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PLASMA-ASSISTED CVD OF FLUORINATED, HYDROGENATED
AMORPHOUS SILICON

Final Technical Report for September 15, 1979—September 15, 1980

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Solar Energy

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Plasma-Assisted CVD of Fluorinated,
Hydrogenated Amorphous Silicon

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FINAL TECHNICAL REPORT

September 15, 1979 - September 15, 1980

Written by

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1. ABSTRACT

During the past year, approximately 300 large-area (400cm^2) PIN hydrogenated amorphous silicon (a-Si:H) solar cells were fabricated and tested. a-Si:H PIN cells which were plasma deposited at 200° to 350°C were found to have high internal currents ($13\text{mA}/\text{cm}^2$), whereas those which were deposited by CVD at 500° to 650°C had low internal currents. When corrected for optical losses in the top electrode, the internal quantum efficiency vs wavelength for the PIN cells indicated a peak value above 80% at about 525nm, which decreased monotonically to zero at about 725nm. When the published values of RCA and EXXON were corrected similarly for optical loss, nearly identical values of internal quantum efficiencies were found. Calculations based on a model proposed by Cody et al of EXXON indicated that the depletion width was less than 0.4 microns for all PIN cells, thereby limiting junction efficiency in the red portion of the solar spectrum since the $1/e$ photon range exceeds this value. A novel inverted NIP cell was tested and found to have its maximum quantum response shifted to 625nm. Also, an amorphous boron (a-B) layer deposited on a-Si:H to form a PIN heterojunction improved blue response and Voc. A combination of the red-responsive cells and the a-B heterojunction cells could raise efficiency to 8%.

2. BACKGROUND

Plasma-deposited amorphous silicon was produced originally in our lab in 1957 using SiF_4 and H_2 as the starting gases. The resulting material a-Si:H:F had a high resistivity and good dielectric properties. Subsequently, we designed and developed a pilot plant to plasma deposit one micron films of C_2F_4 dielectric films on a metallized Mylar substrate in kilometer lengths.

Under test, the pilot plant was found to operate relatively trouble free and to produce high-quality films with a pin hole count of less than one per square meter. Although dielectric film is easier to produce than semiconducting film, our experience indicates that low-cost a-Si:H film can be produced continuously in large areas using our new electrode design described in the next section 3B.

3. APPARATUS

3A CVD Apparatus

The CVD apparatus used to grow a-Si without plasma assistance was a conventional quartz reactor tube with external quartz-iodide IR lamps. The Mo foil substrate is held on a graphite susceptor plate. Thermocouples are attached to the substrate and IR lamp intensity controlled manually to maintain the substrate

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temperature in the 500° to 600° range.

About 50 sample runs were made in which a-Si:H was deposited on Mo substrates 1" x 8" by CVD in a quartz reactor. A mixture of 1% silane in He carrier gas was used to increase the safety since the deposition was made at atmospheric pressure. The deposition temperatures were varied between 500° and 600°C to avoid crystallization.

Subsequently, one half of the a-Si:H films were hydrogenated in a plasma and half of these samples were top-coated with an a-B top layer to form a PIN junction. Similarly, half of the unhydrogenated samples were top-coated with a-B.

Under solar simulation tests, the Isc and Voc were found to be best for the a-B coated, unhydrogenated samples, but the efficiencies of the samples were quite low due to de-hydrogenation that occurs at the High CVD temperatures 500° - 600°C. Tests will be repeated when disilane is available. As the decomposition temperature of disilane is lower than that of silane, lower CVD temperatures should result in higher retained hydrogen, as was recognized by Dr. Jack Stone. In the meantime, plasma-assisted CVD was used to attain high efficiencies and to provide a basis for studying junction properties which contribute to higher cell efficiency.

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3B Plasma Deposition Apparatus

In the plasma deposition runs, the apparatus is essentially the same as that used previously to deposit a-Si:H and a-B (1). Referring to Fig 1, the substrate 11 is held on the cathode 2 heated by resistance heater 3. The anode enclosure 4 is an aluminum cylinder 8 with end plate 9. Electrical power is supplied from supply 24 through resistor 23 and leads 21, 22. Feed-thrus 18, 19, baseplate 12 and Pyrex pipe 6 form a vacuum tight enclosure. The silane and dopant gases are introduced from tanks 17 a-e through valves 16 a-e through tube 5 and out through nozzle 7. This apparatus was modified to hold two 4" x 8" (200cm² each) substrates 11 on both sides of electrode 1.

In operation, the glow discharge is initiated in the gap "d" which has the most intense electric field, and the pressure and voltage are adjusted to move the plasma P into the weak electric field E over the substrate 11. Thus, any sparking to the substrate 11 cannot be sustained by the weak electric field and the sparking terminates. Large, uniform areas of a-Si:H can be produced by this process.

Using the apparatus illustrated in Fig 1, about 100 sample runs were made producing a-Si:H on two pieces of 4" x 8" stainless steel (200cm² each). Half of the samples were sent to Professor Wayne Anderson and Dr. Min-Koo Han at SUNY-Buffalo for fabrication

into solar cells. The other half of each sample was sent to Dr. Harold Wiesmann at Brookhaven National Labs where he has an appointment as a Guest Scientist in Dr. Myron Strongin's Physics group. Thus, two independent measurements were made on each sample. The data taken by Plasma Physics at Brookhaven are given in the following sections, while the SUNY-Buffalo data are presented separately in their report, using Cr contacts with different areas.

4. TEST RESULTS FOR PLASMA DEPOSITION

A. Spectral Response

Referring to Fig 2, the internal yields of a selection of the best PIN a-Si:H cells published by others in the literature as of 1/1/80 are plotted after correction for absorption in the semitransparent contact metal. The fall off in yield at short wavelengths in all a-Si:H cells is assumed to be due to the adsorption in the top P layer. Plasma Physics cell #43 is superior to the other cells in the blue since the a-B:H layer was only 100A thick. RCA has more recently reported a thinner P layer which presumably has a higher blue yield and Isc.

The yield curve Y is most important since its integral is proportional to the internal short circuit current. For example, when the AM1 solar spectrum F is applied to cell #93 using:

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$$I_{SC} = \int Y(\lambda) F(\lambda) d\lambda \quad (1)$$

For cell #43 the internal $I_{sc} = 13\text{mA}/\text{cm}^2$. This assumes, of course, that the yield curve does not change under high intensity illumination. The value obtained independently by SUNY-Buffalo was internal $I_{sc} = 13.8\text{mA}/\text{cm}^2$ on the mating piece which corroborates our procedure.

As cell #43 was approximately $1\mu\text{m}$ thick, the fall off in the red region is not limited by the adsorption constant but rather by insufficient carrier collection in the rear of the cell. It should be noted that the intrinsic material is slightly N-type and the depletion region is located at the front of the cell. If carriers are collected only in the high field region, the data implies that the depletion region width is the limiting factor determining the shape of the yield curve and hence the internal I_{sc} .

It should be noted again that cell #43 uses a novel amorphous boron layer as the top P contact. A SIMS analysis was made of the amorphous boron/a-Si:H interface at the National Physical Labs in the UK, which was reported jointly in a paper presented at the Ion Plating Conference in London in July 1979, which indicated the boron layer is about $100\text{\AA}$ thick. Minimizing diffusion raised V_{oc} by about 200mV .

Also plotted in Fig 2 is quantum yield for a commercial PN junction crystal-Si solar cell being manufactured currently for comparison with a-Si:H cells. As seen, the

the internal blue responses of the a-Si:H cells are better than the commercial crystal-Si, although the red responses of the a-Si:H cells are lower for the reasons given above. Of course, the blue response of the crystal-Si PN junction can be increased by reducing the depth of P layer by carefully controlling B diffusion. However, such steps add to the production costs which are high due to costs associated with crystal growth.

B. Internal Yield and Depletion Width

The internal yield Y is defined as:

$$Y(\lambda) = n(\lambda)/T(\lambda) \quad (2)$$

Here, $T(\lambda)$ is the transmissivity of the Pd top layer. In all our PIN cells the Pd is 100A thickness. The Pd transmission was measured on glass and found to be 30% and relatively flat throughout the visible region.

Knowing the interval yield, the depletion width and other properties can be calculated if accurate values of the adsorption coefficient, $a(\lambda)$, are known. In theory, one can measure the reflectance, R , adsorption, A and transmission, T , as a function of wavelength, λ . Knowing any two quantities allows one to extract the index of refraction, n , and the adsorption coefficient, a . As we had no means available for measuring the reflectance we used values reported in the literature for appropriate values of the index of refraction. It has been shown that the concentration of hydrogen in amorphous silicon films is a function of temperature.³

It is expected that the hydrogen concentration is the determining factor in modifying n and a . Therefore data were used only for films made at the same temperature, 250°C , and is shown in Fig 3. The data of Weiser (V) was calculated from reflectance measurements assuming

$$K = \frac{4\pi a}{\lambda} = 0. \quad (3)$$

As a first order correction the a values of Cody et al, were used to correct Weiser's data (V). The agreement is excellent.

(The solid line is the values of n used in the a calculations.)

The data of Jong et al. is characteristic of electron beam evaporated material in that n is anomalously low. One of us (Weismann) has also observed such trends in E-beam material and is attributable to the high void content characteristic of such films. For comparison the index of crystalline-Si is shown. It is seen that the sharp structure at ~ 3 e.v. generally associated with a direct transition is washing out. This implies that it should be easier to design A-R coatings for a-Si as compared to crystalline Si.

Having found a mean value for the index of refraction, we can now define a procedure for calculating the adsorption coefficient. In order to avoid proximity effect measurements the a-Si was deposited on ITO-coated glass. Depositions were made at a variety of thicknesses and the transmission was measured in the high adsorption region which limits the error to the uncertainty in the value of the index of refraction. The exact three layer transmission

FIG 3

equation was solved and the theoretical value was adjusted by varying n until it agreed with the measured value of the transmission. It is of course necessary to know the value of the n -Si top layer. This was measured via interference color fringes, diamond stylus (Linear Differential Transducer) and interferometer. The ITO thickness was supplied by the manufacturer. A schematic for the procedure used is shown in Fig 4. It should be noted that the multiple internal reflection coefficient for the glass-air interface is also included.

FIG 4

$$T = f \left[q_1, q_2, q_3, h_1, h_2, \alpha_1, \gamma_1, \gamma_2 \right] \frac{h_3}{h_0} \left(\frac{1 - R_4}{1 - R_3 R_4} \right)$$

$$q_1 = \frac{n_0^2 - n_1^2 - k_1^2}{(n_0 + n_1)^2 + k_1^2}, \quad q_2 = \frac{n_1^2 - n_2^2 + k_1^2}{(n_1 + n_2)^2 + k_1^2}, \quad q_3 = \frac{n_2 - n_3}{n_2 + n_3}$$

$$h_1 = \frac{2n_0 k_1}{(n_0 + n_1)^2 + k_1^2}, \quad h_2 = \frac{-2h_1 k_1}{(n_1 + n_2)^2 + k_1^2}$$

$$\alpha_1 = 2\pi k_1 d_1 / \lambda, \quad \gamma_1 = 2\pi n_1 d_2 / \lambda, \quad \gamma_2 = 2\pi n_2 d_2 / \lambda$$

$$e^{\pm i\alpha_1}, \sin \gamma_1, \cos \gamma_1, \sin \gamma_2, \cos \gamma_2$$

The raw data of figure 5 was averaged at each energy according to the formula

$$\sqrt{\alpha E} = \sqrt{\left(\sum_{N=1}^N \alpha/N \right) \cdot E} \quad (4)$$

and plotted in the usual form $\sqrt{\alpha E} (10^4 \text{ cm E.V.})^{1/2}$ vs. energy (E.V.). The data (figure 6) is seen to generate a reasonably straight line. The open circles indicate the scatter needed to generate 50% error in the measurement. The data can be fit by the equation

$$\alpha = (6.90)^2 \frac{(E - 1.68)^2}{E} \quad (5)$$

which is the usual form for optical adsorption in amorphous materials. The value of the optical gap, $E_g = 1.68 \text{ E.V.}$, indicates approximately 15% incorporated hydrogen which is consistent with the method and temperature of formation, D.C. glow discharge at $\sim 250^\circ\text{C}$. For comparison the R.F. data of Cody et al.⁴ is included for comparison. The break present in Cody's data is indicative of an inhomogeneity in the material which is ascribed to two different local coherence volumes in the adsorption matrix elements. No such structure is present in our data which generally indicates a superior material. These expectations are borne out when depletion measurement comparisons are made.

Fig 7 shows internal yield measurements for a variety of Plasma Physics D.C. glow discharge solar cells. These cells all have the structure Pd-P-I-N-S.S. except for cell #30 which had an ITO-glass base. Most of the structure in these curves can be ascribed to variations in the top P layer thickness, T_p , intrinsic layer thickness, T_i , depletion width, X_C , and substrate reflectivity, R.R. For example, the fall off in internal yield at high photon energies is due to adsorption in the top P layer. This implies that there is an optimum P layer thickness. Due to the short diffusion length in doped a-Si (200A), almost all of the carriers generated in the P layer are lost. Therefore the P layer should be as thin as possible. However, due to the low doping efficiency (it is estimated that the fermi level can only be moved to within 0.2 E.V. of the valence "conduction" band) if the P layer is too thin there will be incomplete ionization of the intrinsic region leading to a loss in depletion width. The fall off in internal yield at long wavelengths is due to the finite thickness of the cells (1 μ m) coupled with the fact that only carriers generated within the depletion width are assumed to be collected.

FIG 7

The model used to calculate the depletion width is shown in Fig. 8. The model is exact but it does ignore any contributions to the photocurrent from carriers generated outside the depletion width, i.e. the diffusion length, L , is assumed to be equal to zero. The "primed" regions in the figure represent the layers of the solar cell which are successively transversed by the photons reflected from the intrinsic a-Si, S.S. interface. In the equation for the depletion width, X_C , all the necessary parameters are either known or can be measured separately. To a good approximation the adsorption in the N region can be well approximated by setting it equal to the adsorption in the intrinsic region, I . The P layer is amorphous boron and the approximation is not quite as good but due to the thinness of the layer the error is negligible except in the regions of photon energy ≥ 2.5 E.V. The stainless steel reflection coefficient, R.R., was set equal to 0.7.

FIG 8

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$$Y = \frac{N_p}{N_o T(\lambda) B} \quad , \quad X_c \equiv X'_c \quad , \quad T_I \equiv T_I \quad , \quad T_N \equiv T_N'$$

$$Y = e^{-\alpha T_p} [1 - e^{-\alpha X_c}] + RR \cdot e^{-\alpha T_p} e^{-\alpha X_c} e^{-2\alpha T_N} e^{-\alpha 2(T_I - X_c)} [1 - e^{-\alpha X'_c}]$$

Here we present the results (Fig 9) of the depletion width calculation for four solar cells at a variety of wavelengths. The depletion width, x_c , for cell #43 is quite large, approximately .37um. This value is equal to the best reported values of ECD's ⁵ a-Si:F:H films, which are claimed to have the lowest density of states yet measured in the center of the gap. Cell #30 is representative of the poor depletion width values achieved on ITO to date. The reason for this is not known but could be due to a resistive interfacial layer between the ITO and N layers. At short wavelengths the depletion widths are seen to increase. This is due to the uncertainty in the values of the adsorption coefficient of the top amorphous boron P-layer. For cells #43 and #22 the increase in x_c at long wavelengths may be indicative of a weak field region at the I-N layer interface. This field would be weak however because the intrinsic a-Si is slightly N type with the fermi level displaced approximately 0.2 E.V. above midgap.

Using the following equation:

$$I_{S.S} = \int Y(\lambda) F(\lambda) d\lambda \quad (6)$$

where $F(\lambda)$ = AM1 spectral curve, we can predict a short circuit current of approximately 13 mA/cm² under AM1 illumination.

Wayne Anderson et al.⁶ have measured short circuit currents on a variety of films having approximately 50% transmissive top contacts. Some films have shown short circuit currents of approximately 6mA/cm² which translates into approximately 12mA/cm² for a clear top contact under AM1 insolation. Some collapse of the depletion width does

Pd-P-I-N-S.S.

FIG 9

FIG 10

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indeed occur but above approximately $10\text{mA}/\text{cm}^2$ the relation between short circuit current and insolation is linear.

As was previously shown in Fig 2, the internal yield curve corrected for optical losses for all the a-Si:H solar cells reported in the literature, decreases similarly from a peak in the green at about 525nm. An inverted NIP/stainless steel geometry with the light incident on the N layer was next investigated in an attempt to improve the red response. This geometry was fabricated successfully prior to the present contract, but no detailed spectral measurements were made. A number of such cells were constructed and the internal yield of two such cells, #87 and #93, are plotted in Fig 10 along with the internal yields of some PIN stainless steel cells, including our best PIN cell, #43.

Referring to Fig 10, note that the internal yield is quite remarkable in that the response is peaked in the red and falls off to zero both in the blue and far red, contrary to all published results on PIN stainless steel cells. Also note that the peak is quite high, approximately 80% for the cells shown here. PIN cell #43 is .84 μm s thick and according to equation (5) and those shown in Fig 8, the yield in the red is limited by insufficient carrier collection outside the depletion region and not the cell thickness. The situation is reversed for the inverted NIP cells #89 and #93.

Next using the model illustrated in Fig 8, except introducing the illumination through the N layer instead of the P layer, the depletion width for cell #93 at its 625nm peak is 1.6 μm out of a total thickness of 1.7 μm . This width is substantially larger than the depletion width shown above in Fig 9 for PIN cells or for any cells reported in the literature! The depletion width at 525 nm is 1.4 μm , leaving a thin inert intrinsic layer between the N^+ layer and the depleted intrinsic layer.

Thus, in the case of the blue photons, most of the carriers are generated in an 0.1 μm inert intrinsic (I) layer adjacent the top N^+ layer and are lost. Under white light the blue response improves significantly, as will be investigated and reported in the next contract period. These calculations indicating a depletion region in the red portion of the spectrum nearly filling a 1.7 μm thick inverted NIP cell cannot be explained at present; however, there are two possible hypotheses.

First, the simplest explanation is afforded by the model for the electric field as derived in (7). In the first model the electric field of the junction has a long tail extending approximately 1 μm into the intrinsic region, with a residual value of approximately 10^3 V/cm . The carriers generated by the red light are collected because the optical generation is gradual enough and the intensity low enough so that the weak electric field is not inverted by space charge of the charge carriers.

The same effect should be present in PIN stainless steel cells and such behavior is suggested in Fig 9 where the calculated depletion width is seen to increase slightly in the red region, although these values are substantially lower than the peak depletion widths in the inverted NIP cells.

Also, using the same model, note that the optical absorption coefficient is maximum for blue photons; thus, the optical generation for the blue photons is strongest where the electric field is weakest in the inverted NIP cell, and the space charge could invert the electric field. If this explanation is correct, then the effect should disappear at a red light intensity great enough to overcome the electric field. Such an experiment is planned.

A second possible explanation is that the deep trap states are neutralized excitonically increasing the ambipolar diffusion in the intrinsic a-Si:H adjacent the N^+ layer. This picture is consistent with the #93 yield curves since the red photons penetrate the entire intrinsic region providing neutralization throughout the intrinsic region and consequently with a high yield; whereas, the blue photons are absorbed in a thin top layer leaving an inert intrinsic layer between the generated carriers and the depletion region, and a correspondingly low yield.

5. PROJECTED SOLAR CELL EFFICIENCIES

We have used simple techniques to measure the internal yield, adsorption coefficient and depletion width of Pd-P-I-N-S.S. (or ITO) a-Si solar cells. The best values achieved to date are:

$$V_{a.c.} = 800 \text{ M.V.}$$

$$I_{SC} \text{ (extrapolated by a factor of 2)} = 12 \text{ mA/cm}^2$$

$$X_C = 0.37 \text{ um}$$

$$\text{Fill Factor (F.F.)} = 0.55$$

which, when combined, yield an AM1 efficiency of approximately 5%. This compared favorably with the recent 5.5% efficiencies reported by RCA on their best cells with optimized P^+ and N^+ layers. Currently we are producing our cells on stainless steel which has an extremely rough surface finish. One of the authors has observed that surface roughness on the order of the film thickness affects the growth kinetics even though no chemical reaction takes place. Hence we expect large improvements in our cell properties, especially fill factor and open circuit voltage.

Most importantly, the red response of the inverted NIP cell #93 indicates the possibility of increasing cell efficiency by two or more percentage points in a tandem cell. Thus 8% efficiency appears possible in principle at this time.

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