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AMORPHOUS SILICON SOLAR CELLS

Quarterly Report No. 1 for Period October 1—December 31, 1980

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Solar Energy

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PREFACE

This Quarterly Report covers the work performed by the Display and Energy Systems Research Laboratory of RCA Laboratories, Princeton, New Jersey, for the period 1 October 1980 to 31 December 1980 under Contract No. XG-0-9372-1. The Staff Vice President is B. F Williams; D. E. Carlson is the Group Head and Project Scientist. The staff members and associate staff personnel who have contributed to the report, and their areas of specialization, are listed below.

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SUMMARY

We have modeled the photocapacitance of p-i-n cells assuming that the undoped layer is free of space charge with a uniform electric field extending across it. The theory provides a good fit to both the field dependence and light intensity dependence of the photocapacitance.

Probe measurements in a dc SiH_4 discharge indicate the presence of two groups of electrons in the plasma and a positive ion flux of $\sim 10^{13}$ ions $\text{cm}^{-2} \text{s}^{-1}$.

The positive ion flux is ~ 10 to 100 times smaller than the particle flux determined from the film deposition rate; thus, neutral species are primarily responsible for the film growth.

A series of experiments showed that PF_5 and BCl_3 could be used to make n- and p-layers respectively, in p-i-n cells, but there was no evidence of improved performance as compared to cells made using PH_3 and B_2H_6 as dopant sources.

A new technique has been developed to measure the diffusion length in amorphous silicon. This technique is based on a variation of the Surface Photovoltage Method used to characterize single-crystal semiconductors. Diffusion lengths as long as $0.4 \mu\text{m}$ have been measured in undoped a-Si:H at light levels corresponding to $\sim 0.1 \text{ AM1}$.

Electron irradiation effects are similar in both a-Si:H and a-Si:D so that the electron-induced defects are not caused by atomic displacements of H or D.

Conductance and capacitance studies of a-Si:H:F alloys indicate that fluorine may be either adding donor-like states to phosphorus-doped a-Si:H:F or may be removing some defect states in the central position of the energy gap. The improvement in conductivity caused by adding fluorine is small compared to the changes observed when the films become microcrystalline. No improvement was observed in the performance of p-i-n solar cells made with varying amounts of fluorine-containing gases present during the deposition of the different layers.

Several p-i-n a-Si:H solar cells were fabricated using a glow discharge in Si_2H_6 (disilane) for the undoped layer. These cells exhibited higher values of V_{oc} (~ 850 to 890 mV) and lower values of J_{sc} (~ 7 to 10 mA/cm^2) than cells made in SiH_4 discharges.

An experimental optimization of p-i-n cell performance in an rf capacitive system showed that the best cells were obtained when the rf power was relatively low (60 mW/cm^2) and the substrate temperature was $\sim 230^\circ\text{C}$. Other studies have shown that good p-i-n cells can be fabricated on ITO-coated glass without the use of a cermet contacting layer.

Interfaces are being studied by measuring work functions of various surfaces. A correlation has been found between poor performance of p-i-n cells and relatively low work functions for the n-layer and the top ITO contact.

While light-induced degradation has been observed in some p-i-n cells, the extrapolation of results for present cells indicates that the conversion efficiency will still be in excess of 4.0% after 10 years of normal operation. Some cells have been fabricated that exhibit an improvement in performance under prolonged light exposure.

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SECTION 1.0

INTRODUCTION

A review of the history of hydrogenated amorphous silicon (a-Si:H) and the a-Si:H solar cell can be found in Ref. 1. The present program involves six research tasks: theoretical modeling, deposition and doping studies, experimental methods for the characterization of a-Si:H, formation of solar-cell structures, theoretical and experimental evaluation of solar-cell parameters, and stability studies.

In a separate program, researchers at RCA Laboratories are developing the technology to fabricate large-area a-Si:H solar cells. This program has the objective of developing low-cost, large-area a-Si:H solar panels.

1. D. E. Carlson, I. Balberg, R. S. Crandall, B. Goldstein, J. J. Hanak, J. I. Pankove, D. L. Staebler, H. A. Weakliem, and R. Williams, Final Report ET/21074-4, prepared for the Department of Energy under Contract No. AC03-78-ET-21074, February 1980.

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SECTION 2.0

THEORETICAL MODELING - PHOTOCAPACITANCE OF p-i-n SOLAR CELLS

Measurements of the photocapacitance on the presently constructed p-i-n solar cells show a dependence on illumination that is much different from that observed in Schottky-barrier cells [2]. In these structures a weak increase in capacitance with light intensity was explained [2] by hole trapping causing a decrease in the depletion width and hence an increase in the capacitance. In these Schottky barrier cells the hole traps can be readily studied by populating them with a light flash and probing them by using deep-level transient spectroscopy (DLTS) techniques.

In the p-i-n structures, on the other hand, we can not observe any hole trapping using DLTS techniques. Thus, the photocapacitance observed in the present p-i-n cells is likely due to free electrons and holes and not trapped charge.

The data is presented below and then a simple model of the transport in the p-i-n cell is used to explain the light intensity and voltage dependence of the photocapacitance (C_p).

In Fig. 2-1 the fractional change in the photocapacitance (capacitance under illumination (C_p) divided by capacitance in the dark C_D minus 1) is plotted versus illumination intensity for a p-i-n solar cell at room temperature and a measuring frequency of 1000 Hz. The bias is zero. The data are well represented by a linear variation with light intensity. Similar results were obtained at other frequencies between 10 and 10^5 Hz.

In Fig. 2-2 the photocapacitance for a fixed illumination is shown as a function of bias. Here, the data are plotted as $(C_L/C_D - 1)^{-1/2}$ versus applied bias for a reason that will become apparent after the model for the photocapacitance is presented.

2. R. Williams and R. S. Crandall, RCA Rev 40, 371 (1979).

Figure 2-1. FRACTIONAL CAPACITANCE CHANGE UNDER ILLUMINATION MEASURED AT ROOM TEMPERATURE USING A FREQUENCY OF 1000 Hz and 0-V BIAS.

Figure 2-2. RECIPROCAL OF SQUARE ROOT OF FRACTIONAL CAPACITANCE CHANGE UNDER ILLUMINATION VERSUS APPLIED BIAS. SAME CONDITIONS AS FIG. 2-1.

To explain the origin of the photocapacitance as well as its dependence on light intensity and voltage we use a simplified picture of a p-i-n solar cell. Namely, that it is an insulator between blocking contacts. This is because under solar-cell operation the holes that flow away from the n-type contact are not replenished there. A similar situation applies for the electrons.

leaving the p-type contact. Because there is no evidence to the contrary, we take the i-layer to be space-charge free with a uniform electric field throughout it. This simplification does not change the character of the final result but simplifies the mathematics.

To calculate the capacitance we need an expression for the small-signal ac currents. For this we follow the standard approach of a small signal approximation to the continuity equations which, in the limit of no recombination, are

$$\frac{\partial n}{\partial t} = G + \frac{1}{q} \frac{\partial J_n}{\partial x}; \quad \frac{\partial p}{\partial t} = G - \frac{1}{q} \frac{\partial J_p}{\partial x} \quad (2-1)$$

for electrons (n) and holes (p), respectively. The quantity G is the rate of generation per second per unit volume of electron-hole pairs, q is the elemental charge, x is the coordinate through the plane of the solar cell, and J_n and J_p the electron and hole-current densities, respectively. The light is assumed to be uniformly absorbed so that G is independent of x. The electron and hole densities are separated into dc and ac parts, i.e.,

$$n = n_0 + n_1 e^{i\omega t}; \quad p = p_0 + p_1 e^{i\omega t} \quad (2-2)$$

where n_0 and n_1 depend on position only and $n_1 \ll n_0$; a similar consideration applies to holes. The electric field E is similarly expanded into dc and ac parts E_0 , E_1 respectively.

Because diffusion will be unimportant at the high fields under consideration here, the currents are

$$J_n = q \mu_n \left[n_0 E_0 + n_1 E_0 e^{i\omega t} + n_0 E_1 e^{i\omega t} + n_1 E_1 e^{2i\omega t} \right] \quad (2-3a)$$

$$J_p = q \mu_p \left[p_0 E_0 + p_1 E_0 e^{i\omega t} + p_0 E_1 e^{i\omega t} + p_1 E_1 e^{2i\omega t} \right] \quad (2-3b)$$

where μ_n and μ_p are electron and hole mobilities, respectively.

Substitution of Eqs. (2-3a) and (2-3b) into the continuity equations (2-1) results in expressions that cannot be solved except numerically unless we make the simplifying assumption that the photocarriers do not significantly distort the electric field. It can be readily shown that this assumption is well

justified as long as the currents vary linearly with the generation rate G . With this assumption, the dc components of the continuity Eq. (2-1) becomes

$$0 = G + \mu_n E_o \frac{\partial n_o}{\partial x}; \quad 0 = G - \mu_p E_o \frac{\partial p_o}{\partial x} \quad (2-4)$$

and the ac components are

$$i\omega n_1 = \mu_n E_o \left[\frac{\partial n_1}{\partial x} + \frac{E_1}{E_o} \frac{\partial n_o}{\partial x} \right] \quad (2-5a)$$

$$i\omega p_1 = -\mu_p E_o \left[\frac{\partial p_1}{\partial x} + \frac{E_1}{E_o} \frac{\partial p_o}{\partial x} \right] \quad (2-5b)$$

With the appropriate boundary conditions that

$$p(0) = p_1(0) = n_1(L) = n_o(L) = 0 \quad (2-6)$$

where 0 is the coordinate of the n-i interface and L is the coordinate of the i-p interface. The Eqs. (2-4) and (2-5) can be readily integrated to yield

$$n_o = \frac{G}{v_n} (L-x); \quad p_o = \frac{G}{v_p} x \quad (2-7)$$

$$n_1 = \frac{G E_1}{E_o} \left[\frac{\exp\left(\frac{-i\omega(L-x)}{v_n}\right) - 1}{i\omega} \right] \quad (2-8a)$$

$$p_1 = G \frac{E_1}{E_o} \left[\frac{\exp\left(-\frac{i\omega x}{v_p}\right) - 1}{i\omega} \right] \quad (2-8b)$$

where

$$v_n = \mu_n E_o; \quad v_p = \mu_p E_o \quad (2-9)$$

are the electron and hole drift velocities, respectively.

The expressions (2-7) and (2-8) for the free-carrier densities are then substituted into (2-3) to find the current.

The dc component of the current is

$$J_{dc} = q G L \quad (2-10)$$

a saturated current, as it should be, since recombination has been neglected.

The total ac current is the sum of the electron and hole currents plus the displacement current. The displacement current has two contributions: One is independent of light intensity and is associated with the geometrical capacitance; The second is linear in G and arises from the small electric field distortion due to the photogenerated space charge. This contribution is zero at the point where $p = n$. Therefore, if the ac current is evaluated at this point, $x = x_c = L/(1 + \mu_n/\mu_p)$, then the only contribution to the ac photocurrent is the conduction current found by substituting Eqs. (2-7) - (2-9) into Eqs. (2-3a) and (2-3b). The result is

$$J_{ac} = qGe \left\{ \frac{2L}{E_o} + \frac{\mu_n}{i\omega} \left[\exp\left(-i\omega \frac{(L-x_c)}{v_n} - 1\right) \right] + \frac{\mu_p}{i\omega} \left[\exp\left(\frac{-i\omega x_c}{v_p} - 1\right) \right] \right\} \quad (2-11)$$

The capacitance C_p and conductance (G) are found from expression (2-11) using the definition

$$\frac{J_{ac}}{E_1 L} = G_p + i\omega C_p$$

Thus, to first order in ω

$$C_p = \frac{q G L^3}{v_o^2} \left[\frac{1}{\mu_n} + \frac{1}{\mu_p} \right] \quad (2-12)$$

The conductance to first order in ω is zero. Since it is the slope of the I-V curve it should be zero for a saturated photocurrent.

Referring to Eq. (2-11) we see that the expansion parameters are

$$\frac{\omega L}{v_n} = \omega t_n \quad ; \quad \frac{\omega L}{v_p} = \omega t_p$$

where t_n and t_p are the electron and hole transit time, respectively. Thus, one does not expect any high-frequency effects below about 10^6 Hz.

Eq. (2-12) has three functional dependences that can be verified experimentally. They are the strong dependence on sample thickness, the linear dependence on light intensity through G , and the inverse quadratic dependence on voltage. The data shown in Figs. 2-1 and 2-2 are presented to test these dependencies. The straight line through the data shows that $C_p = C_L - C_D$ does vary linearly with light intensity. The data in Fig. 2-2 similarly show the voltage dependence expected from Eq. (2-12). Namely,

$$1/\sqrt{C_p} \propto V_o$$

SECTION 3.0

DEPOSITION AND DOPING STUDIES

3.1 PROBE MEASUREMENTS OF A dc SILANE GLOW DISCHARGE

A dc silane discharge using a proximity electrode assembly has been shown to be an important method for the deposition of thin-film a-Si:H solar cells [3]. A preliminary mass spectroscopic analysis of this discharge was done recently; however, quantitative measurements of the ion flux, plasma density, and electron temperature could not be made [4]. Under some circumstances, measurements made using an electrostatic probe can be used to determine these plasma parameters, as well as others. Therefore, to complement the mass spectroscopic study, a flat probe mounted behind a fine mesh screen covering a hole in the substrate plate of a dc proximity electrode assembly was used to measure the current-voltage characteristics of silane glow discharges. This configuration was used to obtain the ion flux and other plasma parameters at or near the surface on which solid a-Si:H films are grown.

The single-probe characteristic (SPC) was measured for several different operating pressures in the range 0.3 to 0.5 Torr, and silane flow rates of 25 and 90 cm³/min at STP (SCCM). In almost all cases the shape of the SPC is consistent with the presence of two groups of electrons in the plasma having Maxwell distributions at different temperatures which we shall refer to as $T_e^{(1)}$ and $T_e^{(2)}$. For low flow rate and pressure, the negative current part of the SPC is quite flat and fails to saturate for large positive probe voltages, indicating the presence of very energetic electrons and perhaps a breakdown in the applicability of the probe theory [5]. The positive ion flux at the floating potential in those cases where probe theory seems applicable ranges from 2.9×10^{12} ions cm⁻²/s⁻¹ to

3. D. E. Carlson, R. S. Crandall, B. Goldstein, J.J. Hanak, A. R. Moore, J. I. Pankove, and D. L. Staebler, Final Report, prepared for DOE under Contract No. EY-76-C-03-1286, October 1978.
4. H. A. Weakliem, to be published.
5. F. F. Chen in Plasma Diagnostic Techniques, R. H. Huddleston and S. L. Leonard, (eds.). (Academic Press, New York, 1965).

3.2×10^{13} ions $\text{cm}^{-2}/\text{s}^{-1}$. This positive ion flux is 1 to 10 percent that of the atomic flux corresponding to typical a-Si:H film growth rates for the same discharge conditions.

The current was collected by a flat stainless steel probe mounted behind a 240 mesh stainless steel screen which covered a 0.25-in.-diam hole in the substrate plate. The size of the individual openings in the mesh, ca. $65 \times 65 \mu\text{m}$, is smaller than the estimated sheath thickness and mean free path, which should ensure minimum perturbation of the plasma boundary. A 1-mm-thick Teflon washer was used to electrically isolate the probe from the substrate, and a Teflon cover surrounding the probe served to attach it in position behind the screen and to shield its rear surface from stray charged particles. The measured optical transmission of the screen is 0.40, therefore, the effective area of the particle beam is 0.13 cm^2 . A power supply was used to bias the probe with respect to the grounded substrate, and a Keithley 602 electrometer was used to measure the probe current. The anode-cathode and cathode-substrate separation were both 1.6 cm. The anode and cathode were connected to floating positive and negative outputs of a dc power supply, and the substrate was grounded. The probe, dc proximity assembly, and circuit diagram are shown in Fig. 3-1. The probe voltage was measured with a high impedance voltmeter and care was taken to ensure that the voltmeter did not affect the probe current measured by the electrometer. A probe voltage of a few volts negative was found necessary to give zero net current flow in the probe to substrate circuit. The probe current was measured as a function of applied voltage for both positive and negative voltages.

The negative current part of the SPC is shown in Fig. 3-2 as a plot of $\ln I$ vs V_c , where V_c is the probe collector voltage, and the positive current part of the SPC is shown in Fig. 3-3 for a silane discharge operated at $p = 0.48$ Torr, flow = 90 SCCM, $V_{a-c} = 790$ V, and $I_{a-c} = 30$ mA. Note that the positive current increases rapidly with increasing negative voltage for small values of V_c , gradually reaching a nearly saturated value for large negative V_c (see Fig. 3-3). The saturated part of the positive current SPC was fit to a straight line, and extrapolation to $V_c = 0$ gives a value I_+ that is taken to be the value of the positive ion current at the floating potential V_f . Since the floating potential is only a few volts negative and the linear dependence of $\ln I$ on V_c

Figure 3-1. DIAGRAM SHOWING THE dc PROXIMITY ASSEMBLY, THE PLANE PROBE BEHIND A SCREEN IN THE SUBSTRATE, AND THE PROBE CURRENT-VOLTAGE MEASURING CIRCUIT.

Figure 3-2. MEASURED NEGATIVE CURRENT VS PROBE VOLTAGE CHARACTERISTIC FOR A SILANE DISCHARGE OPERATED AT $p = 0.48$ TORR, FLOW = 90 SCCM, $V_{a-c} = 790$ V, AND $I_{a-c} = 30$ mA.

Figure 3-3. MEASURED POSITIVE CURRENT VS PROBE VOLTAGE CHARACTERISTIC FOR THE SAME DISCHARGE CONDITIONS AS GIVEN IN Fig. 3-2.

is slight, only a small error is introduced by using $V_c = 0$ rather than $V_c = V_f$ to determine the value of I_+ . The positive ion flux is given by

$$J_+ = I_+/eA \quad (3-1)$$

where e is the electronic charge and A is the effective probe collection area. An assumption implicit in Eq. (3-1) is that all the positive ions are singly charged. The results of the mass spectroscopic studies show this to be a valid assumption in the present case, since no doubly charged ions were detected [4]. Using Eq. (3-1) and the SPC shown in Fig. 3-3, we find $J_+ = 2.9 \times 10^{12}$ ions $\text{-cm}^{-2}/\text{s}^{-1}$.

The SPC for positive probe voltages, shown in Fig. 3-2, has two distinct segments for which $\ln I$ depends linearly on V_c . The SPC finally shows a departure from the linear dependence of $\ln I$ on V_c , and the current gradually approaches saturation for large positive values of V_c . The Langmuir theory

for the case of no collisions in the sheath [5] may be used to interpret the two linear segments of the SPC as arising from two groups of electrons at different temperatures, each group having a Maxwellian distribution. The slope of $\ln I_e$ vs V_c is equal to e/kT_e , where I_e is the electron current. The electron current is obtained by subtracting the value of I_+ from the measured net negative current, however, since I_+ is small compared with the net negative probe current, little error in the determination of T_e is introduced by ignoring the contribution of I_+ . We may also obtain an approximate value of the space potential, V_s , by taking it to be the value of V_c at the intersection of the straight line segments of the saturation negative current and the Maxwell electron current.

The exact relation between the plasma density and J_+ depends on the size and shape of the probe, as well as on some assumptions about the sheath and its boundary. We have obtained values of the plasma density, n_0 , by using the approximate result of the theory of Bohm, Burhop, and Massey [5],

$$J_+ = \frac{1}{2} n_0 \left(\frac{kT_e}{M_+} \right)^{1/2} \quad (3-2)$$

where M_+ is the positive ion mass, and J_+ , n_0 , and T_e have been defined previously. Numerous objections may be raised concerning the applicability of Eq. (3-2) for the present case, however it is probably the best result available and should provide a good set of relative values of n_0 for different discharge conditions. We have used the value 30 amu for M_+ in Eq. (3-2), which is a reasonable average value from the mass spectroscopic studies [4], although there are significant quantities of H_2^+ present, particularly at low pressure and flow rates. We have also used a weighted average of the two electron temperatures observed in the SPC for the value of T_e in Eq. (3-2). A summary of the silane plasma parameters for several different discharge conditions is given in Table 3-1.

The electron temperature, the positive ion flux, and the plasma density all increase as the pressure decreases for fixed flow rate and approximately constant discharge power. The inverse dependence of T_e on pressure, p , is the normal behavior for low current-density discharges where ionization is produced primarily by single-electron collision events. As the flow rate decreases for fixed pressure, there are significant increases in the values of T_e , J_+ , and

TABLE 3-1. PLASMA PARAMETERS FOR SEVERAL dc SILANE DISCHARGES
DETERMINED FROM THE PLANE PROBE CHARACTERISTICS.

p (Torr)	Flow (SCCM)	^(*) V _{a-c} (Volts)	V _s (eV)	⁽¹⁾ T _e (eV)	⁽²⁾ T _e (eV)	J ₊ (ions cm ⁻² /s ⁻¹)	n _o (cm ⁻³)
0.48	90	790	44	13.9	2.4	2.9 x 10 ¹²	2 x 10 ⁷
0.41	90	800	42	17	3.0	5.8 x 10 ¹²	3.4 x 10 ⁷
0.31	90	960	80	17.4	5.6	3.2 x 10 ¹³	1.1 x 10 ⁸
0.50	25	925	64	20.9	8.3	1.9 x 10 ¹³	6 x 10 ⁷

(*) The anode-cathode dc current is 30 mA in all cases.

n_0 . Increased fragmentation of silane by dissociative ionization and large increases in the quantities of H_2 and H_2^+ are observed mass spectroscopically, for both dc [4] and rf discharges [6]. It is not clear why the electron temperature increases so much at low flow rates; little or no low energy electron contribution is observed in the SPC and the electron saturation segment has a greater dependence of $\ln I$ on V_c at low flow rates than at high flow rates. The drastic change in shape of the SPC at low flow rates may indicate that the simple collisionless SPC theory is no longer applicable.

There is no general theory for probe characteristics of a reactive discharge and the SPC theory we have used is that for a collisionless, nonreactive discharge. In the present case, we estimate that the electron mean free path and the sheath thickness are comparable, therefore we may expect that the shape and value of the electron saturation current I_e may be strongly influenced by the densities and fields at the probe boundaries, but the values of T_e should be little affected [5]. While ion-molecule collisions in the sheath may in principle affect the value of J_+ , many of the known ion-molecule reactions in silane are of the charge exchange type [7], so we think that the values of J_+ obtained are nearly correct.

Contamination of the probe is a severe problem and we have found that the value of I at any given V_c gradually decreases as the discharge continues. This is partly due to the continual reduction of the beam area owing to the deposit of the solid a-Si:H film on the screen and partly due to the screening of the extracting probe voltage caused by the deposit of the dielectric film on the probe surface. All the data given were taken using a freshly cleaned probe, and the data were recorded in as short a time as possible. We repeated the I-V measurements after recording the entire SPC and found changes of a few percent, at most.

We think that the values of the positive ion flux, J_+ , are close to the true values of the flux arriving at the substrate. The flux is between 0.01 and 0.1 times the particle flux corresponding to the measured deposition rate of the a-Si:H films for the plasma conditions studied.

6. G. Turban, Y. Catherine, and B. Grolleau, Thin Solid Films 67, 309 (1980).
7. T. Y. Yu, T. M. H. Cheng, V. Kempter, and F. W. Lampe, J. Phys. Chem. 76, 3321 (1972).

3.2 INVESTIGATION OF PF_5 AND BCl_3 AS DOPANTS

A series of p-i-n cells were made with PF_5 substituted for PH_3 in the n-layer, and another series with BCl_3 substituted for B_2H_6 in the p-layer.

Table 3-2 shows the variation in photovoltaic properties with varying amounts of PF_5 present in the SiH_4 discharge during the n-layer deposition. PH_3 was used only during the fabrication of the control cell. The deposition conditions for all three layers in the p-i-n structure were: dc proximity mode, pressure = 0.5 Torr flow = 50 SCCM, power density at cathode = 0.7 W/cm^2 , and substrate temperature $\sim 330^\circ\text{C}$. The solar-cell structure was ITO/n-i-p/steel.

The data in Table 3-2 indicate that PF_5 can act as an effective dopant source and that the optimum doping level is ~ 5 vol %. PF_5 in SiH_4 . However, these data do not show any advantage over the use of PF_5 in place of PH_3 as a dopant source for producing n-type films.

Table 3-3 shows the variation in photovoltaic properties for varying amounts of BCl_3 present in the SiH_4 discharge during the deposition of the p-layer. These data indicate that BCl_3 is an effective p-type dopant source, but there is no clear-cut advantage over B_2H_6 . The relatively poor fill factor in these devices (1.2 cm^2 in area) is attributed to somewhat resistive ITO ($R_0 \sim 300$ to $1000 \Omega/\square$).

TABLE 3-2. PHOTOVOLTAIC PROPERTIES FOR VARYING AMOUNTS OF PF_5 PRESENT DURING THE n-LAYER DEPOSITION

Amount of PF_5 Present	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η_{AM1} (%)
No PF_5 , 2.0% PH_3	809	11.39	0.504	4.64
0.2% PF_5	399	5.29	0.458	0.97
1% PF_5	730	8.61	0.415	2.60
5% PF_5	803	10.13	0.516	4.20
20% PF_5	782	8.85	0.464	3.21

TABLE 3-3. PHOTOVOLTAIC PROPERTIES FOR VARYING AMOUNTS
OF BCl_3 PRESENT DURING THE p-LAYER DEPOSITION

<u>Amount of BCl_3 Present</u>	<u>V_{oc} (mV)</u>	<u>J_{sc} (mA/cm²)</u>	<u>FF</u>	<u>η_{AM1} (%)</u>
No BCl_3 , 1.3% B_2H_6	783	10.85	0.450	3.83
0.2% BCl_3	767	10.38	0.443	3.53
1.0% BCl_3	787	10.93	0.455	3.91
5.0% BCl_3	771	10.99	0.444	3.77

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SECTION 4.0

EXPERIMENTAL METHODS FOR CHARACTERIZING a-Si:H

4.1 DIFFUSION LENGTH OF HOLES IN a-Si:H BY THE SURFACE PHOTOVOLTAGE METHOD

The minority carrier diffusion length L is one of the most important parameters defining the quality of a semiconductor and it also clearly plays a crucial role in determining the performance of a solar cell. In the past quarter we have succeeded in measuring L in undoped a-Si:H. We now have a method for measuring the quality of a-Si:H directly without having to construct a complete solar cell. We have also shown that prolonged illumination can decrease L and that subsequent annealing will restore the original value.

The measurements were performed using a variation of the Surface Photovoltage Method (SPV). The theory of the method is well known [8,9,10], and some of the limits of its application have been studied [11,12]. In the SPV method one illuminates the surface of the semiconductor with monochromatic radiation of variable $h\nu > E_g$. A photovoltage is then detected between the surface and an unilluminated back contact which is caused by the increase in minority carrier concentration at a surface barrier. The surface barrier may be that due to surface states or alternatively, one can use a thin diffused junction or a transparent Schottky barrier. One then adjusts the incident photon flux I at every λ to yield the same photovoltage ΔV . If certain conditions are met it can be shown [8] that

$$I(1-R) = \text{constant} \left(\frac{1}{\alpha} + L \right) \quad (4-1)$$

where α = the absorption coefficient and R the reflection coefficient of the incident light. The intercept of Eq. (4-1) on the abscissa yields L . The

8. A. M. Goodman, J. Appl. Phys. 32, 2550 (1961).
9. E. O. Johnson, Phys. Rev. 111, 153 (1958).
10. T. S. Moss, J. Electronics and Control 1, 126 (1955).
11. W. E. Phillips, Solid-State Electron 15, 1097 (1972).
12. E. Y. Wang, C. R. Baraona, and J. W. Brandhorst; J. Electrochem. Soc. 121, 973 (1974).

conditions which must be met are:

$$W < 1/\alpha < d \quad (4-2)$$

$$L \ll d \quad (4-3)$$

$$L \gg W \quad (4-4)$$

$$n_0 \gg p \quad (4-5)$$

where W is the depletion width at the surface, d is the thickness of the semiconductor layer, and n_0 is the density of the majority carriers. Eqs. (4-2) and (4-3) are easily met by making the sample sufficiently thick [11,12]. Eq. (4-5) states that the lifetime for photogenerated holes is to be constant under changes of the illumination level. Since in our measurements the a-Si:H samples are photoconductive insulators, the values of L obtained will be strictly valid only for the light levels used in the experiment. Eq. (4-4) may be the most difficult to satisfy a priori since previous measurements of L by other methods [13,14] indicate that it may be smaller than 1000 Å; this condition will be discussed further below.

In these experiments the sample was illuminated with unmodulated light and the surface photovoltage ΔV was measured with a vibrating Kelvin probe. The measurements were performed in high vacuum ($\sim 5 \times 10^{-9}$ Torr); this made it possible to remove the surface oxide by argon ion sputtering and thus vary the nature of the surface barrier. The composition of the surface was monitored by Auger Electron Spectroscopy. All measurements of L were made at room temperatures. We have chosen to perform these measurements in high vacuum because this made it easy to work with a well-defined surface; it also facilitates measurements of L as a function of temperature which are now in progress. The method can be used in a room ambient when one wishes to do routine testing of material quality.

The samples were prepared by decomposition of SiH_4 in a dc glow discharge at substrate temperatures of $T_s = 330^\circ\text{C}$ and $T_s = 240^\circ\text{C}$. An n^+ layer 200 Å thick

13. D. L. Staebler, J. Non-Cryst. Solids 35 & 36, 387 (1980).

14. A. R. Moore, Appl. Phys. Lett. 37, 327 (1980).

was first deposited on a stainless steel substrate, followed by 2.3μ of undoped material. The room-temperature dark resistivities for the samples were respectively $\rho = 2.6 \times 10^8 \Omega\text{-cm}$ and $\rho = 10^{13} \Omega\text{-cm}$ for the samples made at $T_s = 330^\circ\text{C}$ and $T_s = 240^\circ\text{C}$. The samples were illuminated through interference filters, a water filter and an infrared reflecting filter to pass only $\lambda < 0.76 \mu$.

Fig. 4-1 shows two plots of I vs α^{-1} for the sample made at $T_s = 330^\circ\text{C}$. The upper curve was measured with the surface oxide present. The maximum surface band-bending was measured by illuminating the barrier with an intense Xe arc to yield a saturated photovoltage of about 75 mV. A straight line was obtained for $\alpha^{-1} > 0.15 \mu$. The second curve was measured after sputtering the surface with 500-eV argon ions until no oxidized Si could be detected, and annealing the sample for 30 min at 200°C to minimize surface damage. Under these conditions the surface band-bending is approximately 180 mV. Measurements were made with $\alpha^{-1} \leq 1.5 \mu$ to ensure that there would be no interfering photovoltage or reflection of light from the back contact. Both curves intersect the abscissa at nearly the same point yielding a value $L = 0.44 \mu$. Although both curves are shown plotted with the same relative intensity for the ordinate, the incident light intensities needed for $\Delta V = 50$ mV with the surface oxide were actually five to ten times larger than those needed with the oxide removed; these intensities were in the range 5×10^{14} to 10^{16} photons $\text{cm}^{-2} \text{s}^{-1}$.

Fig. 4-2 shows I vs α^{-1} for the same sample after illumination with white light ($\lambda < 0.76 \mu$) for 60 h at $\sim 1 \text{ W/cm}^2$ (10 Sun). This light soaking reduced the diffusion length to $L = 0.17 \mu$. After annealing for 30 min at 250°C in the dark, a new plot yielded the original value $L = 0.45 \mu$ as in Fig. 4-1. This experiment appears to be related to the well-known Staebler-Wronski effect [15]. In this effect, which is thought to be associated with changes in the occupation or density of deep states, a decrease in dark current and photocurrent occurs after prolonged illumination. Its magnitude varies with sample preparation and it is not seen in all specimens of undoped a-Si:H. The effect is reversible and the original conductivities are recovered after heating above 150°C . Our results show that in addition to decreasing the

15. D. L. Staebler and C. Wronski, Appl. Phys. Lett. 31, 292 (1977);
J. Appl. Phys. 51, 3262 (1980).

Figure 4-1. RELATIVE PHOTON FLUX FOR CONSTANT SURFACE PHOTOVOLTAGE WITH SURFACE OXIDE AND AFTER SPUTTERING OFF THE OXIDE AND ANNEALING AT 200°C .

Figure 4-2. SURFACE PHOTOVOLTAGE DATA ILLUSTRATING THE REDUCTION IN L AFTER PROLONGED ILLUMINATION. AFTER SUBSEQUENT ANNEALING L RECOVERS ITS ORIGINAL VALUE OF Fig. 4-1.

recombination time for electrons, prolonged illumination of a-Si:H can also substantially reduce the hole lifetime.

A similar set of experiments were performed on the sample made at $T_s = 240^\circ\text{C}$; it behaved qualitatively like that above under illumination and annealing. Also, the magnitudes of the surface band-bending with and without oxide were the same as those for $T_s = 330^\circ$. However, the shape of the plot of I vs α^{-1} was often seen to deviate from a straight line for strongly absorbed light as shown in Fig. 4-3 for the sputtered surface. Extrapolation of the straight line portion yields $L = 0.39 \mu$ in good agreement with the value obtained from another measurement with the surface oxide, $L = 0.40 \mu$. We suggest that the deviation from the straight line is probably due to the width of the space charge layer being no longer negligible compared to α^{-1} , which violates condition Eq. (4-2). Note that this would be consistent with the higher resistivity of the 240°C sample. It is clear that as α^{-1} becomes larger, the influence of the surface on the shape of the curve becomes progressively smaller.

Figure 4-3. SURFACE PHOTOVOLTAGE DATA FOR SAMPLE DEPOSITED AT $T_s = 240^\circ\text{C}$ AFTER SPUTTERING OFF THE SURFACE OXIDE.

The measured values of L for both samples are not sensitive to a doubling of the surface band-bending and to the concomitant decrease of photon flux (greater than fivefold) needed to obtain $\Delta V = 50$ mV. In addition, for light absorbed deeply into the sample, a straight-line plot is always observed. Hence, the values of L obtained by extrapolation of these curves are not sensitive to surface conditions and can be taken as a bulk property of the a-Si:H films. These values are larger than those previously reported. Staebler reported $L < 350$ Å by measuring the transport of holes through a wedge-shaped sample [13]. More recently, Moore reported $L \sim 0.09$ μ from measurements of the PEM effect [14]. Our larger values of L may reflect the continued improvement in quality of the a-Si:H, the use of a different technique, or the fact that our films are considerably thicker than those used in the earlier measurements.

4.2 ELECTRON IRRADIATION EFFECTS

4.2.1 Comparison of a-Si:H and a-Si:D

Recently we have concluded from electron irradiation effects in undoped samples of a-Si:H with high and low H content that hydrogen plays a role in the nature of the electron-induced defects [16]. Using Auger scanning microprobing as previously described [17], we now have compared the extent of electron irradiation damage in undoped samples of a-Si:H and a-Si:D deposited onto stainless steel at various substrate temperatures for different H and D content. If the electron-induced defects were caused by the atomic displacement of H and D, respectively, we would expect, due to the mass difference, a distinctly higher threshold electron energy for damage in a-Si:D. This, however, was not observed. Instead, we have found very similar damage behavior in a-Si:H and a-Si:D; moreover, the extent of damage is larger for lower deposition temperatures, i.e., presumably for both high H and D content (the H and D concentrations are currently being determined by SIMS). From these measurements we conclude that electron-induced defects are not caused by atomic displacements

16. H. Schade, Electron Irradiation Damage in a-Si:H, in D. E. Carlson, et al., "Amorphous Thin Films for Solar-Cell Applications," Final Report, SERI/PR-08254-F, Oct. 1980, pp. 44-46.

17. H. Schade, Le Vide, Les Couches Minces 201 (Suppl.), 999 (1980).

of H or D but rather involve the breaking of bonds due to Franck-Condon-type processes, which conceivably require similar energies in hydrogenated and deuterated material.

4.2.2 Photoluminescence of Undoped a-Si:H and a-Si:D

The samples described under Section 4.3.1 were partly electron-irradiated with an energy of 5 keV and a dose of about 10^{19} electrons/cm², and subsequently analyzed by photoluminescence. In all cases, the main luminescence at 1.2 keV peak was substantially reduced by 80% to 90%, whereas the luminescence at about 0.8 eV was either only slightly reduced or even increased. Only minor luminescence changes for the electron-irradiated areas were detected after a period of 45 days.

The differences between the 4 samples are summarized in Table 4-1.

TABLE 4-1. PHOTOLUMINESCENCE (PL) INTENSITY AT 0.8 AND 1.2 eV BEFORE, AND 5 AND 45 DAYS AFTER ELECTRON IRRADIATION.

	PL INTENSITY (Arbitrary Units)					
	ORIGINAL		e-IRRADIATED			
			5 days Before PL		45 days Before PL	
PL Energy [eV]	0.8	1.2	0.8	1.2	0.8	1.2
<u>a-Si:H</u>						
high - H	0.14	11.6	0.12	1.3	0.14	2.1
low - H	0.17	9.2	0.13	1.0	0.16	1.6
<u>a-Si:D</u>						
high - D	0.73	23.1	1.2	3.8	1.5	7.5
low - D	0.38	10.0	0.61	2.4	---	---

It is interesting to note that in the case of the a-Si:D sample, the 0.8-eV luminescence intensity further increases from its original value upon room-temperature annealing ($0.73 \rightarrow 1.2 \rightarrow 1.5$), while at 1.2 eV, as normally expected, the intensity recovers towards its original value (see also Fig. 4-4). From this finding we infer, that the centers responsible for the luminescence at 0.8 eV are increasing due to a rearrangement of the defect structure. This behavior may be correlated with the observed increase in the 0.8-eV luminescence with the temperature during photon irradiation reported in [18].

Before trying to draw any other conclusions from the results in Table 4-1 the H and D contents of these samples have to be determined, as mentioned above.

Figure 4-4. PHOTOLUMINESCENCE (PL) INTENSITIES (ARBITRARY UNITS) AT 0.8 AND 1.2 eV ALONG A PARTIALLY ELECTRON-IRRADIATED UNDOPE a-Si:D SAMPLE. THE STEPS ABOUT HALFWAY THROUGH THE ELECTRON-IRRADIATED AREA MARK THE BOUNDARY BETWEEN AREAS THAT HAD BEEN IRRADIATED 45 DAYS AND 5 DAYS BEFORE THE PL MEASUREMENTS.

18. J. I. Pankove and J. E. Berkeyheiser, Appl. Phys. Lett. 37, 705 (1980).

4.2.3 Solar-Cell Properties

Two ITO/n-i-p/steel solar cells, known to be "stable" and "unstable" after light-soaking were irradiated with an electron dose of about 10^{19} electrons/cm². The electron energy (7 keV) was chosen such that the estimated electron penetration reached through half the i-layer. The electron irradiation resulted in a drastic degradation of the cell properties - too large to draw any conclusions with regard to the original difference "stable" vs "unstable." Both cells initially with $\eta > 4\%$, and otherwise typical properties, degraded to $\eta = 0.1\%$, with a loss in V_{oc} by a factor of 2, and in I_{sc} by a factor of 15. After annealing at 200°C for 45 min, both cells regained their original properties to within 5%. In order to compare the effects of light-soaking and electron irradiation, we will reduce the electron dose in future experiments, and thus hope to resolve, whether cells can be stable with regard to light-soaking as well as electron irradiation.

4.3 CONDUCTANCE AND CAPACITANCE STUDY OF a-Si:H:F ALLOYS

4.3.1 Introduction

In the last few years the interest in low-cost solar cells has yielded many studies of the amorphous silicon-hydrogen alloys prepared by glow-discharge decomposition of silane, SiH₄. At present, it appears that by using different preparation conditions and different hydrogen contents, it is impossible to improve the semiconducting properties of a-Si:H beyond a photoconductivity of $10^{-3} (\Omega\text{-cm})^{-1}$ under AM1 illumination, a dark conductivity of $10^{-1} (\Omega\text{-cm})^{-1}$ and a dark conductivity-activation energy of less than 0.15 eV. The accepted explanation to these limitations is the high density of states in the forbidden gap which increases from about $10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ at the midgap to about $3 \times 10^{21} \text{ cm}^{-3} \text{ eV}^{-1}$ at the band edges.

Recently, Madan and co-workers have reported reasonably efficient solar cells ($\eta \approx 6.3\%$) using glow discharge decomposition of H₂ and SiF₄. [19,20]. Comparison of this material with a-Si:H shows that it has the same photoconductivity but a significantly improved doping efficiency. In particular conductivities

19. W. Czubytyj, M. Shur, K. Ng, and A. Madan, Proceedings of the IEEE 14th Photovoltaic Specialists Conf., San Diego, CA, 1980, p. 1214.

20. A. Madan, J. McGill, W. Czubytyj, J. Yang, and S. R. Ovshinsky, to be published.

as high as $10^{-1} (\Omega\text{-cm})^{-1}$ and activation energies as low as 0.02 eV were reported for phosphorus- or arsenic-doped materials. These observations were attributed to the reduction of the density of states near midgap to $\sim 10^{16} \text{ cm}^{-3} \text{ eV}^{-1}$ [21-25].

In order to evaluate the role of the fluorine on the density of states and the doping efficiency, we have carried out a systematic study of the G-V and C-V characteristics of MIS (metal-insulator-semiconductor) structures where S was an a-Si:H:F alloy. To confirm the generality of the results we have used materials that were prepared in four different glow-discharge systems (dc, ac, rf, magnetron rf) and over a range of substrate temperatures [26]. While in the previously reported works on the Si:H:F alloys [19,27] the materials were prepared by the decomposition of H_2 and SiF_4 , in the present case they were prepared by the decomposition of a mixture of SiH_4 and SiF_4 .

4.3.2 Experimental Conditions

The MIS junction used for the present study had the same structure as the four terminal devices described in earlier studies [26]. The junction was made by the evaporation of Cr strips on a glass substrate, deposition of the amorphous film, oxidation of the top of the film, and then the evaporation of a Cr or Au strip perpendicular to the strips on the substrate. The area of the junctions used was always $3 \times 10^{-3} \text{ cm}^2$, the thickness of the amorphous film was between 3000 and 6000 Å, and the oxide thickness was about 40 Å [26].

The amorphous material was deposited in one of four glow-discharge systems, a dc system, an ac (60 Hz) system, an rf (13.56 MHz) system, and an rf magnetron-diode glow-discharge system. The flow rates and pressures of the gas used for the decomposition were the same as in our previous work [26]. The effect of the substrate temperature, T_s , on the material was studied for the temperature

21. S. R. Ovshinsky and A. Madan, *Nature* 276, 482 (1978).
22. A. Madan, S. R. Ovshinsky, and E. Benn, *J. Philos. Mag.* 40, 259 (1979).
23. A. Madan, S. R. Ovshinsky, W. Czubytyj, and M. Shur, *J. Electron. Mat.* 9, 385 (1980).
24. A. Madan and S. R. Ovshinsky, *J. Non-Cryst. Solids* 35-26, 171 (1980).
25. R. Risch and D. C. Licciardello, *Phys. Rev. Lett.* 41, 889 (1978).
26. I. Balberg, *Phys. Rev. B* 22, 3853 (1980).
27. M. Konagai and K. Takahashi, *Appl. Phys. Lett.* 36, 599 (1980).

interval $300 \geq T_s \geq 200^\circ\text{C}$. It was always found that the higher T_s (in this temperature interval), the lower the resistivity of the material. In accord with this observation the corresponding G-V and C-V characteristics were changing into the typical characteristics of the lower resistivity material. The results to be shown below are all associated with materials prepared with $T_s \sim 300^\circ\text{C}$. The doping levels, to be quoted below, are given by the ratio of the dopant gas, (PH_3 or SiF_4), to the silane in the gas mixtures. Secondary ion mass spectroscopy and electron probe microanalysis have indicated the following relationships between this ratio and the actual impurity concentration in the Si:H alloy (P/Si or F/Si):

$$\text{P/Si}_i \sim 2.0 - 3.5 \times (\text{PH}_3/\text{SiH}_4)$$

and

$$\text{F/Si}_i \sim 0.04 - 0.06 \times (\text{SiF}_4/\text{SiH}_4)$$

(4-6)

Both relationships in Eq. (4-6) were found to hold as long as there is more than 50% silane in the gas mixture. We should note that in the material studied by Madan et al. [21,22] ($\text{SiF}_4/\text{H}_2 \sim 5$) SIMS analysis has indicated that $\text{F/Si} \sim 0.025$ [28]. Hence, our materials fabricated with $\text{SiF}_4/\text{SiH}_4 = 10^{-1}$ contain ~ 5 times less fluorine, but those fabricated with $\text{SiH}_4/\text{SiF}_4 = 10^1$ (or $\text{SiF}_4/\text{SiH}_4 = 10$) should contain on the order of a few at % of fluorine. Electron diffraction measurements taken on the films used in the present measurements have not revealed any evidence for crystallinity.

In the materials studied here it was found that for a doping level of $\text{PH}_3/\text{SiH}_4 \sim 10^{-3}$ the resistivities were of the order of $10^3 \Omega\text{-cm}$ and the activation energies were about 0.4 eV. For doping levels of the $\text{PH}_3/\text{SiH}_4 \sim 10^{-2}$ the resistivities were of the order of $10^2 \Omega\text{-cm}$ and the activation energies were about 0.2 eV. These relationships between the resistivity and activation energies are in general agreement with values quoted previously in the literature [29]. One should note however that variations by less than an order of

28. A. Madan, private communication.

29. W. E. Spear, Adv. Phys. 26, 312 (1977).

magnitude in the resistivity and by 0.05 eV in the activation energies are quite common for materials prepared with the same PH_3/SiH_4 gas mixture under different conditions. The smallest resistivity and the lowest activation energy found in the present study were for $\text{PH}_3/\text{SiH}_4 = 4 \times 10^{-2}$ with values of 75 $\Omega\text{-cm}$ and 0.17 eV, respectively. The effect of fluorine, as will be demonstrated below, was to reduce the resistivity and the activation energy somewhat (see Section 5.2). However, these changes were small compared with the fluorine effect on the G-V and C-V characteristic suggesting a reduction of the mobility by the fluorine. The lowest resistivity and activation energy for the fluorinated materials were found to be 140 $\Omega\text{-cm}$ and 0.17 eV, respectively, for a doping level of $\text{PH}_3/\text{SiH}_4 = 10^{-2}$ and fluorination level of $\text{SiF}_4/\text{SiH}_4 = 10^{-1}$.

The measurement technique which has been described in detail previously [26] is based on a modulation of the applied dc bias by a small test signal and the detection of the ac current through the MIS device. The in-phase current is proportional to the conductance of the device, G , while the out-of-phase current is proportional to ωC where ω is the test signal frequency and C is the capacitance of the device. In the present study all measurements have been taken using a test signal amplitude of 1 mV and a frequency of $2\pi \times 10^3$ rad/s. The measurement of the dc I-V characteristics were taken using a logarithmic picoammeter that was connected in series with the device.

4.3.3 Experimental Results

In order to appreciate the role of the fluorine in the amorphous alloy let us examine first the behavior of the nonfluorinated material. In Fig. 4-5 we show typical characteristics of undoped a-Si:H. The observed "conductance well" is associated with tunneling of electrons from the metal into the semiconductor conduction band, for a negative bias, and from the semiconductor valence band to the metal, for a positive bias. In cases where the semiconductor is of very high resistivity (as is the present case) the voltages V_c and V_v at which the conductance rises sharply are proportional to the energy separation of the conduction band edge and the Fermi level, $E_c - E_F$, for V_c (<0) and the separation of the Fermi level and the valence band edge $E_F - E_v$, for V_v (<0). The proportionality is determined by the capacitive voltage distribution between the insulator and the semiconductor. If the semiconductor film is of a high enough resistivity its capacitance is the geometrical capacitance. In

Figure 4-5. TYPICAL G-V AND C-V CHARACTERISTICS OF A MIS DEVICE WHERE S IS UNDOPED a-Si:H. THE a-Si:H WAS DEPOSITED IN AN rf-MAGNETRON GLOW-DISCHARGE SYSTEM. THE U-SHAPED G-V CHARACTERISTIC IS USUALLY REFERRED TO AS THE "CONDUCTANCE WELL".

Fig. 4-5 the capacitance is indeed the geometrical capacitance and is thus independent of the applied voltage. As is apparent then, the ratio:

$$V_C/V_V = (E_C - E_F)/(E_F - E_V) \quad (4-7)$$

is a good measure of the location of the Fermi level [26]. When the material becomes more conducting the ratio, V_C/V_V , say for an n-type material, will be always larger than $(E_C - E_F)/(E_F - E_V)$. For crystalline semiconductors this ratio as a function of carrier concentration has been worked out in detail [30,31].

In Fig. 4-6 we show the effect of doping on the G-V and C-V characteristics of a-Si:H. The doping level is marked in the figure by the ratio of PH_3 and SiH_4 gas concentrations in the glow discharge. For phosphorus-doped materials with very small doping levels the results are much the same as in the undoped material shown in Fig. 4-5. At intermediate doping levels ($\text{PH}_3/\text{SiH}_4 \sim 10^{-3}$)

30. I. Balberg and D. E. Carlson, Phys. Rev. Lett. 43, 58 (1979).

31. I. Balberg, J. Electron Mat. 9, 797 (1980).

(a)

(b)

Figure 4-6. THE EFFECT OF INCREASING PHOSPHORUS DOPING LEVEL FROM 10^{-3} (a) THROUGH 5×10^{-3} ; (b) to 4×10^{-2} ; (c) ON THE G-V AND C-V CHARACTERISTICS OF A MIS DEVICE, WHERE S IS n-TYPE a-Si:H. THE AMORPHOUS MATERIAL WAS DEPOSITED IN AN ac GLOW-DISCHARGE SYSTEM.

Figure 4-6. THE EFFECT OF INCREASING PHOSPHORUS DOPING LEVEL FROM 10^{-3} (a) THROUGH 5×10^{-3} ; (b) to 4×10^{-2} ; (c) ON THE G-V AND C-V CHARACTERISTICS OF A MIS DEVICE, WHERE S IS n-TYPE a-Si:H. THE AMORPHOUS MATERIAL WAS DEPOSITED IN AN ac GLOW-DISCHARGE SYSTEM.

one obtains the results shown in Fig. 4-6(a). The G-V characteristic is rounded and there is a peak in the conductance which depends on the test signal frequency [30,31]. The capacitance is increasing from positive to negative voltages and there is a capacitance peak at the same voltage as the conductance peak. The magnitudes of these peaks are related by the well-known relation of the generation-recombination mechanism [26,31]. These results, as well as the relatively high capacitance values can be interpreted by assuming that the doped a-Si:H behaves as a crystalline semiconductor which has a peak in the density of surface states, at the energy level $E = E_c - 0.45 \text{ eV}$ [30]. With increasing doping levels the conductance peak disappears while the capacitance peak appears to move towards larger negative voltages. This is shown in Fig. 4-6(b), where one finds a steplike structure in the conductance. This step was interpreted as due to tunneling into states which are located below

the midgap [32]. The density of these states is known to be enhanced by phosphorus doping and this is the reason for their observation in the doped material [26,32].

The behavior of the capacitance is more complicated. The apparent sharp decrease of the capacitance at voltages for which the conductance rises sharply is due to the phase variation in the lock-in detector. The increase of the capacitance from positive to negative voltages may be a combination of the capacitance peak shift (to be expected with the rise of E_F) and a capacitance increase associated with the sensing of the below-midgap states (to be expected in view of the G-V result). The narrowing of the conductance well is associated with the increasing conductivity of the semiconductor which causes an increase in the voltage drop across the oxide for a given applied bias. The narrowing of the "conductance well" and the shift in the Fermi level towards higher energies thus moves the peak, in the G-V and the C-V characteristics, out of the "well." This explanation is in accord with our findings as well as other reports [33] that the Fermi level moves from midgap to about $E_C - 0.2$ eV upon increasing the doping level to $\text{PH}_3/\text{SiH}_4 = 10^{-2}$ and the pinning of the Fermi level there for higher doping levels. In Fig. 4-6(c) we see the effect of a further increase in the doping. The most apparent is the narrowing of the "well" due to the increasing conductivity of the semiconductor. The conductivity increase is also the reason for the disappearance of the structure in the G-V characteristic which is masked now by the sharp rise of the metal-to-bands tunneling conductance. The capacitance has now an additional increase for an applied positive bias. This increase is due to the ionized donors (as is the case in MOS devices) and/or to the sensing of the states above the midgap which can be achieved in the highly conducting materials [31] (having a shorter time constant for the generation-recombination process). Comparison of the present results on tunnelable MIS structures with nontunnelable MOS devices can shed light on the contribution of each effect to the observed capacitance. This comparison will be made elsewhere. To show that the results shown in Fig. 4-6 are independent of the deposition method we show in Fig. 4-7

32. I. Balberg, J. J. Hanak, and H. A. Weakliem, to be published.

33. A. J. Harris, R. S. Walker, and R. Sneddon, J. Appl. Phys. 51, 4287 (1980).

Figure 4-7. THE EFFECT ON INCREASING PHOSPHORUS DOPING LEVEL FROM 10^{-3} (a) TO 2×10^{-2} ; (b) ON THE G-V AND C-V CHARACTERISTICS OF A MIS DEVICE WHERE S IS n-TYPE a-Si:H. THE AMORPHOUS MATERIAL WAS DEPOSITED IN A dc GLOW-DISCHARGE SYSTEM.

the G-V and C-V characteristics obtained on samples which were made in a dc glow-discharge system.

The effect of the fluorine ($\text{SiF}_4/\text{SiH}_4 = 10$) on a material which is intermediately ($\text{PH}_3/\text{SiH}_4 \sim 10^{-3}$) doped is demonstrated in Figs. 4-8 and 4-9. We see that the effect of the fluorine is to lower the resistivity and to eliminate the peak in both the G-V and C-V characteristics. Comparison of these figures to Fig. 4-6 indicates that the effect of the fluorine is the same as increasing

Figure 4-8. THE G-V AND C-V CHARACTERISTICS OBTAINED FOR A MIS DEVICE WHERE S IS INTERMEDIATELY DOPED a-Si:H ($\text{PH}_3/\text{SiH}_4 = 10^{-3}$) WITH A HIGH (~ 2 at.%) FLUORINE CONTENT. THE AMORPHOUS MATERIAL WAS DEPOSITED IN AN ac GLOW-DISCHARGE SYSTEM. THE EFFECT OF THE FLUORINE CAN BE APPRECIATED BY COMPARISON WITH FIGS. 4-6(a) AND 4-7(a).

Figure 4-9. THE G-V AND C-V CHARACTERISTICS OBTAINED FOR A MIS DEVICE WHERE S IS INTERMEDIATELY DOPED a-Si:H ($\text{PH}_3/\text{SiH}_4 = 10^{-3}$) WITH A HIGH (~ 2 at.%) FLUORINE CONTENT. THE AMORPHOUS MATERIAL WAS DEPOSITED IN AN rf-MAGNETRON-DIODE GLOW-DISCHARGE SYSTEM. THE DIFFERENT "CONDUCTANCE WELL" WIDTHS IN THIS FIGURE AND IN FIG. 4-8 ARE CONSISTENT WITH THE HIGHER CONDUCTIVITY ACHIEVED IN THE rf SYSTEM MATERIAL.

the doping from about $P/Si \approx 10^{-3}$ to about $P/Si = 10^{-2}$. Hence, while there is a clear increase in the doping efficiency there is no evidence for changes in the material other than the elimination of the $E_c - 0.45$ eV peak. These results may be interpreted as indicating that the fluorine acts as an additional dopant. A comparison of Fig. 4-8 and Fig. 4-9 shows again that there is no significant difference between materials prepared by different glow-discharge methods, and that the conductivity increases (the "conductance well" width decreases) with increasing fluorine content. To see that the same conclusion applies to the higher dopings we show in Fig. 4-10 the effect of an order of magnitude increase in the fluorine content on a highly doped ($PH_3/SiH_4 \approx 10^{-2}$) material. It is clearly seen that the behavior shown in Fig. 4-10(a) is similar to the behavior shown in Fig. 4-6(b) and the behavior shown in Fig. 4-10(b) is similar to the behavior shown in Fig. 4-6(c). These results confirm then that the effect of fluorine is similar to the effect of increasing the doping level. Again, we see that there are no drastic changes in the resistivity or the characteristics which may indicate changes in the density of states close to the band edges or the shift of the Fermi level beyond the energies which were obtained by heavy ($PH_3/SiH_4 > 10^{-2}$) dopings. Comparison of Fig. 4-9 and Fig. 4-10 indicates that the doping efficiency does not improve significantly when the ratio SiF_4/SiH_4 exceeds 10^{-1} . We may conclude then that a large F/Si content is ineffective in improving the doping efficiency. Moreover, the amount of fluorine in the films does not appear to exceed a few atomic % even for discharges containing 90% SiF_4 [28].

The relative position of the Fermi level in the fluorinated material can be studied by the I-V characteristics [26]. Such a characteristic for a relatively high resistivity material is shown in Fig. 4-11. Using the criterion given by Eq. (4-7) we find that the Fermi level is at about 0.2 eV below E_c . For high-resistivity, nonfluorinated material having the same dopant concentration we found (see Fig. 6(c) of Ref. 26) by using the same criterion that the Fermi level is about 0.5 eV below E_c . From this comparison we also find an order of magnitude decrease in the resistivity due to the fluorine. These two results are in accord with the effect of fluorine on the doping efficiencies as discussed above.

Figure 4-10. THE EFFECT OF INCREASING FLUORINE CONTENT FROM ~ 0.05 at.% (a) to ~ 0.5 at.%; (b) ON THE G-V AND C-V CHARACTERISTICS OF A MIS DEVICE WHERE S IS HIGHLY DOPED n-TYPE a-Si:H. THE AMORPHOUS MATERIAL WAS DEPOSITED IN A dc GLOW-DISCHARGE SYSTEM.

Figure 4-11. THE I-V CHARACTERISTIC OF A MIS DEVICE WHERE S IS INTERMEDIATELY DOPED n-TYPE a-Si:H AND THE FLUORINE CONTENT IS ~ 0.5 at.%. THE AMORPHOUS MATERIAL WAS DEPOSITED IN AN ac GLOW-DISCHARGE SYSTEM.

4.3.4 Discussion

The above results indicate that by including fluorine in a-Si:H alloys one is either eliminating states at about 0.45 eV below the conduction band edge or adding new donor levels, but one cannot eliminate states closer to the band edges. We should stress that this last conclusion is in accord with the density of states which was determined by Madan et al. [22] using the field-effect method. Another finding is that the fluorine does improve the doping efficiency and this improvement is proportional to the $\text{SiF}_4/\text{SiH}_4$ ratio in the glow discharge as long as this ratio does not exceed 10^{-1} . The above results are in sharp disagreement with the low resistivity and low activation energies reported by Madan et al. [21,22]. It is found that the fluorine has the same effect as an increase in the phosphorus dopant and that the limitations which are applicable to a-Si:H materials made with this dopant ($\rho > 10^2 \Omega\text{-cm}$, $E_a > 0.15 \text{ eV}$) are applicable to the doped a-Si:H:F material.

The role of fluorine which was found here may be due either in providing another dopant or by removal of states from the gap which enables the shift of the Fermi level from the midgap towards $E_c - 0.2 \text{ eV}$. The first effect may be borne out by the known fact [34,35] that fluorine has donor levels in crystalline silicon which are located at $E_c - 0.21 \text{ eV}$ and $E_c - 0.66 \text{ eV}$. The first level may act then as a donor level as long as it is above E_F . Hence, it cannot yield the much lower activation energies reported by Madan et al. [21,22]. The second effect, the elimination of deep trapping states below $E_c - 0.4 \text{ eV}$, enables the shifting up of the Fermi level at lower phosphorus dopings in the range where the position of E_F is sensitive to the doping level. Indeed, it was found from other measurements [33] that the position of E_F is sensitive to the dopant concentration as long as $E_c - 0.2 \geq E_F \geq E_c - 0.5 \text{ eV}$. The important point to note is that neither of the above possibilities can explain an E_F which is closer to E_c than about 0.2 eV. As pointed out above, the field effect measurements of Madan et al. [21,22] have not indicated any change in the density of states in the energy interval $E_c \geq E \geq E_c - 0.2 \text{ eV}$ due to the inclusion of fluorine in their material. The density of states

34. P. Su, A. Sher, Y. H. Tsuo, and J. A. Moriarty, Appl. Phys. Lett. 36, 991 (1980)

35. A. Goetzberger, E. Klausmann, and M. J. Schulz, CRC Critical Reviews in Solid State Sciences 6, 1 (1976).

in this interval for the fluorinated material as well as for the nonfluorinated material is of the order of $10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$ and there is no way to avoid the pinning of the Fermi level in such a high density of states. It seems then that the density of states of Madan et al. [21,22] cannot be reconciled with their own high-conductivity and low-activation energy data. In fact, contrary to their report one would expect from their states distribution an improved photoconductivity (due to the elimination of deep traps) rather than a remarkable shift in E_F .

In view of the above discussion it appears that neither fluorine doping or elimination of deep traps can explain the low values of the resistivity and activation energy reported by Madan et al. [21,22]. The explanation has to be based on a mechanism of elimination of states close to the band edges. Since these states are usually tail states which are due to the disordered nature of the amorphous material, they can be eliminated naturally by the material ordering, i.e., by crystallization. That such an effect can be achieved in a-Si:H materials prepared by glow discharge was demonstrated by very recent studies of Matsuda et al. [36], and by Hamasaki et al. [37]. They found that at high rf power deposition or at low deposition rates the Si:H alloy crystallizes yielding a P-doped material with a conductivity of about $10 (\Omega\text{-cm})^{-1}$ and an activation energy of 0.02 eV. The resemblance between these values and the values found by Madan et al. [21,22] seems to be more than accidental. The fact that the crystallization is enhanced by the dopants can explain the discrepancy between Madan's density of states and their resistivity and activation energy results. The field-effect measurements were carried out on a material which has not been heavily doped while the low resistivity and activation energy are associated with heavily doped material, where crystallization is more likely.

Hence, the effect of crystallization can explain the low-resistivity and the low-activation energy found in some Si:H or Si:H:F alloys. The effect of fluorine in the amorphous Si:H:F alloys is to either eliminate deep defect-

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- 36. A. Matsuda, S. Yamasaki, K. Nakagawa, H. Okushi, K. Tanaka, S. Iizima, M. Matsumura, and H. Yamamoto, Jpn. J. Appl. Phys. 19, L305 (1980).
 - 37. T. Hamasaki, H. Kurata, M. Hirose, and Y. Osaka, to be published.

states in the gap or add new donor levels, and thus improving the doping efficiency as long as the Fermi level is below the bandtail states ($E_c - E_F > 0.2$ eV).

Recently, we have produced high-conductivity ($\sigma \sim 10 \Omega^{-1} \text{ cm}^{-1}$) Si:H:F material using dc glow discharges in SiF_4 and H_2 , and electron diffraction studies confirm that the films are microcrystalline.

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SECTION 5.0

FORMATION OF SOLAR-CELL STRUCTURES

5.1 AMORPHOUS SILICON CELLS MADE IN DISILANE DISCHARGES

Several p-i-n cells (ITO/n-i-p/steel) were made in discharge atmospheres containing disilane (Si_2H_6). The deposition conditions were dc proximity mode, 0.55-Torr pressure, flow = 50 SCCM, power density at cathode = 0.7 W/cm^2 , and substrate temperature = 330°C .

As shown in Table 5-1, the cells made in Si_2H_6 discharges all exhibit larger values of V_{oc} than the control, but smaller values of J_{sc} . This is probably due to a somewhat thicker n-layer for the devices made in Si_2H_6 discharges. The deposition rate is higher for the Si_2H_6 discharge ($\sim 50 \text{ nm/min}$) as compared to SiH_4 ($\sim 32 \text{ nm/min}$) for the dc proximity mode, but the enhancement is small compared to that observed by Brodsky [38] for the rf electrodeless mode. These preliminary experiments indicate that Si_2H_6 can be used to make a-Si:H solar cells, but further tests are necessary to see if there are any advantages other than enhanced deposition rate.

TABLE 5-1. PHOTOVOLTAIC PROPERTIES FOR p-i-n DEVICE
MADE IN Si_2H_6 DISCHARGES

Conditions	V_{oc} (mV)	J_{sc} (mA/cm)	FF	η_{AM1} (%)
Control (SiH_4)	819	12.8	0.500	5.27
Si_2H_6 discharge	891	9.73	0.525	4.55
Si_2H_6 , but higher/power (110 nm/min)	853	7.74	0.477	3.15
Si_2H_6 , 0.3 Torr (75 nm/min)	862	10.24	0.497	4.39

38. B. A. Scott, M. H. Brodsky, P. B. Kirby, R. M. Plecenik, D. C. Green, E. E. Simonyi, and J. Kucza, Bull. Am. Phys. Soc. 25, 294 (1980).

5.2 THE EFFECTS OF FLUORINE ON DEVICE PERFORMANCE

In Ref. 39 we described a series of experiments where various fluorine-containing gases were added to the discharge atmosphere during the deposition of the different layers in a p-i-n solar-cell structure. We found that adding > 1 vol % of HF or F₂ to a SiH₄ discharge atmosphere caused a significant decrease in the conversion efficiency, but the addition of SiF₄ (99.6% purity) caused only a modest decrease (from ~5.5% for no SiF₄ to ~4.0% for 20 vol % SiF₄).

We recently repeated those experiments using relatively pure SiF₄ (99.99%) and find the conversion efficiencies to be similar to those observed earlier (see Fig. 5-1). As also observed earlier [39], we found that the presence of SiF₄ during the deposition of either the p- or n-layer had no significant effect on device performance. These depositions were all made in a dc proximity made at a pressure of 0.5 Torr flow of 50 SCCM, power of ~0.7 W/cm² at the cathode screen and substrate temperature of ~330°C. The structure was ITO/n-i-p/steel.

For a discharge atmosphere containing 17 vol % SiF₄ and 83.3 vol % SiH₄, the fluorine content of the film was estimated to be ~0.76 at.% from electron-probe microanalysis. The hydrogen content was determined to be ~12 at.% from secondary ion mass spectroscopy.

We have also made resistivity measurements to test the effects of adding SiF₄ to the discharge during the deposition of the doped layers. Fig. 5-2 shows the resistivity as a function of substrate temperature for a series of phosphorus-doped films deposited with varying amounts of SiF₄ present. The resistivity is decreased slightly by the presence of SiF₄ except for the case of 10% SiF₄ present at substrate temperatures below ~260°C. This same trend was evident in data presented in an earlier report [38] for varying amounts of HF present during the deposition phosphorus-doped films (see also Section 4.4).

39. D. E. Carlson, R. S. Crandall, J. Dresner, B. Goldstein, J. J. Hanak, A. R. Moore, H. E. Schade, D. L. Staebler, and H. A. Weakliem, Final Report SERI/PR-0-8254-F, prepared for the Solar Energy Research Institute under Subcontract No. XJ-9-8254, October 1980.

Figure 5-1. THE CONVERSION EFFICIENCY AS A FUNCTION OF THE AMOUNT OF FLUORINE-CONTAINING GAS PRESENT DURING THE DEPOSITION OF THE i-LAYER FOR A p-i-n STRUCTURE.

Figure 5-2. RESISTIVITY AS A FUNCTION OF SUBSTRATE TEMPERATURE FOR A SERIES OF PHOSPHORUS-DOPED FILMS DEPOSITED WITH VARYING AMOUNTS OF SiF₄ PRESENT.

Fig. 5-3 shows the resistivity as a function of substrate temperature for a series of boron-doped films. In this case, 10% SiF_4 increases the resistivity at all substrate temperatures investigated but the effect is larger at low substrate temperatures.

Electron diffraction measurements indicate that the present films are amorphous. Thus, fluorine does not appear to strongly influence the properties of hydrogenated amorphous silicon, and we believe that the high conductivity films reported by others [21,22] are the result of a microcrystalline structure (see Section 4.4).

Figure 5-3. RESISTIVITY AS A FUNCTION OF SUBSTRATE TEMPERATURE FOR A SERIES OF BORON-DOPED FILMS DEPOSITED WITH VARYING AMOUNTS OF SiF_4 PRESENT.

5.3 EXPERIMENTAL OPTIMIZATION OF MATERIALS FOR p-i-n a-Si:H SOLAR CELLS ON GLASS SUBSTRATES

Materials optimization studies reported here are a continuation of work reported previously [1,39], for a-Si:H materials deposited by the rf-capacitive (rf(c)) glow discharge from silane. As described previously, samples having graded

parameters and an automated technique of measuring cell performance are used that was described previously. The cell structure consisted of glass substrate/ITO (62.5 nm)/ Pt-Y₂O₃ (10 nm, 10 vol % Pt)/p a-Si:H (5 nm)/i a-Si:H/n a-Si:H (30 nm/Ti(100 nm)/Al(100 nm). For the deposition of the p- and n-doped layers, 1% B₂H₆ and 2% PH₃ in Si:H₄ were used. Otherwise, previously optimized parameters for the fabrication of the solar-cell samples were used including a gas flow of 20 SCCM and gas pressure of 20 mTorr.

5.3.1 Dependence of Performance on the Thickness (D_i), Deposition Temperature (T_s), and rf-Power Density (W_{rf}) of the i-Layer

We carried out a three-parameter simultaneous optimization of D_i , T_s and W_{rf} for the i-layer, in which the first two parameters were graded at right angles in each sample and W_{rf} was varied stepwise (30, 60, 150, 300, and 600 mW/cm²) in five samples. Testing of the cell performance was done under 33% AM1 illumination to minimize any degradation effects due to the exposure to light (see Section 5.4 and 7.0); the resulting V_{oc} was typically 30-mV lower than at AM1. The following optimized values of the three parameters were obtained: $D_i \geq 650$ nm, $T_s = 215^\circ\text{C}$, and $W_{rf} = 60$ mW/cm². At this power setting the deposition rate was 10.4 nm/min. The cell performance obtained was $\eta = 4.4\%$, $V_{oc} = 840$ mV (870 mV at AM1), $J_{sc} = 8.6$ mA/cm² (normalized to AM1) and FF = 0.60.

At the optimum rf power the dependences of J_{sc} and V_{oc} on D_i and T_s are shown in the form of contours in Figs. 5-4 and 5-5, respectively. Continued increase of J_{sc} up to the maximum thickness implies that the collection width exceeds the maximum D_i . The dependence of V_{oc} is as expected.

A summary of the values of V_{oc} , J_{sc} , FF and η max at or near D_i max as a function of W_{rf} is given in Fig. 5-6. The data show an inverse relationship between the rf power and cell performance with a maximum in η at 60 mW/cm². The lower cell performance at higher W_{rf} is probably due to the increasing deposition rate and the higher density of defects in the i-layer. The dependence of the deposition rate on W_{rf} is given in Table 5-2 along with η max and the values of D_i and T_s at which η max occurs. Note that at the two highest values of W_{rf} , η max (and J_{sc} max) were attained at low, intermediate values of D_i , indicating a low depletion width and higher density of defects in these materials. Also, note the increase in T_s with W_{rf} ; this behavior can be expected

Figure 5-4. CONTOURS OF J_{sc} OF p-i-n CELLS AS A FUNCTION OF THE DEPOSITION TEMPERATURE AND THE THICKNESS OF THE a-Si:H i-LAYER AT OPTIMIZED rf-POWER DENSITY OF 60 W/cm².

Figure 5-5. CONTOURS OF V_{oc} FOR THE SAME SAMPLE AS FIG. 5-4.

Figure 5-6. MAXIMUM VALUES OF η , V_{oc} , J_{sc} , AND FF AS A FUNCTION OF rf-POWER DENSITY AT OPTIMIZED THICKNESS AND SUBSTRATE TEMPERATURES OF THE i-LAYER.

as higher T_s is required to grow material with a similar degree of order at higher deposition rates.

5.3.2 Dependence of the Absorption Coefficient on T_s

In our previous reports we presented the results of optimization of the T_s and thickness of the p layer in p-i-n cells and observed very strong inverse dependence of η and J_{sc} on T_s . This result suggested a strong dependence of the optical absorption coefficient $\alpha(\lambda)$ on T_s . Subsequently, we have found that the Pt-Y₂O₃ cermet used in those cells darkened considerably with T_s . Nevertheless, measurement of the dependence of $\alpha(\lambda)$ on T_s was warranted. We prepared samples having a doping level of 1% B₂H₆ in the gas phase and graded T_s from 130° to 220°C. Measurements of $\alpha(\lambda)$ have shown a modest increase of about a factor of 1.5 with T_s in the range of λ of interest, as shown in Fig. 5-7.

TABLE 5-2. DEPENDENCE OF THE DEPOSITION RATE OF a-Si:H AND THE CELL CONVERSION EFFICIENCY ON rf-POWER DENSITY AT OPTIMIZED THICKNESS AND T_s OF THE i-LAYER.

W_{rf} (mW/cm ²)	Deposition Rate (nm/min)	η max (%)	D_i at η max (nm)	T_s at η max (°C)
30	5.5	4.0	≥ 650	215
60	10.4	4.4	≥ 580	233
150	18.2	3.5	≥ 550	212
300	31.6	2.4	400	270
600	42.6	2.0	290-425	270

Figure 5-7. COMPARISON ON THE OPTICAL ABSORPTION COEFFICIENTS $\alpha(\lambda)$ OF a-Si:H p-LAYER DEPOSITED AT 132° AND 208°C. (OPEN POINTS ARE FOR A THICK SAMPLE $\sim 1.0 \mu\text{m}$, CLOSED FOR A THIN SAMPLE $\sim 0.1 \mu\text{m}$.)

For p-i-n cells having p-layer thicknesses of 5 nm such as used in the present cells, the corresponding decrease in J_{sc} and η would be only a couple of percent.

5.3.3 Dependence of Solar-Cell Performance on the T_s of the p-Layer

(Redetermined)

In view of the weak dependence of $\alpha(\lambda)$ on T_s , we fabricated a p-i-n solar cell sample having a p-layer with T_s graded from 130° to 210°C and an improved cermet substrate (with respect to darkening). For this sample η remained approximately constant over the range of T_s from 130° to about 187°C, thereafter decreasing by about 20% before reaching 230°C. This variation is much smaller than our previous results, but larger than what would be expected from the $\alpha(\lambda)$ variation with T_s . Hence, progressive darkening of the cermet contacting the p-layer, is still suspected above 190°C.

5.3.4 Comparison of Performance of Cells With and Without Pt-Y₂O₃ Cermet

Contacts

In the past (Ref. 1), we have demonstrated that the V_{oc} of p-i-n cells can be improved about 200 mV by interposing a high work function cermet layer between the ITO electrode and the p-layer. At that time relatively low doping level was used (0.1% B₂H₆ in Si:H₄). Subsequently we have adopted higher doping level (1% B₂H₆ in Si:H₄) and lower rf power (30 mW/cm²) whereby further improvements in V_{oc} (911 mV) have been realized [40]. Increased doping has also enabled us to reduce the p-layer thickness from 35 to 5 nm, thereby improving the J_{sc} . The use of the cermet has been retained until now. Recent reports [41] of V_{oc} in excess of 800 mV without the use of cermets has raised the possibility that higher doping of the p-layer might eliminate the need for the

40. D. C. Carlson, R. S. Crandall, J. Dresner, B. Goldstein, J. J. Hanak, H. E. Schade, D. L. Staebler, H. A. Weakliem, and R. Williams, Quarterly Report No. 3, SERI/PR-0-8254-3, prepared for the Solar Energy Research Institute under Subcontract No. XJ-9-8254, June 1980, p. 45.
41. Y. Kuwano and M. Ohnishi, Proc. 1980 Photovoltaic Solar Energy Conf., Cannes, Frances, Nov. 1980.

cermet. Hence, we made a-Si:H solar-cell samples on glass substrates coated with ITO on one half and ITO/Pt-Y₂O₃ cermet on the other. Preliminary results indicate virtually the same performance in the two halves of the sample (at 33% AM1, $V_{oc} = 0.805$ V). Thus, the higher doping of the p-layer indeed appears to eliminate the need for the cermet. Further work is under way to confirm these results including testing of additional cells, fabrication of samples by both rf(c) and dc(p) techniques, and the study of interfaces by means of a Kelvin probe (see Section 6.0).

5.3.5 Stacked Cells with Improved p-n Dummy Junction

Initially, when we pioneered a-Si:H stacked cell [42], we used low doping (0.1% B₂H₆ and 0.2% PH₃) levels in the gases for our p- and n-doped layers. The resulting p-n dummy junction introduced a barrier which reduced the V_{oc} . The use of transparent cermet and cermet/Ti layers remedied this problem at the expense of lowering the J_{sc} . The use of higher doping levels by other laboratories [43,44] produced progressively higher V_{oc} for the stacked cells using only p-n dummy junctions. Because of possible future potential of the stacked cells in achieving higher η and good stability (see Sections 5.4 and 7.0), we fabricated a two-cell and a three-cell stacked cell in which the doping levels have been increased tenfold. In AM1 illumination the values of V_{oc} were 1.52 V and 2.03 V, and values of η were 2.6 and 3.0%, respectively. An increase of ~0.5 V in V_{oc} for the two-cell sample has been realized over the cells using the lower doping in the p/n layer junctions. The fill factors are still low (0.43 to 0.50), indicating that an undesirable barrier is still present. Hence, further improvements in the doped layers are desired.

5.3.6 Improved Performance Parameters in Monolithic Solar-Cell Panels (MSCP)

We have fabricated three 3" x 3" MSCPs, each having 13 series connected cells. Updated optimized materials parameters were used. We obtained the following improvements in V_{oc} and J_{sc} over our previous results: 885 vs 844 mV/cell and 8.66 vs 7.80 mA/cm². The FF was however much lower (0.43 vs

42. J.J. Hanak, J. Non-Cryst. Solids 35 & 36 755 (1980).

43. Y. Hamakawa, H. Okamoto, and Y. Nitta, *ibid.*, p. 749.

44. M. Ondris and W. Den Boer, Proc. 1980 Photovoltaic Solar Energy Conf., Cannes, France, Nov. 1980.

previous 0.56) due to high cell-to-cell series contact resistance ($\sim 15 \Omega\text{-cm}^2/\text{cell}$) and a comparably high contribution to R_s from the ITO electrode. Hence, the best η was 3.2%. (With better contacts and previous FF of 0.56, η would be 4.2%.)

5.4 OPTICAL STABILITY STUDIES ON DEVICES FABRICATED IN AN rf(C) DISCHARGE

5.4.1 Optical Stability of a-Si:H p-i-n Solar Cells Illuminated Through the p-layer

Upon repeated AM1 testing of p-i-n cells deposited on glass substrates, we have observed gradual degradation of performance in some of the cells. This observation has prompted us to conduct optical stability tests under prolonged AM1 illumination and to find the cause for any instability. We also found that the degradation can be removed by annealing the sample for about 15 min at 200°C and also at lower temperature for longer periods of time.

5.4.2 Optical Stability of a Large MSCP

As an example we subjected a large (64 cm^2), 16-cell series-connected MSCP to natural AM1 illumination. In a six-hour period the efficiency decreased from 3.6 to 3.1% accompanied by decreases in FF, J_{sc} , and to a small extent, in V_{oc} . Upon annealing the sample overnight at 100°C, the collection efficiency has been restored to 3.6%. Subsequently, we placed the device on a continuous test on the rooftop. The performance data taken over a 95-day period are shown in Fig. 5-8. A fair amount of noise is present in the curves (particularly in V_{oc} and J_{sc}), most of which is due to ambient temperature. After about 45 days, η appears to saturate at about 2.5%, thereafter showing minor changes due to seasonal temperature. (After the first frost, a-Si:H began peeling, thereby destroying the device, apparently due to insufficient encapsulation.)

5.4.3 Dependence of Optical Instability on the Thickness of the i-Layer of a-Si:H Cells

(a) Cells Without p-Layer (i-n) - Acting on the hypothesis that the optical instability of a-Si:H cells might be related to an increase in the density of defects and thereby a decrease in the depletion width, we carried out tests of optical stability dependence on the thickness of the i-layer. First, we used a sample having the structure of glass/ITO/Pt-SiO₂ cermet/ i-n a-Si:H/Ti/In (Note: no p-layer) and having the i-layer graded from 0 to 800 nm. The T_s was 220°C, the rf-power density was 0.09 W/cm^2 for the i-layer and 0.12 W/cm^2

Figure 5-8. OPTICAL STABILITY OF A 16-CELL MSCP EXPOSED TO DAYLIGHT OUTDOORS.

for the n-layer which was doped with 1.2% PH_3 in the gas phase. The cell was illuminated through the glass side.

First, the cell performance at AM1 illumination was determined. Then it was illuminated for 64 h at AM1 and the cell performance was retested. Dependences of the FF and series resistance at 1-V forward bias (R_4) are shown in Figs. 5-9 and 5-10, respectively. There were minor improvements in V_{oc} and J_{sc} which may or may not be relevant such as J_{sc} "improving" over the range of 0 to 200 nm and subsequently decreasing at large i-layer thicknesses. The increase in R_4 above 200 nm for the light-quenched samples shows thickness dependence and probably is due to the Staebler-Wronski effect. In this case the increase in internal series resistance appears to be the direct cause of the lowering of the FF. A decrease in η at higher thicknesses is a consequence of the decrease in FF. One consequence of these tests is that stacked cells made of thin enough layers (the usual case) should not degrade.

Figure 5-9. DEPENDENCE OF FF ON i-LAYER THICKNESS FOR AN a-Si:H i-n CELL BEFORE AND AFTER A 64-h AM1 ILLUMINATION.

Figure 5-10. DEPENDENCE OF SERIES RESISTANCE AT 1-V FORWARD BIAS FOR SAMPLE AND CONDITIONS OF FIG. 5-9.

(b) Cells Having the p-i-n Structure - For p-i-n cells deposited on and illuminated through glass and having the i-layer graded in thickness and T_s , we have measured optical stability after a 67-h AM1 exposure. The cells were stable up to i-layer thickness of about 200 nm, thereafter experiencing increasing deterioration with thickness as shown in Figs. 5-11 to 5-14 for η , V_{oc} , J_{sc} , and FF, respectively.

The observed optical stability in a-Si:H cells in which the i-layer thickness is < 200 nm appears to give support to a conclusion by Rose [45] who has calculated that in thin cells ($\sim 0.1 \mu\text{m}$) a very high density of states ($\sim 10^{17} \text{ cm}^{-3}$) can be tolerated before problems with carrier extraction arise.

Figure 5-11. DEPENDENCE OF CONVERSION EFFICIENCY OF p-i-n CELLS ON i-LAYER THICKNESS BEFORE AND AFTER A 67-h AM1 ILLUMINATION.

45. A. Rose, Phys. Status Solidi. A 56, 11 (1979).

Figure 5-12. DEPENDENCE OF V_{oc} FOR SAMPLE AND CONDITIONS OF Fig. 5-11.

Figure 5-13. DEPENDENCE OF J_{sc} FOR SAMPLE AND CONDITIONS OF Fig. 5-11.

Figure 5-14. DEPENDENCE OF FF FOR SAMPLE AND CONDITIONS OF Fig. 5-11.

5.4.4 Effect of the Deposition Ambients of the i-Layer on the Optical Stability of p-i-n Cells

(a) Deposition Temperature - We have made optical stability tests on a p-i-n solar-cell sample having the T_s of the i-layer graded from $\sim 190^\circ$ to 290°C . There was no pronounced dependence of the degradation of η on T_s over this range of T_s .

(b) RF Power Density - Over a range of rf power density of the glow discharge from 30 to 150 mW/cm^2 there is no pronounced effect on cell stability. At 300 mW/cm^2 the cell degradation is lesser, but so is the cell performance. The a-Si:H material deposited at the higher W_{rf} apparently has already higher density of defects as discussed in Section 5.3.1.

5.4.5 Dependence of Optical Instability of p-i-n Cells on Bias Applied During Illumination

We have studied optical instability of p-i-n cells as a function of bias from 4-V reverse to 1-V forward in AM1 illumination for 17 h. As shown in Fig. 5-15

Figure 5-15. DEPENDENCE OF OPTICAL INSTABILITY OF p-i-n CELLS ON BIAS APPLIED DURING 17-h AM1 ILLUMINATION.

the cells are relatively stable at 4-V reverse bias and deteriorate at an increasing rate as the bias is shifted to forward.

5.4.6 Study of Optical Stability of Stacked Cells

We have predicted that stacked cells would be stable because the i-layers are thin. We made a stacked cell in which the thicknesses of the first and second i-layers were 38 and 283 nm, respectively. Its conversion efficiency was 1.77% at the start; after 89-h illumination η was 1.70%; FF decreased from ~59 to ~58. This result demonstrates the potential of good stability of the stacked cells.

5.4.7 Improvement in Solar-Cell Performance Upon Light-Soaking

We have observed an improvement of a-Si:H solar-cell performance upon prolonged AM1 light-soaking. The cell structure consists of glass substrate/ITO/Pt-Y₂O₃ cermet/p-i-n a-Si:H/Ti/Al and is illuminated through the glass. Of 25 cells tested on the same substrate, four were shorted and the rest showed an improvement. Data taken under AM1 illumination for one of the cells is shown in Table 5-3.

TABLE 5-3. EFFECT OF AM1 LIGHT-SOAKING ON CELL ISC-10-140-V

Light Soak (hours)	V_{oc} (mV)	J_{sc} mA/cm ²	FF	R_4 Ω -cm ⁻²	η (%)
0	806	7.33	0.486	14.3	2.87
68	848	7.43	0.520	15.9	3.28
164	845	7.68	0.542	14.3	3.52
226	849	7.68	0.538	13.9	3.51
320	848	7.81	0.526	15.3	3.49
386	844	7.79	0.537	14.6	3.53

The thickness of the i-layer was 283 nm; for the rest of the cells it ranged up to 326 nm. Previously, we have shown stability only up to 200 nm. One of the cells subsequently exposed to a forward bias at 500 mA/cm² in the dark showed a decrease in η from 3.5 to 3.1%.

Another group of cells were annealed (after the 226-h light-soaking) at 200°C for 15 min in vacuo and have shown further improvement. For the best cell η increased from 3.33 to 4.14%, V_{oc} from 839 to 868 mV, J_{sc} from 7.87 to 8.77 mA/cm² and FF from 0.504 to 0.544. Upon subsequent 66-h exposure to AM1 illumination, it returned approximately to the state prior to annealing. At this time the reason for these effects is not known. The sample will be thoroughly analyzed to obtain some clues.

SECTION 6.0

THEORETICAL AND EXPERIMENTAL EVALUATION OF SOLAR-CELL PARAMETERS

6.1 SOLAR-CELL INTERFACES

In an effort to assess the role of interfaces in a-Si:H solar cells, the work-function differences between adjoining layers used in the cells are measured in the dark and under illumination. We have measured the work-function differences and photovoltages for the exposed areas of the n-layer and ITO on various solar cells of different efficiencies. For measurements in the dark, the main results are:

- (a) The work function for the n-layer is about 0.3 to 0.4 eV smaller than for ITO.
- (b) The work functions for both the n-layer and ITO were about 0.3-eV lower for a poorly performing cell compared to a good cell.
- (c) For ITO, preliminary results indicate a correlation between lower work function and higher sheet resistance.

For uncalibrated white-light illumination, the following work-function changes (photovoltages) were obtained:

- (a) The photovoltage for exposed ITO on good cells is 0.5 to 0.6 eV, and on shorted cells, 0 eV.
- (b) The photovoltage of cells measured on the n-layer is always about 0.2 to 0.3 eV, and practically independent of the dark value. This photovoltage is thus attributed mainly to an internal open-circuit photovoltage, and only to a minor degree to surface band-bending changes. It is further concluded that the shorting of cells is caused by the ITO or metal contact.

6.2 AMORPHOUS VS POLYCRYSTALLINE n-LAYERS

A comparison was made between the work functions of hydrogenated amorphous and microcrystalline n-type Si grown on stainless steel: the work function of the microcrystalline material is about 0.4-eV higher than for the amorphous material; it is thus about equal to the work function of the ITO. Microcrystalline n-layers, therefore may be better suited, apart from their higher conductivity, to be contacted by ITO, since, based on work-function considerations, less band-bending at the n-Si/ITO contact may be expected.

6.3 THE ITO/p- TYPE a-Si:H AND ITO/Pt-Y₂O₃/p- TYPE a-Si:H INTERFACES

We have measured the work function as a function of position on a sample of thickness-graded p-type a-Si:H deposited concurrently on ITO and ITO/Pt-Y₂O₃. Before and after Si deposition, the work function of ITO/Pt-Y₂O₃ was about 0.1 eV higher than for ITO. For the p-layer, the work function is essentially independent (exception see below) of the substrate material ITO or ITO/Pt-Y₂O₃. However, a significant time dependence has been observed: shortly after deposition, the p-layer work function is about 0.1-eV higher than that of the substrate material, but over a period of two weeks steadily decreases to a value 0.3- to 0.4-eV lower than that of the stable substrate. For the ITO substrate only, the work function vs sample location passes through a minimum going from the ITO across the ITO/p-Si boundary at which the p-layer has its smallest thickness. This minimum is most pronounced shortly after the p-layer deposition; its value about equals that of the thicker p-layer after two weeks.

From these measurements, we draw the following conclusions:

- (a) Based on work-function considerations, the ITO/Pt-Y₂O₃ with its higher work function may provide a better (smaller barrier) contact to the p-layer. Earlier experiments seem to have provided evidence for this.
- (b) The observed minimum of the work function at the ITO/p-Si boundary indicates, that ITO, but not ITO/Pt-Y₂O₃, causes oxidation of the p-layer probably during the deposition. The 2-week decrease of the p-layer work function is attributed to an oxidation of the p-layer surface in the room ambient.

SECTION 7.0

STABILITY STUDIES

7.1 STABILITY OF (ITO/n-i-p/STEEL) CELLS

Our best-efficiency large area cells are n-i-p structures; their efficiencies are regularly above 5% in areas larger than 1 cm^2 [46]. We have now studied the stability of these cells. There is a great variety of results, depending on the deposition conditions. Some cells are very unstable to optical exposure, others are not. In the following, we show our results and discuss some models. In brief, the changes occur in the amorphous silicon and are due to a reduction in the hole collection efficiency.

We also present our first results on long-term life tests. They are promising since tests on our more stable cells predict an efficiency above 4% after 10 years in sunlight. The optical stability of a-Si:H solar cells should not be a practical problem. Good stability is not automatic, however, and requires the proper deposition conditions. Our research in this important area continues.

7.1.1 Experiment

All cells reported here were made in one of three dc systems, using a discharge of pure SiH_4 at 0.5 to 0.6 Torr. The doped layers were made by adding a few percent at PH_3 or B_2H_6 to the discharge. The structure was: stainless steel substrate thin p-layer/0.5 μm i-layer/thin n-layer/ITO semitransparent contact and AR coating. The top contact is important for high efficiency, but not for cell stability. Effects similar to these reported below were also seen in cells in which the ITO was replaced by thin Ti contacts.

Optical illumination came from GE, ELH, or ENH tungsten lamps. The illumination level was usually set to AML, using amorphous silicon calibration cells. Temperature during illumination was $\sim 40^\circ\text{C}$. The cell parameters were measured with the automated testing facility of G. Nostrand at RCA Laboratories.

46. D. E. Carlson, R. W. Smith, G. A. Swartz, and A. R. Triano, Electrochemical Society Meeting, Hollywood, FL, October 1980.

7.1.2 Stability Results

The range of stabilities that we found is shown in Fig. 7-1. The bottom curve represents our most unstable cells, the top our most stable cells. All others fell within these extremes. Even in the worst case, it takes at least an hour or so in AM1 illumination to see a change. In addition, the efficiency tends to saturate at longer exposures. No cell dropped below 2.8%. The results shown here are for cells in open circuit during illumination. Slightly less degradation occurred for cells in short circuit during illumination. Little or no degradation occurred in cells under a reverse bias larger than 1 V.

Most measurements were made in simulated AM1 ($\sim 100 \text{ mW/cm}^2$). A few tests at ~ 0.1 AM1 suggested that the effect is reciprocal; the rate of change seems to be linear with light intensity. A test in real sunlight gave results similar to these shown in Fig. 7-1.

Figure 7-1. RANGE OF CELL STABILITIES TO WHITE LIGHT EXPOSURE. THE MAXIMUM EXPOSURE CORRESPONDS TO ~ 2 CONTINUOUS DAYS OF SIMULATED AM1.

Two of the stable cells were given a long term life test in continuous AM1 (simulated) while biased at the maximum power point. The results are shown in Fig. 7-2. The upper line is for a cell that was masked from the light during the test. It did not change at all; demonstrating the excellent shelf life of our cells. The lower line is for the exposed cells. The efficiency gradually

Figure 7-2. LONG-TERM LIFE TEST OF TWO OF THE MORE STABLE CELLS. THE UPPER CURVE IS FOR A DIODE THAT WAS MASKED FROM THE LIGHT.

decreases, following a straight line on the log-log plot. By extrapolation one expects that the efficiency will remain above 4% for ~ 100 weeks. Assuming a factor of 5 between AMI and a daily averaged illumination; this predicts that the efficiency will stay above 4% for 10 years in real sunlight.

7.1.3 Changes in Cell Properties

To study the degradation process we concentrate on the unstable cells. Fig. 7-3 shows the IV curves before and after a 10 Wh/cm^2 exposure of such a cell. The efficiency decreases from $\sim 5.0\%$ to $\sim 3.0\%$. Most of this is due to the fill factor, and J_{sc} . The V_{oc} changes only slightly. Although the J_{sc} changes, the saturated photocurrent in reverse bias does not. The two curves tend to merge at a reverse bias larger than 2 V.

The spectral response of the curves also change. Fig. 7-4 shows the collection efficiency before and after exposure in a similar cell. The largest drop is in the blue side of the spectrum. The blue response also becomes more sensitive to an applied bias. It increases in reverse bias more than the red. Also, curves A and B are similar to each other if measured at a reverse bias more than $\sim 2 \text{ V}$.

7.2 MECHANISMS

We now comment on the degradation mechanism. First, it is not an increase in series resistance. This is clear from the I-V curves in Fig. 7-3. The slope at V_{oc} is a good measure of the series resistance and it changes little, if at

Figure 7-3. I-V CURVES OF AN UNSTABLE CELL, MEASURED IN SIMULATED AM1. A IS THE INITIAL CURVE. B IS THE CURVE AFTER A LONG OPTICAL EXPOSURE.

Figure 7-4. COLLECTION EFFICIENCY VS WAVELENGTH FOR A SIMILAR CELL (A) BEFORE AND (B) AFTER A LONG OPTICAL EXPOSURE MEASURED AT ZERO BIAS.

all. We have also confirmed this with measurements at low light intensity; the fill factor does not improve.

Second, the mechanism does not involve a change in the optical properties of the cell. This follows from the similarity of the A and B photoresponses when measured at saturation in reverse bias. In saturation, the internal quantum efficiency should be unity [47], i.e., each photon absorbed in the active region of the cell should produce one pair of collected charges. If the saturation current does not change, then the optical properties have not changed either. Direct measurements on the cell reflectivity have confirmed this result; the reflectivity is unaffected by the optical exposure.

Our results show, instead, that the changes are due to a degradation in the collection efficiency of carriers generated in the n-side of the cell. This accounts for the drop in the blue response of the cell, and for the decrease in fill factor. Tests on cells fabricated with no n-layer show similar effects. Thus, it is the undoped a-Si:H that is changing. One possibility is that this effect is related to similar ones seen in previous work on optically induced changes in conductivity [48] and luminescence [49]. In other words, the recombination rate increases due to formation of new defects or sensitization of old ones. Another possibility is field distortion; the built-in field may become lower on the n-side of the cell due to a build-up of positive space charge in the i-layer. The collection efficiency depends on both factors, the internal field and the recombination rate. We are still working on this question.

One definite conclusion can be made here, nevertheless. That is that the absorbed photons do not directly change the a-Si:H. Instead, it is due to the free carriers they produce. This follows from one powerful experimental result. An unstable cell does not change when it is exposed to light while under far reverse bias. This happens because all the carriers are collected. They don't stay inside the cell and damage the a-Si:H. In this model the origin of the free carriers is not important. Indeed, we find changes similar to those produced by light are found after forward-bias charge injection in the dark.

47. R. S. Crandall, J. Non-Cryst. Solids 35 & 36, 381 (1980).

48. D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. 31, 292 (1977), and Appl. Phys. 51, 3262 (1980).

49. J. I. Pankove and J. E. Berkeyheiser, Appl. Phys. Lett. 37, 705 (1980).

The damage process itself is not yet known. It may come from energy released when the carriers are trapped or recombine. This could cause, for example, a metastable reorientation of weak hydrogen bonds in the a-Si:H [48]. A change in charge state of the defect, as seen in similar measurements on single-crystal silicon cells [50], may also be involved.

7.3 FABRICATION OF STABLE CELLS

The most important question remaining is why some of our cells are relatively stable. One possibility is that the a-Si:H contains fewer "bad" defects, e.g., those defects that can undergo a metastable change. Another possibility is that the built-in field is higher. This then could keep the field on the n^+ side from dropping; as yet, we are not certain which is more important.

It must be pointed out, however, that we have been able to reproduce our results. Continued research will lead us to better understanding and better cell stability. For example, the two cells given the life test of Fig. 7-2 were made in different systems, yet followed the same flat decay line. Thus, there is reasonable promise that our continued research in this area will lead to better understanding of this problem, and to better cells.

50. V. C. Weizer, H. W. Brandhorst, J. D. Broder, R. E. Hart, and J. H. Lamneck, J. Appl. Phys. 50, 4443 (1979).

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