

Amorphous and Microcrystalline Silicon Solar Cells

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AMORPHOUS AND MICROCRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT

We review the progress made by amorphous silicon solar cells, including the emerging technology of solar cells of microcrystalline silicon. The long-term trend in the efficiency of stabilized laboratory cells based on a-Si:H has been a rise of ~ 0.6 % per year. The recent trend in the a-Si,Ge:H cell efficiency alone, measured in the spectral window assigned to the bottom device in a triple-junction cell, has been an increase of ~ 0.16 % per year. These improvements have brought within reach the target of 15 % efficiency identified by EPRI and DOE for widespread application. Our review leads to an identification of areas of promising research, with emphasis on the fundamental science required to reach the 15 % target, and then to move to the next-level efficiency goal.

INTRODUCTION

Solar cells of hydrogenated amorphous silicon and microcrystalline silicon are archetypal thin-film cells. They are thin, can be made in large area, and are made at low substrate temperatures. The low substrate temperatures of $\sim 150^\circ\text{C}$ to $\sim 400^\circ\text{C}$ provides flexibility in the choice of substrates, which includes plate glass and foils of steel or plastic. Hydrogenated amorphous silicon (a-Si:H) is finding growing use in other industries, which include active-matrix, liquid-crystal displays (AMLCDs), electrophotography, application-specific sensor arrays on complementary metal-oxide semiconductor (CMOS) circuits, photosensor arrays for electronic cameras, and antifuses. This broadening range of applications multiplies the number of scientists and engineers that contribute to a-Si:H technology and provides increasing leverage to a-Si:H solar cell work. For example, equipment suppliers to the AMLCD industry are designing deposition systems for motherglass areas of 1-m^2 to 2-m^2 size, thereby helping solve questions of productivity, and of film uniformity over large area.

The prospect for high efficiency.

The present efficiencies of stable cells based on a-Si:H are [1]:

Single-junction a-Si:H	9.3 %
Triple-junction a-Si:H/a-Si,Ge:H/a-Si,Ge:H	13.0 %

The microcrystalline cell has reached an efficiency of 8.5% [2]. Because predictive theories for the optical and electronic properties do not exist, cogent forecasts cannot be made of the efficiencies that are achievable with a-Si:H and $\mu\text{c-Si:H}$. However, the steady efficiency increase of amorphous silicon cells documented in Figure 1 suggests that no plateau is in sight [3]. We proceed with a working assumption of physically achievable cell efficiencies in the neighborhood of 20% for single junctions and 30% for multijunctions.

RESEARCH ISSUES OF THE PAST SEVEN YEARS

In a previous workshop [4] seven groups of research issues with a-Si:H and its alloys were identified. The $\mu\text{c-Si:H}$ cell was not yet known at the time of the 1992 workshop. The a-Si:H research issues were:

- Novel materials and growth methods
- Nanoscale structures and their effects on the electronic properties: structural and chemical heterogeneity
- Hydrogen configurations and their role in metastability
- Renewed studies of electronic transport
- Heterostructures and interfaces
- Impurities and defects
- Device modeling

FUNDAMENTAL RESEARCH DONE IN THE PAST SEVEN YEARS

Because of the large world-wide community in R&D on a-Si:H, an enumeration of all research accomplishments would go beyond the bounds of this report. Although the emphasis during this recent period lay on device work, very interesting fundamental results have been obtained and new techniques are coming to the fore. We first enumerate areas in which progress has been made, and then we illustrate the progress with a few arbitrarily chosen highlights.

Areas in which progress was made.

Novel materials and growth methods.

- Protocrystalline silicon
- Microcrystalline silicon
- Hot-wire catalyzed growth

Nanoscale structures and their effects on the electronic properties:
structural and chemical heterogeneity.

- SAXS
- TEM microcrystalline inclusions

Hydrogen.

- H-diffusion
- H-recombination
- Internal friction
- Low H in hot wire

Transport.

Hole transport

Alloys.

H dilution

Deposition.

High rate

Cluster formation

Impurities.

Correlation between impurity content and SW effect

Modeling.

AMPS established material property targets for stable 15% triple-junction. AMPS modeling of device performance led to a revision of the mobility gap of a-Si:H and to a value for the discontinuity of the conduction-band edge between a-Si:H and $\mu\text{c-Si:H}$.

The progress is easiest seen in illustrations that we provide in the following for some of the areas.

Progress in cell efficiency.

The steady rise in cell efficiency at an average rate of 0.6% per year has been maintained over the past seven years. Figure 1 [4] tracks the efficiency of a-Si:H based cell technology in the form of single-junction and multi-junction cells, and also shows the efficiency of modules. Note that the time delay between cell and module efficiency is only ~ 5 years, which reflects the fast technology transfer in the a-Si:H community. Recent progress in the efficiency of the low-gap, a-Si,Ge:H cell, used as the bottom device of triple-junctions, is shown in Figure 2 [5]. The efficiency of Figure 2 is measured in the spectral window assigned to the bottom device in a triple-junction cell. It has been increasing at a rate of ~ 0.16 % per year. The efficiency improvements documented in Figures 1 and 2 have brought a-Si:H cell technology within reach of the present target of 15 %.

Hole mobility. The 1990s have seen widespread use and investigation of the techniques of hydrogen dilution [6] and of hot-wire catalyzed deposition [7, 8]. Their application has produced a-Si:H with hole mobilities in the 0.1 to 1 cm^2/Vs range [9].

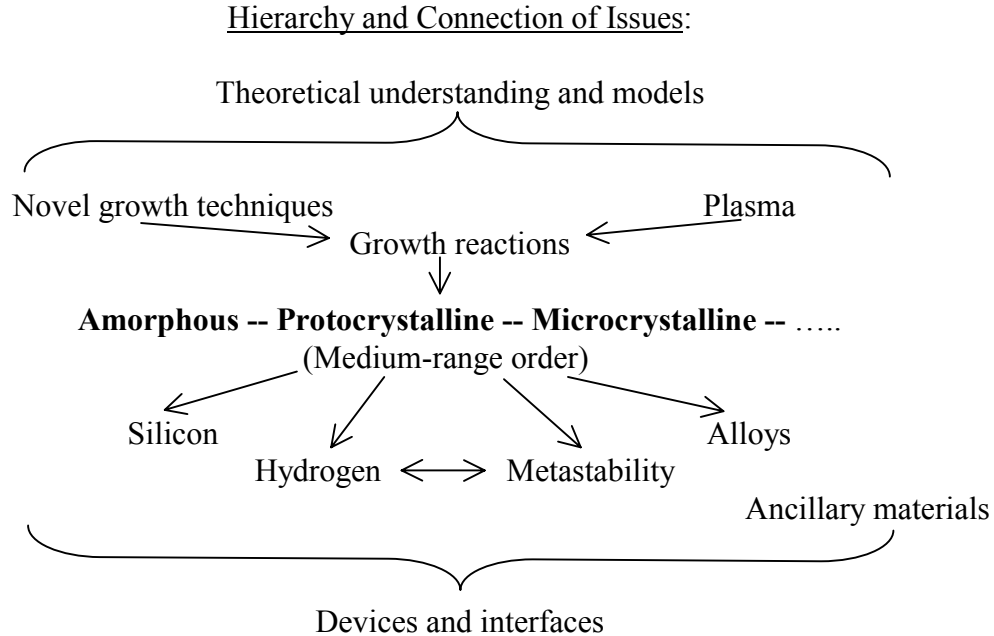
High-purity a-Si:H. Foreign impurities have been one suspected cause of metastable, light-induced defects. In a series of experiments that included deposition of a-Si:H from highly-purified source gas in UHV-quality deposition systems, and secondary ion mass spectrometry (SIMS) at a high sputtering rate, the concentration of the atmospheric impurities of carbon, nitrogen, and oxygen in a-Si:H was brought to below the density of light-induced dangling bonds. This result rules out a one-to-one correspondence between light-induced defects and these impurities [10]. The concentration profiles of O, C and N in the a-Si:H layer deposited on x-Si is shown in Figure 3 [11]. The subgap optical absorption spectra before and after light-soaking are shown in Figure 4 [11].

Models of hydrogen in metastability. The role that hydrogen may play in the creation of metastable defects found ample attention during the period in review. One very interesting proposed mechanism of dangling-bond defect creation is by hydrogen collision [12]. In this model, shown in Figure 5, an incoming photon or an injected charge carrier releases a hydrogen atom from an Si-H bond. The H atom diffuses through the network. If two diffusing hydrogen atoms open a weak Si-Si bond and form two Si-H bonds, the original sites that these two hydrogen atoms left behind remain dangling bonds. A new type of metastable defect associated with hydrogen is the H-flip defect [13]. The partial result of a molecular dynamics calculation of Figure 6 shows at the top the creation of the metastable H configuration as a result of a flip. The bars illustrate the change in electron density of several H atoms as a consequence of the flip. The flip changes the local structure around the H atom in question, but are not necessarily associated with the creation of a dangling bond.

Medium-range order, protocrystalline and microcrystalline silicon. Our view of the atomic arrangement in a-Si:H has become more refined in recent years, in part because of results obtained by new tools, and in part by the introduction of deposited microcrystalline silicon as a solar cell material. Small-angle X-ray scattering (SAXS) has shown that it is possible to make a-Si:H so free of micropores that the SAXS signal drops to the background level [14]. On the other hand, SAXS data from alloys clearly show microvoids, which may be preferentially oriented. Although voids have been drawing attention, crystalline inclusions also have come into focus. Under some growth conditions, such inclusions may be produced from clusters formed in the glow discharge [15, 16] Figure 7 illustrates the growth of negatively-charged clusters into particles that eventually become occluded in the growing film. A different path toward forming crystalline inclusions is taken when a-Si:H is grown under strong hydrogen dilution. Under these conditions, an initially pure a-Si:H film develops first protocrystallinity in the form of ordered regions and eventually microcrystalline inclusions. The transition from purely amorphous to microcrystalline silicon has been followed by ellipsometry, and characterized so extensively, that an a-Si:H - μ c-Si:H has been established [17]. Figure 8 illustrates this phase diagram as a function of film thickness and hydrogen dilution, and shows that the transition depends on the type of substrate [18]. A new tool based on transmission-electron microscopy, fluctuation microscopy, is sensitive to variations in medium-range order and thus promises to provide information about the protocrystalline state [19]. The development of the microcrystalline silicon solar cell [2] showed that μ c-Si:H is a semiconductor capable of bipolar operation, and has opened a new era in thin-film silicon technology. State-of-the-art cell performance is illustrated by Figure 9. [20].

ISSUES THAT REMAIN RELEVANT

Although the research emphasis in a-Si:H and $\mu\text{c-Si:H}$ has varied over the years, most issues remain active, if only because the rising demands on cell performance require ever deeper understanding. Solar cells are high-performance analog devices, with highly interrelated parameters. Therefore, it is not surprising to see that solving one issue exposes another issue that must be solved. All issues in a-Si:H and $\mu\text{c-Si:H}$ are connected. We seek to illustrate this connection with the following table.



Discussion of issues.

In this section, we list input collected from our colleagues in the a-Si:H and $\mu\text{c-Si:H}$ research community. The input is grouped by entries in the table above.

1. Amorphous -- Protocrystalline -- Microcrystalline -- .

a-Si is the end point of a continuum

Is the in-between (protocrystalline, on-the-edge) material really different?

Develop quantifiable measures for this difference

Difficulty of controlling large-area uniformity of protocrystalline silicon

Make the ideal material: absorption of a-Si, transport of x-Si

Understand and control the a/c transition

Nanocrystalline Si: electron states, doping, recombination, and confinement effects?

Relation between crystallinity and optical-absorption coefficient

Grain boundary properties, including those of Si,Ge and Si,C alloys

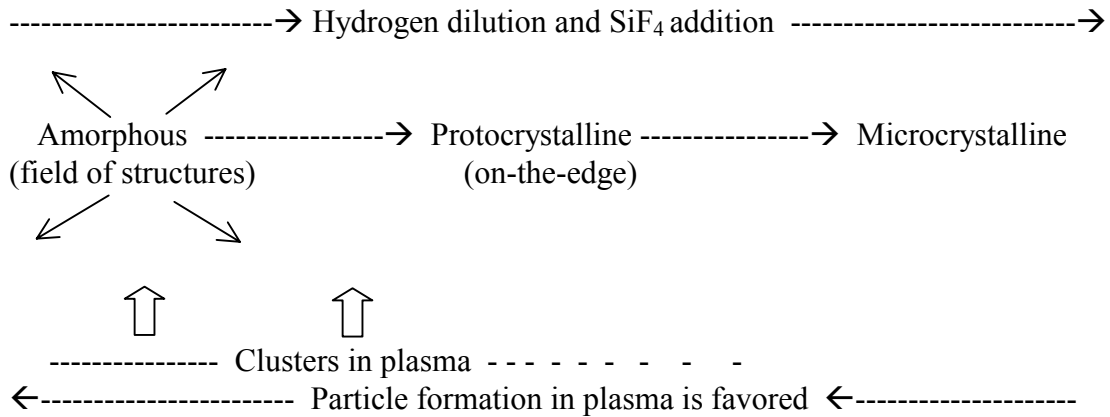
Need methods for characterizing electronic and optical properties of mixed-phase materials, and materials with continuously varying structure

Need more and cleverer structural probes

Transport properties: compare materials for high hole mobility

What are the commonalities in structure that provide high mobility (substrate, growth)?

Growth parameters that affect medium-range order, protocrystallinity and microcrystallinity:



2. Medium-range order.

Which difference between PECVD a-Si:H, H-diluted a-Si:H, hot-wire a-Si:H
 Techniques for measuring MRO

3. Theoretical understanding and models.

Medium-range order, dangling bonds, amorphous/crystalline interfaces, transport, recombination in materials
 Need first-principles calculation of electronic structure
 More extensive use of molecular dynamics computation
 Model growth: gas phase and surface
 Lack of critical mass in theory
 Growth, electronic, device, optical models

4. Metastability.

Theory of light induced degradation
 Does a single event produce dangling bonds and structural changes?
 Do structural changes precede the creation of dangling bonds? Which precedes what?
 Time-resolved measurements
 Sources of irreversibility
 Irreversibility arising from trace amounts of boron

5. Hydrogen.

How does H affect the network, how does the network affect H?
 Structure/configuration and topology
 H microstructure other than by (gross) IR absorption
 H models for a-Si:H with inhomogeneous structure
 Describe how H breaks bonds as it moves and leaves structural changes in its wake
 Localized H motion
 Effect of charge state on H motion

Relation to metastability of H structures

H vs. D: changes discharge kinetics, not film itself? Make the same films with H and D to test

Effect of other bond terminators, F, Cl on discharge and in film

6. Plasma.

Physics and chemistry of plasma processes, dependence on excitation frequency

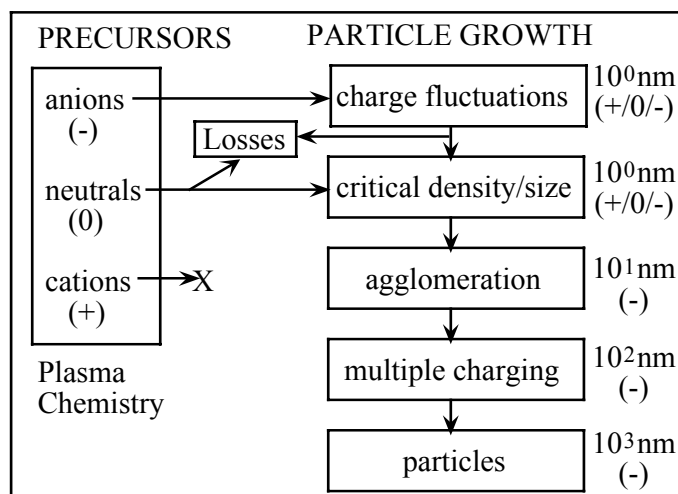
Transients in plasma deposition

High deposition rate (importance for capital cost), indispensable for practical use of μ c-Si

What to do to keep particles out (a-Si:H) or to include them (protocrystalline Si)

Homogeneity over large area. Electrode spacing, showerhead structure, excitation frequency

The following schematic diagram [16] illustrates the relation between precursors and particle growth:



7. Novel materials and growth techniques.

Create materials with designed optical absorption and transport properties. Can we make a material with the optical-absorption characteristics of a-Si:H (Figure 10) [20] and the transport properties of x-Si?

Designed mixtures of amorphous and crystalline, design quantum properties

Low-pressure, plasma-free techniques: hot wire, ...

Hot wire: filament stability and life, chamber-induced differences

Design remote reactors to separately control feed of reactive species and of particles, and of growth reactions on the surface

Develop techniques for designing clean reactors

8. Growth reactions.

Systematic study of the chemistry of growth reactions

Relation between growth chemistry - structure- electro-optic properties - device performance

Material and device must be made in the same system

Multiple-zone reactors for the manipulation of film properties (e.g., a small density of nuclei is established in zone 1, and is injected as seed into surface in zone 2 to control growth)

Reactions in hot wire deposition

Induction period for microcrystalline growth

Raise growth rate of microcrystalline silicon

Microcrystalline Si for tunnel junctions is the least controlled industrial material at present

Effect of substrate on film structure (High- μ_p material grows best on x -Si. Hot wire produces epitaxial Si at 300°C if surface is cleaned properly.)

Growth chemistry of alloys

9. Alloys.

Bring understanding and control of a-Si,C:H and a-Si,Ge:H to the level of a-Si:H

What did improve in a-Si,Ge:H when USSC raised a-Si,Ge:H cell efficiency?

Different role of H in different alloys: clustered on C in a-Si,C:H, clustered on Si in a-Si,Ge:H

Understand doping of alloys

To date mostly alloys with group IV partners: explore others, Si-Se, Si-metals

Precursor molecules for alloys

Very little basic work now

10. Devices and interfaces.

Fundamentals of devices: assemblies of thin films of varying structure, interfaces
Superlattice structures for the study of interfaces

Limits to V_{oc} : band tails, interfaces, band alignments

Devices including a range of structures: amorphous in-between, microcrystalline

Measure device physics by other than solar cell parameters (e.g., EL, capacitance, transient transport)

Interfaces: measure, describe, and model

Understand role of buffer layers. Why are they needed?

Connection between device performance and material quality: how strong is it?

11. Ancillary materials.

Transparent conductors

Formulation of optical waveguiding

Minimizing materials use with thin materials

Flexible substrates

Mechanical properties, stress

12. Combinatorial techniques for speeding up research.

NEW FUNDAMENTAL RESEARCH OPPORTUNITIES

The preceding list of research issues already implies and reflects a host of research opportunities. With the following list we take a step back and survey the broader areas of

research that we consider important to continued progress in a-Si:H and $\mu\text{c-Si:H}$ solar cell technology.

Experiment with new growth techniques
Gas-phase chemistry of glow discharge and hot wire
Surface reactions, nucleation and growth, substrate effects
Molecular dynamics of large cells: 10^8 atoms
Techniques to measure and interpret medium-range order
Protocrystalline material: how does it differ from a-Si:H
Nano-, microcrystalline material: induction period, substrate effect,
 optical and electronic properties, quantify grain boundaries, doping
Design silicon with a high optical-absorption coefficient and long transport length
Early kinetics of metastability: sequence of changes in structure and defects
Probes for hydrogen topography
Role of alternative bond terminators: F, Cl
Alloys: what makes a-Si,Ge:H and a-Si,C different from a-Si:H
 Doping of alloys
 Make and measure microcrystalline alloys
 Make alloys with non-column IV elements
Establish complete models: Growth, structure, electrical, optical, including interfaces

COMMONALITIES WITHIN PHOTOVOLTAICS

Amorphous -- Protocrystalline -- Microcrystalline --, Hydrogen
 Relation to single-, polysilicon
Plasma, Novel growth techniques, Growth reactions
 Plasma processing, surface reactions
Devices and interfaces
 Numerical modeling for all thin-film cells: Optical, electronic,
Ancillary materials: TCOs

OUTLOOK

We consider the following three directions of basic research crucial to continued progress in a-Si:H and $\mu\text{c-Si:H}$ solar cell technology.

1. The understanding and control of Si and alloy film structure, ranging from amorphous over MRO and protocrystalline to μc material, with increasing emphasis on high deposition rate as the structural order increases.
2. The acquisition of a comprehensive understanding of the role of H in establishing nanostructure, in alloying and doping, in metastability, and as a structural modifier during solar cell operation.
3. The understanding and control of the gas-phase chemistry, the reactions on the growing surface of Si and alloy films, and their effect on device properties.

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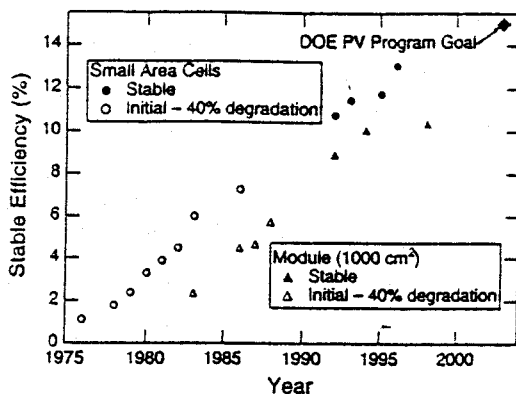


Figure 1. Chronological record of the efficiencies of a-Si:H based solar cells and modules (Ref 3).

Progress in Power Output for Low-Bandgap a-SiGe Alloy Solar Cells made at United Solar and Measured under AM1.5 with a $\lambda > 630\text{nm}$ Filter

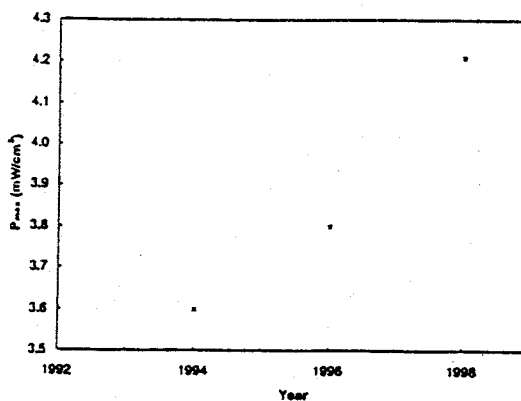
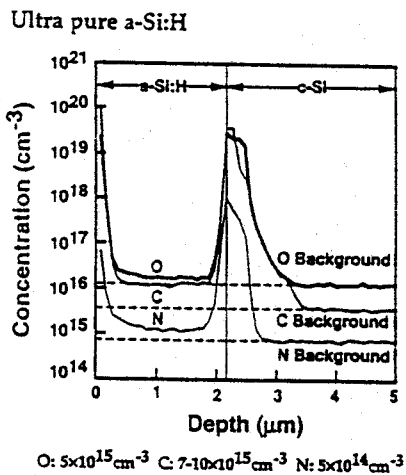


Figure 2. Chronological record of the efficiency of the low-gap a-Si.Ge:H cell for use in a triple junction devices. Efficiency measured under filtered red light (Ref. 5).

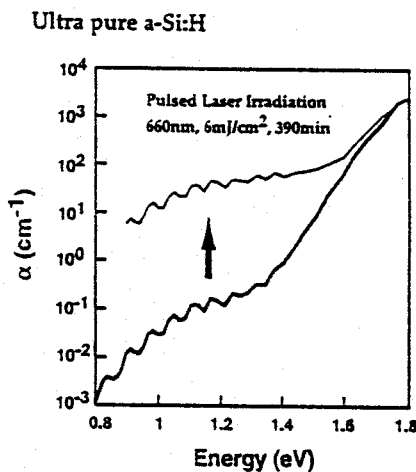


Very high primary ion beam current density
high rate sputtering by primary ions

Low depth resolution $> 1000\text{\AA}$

High Sensitivity
(Normal detection limit of SIMS: 10^{17}cm^{-3} for O or C, 10^{16}cm^{-3} for N)

Figure 3. SIMS profile of an ultra-high purity sample of a-Si:H, made to correlate impurity content and light-induced defect generation (Ref. 10).



LID density \gg Impurity contents

~~X~~ Extrinsic model which postulates one-to-one correlation between LID and impurity

Figure 4. Subgap optical absorption of an ultra-high purity sample of a-Si:H, which exhibits a saturated density of defects higher than the concentration of atmospheric impurities (Ref. 10).

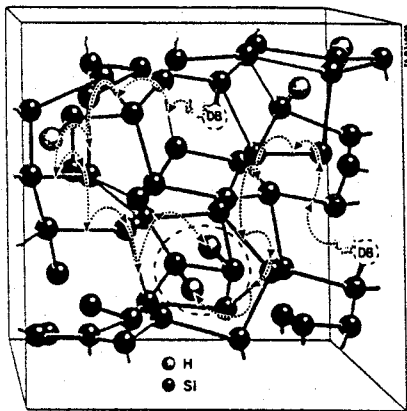


Figure 5. Illustration of the hydrogen collision model for the generation of metastable dangling bonds in a-Si:H (Ref. 12).

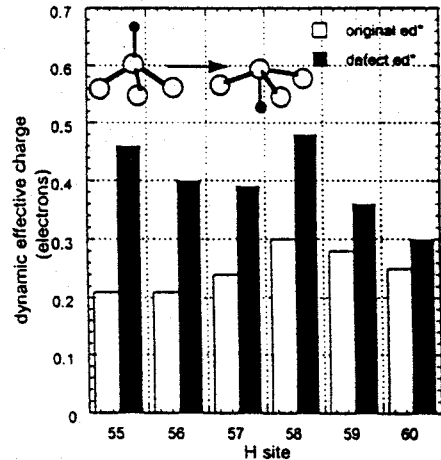


Figure 6. Illustration of the hydrogen flip metastability, and of the effective electron charge on a set of hydrogen atoms before and after the flip process (Ref. 13).

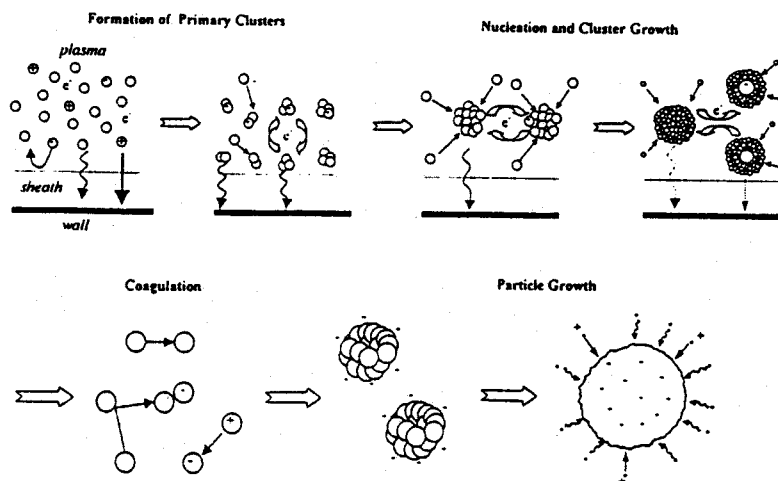


Figure 7. Formation of particles in a silane glow discharge in four steps: cluster formation, particle nucleation, coagulation, and independent growth of trapped multiply-charged macroscopic particles by condensation. (Ref. 16).

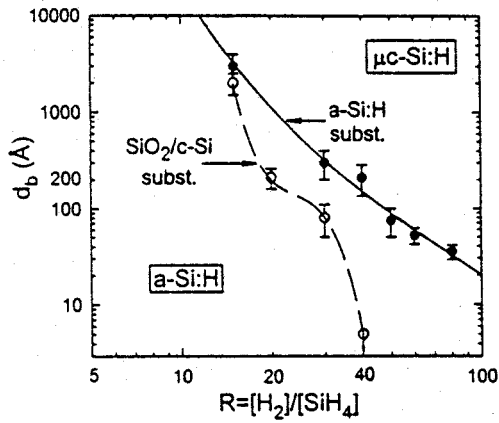
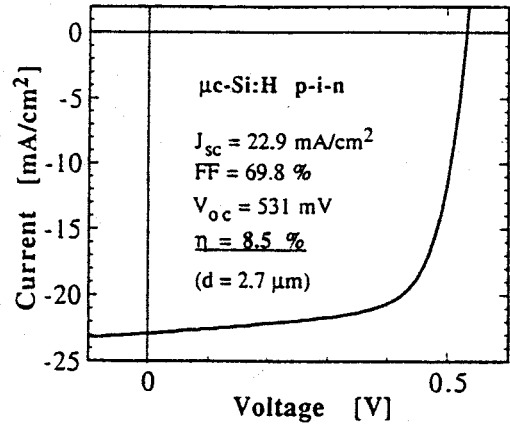


Figure 8. "Phase diagram" of a-Si:H and $\mu\text{c-Si:H}$ as a function of hydrogen dilution and film thickness. Note that the "phase boundary" depends on the type of substrate on which the film is grown (Refs. 17 and 18).



η [%]	7.7	8.3	7.7	8.1	8.5	3.2	4.4
J_{sc} [mA/cm ²]	25.3	25.2	21.5	23.2	22.9	18.4	17.9
FF [%]	67.9	68.2	71.1	68	69.8	30.5	41.8
V_{oc} [mV]	448	483	503	512	531	568	592

Figure 9. Current-voltage characteristic of a state-of-the-art solar cell made with a $\mu\text{c-Si:H}$ absorber layer. The table lists the characteristics of several such cells and highlights the ability to exceed a V_{oc} of 0.5 V (Ref. 20).

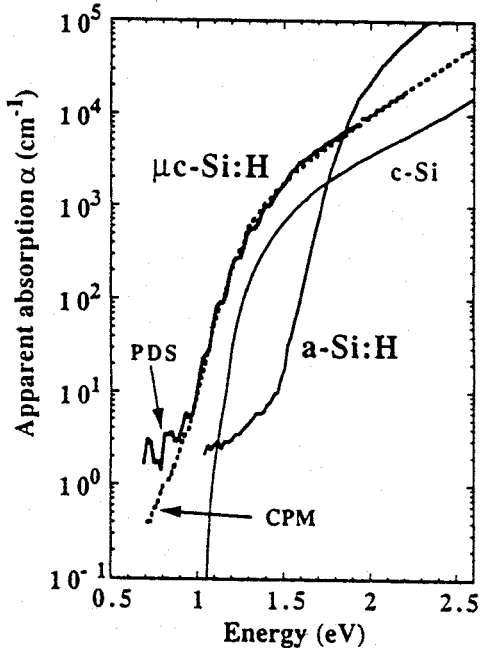


Figure 10. Optical absorption spectra of $\mu\text{c-Si:H}$, a-Si:H and x-Si (Ref. 20).