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AMORPHOUS SILICON SOLAR CELLS: A REVIEW

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ABSTRACT

Recent developments in the production and study of the properties of amorphous silicon containing hydrogen and fluorine impurities are reviewed. Especially emphasized are the properties of the material in regard to its photovoltaic potential and the roles of hydrogen and fluorine in modifying such properties as band gap and mobility from those of the pure amorphous and crystalline material.

1. INTRODUCTION

The hydrogenated form of amorphous silicon (a-Si:H) was first studied by Chittick and collaborators in 1969.[1] Later work was performed by Spear, and LeComber[2] who noted that glow discharge deposited a-Si had a much higher resistivity than evaporated or sputtered a-Si. Subsequently, these workers succeeded in substitutional doping of glow discharge a-Si, with a corresponding increase in conductivity. Although the advent of substitutional doping promoted the possibility of manufacturing a photovoltaic device, Adler, in a 1977 Scientific American article about amorphous materials made no mention of a-Si other than to express the notion that it differs little from its crystalline counterpart.[3]

In 1978, Stanford Ovshinsky, President of Energy Conversion Devices (ECD), reported that a new material, an amorphous silicon fluorine-hydrogen (a-Si:F) alloy, had been produced by the glow discharge method.[4] This material is apparently superior to other forms of a-Si for the fabrication of photovoltaic (PV) devices.

This paper deals exclusively with a-Si:H and a-Si:F materials made by the glow discharge technique because these materials exhibit the best PV properties to date.

The glow discharge process itself is fairly simple.[5] Constituent gases (SiH_4, BH_3, and SiF_4 in the proper combination and ratio) are fed into a plasma region over a substrate. Substrates used have included Cr, Ti, V, Nb, Ta, Mo,[5] fused quartz,[6] glass,[7] and stainless steel.[8]

2. EFFICIENT ENERGY CONVERSION CRITERIA

Boone, Van Doren, and coworkers[9] have outlined the parameters which characterize a solar cell material candidate. These may be summarized as follows.

(1) The absorption coefficient must be large for the solar spectrum, typically $> 10^4$ cm^{-1} for a thin film device. (2) There must be efficient generation and collection of free charge. (3) The total device resistance must be small. (4) The built-in potential must be large enough to ensure a useful output voltage.

The absorption coefficient criterion is satisfied only for those materials with the proper energy band gap. The band gap is also a critical determinant in the magnitude of the open circuit voltage mentioned above. It turns out that the optimum band gap for solar cell operation is near 1.5 eV. Efficient generation and collection of carriers and a low device resistance demand a long diffusion length through large carrier mobilities and lifetimes. Also, a large output voltage requires that either a p-n junction, through material doping, or a metal - semiconductor (Schottky) barrier be produced in the material.

3. THE ROLE OF HYDROGEN AND FLUORINE

Samples prepared by the glow discharge of silane (SiH_4) are not composed entirely of silicon. Substantial amounts of hydrogen (and fluorine if injected into the source stream) are incorporated into the films, which are properly described as alloys. The respective roles of H and F in the alloys are of interest in developing techniques for producing devices with more desirable performance characteristics.

There are several means of hydrogen detection available: nuclear resonance^{10}, absorption peaks of the Si-H vibrational spectrum,^{11,12} thermal evolution.^{11,13,14} The amount of H incorporated into a-Si:H films is dependent on deposition parameters.^{15,16} The H content of capacitively coupled systems is smaller than that of inductively coupled systems.^{17} Hydrogen content, in general, will decrease with increasing substrate temperature, and increase with power in inductively coupled systems.^{6} The idea that the H is desirable for saturating dangling bonds has been investigated with spin resonance techniques.^{18,19,20}

Glow discharge a-Si specimens deposited near 250°C show a spin desity of about $10^{15}/cm^3$. When the H is driven off by heating, the spin density reaches a maximum value of $10^{19}/cm^3$. If one associates 10 dangling bonds with each unpaired spin^{21}, then with 5×10^{22} Si atoms in the film, 0.1 - 0.2 at% H is required to saturate all of the dangling bonds. The question arises whether the excess of H is essential for the desired electrical properties.^{16}

For deposition temperatures greater than 200°C, H appears to exist only in the monohydride form, that is, in Si-H groups.^{11} There is no evidence for interstitial or molecular species.^{22}

The Carnegie group believes that addition of H to a-Si causes the valence band to move downward, increasing the band gap.^{23} The role of F in a-Si:F alloys may be the same as that of H, to reduce the density of states in the band gap by controlling the number of dangling bonds. Stanford Ovshinsky of Energy Conversion Devices (ECD) stresses the similarity between a-Si alloys and the multicomponent amorphous chalcogenides. He proposes that the reason a-Si:F alloys have a band gap density of states an order of magnitude less than that of the a-Si:H material is that the a-Si:H is not "multi" enough.^{4} The F content of ECD a-Si:F is approximately 4 at% and the hydrogen content of this material is approximately 0.5 at%. The a-Si:H material contains typically 5-50 at% H.^{5}

4. ANALYSIS OF TRANSPORT

Transport results for amorphous materials are interpreted on the basis of a band model of the solid. The relevant energy levels of conducting and nonconducting states are identified, as well as the source of the states, e.g. donors, acceptors, defects, traps and vacancies. Various optical, electrical, and thermal stimuli are used to piece together the puzzle of the band model.

An important technique for determining the density of states at the Fermi level is the field effect technique. One displaces the localized state distribution with respect to the Fermi level in small increments by means of an externally applied electric field. Excess charge is induced and the change in surface energy is deduced from measured conductivity changes.^{25} Early work on a-Si:H identified the effect of deposition temperature on the tail states and the position of the Fermi level.^{25}

In the past, there have been two problems in the interpretation of field effect measurements: 1) There are shifts in the reference energies with respect to the state distribution as temperature is varied. 2) Transport results from different specimens did not lend themselves to comparison. These difficulties appear to have been recently resolved.^{26}

A group at Stanford has used field effect and thermoelectric power measurements to determine conduction mechanisms in boron and arsenic doped a-Si:H.^{27} In B-doped material, conduction occurs in both extended states and in acceptor states 0.42 eV above E_v. Similar results were found in As doped a-Si:H.^{28}

With low As concentrations, conduction occurs in extended states and also through localized states at 0.5 eV below E_c. For a high As concentration, conduction is entirely through extended states. The path for hopping conduction in doped a-Si is associated directly with impurities. The Dundee group of Spear, LeComber, and others, has performed studies of transport in doped a-Si:H by means of drift mobility, Hall mobility, and photoconductivity.[17] A difference in the sign of charge carriers indicated by Hall effect and thermoelectric power has been observed for both p and n type materials and a possible explanation was given by Emin.[29]

5. OPTICAL PROPERTIES

The absorption coefficients for both a-Si:H and a-Si:F are both reported to be greater than 10^4 cm^{-1} in the visible wavelength range.[6,8] Thus, a 1 micron thick device will absorb most of the incident illumination. The absorption spectrum of a-Si:H has been studied[30] and the results show that broadening of the crystal spectrum due to disorder is insufficient to explain the shape and position of the spectrum observed for a-Si:H.

Photoluminescence (PL) experiments have generated more questions than they have answered. Presently the temperature dependence of the PL, and the role of the electron-phonon coupling in PL are little understood.[31]

The optical band gap, E_o, is determined primarily by the ratio of constituents in the alloy. A higher H or F content results in a higher band gap energy.[5] The band gap is larger for a-Si:F than for a-Si:H because of the greater Si-F bond energy.[32] The optical band gap can be deduced from photoconductivity data, plotting $[i_p h\nu/eN_o(1-R)]^{\frac{1}{2}}$ versus $h\nu$.[33] A more conventional method[34] is to plot $(\alpha h\nu)^{0.5}$ versus $h\nu$. This method assumes parabolic band edges and optical matrix elements independent of energy.[35]

Anderson and Spear[36] show that σ_{pc}, the photoconductivity, is critically dependent on the Fermi energy position and the density of empty, positively charged recombination centers lying just above E_F in the updoped specimen. Slight n-type doping moved E_F through these states and produced a factor of twenty increase in σ_{pc} as a result of an increase in the recombination lifetimes of excess electrons. Transitions involving an absorbed photon exciting an electron from the valence band to a donor band have been studied with the observation of σ_{pc}.[17] The value of σ_{pc} observed for updoped and lightly doped a-Si:F is $10^{-3}(\Omega\text{-cm})^{-1}$.[6,37] The radiation damage suffered by ion-implanted doping can be studied with observation of σ_{pc}.[38]

The index of refraction of a-Si:H is nearly the same as that of crystalline Si.[5] Carrier generation efficiency of a-Si:F can exceed 95% for illumination in the visible range.[7]

The concern was raised that rapid, level-assisted, recombination might dominate in amorphous alloys and severely limit the performance of a solar cell.[39] Evidence has been presented that this process does not occur in a-Si:F.[7]

6. ELECTRICAL PROPERTIES

The electrical properties of interest for the production of a solar cell include the lifetime, conductivity, photoconductivity, drift mobility, and conductivity activation energy. The table below lists some of the best achieved values to date.

TABLE 1

a-Si:H			
	n type	p type	Ref.
$\sigma(\Omega\text{-cm})^{-1}$	10^{-2}	10^{-2}	5
ΔE(eV)	0.2	0.2	34
σ_{pc} $(\Omega\text{-cm})^{-1}$	10^{-3} (undoped)		6
μ_{el} (cm^2/Vs)	10^{-1}	--	40
μ_{hole} (cm^2/Vs)	--	10^{-3}	40

a-Si:F			
	n type	p type	Ref.
$\sigma(\Omega\text{-cm})^{-1}$	10	1	34,37
ΔE(eV)	<0.05	0.2	39
σ_{pc} $(\Omega\text{-cm})^{-1}$	10^{-3} (undoped)		37
μ_{el} (cm^2/Vs)	--	--	--
μ_{hole} (cm^2/Vs)	--	--	--

The diffusion length of minority carriers in these materials is very small and the diffusion current contribution in PV devices is usually neglected.[7] This assumes that only those carriers generated in the depletion region and, hence, transported under influence of the built-in field contribute to the photocurrent.[7] Electron lifetimes between 10^{-3}s and 10^{-7}s have been observed in undoped a-Si:H films.[9] Minority carrier lifetimes have not been measured, but an indirect estimate has been given for holes in n-type a-Si:H as 10^{-8}s.[5]

Excitons play a substantial role in thin film amorphous solar cells.[7] Many photons generate excitons and the large field in the depletion region is able to split (or ionize) the excitons into electron-hole pairs.

7. DEVICES

There are three basic types of device structures which have been successful for the fabrication of a-Si solar cells: (1) the p-n junction, (2) the Schottky barrier, and (3) metal-insulator-semiconductor (MIS) configurations. More exotic structures such as the reflection-enhanced cell and the tandem junction cell[41] have been proposed for a-Si.[32]

Dey[8] recently examined the performance of p^+n and Schottky barrier cells made with a-Si:H. The fill factors of the devices tested (0.29 and 0.22, respectively) were so low that one doubts that this work is representative of the best technology.

Wronski[41] has studied Schottky barrier structures on a-Si:H. This author finds that the current-voltage characteristics are properly described by the diffusion theory rather than the thermionic emission theory of metal-semiconductor rectification. The device configuration consisted of a stainless steel substrate, a 300 Å thick n layer, a 1 micron thick undoped layer, and a thin Pt metallization. The maximum efficiency achieved with a Schottky barrier cell on a-Si:H is 5.5%.[37]

The most efficient device made from a-Si is a MIS structure on a-Si:F.[37] A Mo substrate was covered with a thin (800 Å) n^+ layer. Next, a 5000 Å layer of undoped material was deposited, followed by a 20 Å thick oxide layer (Nb_2O_5). Contact was made with 70 Å of high work function Au:Pd (90:10) metal, and a ZnS layer (350 Å) served as an anti-reflection coating. This device has achieved a 6.3% efficiency.

The a-Si:F material made into a gold Schottky barrier device has demonstrated nearly unity (>95%) carrier generation efficiency in the visible region of the spectrum. High collection efficiencies have been reported for both a-Si:H and a-Si:F and may be attributed to Poole-Frenkel[42] field assisted ionization from traps.

8. CONCLUSION

Because PV devices on a-Si:F and a-Si:H exhibit desirable performance and can be manufactured at a low cost, it is expected that devices, especially a-Si:F solar cells, will eventually serve as competitive, low cost energy conversion devices. It appears the a-Si may be produced by a variety of procedures and exhibits different properties, depending on deposition conditions and impurities. Thus, it may be possible to optimize both the deposition method and material properties in regard to an efficient, low cost solar cell.

9. ACKNOWLEDGEMENT

The authors would like to take this opportunity to thank Stanford Ovshinsky. The use of his prepublication data for a-Si:F is greatly appreciated.

10. LIST OF SYMBOLS

α	optical absorption coefficient
at%	atomic percent
A	angstrom, 10^{-8} cm
eV	electron volt
N_o	photon flux
i_p	photocurrent
R	reflectivity
$h\nu$	photon energy
σ	dark conductivity
σ_{pc}	photoconductivity
Ω	ohm
ΔE	conductivity activation energy
μ	mobility

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12. BIOGRAPHIES

ROBERT D. ENGELKEN was born on November 14, 1955, in Poplar Bluff, Missouri. He received his public school eduation at the Walnut Ridge, Arkansas, Public Schools and he received the B.S. in Physics from Arkansas State University in 1978.

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PHOTOVOLTAIC PERFORMANCE WITH CONCENTRATION THEORY AND EXPERIMENT

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ABSTRACT

A model of a photovoltaic cell having a resistance in series with the load, for use with solar concentration, has been analyzed and tested over a range of concentrations.

Analysis

Figure 1 shows a schematic view of the cell. Using Kirchhoff's law of currents, in Figure 1, gives

$$I_s = I_J + I \tag{1}$$

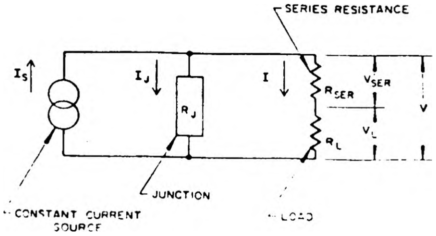


Fig. 1 Photovoltaic Model

The junction current, from E. Spenke [1], is given by

$$I_J = I_o\left[e^{\frac{qV}{kT}} - 1\right] \tag{2}$$

where

I_s is the source current

I_J is the junction current

I is the load current

I_o is the dark current

q is the electrical charge

V is the voltage

k is the Boltzmann constant

T is the temperature

If we define a cell parameter as

$$\Lambda = \frac{q}{kT} \tag{3}$$

Then, we obtain

$$I_s + I_o - I = I_o e^{\Lambda V} \tag{4}$$

and

$$V = \frac{1}{\Lambda}\ln\left[\frac{I_s + I_o - I}{I_o}\right] \tag{5}$$

Using Equation (5), when I=0, we get the open circuit voltage as

$$V_{oc} = \frac{1}{\Lambda}\ln\left(\frac{I_s}{I_o} + 1\right) \tag{6}$$

Additionally, we get the maximum current (short circuit current) when V=0, so from Equation (5), we get

$$\frac{I_s + I_o - I_m}{I_o} = 1 \tag{7}$$

so $$I_s = I_m = I(\text{short circuit}) \tag{8}$$

Also, the source current is given by

$$I_s = \eta_c \dot{N}_{ph}(\varepsilon_g)(1-r)\left[1-e^{-\alpha L}\right]q \tag{9}$$

where [2]

η_c is the collection efficiency

$\dot{N}_{ph}$ is the number of photons per second to the p-n junction of sufficient energy to generate a hole-electron pair

r is the reflection coefficient

α is the fraction of radiation absorbed

L is the thickness of the absorbing semi conductor (p-type layer)

ε_g is the energy gap

Using Equation (6) in Equation (4), we obtain

$$I = (I_s + I_o)\left[1 - e^{\Lambda(V-V_{oc})}\right] \tag{10}$$

From Figure 1, it is seen that,

$$V = V_L + V_{SER} \tag{11}$$

so

$$V_L(I) = V - V_{SER} = \frac{1}{\Lambda}\ln\frac{I_s+I_o-I}{I_o} - IR_{SER} \tag{12}$$

The series resistance is given by

$$R_{SER} = -\frac{1}{\Lambda(I_s+I_o)} + \frac{dV_L(0)}{dI} \tag{13}$$

The external work of the cell is

$$W_L = IV_L = \frac{I}{\Lambda}\ln\frac{I_s+I_o-I}{I_o} - I^2R_{SER} \tag{14}$$

The thermal efficiency of the cell is given by

$$\eta_t = \frac{W_L}{\Phi A_n} \tag{15}$$

where

Φ is the light intensity on the cell

A_n is the area (normal) receiving radiation

Experiment and Results

Experiments were made using Solarex cell #42512A, at solar concentrations of 1, 10 and 36. In the figures following, the experimental data is shown as dots. The theoretical curves are shown as solid lines. Two types of theoretical curves are given: (1) the cell with resistance in series with the load, called the resistance model; and (2) the cell with no resistance in series with the load, called the simple model. The simple model is shown for comparison to show that it does not represent the performance of the cell very well.

Figures 2-4 show the current plotted against V_L for the theory (resistance and simple models) and experiment at concentrations of 1, 10, and 36 respectively.

Figure 5 shows the current plotted against V_L for the resistance model and experiment for all three concentrations.

Figures 6-8 show the efficiency plotted against V_L for the theory (resistance and simple models) and experiment at concentrations of 1, 10 and 36 respectively.

Figure 2
Theoretical and Experimental Response
CR=1

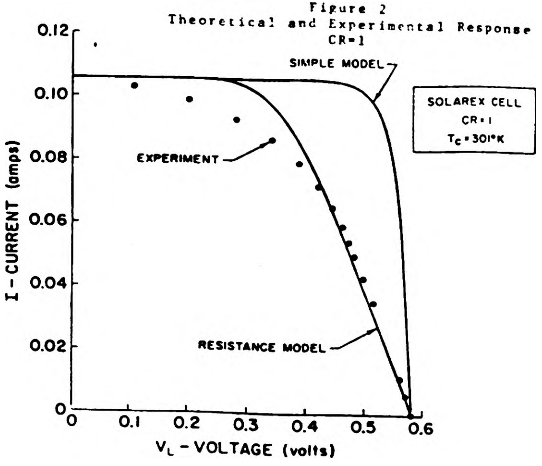


Figure 3
Theoretical and Experimental Response
CR=10

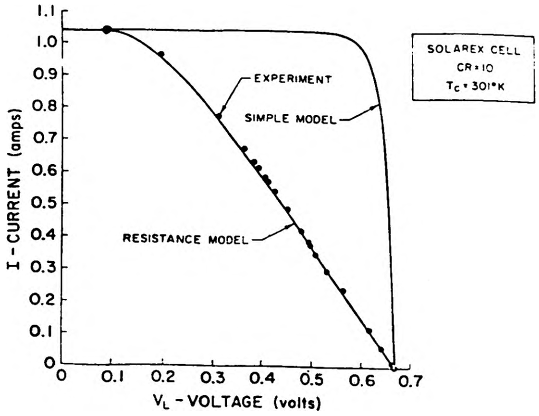


Figure 4
Theoretical and Experimental Response
CR=36

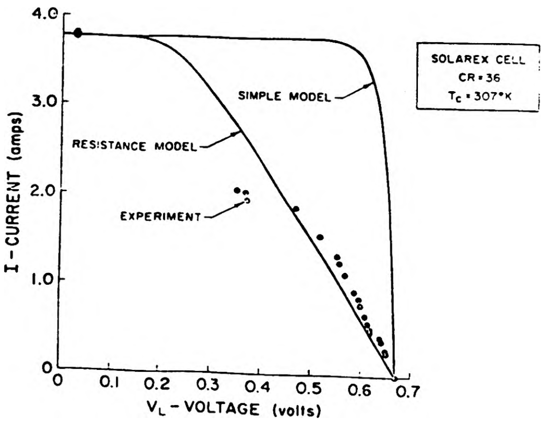


Figure 5
Overall Theoretical and Experimental Response

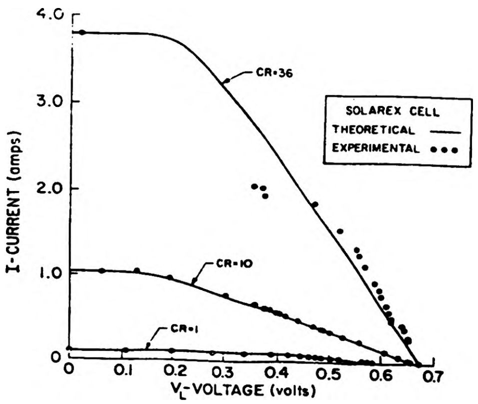


Figure 6
Efficiency of Cell
CR=1

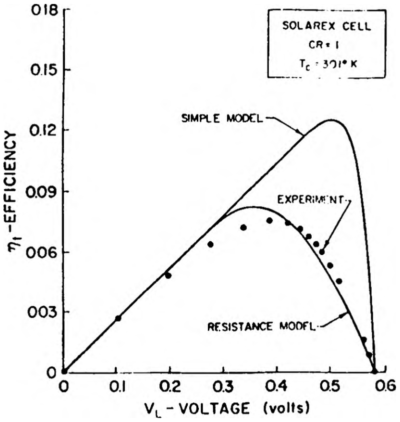


Figure 7
Efficiency of Cell
CR=10

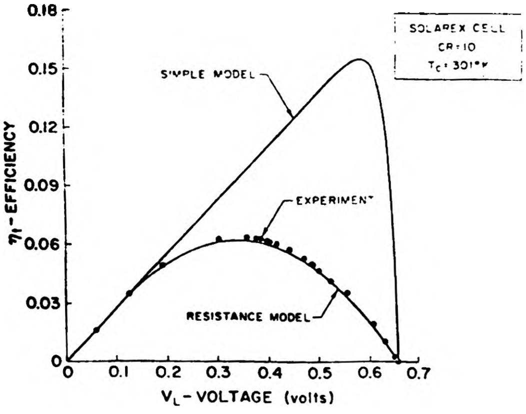
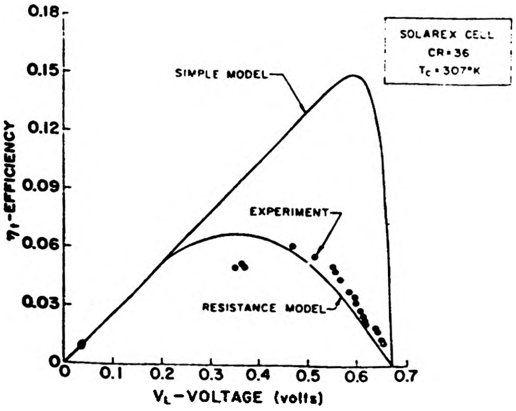


Figure 8
Efficiency of Cell
CR=36



The results of the analysis and the experiments are listed in tabular form in Table I.

Table I

Solarex Cell #42512A (CR=40)

n	CR	V_{oc} Volts	I_s Amps	η_t (exp.)	η_t (resist.)	η_t (simple)	T_c °K	I_{s_1}/I_{s_n}
1	1	0.582	0.1016	0.074	0.082	0.125	301.0	1
2	10	0.659	1.038	0.064	0.062	0.154	301.3	10.21
3	36	0.67	3.78	0.061	0.067	0.149	307.0	37.20

Conclusions

The series resistance model predicts the performance of a photovoltaic cell over a wide range of concentration reasonably well.

The simple model is a very poor predictor of the performance of a photovoltaic cell.

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