Correlation of the Photoelectrochemistry of the Amorphous Hydrogenated Silicon/Methanol Interface with Bulk Semiconductor Properties

To cite this article: Chris M. Gronet et al 1984 J. Electrochem. Soc. 131 2873

View the article online for updates and enhancements.

You may also like

- Growth of Polycrystalline Zn$_{1-x}$Mg$_x$O Thin Films Using EtCp$_2$Mg and MeCp$_2$Mg by Metal Organic Chemical Vapor Deposition
  Yoshiyuki Chiba, Fanying Meng, Akira Yamada et al.

- Physisorption of an organometallic platinum complex on silica: an ab initio study
  Juan Shen, Kallappan Muthukumar, Harald O Jeschke et al.

- Coordination compounds of biogenic metals as cytotoxic agents in cancer therapy
  Dmitry A. Guk, Olga O. Krasnovskaya and Elena K. Beloglazkina

Investigate your battery materials under defined force!
The new PAT-Cell-Force, especially suitable for solid-state electrolytes!

- Battery test cell for force adjustment and measurement, 0 to 1500 Newton (0-5.9 MPa) at 18mm electrode diameter
- Additional monitoring of gas pressure and temperature

www.el-cell.com +49 (0) 40 79012 737 sales@el-cell.com
Correlation of the Photoelectrochemistry of the Amorphous Hydrogenated Silicon/Methanol Interface with Bulk Semiconductor Properties

Chris M. Gronet and Nathan S. Lewis*

Department of Chemistry, Stanford University, Stanford, California 94305

George W. Cogan, James F. Gibbons, and Garret R. Moddel

SERA Solar Corporation, Santa Clara, California 95054

Harold Wiesmann

Vactronic Laboratory Equipment, Inc., East Northport, New York 11731

ABSTRACT

Semiconductor/liquid junctions derived from 0.5 μm thick films of amorphous hydrogenated silicon, a-Si:H, have been investigated in CH₃OH solvent. The a-Si:H films consist of a weakly doped n-type layer over a 200 Å n⁺-a-Si:H layer on a stainless-steel substrate. The low series resistance and high ratio of minority carrier collection length to film thickness in this arrangement allows a study of the properties of semiconductor/liquid interfaces with minimal interference from bulk resistance losses. We find that a-Si:H anodes in 0.02M ferrocene, FeCp, 0.5 mM FeCp₂, 1.5M LiClO₄/CH₃OH solutions exhibit poor short-circuit quantum yields and low fill factors with 632.8 nm irradiation, but that these junctions display internal quantum yields of close to unity and high fill factors with short wavelength (λ < 450 nm) irradiation. Photons absorbed within a distance comparable to the minority carrier collection length are efficiently collected, and the fill factors and quantum yields under such conditions are insensitive to increases in photocurrent density over a range of 0.1-2 mA/cm². Solar-simulated irradiation (88 mW/cm²) from a ELH-type tungsten-halogen lamp in the a-Si:H/0.02M FeCp₂/0.5 mM FeCp₃/1.5M LiClO₄/CH₃OH system yields open-circuit photovoltages of 0.75-0.85V, short-circuit photocurrents of 6-7 mA/cm², and photoelectrode efficiencies for conversion of light to electricity of 2.7%-3.3%. Photovoltages with the acetylferrocene redox system are among the highest reported for any a-Si:H surface barrier system, and can exceed 0.85V under AM1 illumination conditions. Variation in the redox potential of the solution leads to changes in open-circuit photovoltage in accord with theory, and does not yield evidence for pinning of the a-Si:H Fermi level by interface states or artifacts of the semiconductor/liquid interface (13, 14). The observed photoelectrochemical behavior of these a-Si:H films is consistent with documented bulk transport and carrier collection properties of a-Si:H, and does not show evidence for series resistance losses, unusual spectral response characteristics, or recombination sites at the semiconductor/liquid junction. Manipulation of the electronic properties of the a-Si:H films can thus lead to improved energy conversion parameters and a clearer picture of the chemistry at the a-Si:H/liquid interface.

To elucidate the fundamental chemistry at the semiconductor/liquid interface, we have studied photocathodes having liquid contacts derived from nonaqueous solvents. Nonaqueous solvents largely circumvent the photocorrosion and photopassivation processes prevalent in aqueous solution (1-4), and thus provide media which are suitable for reproducible, controlled investigations of the semiconductor/liquid interface. Unfortunately, most semiconductor/liquid combinations in nonaqueous solvents have been reported to exhibit low solar energy conversion efficiencies and generally rather poor interface properties (3-9). The major cause of this behavior has been assigned to interface states at the semiconductor/liquid junction (10-14). These states can act as recombination sites, and thereby lead to low quantum efficiencies and fill factors. Also, these states may serve to pin the surface Fermi level and lead to less than ideal photovoltages at the semiconductor/liquid interface (13, 14).

Of major concern, however, must be the correct assignment of properties to the semiconductor/liquid interface as distinguished from those that are simply electronic properties of the semiconductor itself or artifacts of the method of measurement of current-voltage characteristics. Recent investigations on common semiconductor substrates, such as n-type Si (15) and n-type GaAs (16), have demonstrated that proper attention to bulk electrode properties and control of interfacial chemistry can lead to efficient nonaqueous semiconductor/liquid junc-
tion systems. We have thus turned our attention to thin film materials, such as amorphous hydrogenated silicon (a-Si:H), in an attempt to extend these principles to a wider class of semiconductor materials.

We report herein new data on the photoelectrochemistry of a-Si:H/liquid junctions in nonaqueous solvents. Notably, our results demonstrate that such interfaces exhibit little evidence of recombination sites at the semiconductor/liquid interface which would act to decrease the short-circuit quantum efficiency or to produce unusual wavelength response characteristics. We find that inefficiencies can be ascribed primarily to transport properties in the semiconductor material itself. Control of these parameters can thus lead to improvements in the properties of a-Si:H/liquid junctions. We observe that properly designed semiconductor/liquid combinations with a-Si:H can exhibit internal quantum yields for electron flow which are close to unity over a substantial portion of the solar spectrum. In addition, we observe open-circuit photovoltages and photocurrent efficiencies for conversion of visible light to electricity which are comparable to the best reported values for any surface barrier device fabricated with similar a-Si:H material. An important conclusion of our study is that substantial progress in improving the photocurrent response of a-Si:H/liquid junctions will require improvements in electronic properties of the bulk material itself rather than improvements in the properties of the semiconductor/liquid interface.

**Electronic Properties of a-Si:H**

Amorphous hydrogenated silicon, a-Si:H, has been the subject of intense study for application in terrestrial photovoltaic and photoelectrochemical devices (17-20). This material can be produced by a number of methods (21-23) which yield thin films which are either p-type, "intrinsic," or n-type. In contrast to single-crystal silicon, a-Si:H films possess a strong optical absorption resembling that of a direct gap semiconductor having a bandgap at 1.7 eV (25). The overlap of the absorption spectrum of a-Si:H with the solar spectrum, as well as the ease of deposition of the material itself, are attractive features of these films. An especially critical property in a-Si:H is the relatively short hole-diffusion length. Doping of the film has generally been found to decrease the hole-diffusion length substantially (25-26); thus the preferred structure for photoanode applications consists of a relatively thin, heavily doped n-type layer followed by a thicker "intrinsic" layer (usually weakly n-type), as shown in Scheme I.

Another important property of a-Si:H is that over 2 μm of the material is required to absorb essentially all visible light with energy greater than 1.7 eV. However, film thicknesses significantly below this value are employed in practical solar cells at present. This is because of the low value of the hole-diffusion length, which is typically 0.2-0.7 μm in intrinsic a-Si:H films of the highest quality currently available (27). Thicker films would absorb more light, but electron-hole pairs created at depths large compared to the collection length (at most the sum of the diffusion length and the depletion width) would not be collected and would recombine in the bulk material. Also, the increased series resistance of relatively thick a-Si:H films could produce poor fill factors. Thus, use of relatively thick films would require a detailed analysis of bulk-transport properties in order to isolate those features originating from the semiconductor/liquid interface.

In this study, we have employed 0.5-0.6 μm thick a-Si:H films which have been plasma deposited on a reflecting substrate, stainless steel. The film thickness is on the order of the minority-carrier collection length, Lc, and the reflection of light by the substrate provides an additional pass for light of long wavelengths, effecting increased carrier creation within a distance Lc of the interface. Series resistance losses due to excess bulk thickness have been

---

**Scheme I.** Left: Representation of the thin film a-Si:H photoelectrode structure. The contact to the stainless steel substrate is provided by a 200 Å thick n'-a-Si:H film, followed by a 0.5-0.6 μm thick layer doped weakly n-type. The situation will result in photoanode behavior qualitatively similar to conventional single-crystal photoanodes. Right: Interface energetics for two case of light intensities at a-Si:H/liquid interfaces. The collection length, Lc, is the sum of the minority carrier diffusion length, Lr, plus the depletion region thickness, W. Contraction of the depletion width in a-Si:H with increasing light intensity (-- --) leads to a decrease in Lc at a fixed voltage bias, and yields poor charge collection for light which penetrates deeply into the a-Si:H film. The fill factor and short-circuit quantum yield of these interfaces is thus sensitive to both the intensity and wavelength of light incident on the a-Si:H film.
minimized without sacrifice of light absorption within a distance $L_c$ of the surface. Our films provide an opportunity for detailed examination of the properties of the semiconductor/liquid junction. Information concerning the significance of recombination sites at the semiconducto-liquid interface has been obtained from suitable variations in incident light wavelength and intensity, as well as from photocurrent-voltage properties.

**Experimental**

Experimental techniques and procedures have been described previously (15). CH$_3$OH was distilled from Mg prior to use; no other precautions concerning exclusion of air or water were found necessary to obtain reproducible photocurrent-voltage characteristics. All current-voltage curves were obtained under potentiostatic control of the working electrode vs. a Pt reference electrode, and thus represent photoelectrode efficiencies which measure the properties of the a-Si:H photoanode. These values cannot be compared directly with two electrode solar cell efficiencies without actual fabrication of such devices.

The a-Si:H films were prepared by RF decomposition of silane, and were all prepared at HTP Products by H. Wiesmann. The stainless-steel substrate was maintained at 220°C, with a deposition rate of 1.5 Å/s. A 200Å thick n-doped layer was deposited from silane with 1% phosphine, and was then followed by a nominally intrinsic 0.5-0.6 μm layer of a-Si:H. Infrared absorption measurements indicate that film deposition under these conditions yields a-Si:H with 15% hydrogen content; thus the stoichiometry of our material does not differ substantially from samples used in previous liquid junction studies (9). Slight compositional differences between these samples and previous results (9) do not affect an interpretation of our results, because we obtained excellent agreement with previous data when our a-Si:H samples were tested under experimental conditions identical to those described in other studies.

Photoanodes were fabricated by bonding the stainless-steel substrate to a coil of Cu wire with Ag paint. Insulation from the liquid was obtained with ordinary epoxy resin. Typical photoelectrode areas exposed to the electrolyte were 0.1-0.4 cm$^2$. All electrodes were etched for 10s in 5% aqueous HF and washed with CH$_3$OH immediately before use. Reflectance spectra were obtained by use of spectral response apparatus previously described (15), with reflected light determined by a calibrated Si detector from United Detector Technologies, Incorporated. Spectral response and Schottky barrier measurements were performed using apparatus at SERA Solar, and all other data was collected at Stanford using techniques described previously (15, 16).

**Open-Circuit Photovoltage Measurements to Probe Interface Kinetics**

We have performed cyclic voltammetry and steady-state current-voltage experiments with outer-sphere redox couples in order to establish trends in photovoltages for the a-Si:H/CH$_3$OH interface. The data are summarized in Fig. 1, which indicates the photovoltages, $V_{oc}$ obtained for a-Si:H films in contact with various redox couples, $A'/A$. At sufficiently negative potentials, as in the cyclic voltammetry for (N,N'-dimethyl-4,4'-bipyridinium)$^{+/-}$ (Fig. 1a), we observe dark oxidations and dark reductions near the formal potential of the redox couple, indicating no appreciable photovoltage for this system (10). The (N,N'-dimethyl-4,4'-bipyridinium)$^{+/-}$ redox system does exhibit anodic photocurrent, and the photovoltage [as determined by the difference in anodic peak potential between an a-Si:H photoanode and a Pt electrode (3, 10)] is 0.2V under 100 mW/cm$^2$ of tungsten-halogen irradiation. The dark reductions at a-Si:H films have not been reported in other nonaqueous solvents, and indicate substantial room temperature dark conductivity in this particular sample of a-Si:H material (likely owing to tailing of phosphorus dopant into the intrinsic layer). Accurate values of the conduction band edge position would require measurement of the barrier height, not the photovoltage (28, 29); however, the data do allow us to conclude that $E_{cb}$ is more negative than -0.7V vs. SCE in CH$_3$OH solvent.

We have also employed steady-state photocurrent-voltage techniques to complement the cyclic voltammetry $V_{oc}$ measurements. All experiments were per-
formed with irradiation from a tungsten-halogen lamp, and the solutions contained sufficiently high concentrations of electroactive material to preclude significant photodecomposition processes on the time scale of the measurement. In each cell, the light intensity was adjusted to yield typical AM1 short-circuit photocurrent densities for a-Si:H of 6-7 mA/cm². Voc values obtained through a high impedance voltmeter or from the onset of anodic photocurrent in a steady-state current-voltage scan were in excellent agreement. We observe a linear dependence of Voc vs. E(A'/A) over a wide (1.0 V) potential range, with a slope of Voc vs. E(A'/A) of 1.0 ± 0.2 (Fig. 1b). The data are thus in accord with the ideal model for the semiconductor/liquid interface (30), and do not yield evidence for gap states which pin the surface Fermi level to yield a relatively low photovoltage. Voc values do seem to level off at very positive potentials, photoanodic decomposition processes prevented further variation in the solution potential. For A-acetyl ferrocene, the Voc of 0.88-0.91 V at light levels equivalent to 6-7 mA/cm² photocurrent densities for A = acetylferrocene are among the highest values of Voc reported for any a-Si:H surface barrier device (17, 18, 31).

Cyclic voltammetry measurements of a-Si:H anodes in C₂H₅OH solvent are reported to yield nonideal behavior of Voc vs. E(A'/A) (9). Photoanodic decomposition processes at low concentrations of redox couples and relatively high water content can lead to low values of Voc in cyclic voltammetric experiments, and this is responsible for the discrepancy between our new dependence of Voc vs. E(A'/A) and a previous study of a-Si:H in C₂H₅OH solvent. Our data indicate that measurements of the photocurrent-voltage characteristics of the a-Si:H/CH₃OH interface have yielded excellent agreement with previously reported data (9) in C₂H₅OH and yield similar data in CH₃OH solvent. However, a direct interpretation of these experiments is hindered by concurrent decomposition processes, as is evidenced by the disparity between cyclic voltammetric Voc (0.57 V) and steady-state Voc photocurrent-voltage data (0.75 V) for the ferrocene⁻⁻ system in previous studies (9).

The high concentrations of electroactive reagents and minimal faradaic currents in the direct open-circuit photovoltage determinations (Fig. 1) minimize these complications, and yield an internally consistent set of data which indicate a substantially different range of Voc vs. E(A'/A). Our new data also modify the basic interpretation of the causes of nonideality in the a-Si:H system. We note that a slope of only 0.42 for Voc vs. E(A'/A) has been found by cyclic voltammetry for a-Si:H ч C₂H₅OH (32). In addition, metal/semiconductor Schottky barriers with an a-Si:H have been reported to yield a slope of Voc vs. metal work function of 0.53 (23). This slope in Schottky systems has been attributed to the presence of interface states with a density of 10¹⁵ cm⁻² eV⁻¹ (33). Within this framework, it has been proposed (32) that the native a-Si:H surface oxide is the source of interface states, and that this oxide results in nonideal behavior at all of these a-Si:H interfaces. Our data (Fig. 1b) indicate ideal behavior [slope of Voc vs. E(A'/A) = 1.0 ± 0.2] for a-Si:H/CH₃OH interfaces, and demonstrate that systems consistent with the proposed suggestion, were not observed (9). In fact, exactly the opposite behavior was found, and 454.4 or 514.5 nm light gives lower observed quantum yields than 632.8 nm light. Furthermore, no improvements in fill factor were observed with white light irradiation as compared to 632.8 nm irradiation, and little or no improvement in efficiency was observed with shorter wavelength excitation sources.

In contrast, we observe here substantial improvements in the photocurrent-voltage characteristics of the semiconductor/liquid interface with decreases in the wavelength of the excitation light source. Our data indicate that measurements of the photocurrent-voltage properties at 514.5 nm can yield Voc values which are substantially higher than those at 632.8 nm. This is consistent with the observed decrease in short-circuit quantum efficiency and filling factor with decreasing wavelength (Fig. 2).

Table I. Photocurrent-voltage parameters vs. photon wavelength for the a-Si:H/CH₃OH interface

<table>
<thead>
<tr>
<th>λ (nm)</th>
<th>Input (nW/cm²)</th>
<th>Φ Voc</th>
<th>Voc</th>
<th>Vmax</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>632.8</td>
<td>5.46</td>
<td>0.18</td>
<td>0.69</td>
<td>0.54</td>
<td>3.4</td>
</tr>
<tr>
<td>632.8</td>
<td>11.9</td>
<td>0.16</td>
<td>0.73</td>
<td>0.56</td>
<td>3.2</td>
</tr>
<tr>
<td>632.8</td>
<td>25.1</td>
<td>0.27</td>
<td>0.86</td>
<td>0.57</td>
<td>3.2</td>
</tr>
<tr>
<td>514.5</td>
<td>1.96</td>
<td>0.46</td>
<td>0.84</td>
<td>0.50</td>
<td>6.8</td>
</tr>
<tr>
<td>514.5</td>
<td>3.27</td>
<td>0.57</td>
<td>0.86</td>
<td>0.35</td>
<td>7.6</td>
</tr>
<tr>
<td>514.5</td>
<td>5.30</td>
<td>0.44</td>
<td>0.88</td>
<td>0.52</td>
<td>7.1</td>
</tr>
</tbody>
</table>

* Input at 632.8 nm is from a beam expanded Ar ion laser; input at 514.5 nm is from a beam expanded He/Ne laser. 
* Quantum yield for electron flow at short circuit.
* Voltage at the maximum power point.
* Maximum energy conversion efficiency for monochromatic light corrected for reflectance losses at the a-Si:H/liquid interface. 
* Quantum yield for electron flow at short circuit.
* Efficiency at 632.8 nm is from a beam expanded Ar ion laser. 
* Efficiency at 514.5 nm is from a beam expanded He/Ne laser.
The improvements in our photocurrent-voltage responses with excitation by higher energy photons rule out both of these possibilities in our system. We find that our observations are consistent with the transport and absorption properties of a-Si:H, and we conclude that the behavior of a-Si:H/liquid junctions is dominated by these processes.

In a-Si:H films irradiated with sufficiently short wavelengths, such that the penetration depth $\alpha(k) = 1$ is on the order of 100 nm (24), as typically all of the photogenerated holes will be collected at the junction, resulting in high short-circuit quantum efficiencies. In addition, fill factors should be high, provided that series resistance losses from the use of excessively thick a-Si:H films and highly resistive electrolytes are minimal. As depicted in Fig. 2a, these expectations are in excellent agreement with the photocurrent-voltage characteristics for irradiation of the a-Si:H/CH$_3$OH/FeCp$_2$/FeCp$_2$ interface with light of wavelength $<450$ nm.

The situation for 632.8 nm excitation is substantially different. The $\alpha(k) = 1$ in a-Si:H of 632.8 nm light is typically 1-2 $\mu$m (24); thus, low quantum efficiencies should be expected, since only a fraction of the carriers will be created within a collection length of the interface. Use of material with thicknesses greater than $L_c$ may lead to increased light absorption, but will not necessarily produce substantial increases in photocurrent flow. Quantum yields with 632.8 nm light are rather modest, and therefore fill factors, which do not degrade even at photocurrent densities threefold higher than the onset of decline with the $\lambda > 600$ nm light. (Fig. 2b, Table I), and we conclude that increases in quantum efficiency at this wavelength will require fabrication of material with larger collection lengths, rather than passivation of surface states.

We have noted above that the fill factor at a specific photocurrent density is dependent on the wavelength of the incident photons (31). This can be understood by considering the factors which determine the fill factor of a semiconducting/liquid junction, with emphasis upon the particular electronic properties of a-Si:H. The hole-collection length usually is the depletion width, $W$, plus the diffusion length, $L_d$; thus, only holes produced at depths comparable to $L_d + W$ will diffuse to the depletion region where the built-in field can sweep them to the junction. a-Si:H differs from its crystalline counterparts in that $L_d$ is on the order of, and sometimes less than, $W$ (25-29). Application of an external potential to bias the cell from open circuit to short circuit will serve to increase the field-assisted drift, and thus will lead to collection lengths, and hence photocurrents, which are a strong function of applied voltage. Additionally, in a-Si:H, $L_c$ is known to decrease with increasing light intensity, due to a contraction of the depletion region under illumination (38). Thus, the fill factor should be dependent upon both the light intensity and the penetration depth of the light as compared to $L_d + W$ with shorter wavelengths of light yielding improved photocurrent-voltage characteristics (Fig. 2, 3; Table I).

Clearly, a complete description of the a-Si:H/liquid interface must take these bulk effects into account in order to interpret the photocurrent-voltage data. Quantitative descriptions of the light intensity and potential dependence of the fill factors are being developed, and should yield information concerning carrier transport in a-Si:H similar to that produced by the photovoltage technique. The stability of a-Si:H films in the nonaqueous FeCp$_2$/FeCp$_2$/CH$_3$OH solvent should provide a distinct advantage over the aqueous redox system presently used for these surface photovoltage measurements (38). In this regard, the study of liquid junctions may aid in developing improved techniques for characterizing a-Si:H films, as well as a-Si:H interface properties.

In our discussion of collection lengths, we have implicitly assumed that the hole mobility is sufficiently large that all carriers created in the depletion region are collected. Under this condition, $I_c = 1.0 - W$. However, if the hole mobility is sufficiently small, drift alone will dictate the collection length, and $L_d$ may then only be a fraction of $W$. Our data can be accommodated within the framework of either of these two conditions.

**Fig. 2.** Photocurrent-voltage properties of a-Si:H films (0.35 cm$^2$) in contact with stirred 10 mM FeCp$_2$/0.5 mM FeCp$_2$/1.0M LiClO$_4$ in 
CH$_3$OH solution. The optical path length through the solution is 2 mm. The photocurrent-voltage curves are scanned at 50 mV/s, and potentials were measured vs. a Pt reference electrode poised at the cell potential through a 0.2 mm Al Luggin capillary. (a) Photocurrent-voltage properties with irradiation of $\lambda < 450$ nm obtained from a 200W Hg lamp equipped with a short pass filter. Curves b and c were obtained with neutral density filters transmitting 50% and 25% of the light intensity available in curve a. (b) Photocurrent-voltage properties under identical cell conditions as in Fig. 2a, but irradiation is for $\lambda > 600$ nm from a ELH-type tungsten halogen lamp equipped with a 600 nm long pass colored-glass filter. Curves c and d were obtained with 50% and 25% transmittance neutral density filters from the irradiation in curve b. curve a has the light intensity adjusted to provide similar photocurrent density to curve a in Fig. 2a. Note the pronounced decline in fill factor in Fig. 2b relative to the collection properties displayed in Fig. 2a.
Spectral Response Characteristics of a-Si:H/Liquid Junctions

The spectral response of short-circuit photocurrent vs. photon wavelength lends further credence to the notion that the electronic properties of a-Si:H dominate the photovoltaic behavior. The spectral response data for a-Si:H/CH$_3$OH of 5.0 mM FeCp$_2$/0.5 mM FeCp$_2$ are depicted in Fig. 3. In addition, a reflectivity spectrum of a similar a-Si:H film on a substrate of Pd-coated single-crystal silicon is displayed for reference in Fig. 3b. The spectral response data have been obtained at short-circuit conditions (1 mm optical path length through the solution), with an average light intensity of 1 mW/cm$^2$. As discussed above, the quantum yields obtained for long wavelength excitation at these light intensities will be somewhat higher than differential quantum yields under solar photon fluxes. The measurement in Fig. 3a is based upon light incident upon the photovoltaic cell, and is not corrected for solution absorption or optical reflection losses. For excitation with short-wavelength photons, we observe high quantum yields for electron flow, >0.50. Reference to the reflectivity spectrum at the a-Si:H/air interface (Fig. 3b) indicates that the effective index of refraction of this a-Si:H film at 450 nm is 4.8 (39). Using a value for the index of refraction of 1.0 M LiClO$_4$/CH$_3$OH of 1.35 (40), we calculate that reflective losses from the air/glass/solvent/a-Si:H interfaces will amount to approximately 30% of the incident light. Thus, quantum yields corrected for reflection are greater than 0.8, and would approach unity if corrections for solution absorption were also included.

The effect of small carrier collection lengths in a-Si:H is demonstrated by a comparison of the spectral response curves in the 600-700 nm region to the reflectivity data. In this wavelength region, the absence of interference fringes and the known increase in absorption coefficient with wavelength indicate increasing absorption by the a-Si:H film; however, in the same wavelength region, the short-circuit quantum yield declines noticeably. Long wavelength photons penetrate too deeply into the film to be efficiently collected because of the modest collection lengths of these particular samples of a-Si:H. Thus, low short-circuit quantum yields and low fill factors for excitation of a-Si:H with 632.8 nm light do not necessarily result from recombination sites at the semiconductor/liquid interface, but can be assigned to carrier transport and optical-absorption properties of the material itself.

We note that typical p-i-n solid-state devices show a decline in short-circuit quantum efficiency with short-wavelength excitation because of high recombination rates in the doped layers near the surface (23). However, liquid junctions should benefit from the efficient collection of carriers generated near the interface, and need not possess the surface dead layer present in p-i-n-type systems. In addition, a liquid junction may not exhibit metal/semiconductor interfacial stress, which can induce recombination sites and cause declines in the spectral response for short-wavelength excitation. Ideal semiconductor/liquid junctions should not show a decline in short-circuit quantum efficiency with high energy excitation unless bulk resistivity effects influence majority-carrier collection. Previous investigations of n-i-a-Si:H films in C$_2$H$_5$OH/FeCp$_2$ liquid junctions indicate that the short-circuit quantum yield decreases when the excitation wavelength is changed from 632.8 nm to 514 or 454 nm (9). Recent work on p-i type a-Si:H films in liquid junctions also reveals this effect, and the assumption of low series resistance in these films has led to the suggestion that a decline in short-wavelength response is an intrinsic property of the a-Si:H/liquid interface (32). Different preparations of a-Si:H films could produce different interface properties; however, reference to the spectral response characteristics in Fig. 3 demonstrates that a-Si:H/liquid junctions can exhibit internal quantum yields near unity, and that a decline in spectral response characteristics at short wavelengths is not apparent with our a-Si:H samples under these conditions.

Excessive series resistance losses, especially for majority carriers in p-i a-Si:H films, can lead to decreases in short-circuit quantum yield at short-excitation wavelengths. With excitation of $\lambda < 500$ nm, we can assign reduced quantum efficiencies in our low resistance n-i-a-Si:H films to solution absorption of light, and not to recombination at the semiconductor/liquid interface or to the a-Si:H material itself. Figure 4 depicts the spectral response parameters of a-Si:H films as a function of the concentration of FeCp$_2$ in C$_2$H$_5$OH solvent. We observe that the quantum yield declines severely at short wavelengths, owing to excessive solution absorption, even at relatively modest levels of FeCp$_2$, and with relatively short optical path lengths through the solution (0.5-1.0 mm). Addition of small amounts of the highly absorbing FeCp$_2$ makes the effect more pronounced. Absorption spectra indicate that 0.070 M FeCp$_2$ in C$_2$H$_5$OH in a 2.0 mm thickness absorbs 43% of the light at 514 nm and 97% at 454 nm, and that accurate quantum yields based on photons incident on the a-Si:H electrode surface in these solutions would require extremely short path lengths. Minimization of these losses does not yield evidence for low quantum efficiencies, and yields improved behavior for the a-Si:H/liquid junctions.

Efficiency Parameters for the a-Si:H/FeCp$_2$/FeCp$_2$'/CH$_3$OH System

The photocurrent-voltage characteristics under simulated solar illumination of a-Si:H films in 20.0 mM FeCp$_2$/0.5 mM FeCp$_2$'/1.5M LiClO$_4$/CH$_3$OH are depicted in Fig. 5. Even with the relatively poor long wavelength response of our particular a-Si:H samples and substantial solution absorption for $\lambda < 500$ nm, at 88 mW/cm$^2$ of ELH-type tungsten-halogen irradiation, we observe a short-circuit photocurrent density of 7.8 mA/cm$^2$. Under these conditions...
concentration is 0.5 molar. In curve (b), 13.3 mM FeCp2 is present, in (c) 25.4 mM FeCp2, in (d) 43.4 mM FeCp2, and (e) contains 40.0 mM FeCp2 with 2.0 mM FeCp+ in solution.

conditions, we observe open-circuit photovoltages of 0.75-0.85V and fill factors of 0.5-0.6, with typical photodetector efficiencies for conversion of optical energy to electricity of 2.7%-3.3%. On identical samples of a-Si:H, Schottky barriers fabricated with nominally 50 Å thick Pt films yield short-circuit currents of 5-7 mA/cm² and efficiencies of 1%-2%. We attribute the variation in short-circuit current to differences in transmittance of Schottky barriers and liquid junctions, while the lower efficiency of the Schottky contacts arises from a lower Voc. Open-circuit photovoltages on the best surface barrier-type systems, and would compare favorably to the highest efficiencies obtained for single-crystal silicon semiconductor/liquid junctions under solar conditions (15). It would thus appear that the a-Si:H/liquid interface is not the limiting factor in development of efficient a-Si:H/liquid junctions, but that control and improvement of the electronic properties of the a-Si:H films are the dominant factors at present.

The high quality of the a-Si:H/liquid interface observed in this study is consistent with other recent descriptions of photodetectors in nonaqueous solvents (15, 16, 34), and implies that systematic design and study of efficient photocathodic electronic systems in nonaqueous solvents may be possible with a variety of materials. We have demonstrated that a-Si:H/CH3OH/FeCp2/FeCp+2 junctions can exhibit high quantum efficiencies for electron flow, large photovoltages, and excellent photocurrent-voltage characteristics under the proper conditions. Successes with properly prepared single-crystal photocathodic substrates strongly suggest that future challenges in the area will arise from the chemistry of grain boundaries and recombination sites in polycrystalline materials at liquid junctions, where the unique chemistry at semiconductor/liquid interfaces should allow manipulation of recombination sites through simple chemical processes.

Acknowledgment

We thank L. Christel of SERA Solar Corporation for valuable discussions and supply of computer programs, and Jeff Marks of Stanford University for the use of the arc lamp source. We also thank Professor M. S. Wrighton of MIT for generously supplying a preprint describing work on p-i-a-Si:H.

Manuscript submitted Oct. 26, 1983; revised manuscript received Nov. 4, 1983.

REFERENCES

ABSTRACT

The MeOH/0.1M NaClO$_4$/Pt system is investigated in aerated and deaerated medium, by analyzing the I(t) output signals for a single gating input potential signal [SII(t)] and for a sequence of two isochronic gating input signals [DII(t)] separated by a varying time \( \Delta t \) in open circuit, under the same conditions (\( U = +750 \text{ mV/SCE} \); \( \omega = 12.5 \text{ rps} \); \( \theta = 25^\circ \text{C} \)). Measurements performed with undistilled solvent have indeed shown blockage occurring due to an increase in the rate of oxygen adsorption on the Pt electrode, which is known to exist in methanol oxidation (number and nonrandom distribution, at the atomic level, of the active sites), as was shown for metal systems (titanium or iron) in sulfuric acid (7, 8). To our knowledge, the role of dissolved oxygen on the behavior of the electrode in methanol has not previously been investigated; only deaerated media have been considered. We study here the response of a rotating disk electrode to a potential pulse input. This response depends on the interface topography, i.e., on parameters inherent in the electrode itself (nature, structure, shape, pretreatment etc.), on parameters inherent in the medium (concentration, temperature, viscosity, hydrodynamic conditions, diffusion phenomena, etc.), and on the type of reaction mechanisms taking place at the interface (8, 9).

Experimental

The supporting electrolyte (0.1M) was sodium perchlorate (Merck proanalysis), dried at 150°C under vacuum. Methanol (Baker Absolute) was distilled over Prolabo 99.8% magnesium turnings in order to eliminate water and metallic impurities. Measurements performed with undistilled solvent have indeed shown blockage occurring.