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SOLAR CELLS USING DISCHARGE-PRODUCED AMORPHOUS SILICON

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Thin film solar cells, $\lesssim$ 1 μm thick, have been fabricated in p-i-n and Schottky barrier structures using d.c. and r.f. glow discharges in silane. Conversion efficiencies in the range of 2.5 to 4.0% have been obtained with both structures. The p-i-n cells exhibit built-in potentials of ~ 1.1 V while the Pt Schottky barrier cells have barrier heights of ~ 1.1 eV. The dark currents in the p-i-n cells appear to be recombination-limited while the Schottky barrier cells exhibit near-ideal diode characteristics with diode quality factors near unity.

Key words: solar cells, amorphous silicon, p-i-n devices, Schottky barriers.

Introduction

In a recent paper (1) the authors showed that solar cells could be fabricated from amorphous silicon (a-Si) produced from a glow discharge in silane (SiH_4). Thin film cells, ~ 1 μm thick, were fabricated in a p-i-n structure, and conversion efficiencies as high as 2.4% were obtained in AM1 sunlight. In this paper, we present some new data for p-i-n and Schottky barrier solar cells that have been fabricated using both d.c. and r.f. glow discharges in SiH_4.

Discharge-produced a-Si appears to be a unique semiconductor material. When deposited at a substrate temperature $\gtrsim$ 200°C, it exhibits a lower density of states in the gap than other amorphous semiconductors with comparable energy or mobility gaps (2). Furthermore, the Fermi level in discharge-produced a-Si can be moved with respect to the band edges by substitutional doping (1, 3) or by the creation of a Schottky barrier (4). As a result of the low density of recombination centers, the carrier lifetimes are reasonably long (the electron lifetime has been estimated to be ~ 10 μS) (5). Since the electron mobility in the extended states is ~ 1-10 cm^2/V-S (6), the electron diffusion length is on the order of several microns. The photovoltaic characteristics of p-i-n cells indicate that the hole diffusion length is $\lesssim$ 1 μm (1).

The optical band gap of a-Si is ~ 1.55 eV (5) which is close to the optimum value for photovoltaic energy conversion in semiconductor homojunctions (7). In addition, the optical absorption coefficient of discharge-produced a-Si is much greater than that of crystalline Si over the visible range of the spectrum so that most of the solar radiation with $\lambda < 0.7$ μm can be absorbed in a film only 1 μm thick (1).

All the necessary conditions for efficient photovoltaic energy conversion can be satisfied by a thin film (~ 1 μm) of discharge-produced a-Si. A built-in potential on the order of 1 volt can be achieved by substitional doping or by a Schottky barrier. A significant portion of the solar radiation can be absorbed in a 1 μm thick film, and most of the photogenerated electron-hole pairs can be collected. Also, the series resistance can be kept reasonably low by using doped layers for establishing ohmic contacts to the electrodes (1).

p-i-n Cells

The p-i-n cells were fabricated using substrates of glass coated with indium-tin-oxide (ITO). The doped layers were deposited from an atmosphere of SiH_4 containing ~ 1% of either PH_3 or B_2H_6 and were typically a few hundred angstroms thick. The thickness of the "intrinsic" or undoped layer was usually in the range of 0.3 to 1.0 μm. The top electrode was either Aℓ or Cr evaporated onto the top doped layer (electrode areas were 5 x 10^{-3} cm^2 to 2 x 10^{-2} cm^2).

Figure 1 shows a compositional profile of a p-i-n cell taken with an Auger electron spectrometer. The a-Si films for this device were all deposited at ~ 400°C using d.c. glow discharges in SiH_4 and the appropriate doping gases. The phosphorous and boron concentrations in the cell are ~ 3.5 X and ~ 1.3 X their respective concentrations

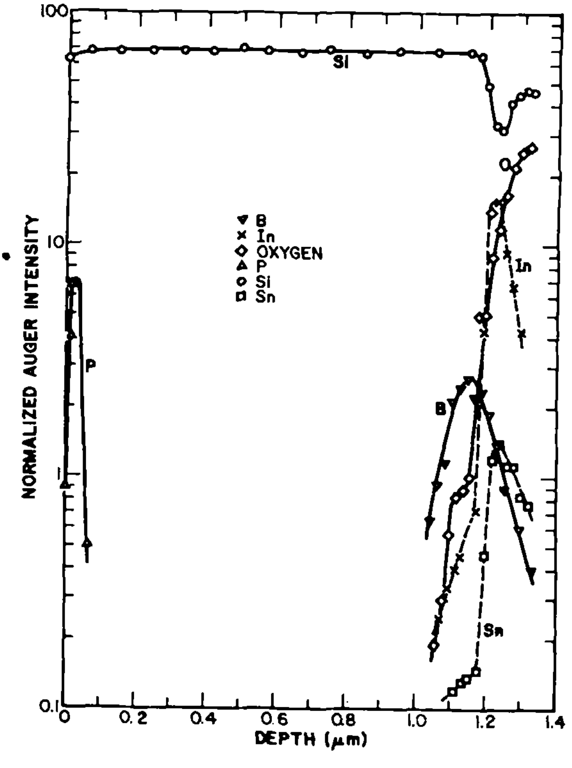

Fig. 1. Compositional profile of p-i-n cell #4-1.

in the discharge atmosphere indicating more rapid deposition rates relative to Si. The data in Figure 1 show that some autodoping of the a-Si does occur and that oxygen appears to diffuse more rapidly than In or Sn (from the ITO film). The boron-doped layer of this cell (#4-1) is ~ 0.15 μm thick as compared to ~ 0.03 μm for the cell reported on in Reference (1).

The illuminated I-V characteristic of this cell (#4-1) is shown in Figure 2. For light comparable to AM1 sunlight (~ 100 mw/cm^2), the open-circuit photovoltage (V_{OC}) was 790 mV while the short-circuit photocurrent (J_{SC}) was 4.8 ma/cm^2 and the fill factor (FF) was 0.39. This value of V_{OC} is the highest observed to date although the conversion efficiency of 1.5% is lower than has been observed in other p-i-n cells (1). The large value of V_{OC} appears to be due to the use of a relatively thick p-layer.

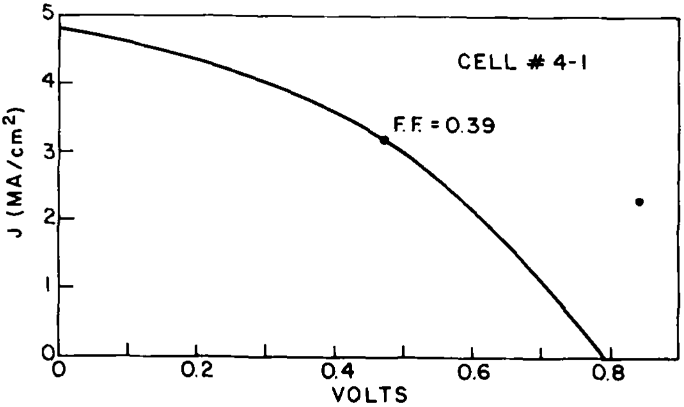

Fig. 2. Illuminated I-V characteristic of p-i-n cell #4-1.

Figure 3 shows the collection efficiency for light incident on the p-layer (through the glass coated with ITO) and for light incident on the n-layer (through semi-transparent Al). The decrease in the collection efficiency for $\lambda \lesssim 0.6$ μm is attributed mainly to recombination of the photogenerated carriers in the doped layers. The data

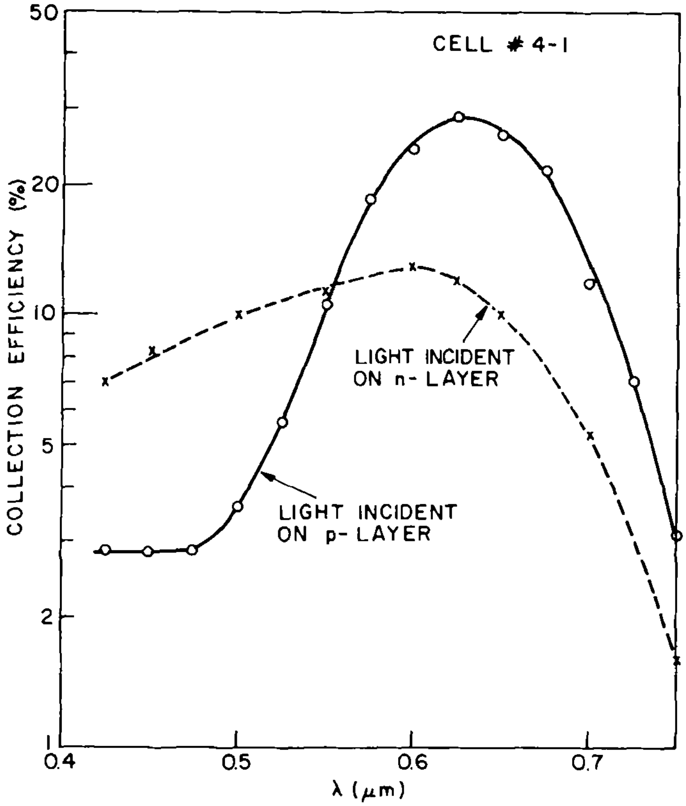

Fig. 3. Collection efficiencies as a function of wavelength for p-i-n cell #4-1.

indicate that recombination effects are more severe in the p-layer than in the n-layer of this cell. However, J_{sc} was larger for the light incident on the p-layer due to the greater average transmission into the cell through the glass and ITO (the average transmission through the Aℓ electrode was estimated to be ~ 30%). In general, J_{sc} decreases as the thickness of the front doped layer increases. However, decreasing the thickness can cause V_{oc} to drop. The best p-i-n cells were obtained with an optimized thickness of ~ 0.03 μm for the p-layer (1).

The dark I-V data for the same cell (#4-1) are shown in Figure 4. Using the expression,

$$J = J_o \left[\exp \left(\frac{eV}{\beta kT} \right) - 1 \right], \tag{1}$$

for the current density in forward bias, the diode quality factor (β) is ~ 2.3 indicating that the currents may be recombination limited. In far forward bias ($\gtrsim$ 1.0 V), the dark I-V data often exhibit a linear series resistance regime before going into a space-charge-limited regime (where $J \propto V^n$, and n is ~ 3). The dark series resistance of cell #4-1 was ~ 20 Ω-cm and this decreased to ~ 14 Ω-cm^2 when illuminated due to a photoconductive effect in the quasi-neutral region (see below).

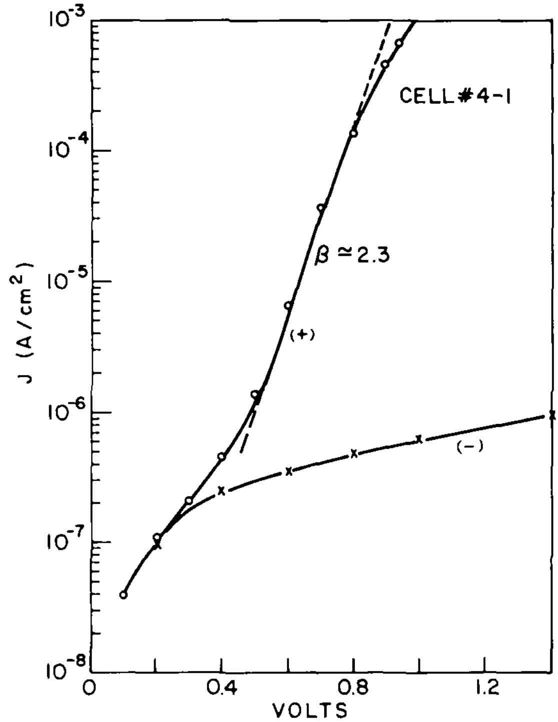

Fig. 4. Dark I-V characteristic of p-i-n cell #4-1.

A further reduction in the series resistance was obtained by depositing a thin semitransparent layer of Cr (~ 20-50 Å) on top of the ITO prior to the a-Si deposition. An effective series resistance may exist at the a-Si (p-type)/ITO (n-type) heterojunction, or possibly a thin resistive oxide layer forms near the interface (see Figure 1).

Capacitance-voltage data, measured at a frequency of 100 Hz, is presented in Figure 5 for a p-i-n device with a thin Cr film next to the p-layer. From the slope of $1/C^2$ versus V, the space charge density of the undoped layer is estimated to be ~ 5 x $10^{15}/cm^3$, which corresponds to zero bias depletion width of ~ 0.55 μm in the dark (8). The saturation of the capacitance at -0.3 V indicates that the space charge density of 5 x $10^{15}/cm^3$ exists over ~ 0.6 μm. Since the thickness of the undoped layer was ~ 0.8 μm, the difference may be due to the diffusion of boron into the undoped layer during deposition. The intercept of the $1/C^2$ versus V plot gives a built-in potential (V_0) of ~ 1.1 V. This value is close to the energy difference between the Fermi levels in the n- and p-regions as determined from resistivity-temperature measurements on doped films.

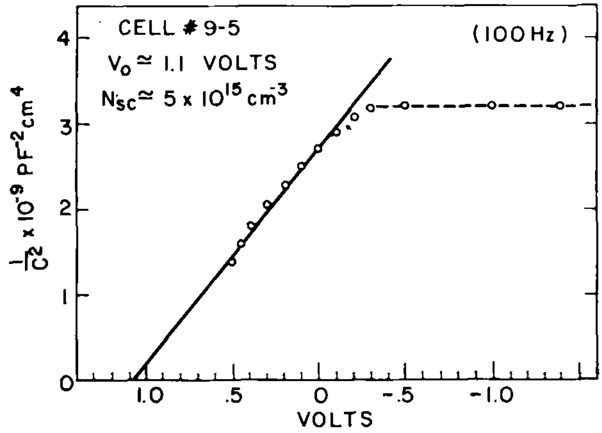

Fig. 5. $1/C^2$ as a function of voltage for p-i-n cell #9-5.

All cells showed a linear dependence of J_{sc} on light intensity over the investigated range of 10^{-4} to 1 sun. Also, over the same range, V_{oc} obeyed the relationship

$$V_{oc} = \frac{\beta' kT}{e} \ln \left(\frac{J_{sc}}{J_o} + 1 \right) \qquad (2)$$

where J_o is the saturation current density and β' is typically ~ 1.5.

Schottky Barrier Cells

The Schottky barrier cells were fabricated by first depositing a phosphorous-doped layer of a-Si on a stainless steel substrate. The doped layer was usually deposited at a substrate temperature of ~ 400°C and was several hundred angstroms thick. Then an undoped layer of a-Si was deposited at ~ 350°C to a thickness in the range of 0.3 to 1.0 µm. The Schottky barrier was formed by the electron-beam evaporation of a Pt film to a thickness of 50-100 Å (electrode areas were 5×10^{-3} to 2×10^{-2} cm^2). An antireflection (AR) coating was subsequently deposited by either electron-beam evaporation of ZrO_2 or by glow discharge deposition of Si_3N_4.

Figure 6 shows the I-V characteristic of an a-Si Schottky barrier cell in light comparable to AM1 sunlight.

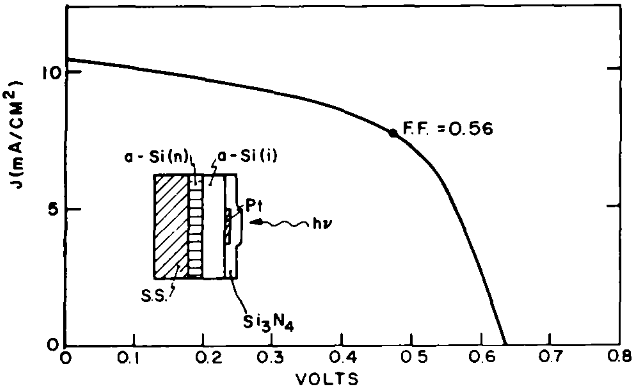

Fig. 6. Illuminated I-V characteristic of a Pt Schottky barrier cell.

This cell was fabricated in a d.c. discharge and exhibited a power conversion efficiency of 4.0%. Comparable efficiencies have been obtained in cells fabricated in r.f. discharges. The largest value of V_{oc} observed to date in a Schottky barrier cell is 765 mV while the best value of J_{sc} is ~ 12 ma/cm^2. The best fill factor obtained so far is ~ 0.61 in sunlight, but values as high as 0.70 have been obtained using only the blue portion of the solar spectrum (J_{sc} ~ 0.4 ma/cm^2). Since blue light generates electron-hole pairs only near the surface, the holes are readily swept out of the a-Si to the Schottky barrier electrode by the large field near the surface. The lower values of FF observed in unfiltered sunlight indicate that some of the holes are being trapped near the back of the cell.

Figure 7 shows the collection efficiency for two Schottky barrier cells, one with an AR coating (curve A) and one without an AR coating (curve B). As shown by curve B, the response of the Schottky barrier cell is relatively

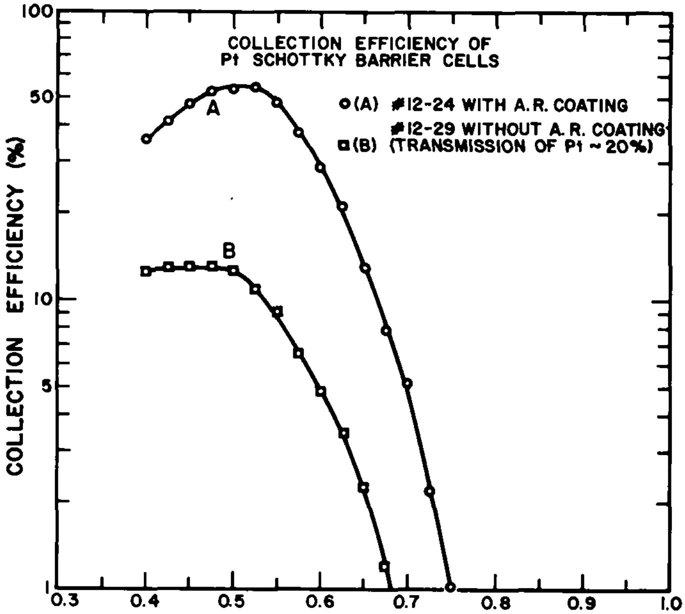

Fig. 7. Collection efficiency as a function of wavelength for two Pt/a-Si Schottky barrier cells.

flat for $\lambda < 0.5$ µm, and the conversion efficiency approaches 100% after correcting reflection and transmission losses due to the Pt. The high collection efficiency at short wavelengths is in contrast to the p-i-n cells where recombination in the top doped layer causes the collection efficiency to decrease for $\lambda < 0.55$ µm. The drop-off in the blue for curve A of Figure 7 is due to the AR layer. The decrease at long wavelengths is caused by the drop-off in the absorption coefficient (1) and the trapping of holes near the back of the cell.

The a-Si Schottky barrier cells are excellent diodes in the dark with diode quality factors close to unity (4). Thus, these cells exhibit near-ideal diode behavior and are not limited by recombination effects as in the case of p-n and p-i-n devices (9,1). Since the depletion widths of the Schottky barrier cells are ~ 0.2-0.3 µm (4), most of the series resistance (R_S) can be attributed to the resistance of the quasi-neutral region. Undoped a-Si exhibits a large photoconductive effect when deposited at ~ 350°C, and the resistivity (ρ) can decrease by several orders of magnitude when illuminated (10). For $\rho \sim 10^4$ Ω-cm and a cell thickness of ~ 1 µm, $R_S A = \rho d \approx 1.0$ $\Omega\text{-cm}^2$ which is close to the observed value in sunlight.

The barrier height (ϕ_B) for a Pt Schottky barrier on a-Si can be determined from the data shown in Figure 8. From Equation (2), $\beta' \simeq 1.15$ and $J_o \simeq 1 \times 10^{-12}$ A/cm^2 so $\phi_B \simeq 1.1$ eV using the diffusion theory for Schottky barrier rectification (4). For a Pt barrier formed on single crystal Si during the same evaporation, $\beta' \simeq 1.08$ and $J_o \simeq 3 \times 10^{-7}$ A/cm^2 so $\phi_B \simeq 0.81$ eV using the thermionic emission expression for J_o (11). Thus, the barrier height on a-Si is 0.3 eV higher than on single crystal Si. This is reflected in the larger value of V_{oc} observed in the a-Si cell (650 mV versus 290 mV for the single crystal Si cell).

Since the maximum efficiency has been estimated to be ~ 15% (1), we believe that further research will eventually lead to conversion efficiencies on the order of 10%. Thus, a-Si solar cells show great promise for low cost terrestrial applications.

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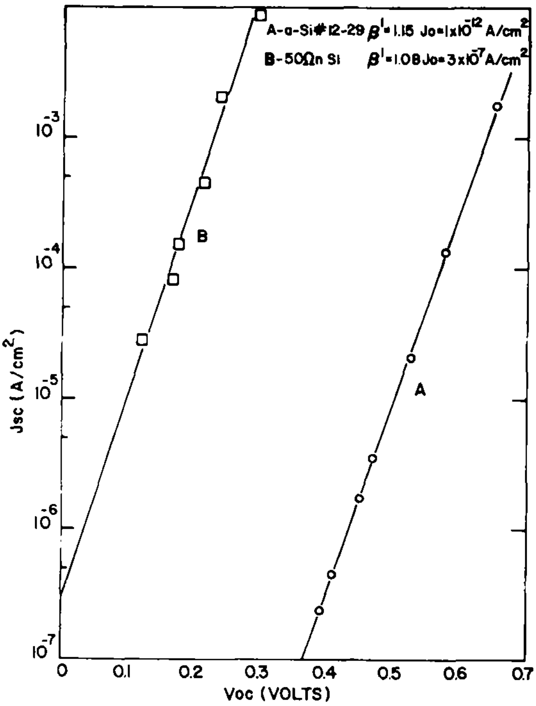

Fig. 8. Short-circuit photocurrent density as a function of open-circuit photovoltage for Pt Schottky barriers on a-Si (A) and single crystal Si (B).

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