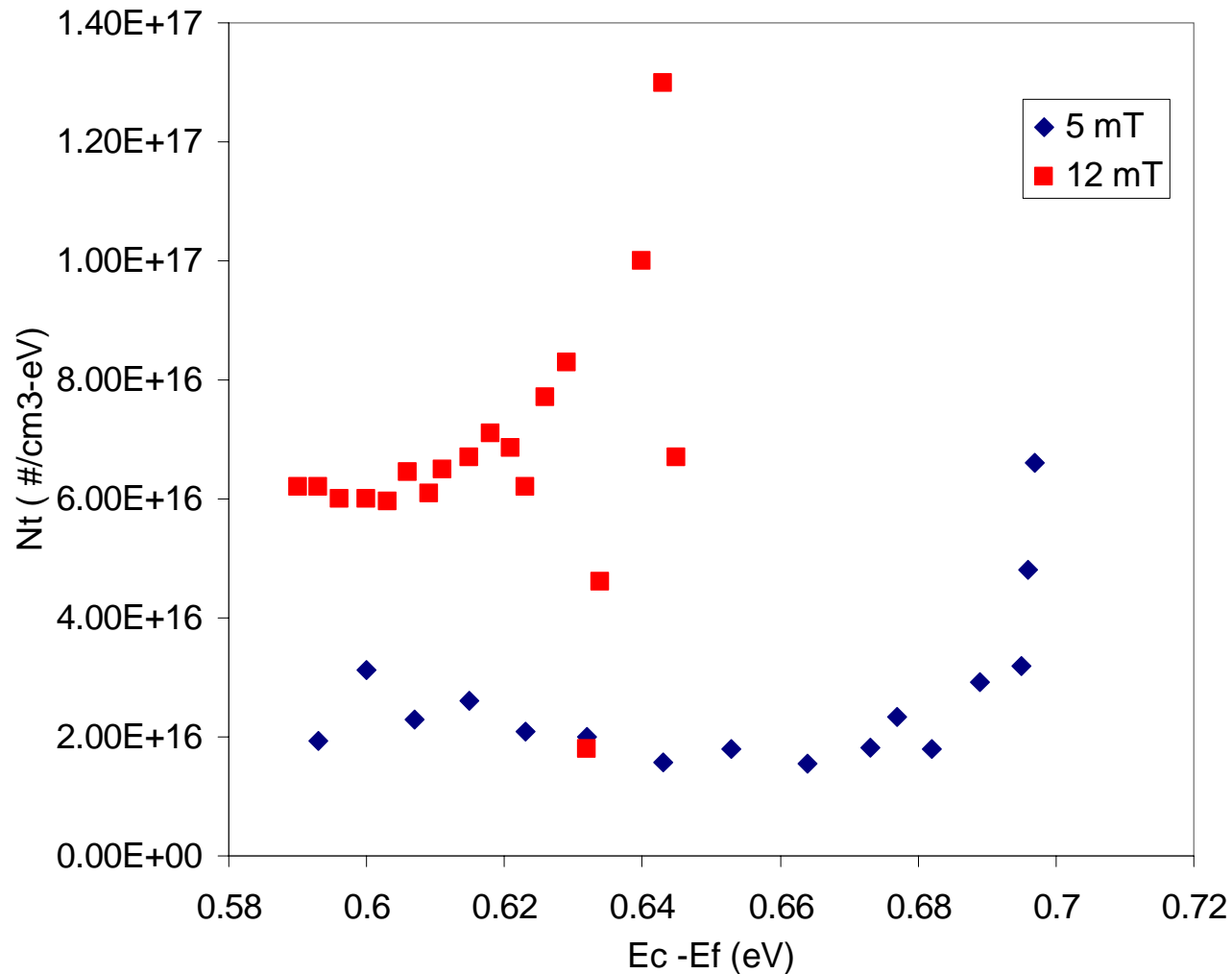


Influence of pressure on H bonding

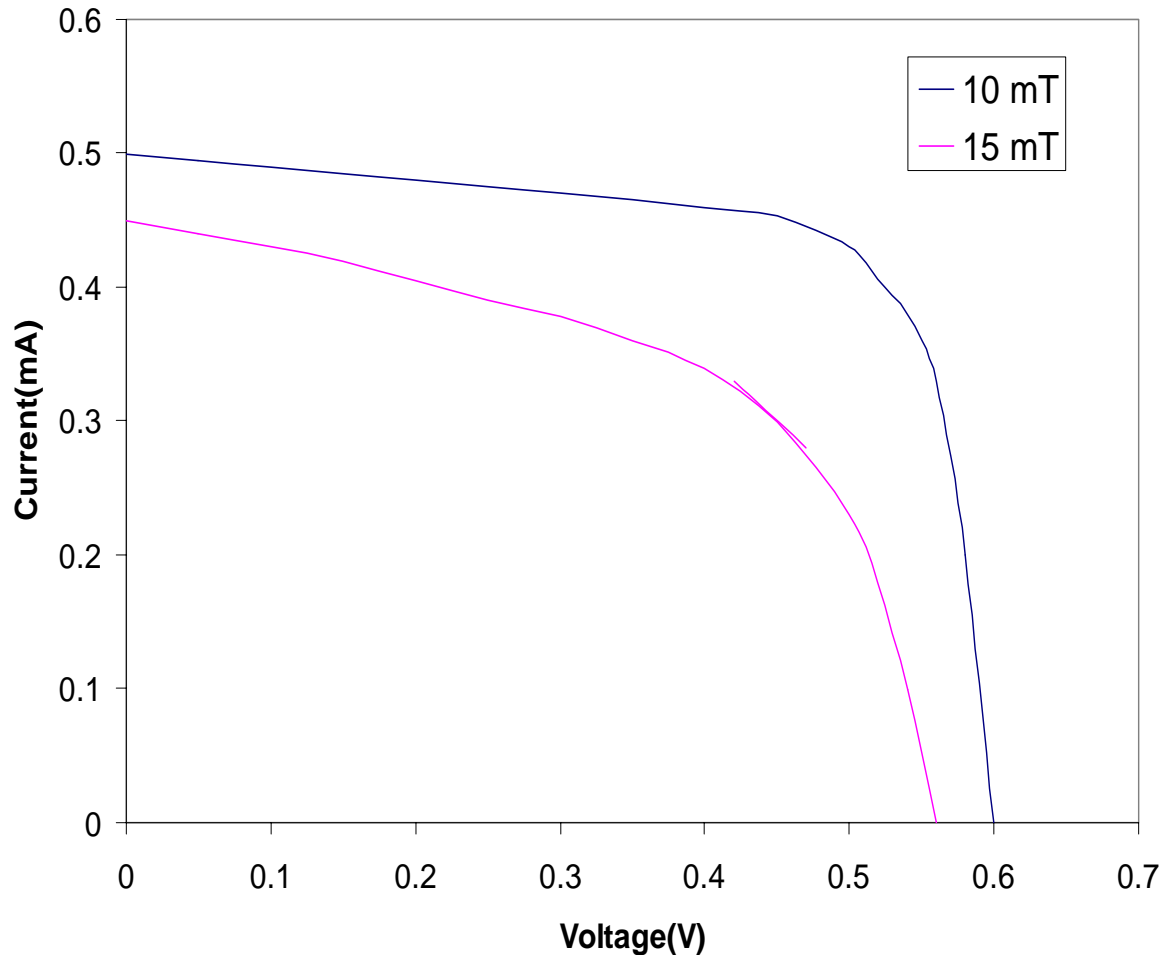
Low pressure – No SiH₂ at 2100 cm⁻¹



Improved defect density at low pressure



Influence of pressure on Devices(Solar cells



Conclusions

Growth chemistry important

- **Standard model is wrong!**
- **H elimination by H radical or ion extraction**

Science advances when conventional wisdom and standard models are challenged.

By controlling chemistry, can produce crystalline materials on unusual substrates (Plastic!) – Potentially revolutionary development

Amorphous materials keep improving

Significant opportunities for novel and original approaches

Future research directions

Increase growth rates of a-Si and a-(Si,Ge) by using combinations of He and H in the plasma

- He to increase decomposition of silane and germane
- H to do chemistry during growth

Improve material and device properties through control of microstructure – mixed phase materials

Experiment on activation energy at surface

Study the stability of a-Si and a-(Si,Ge) alloys made with the new growth chemistry

Supported by:

NREL (US DOE)

NSF

Microelectronics Research Center