n-Type silicon photoelectrochemistry in methanol: Design of a 10.1% efficient semiconductor/liquid junction solar cell

(solar energy conversion/nonaqueous silicon photoanodes)

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Communicated by James P. Collman, November 22, 1982

ABSTRACT n-Type Si electrodes in MeOH solvent with 0.2 M (1-hydroxyethyl)ferrocene, 0.5 mM (1-hydroxyethyl)ferricenium, and 1.0 M LiClO₄ exhibit air mass 2 conversion efficiencies of 10.1% for optical energy into electricity. We observe open-circuit voltages of 0.53 V and short-circuit quantum efficiencies for electron flow of nearly unity. The fill factor of the cell does not decline significantly with increases in light intensity, indicating substantial reduction in efficiency losses in MeOH solvent compared to previous nonaqueous n-Si systems. Matte etch texturing of the Si surface decreases surface reflectivity and increases photocurrent by 50% compared to shiny, polished Si samples. The high values of the open-circuit voltage observed are consistent with the presence of a thin oxide layer, as in a Schottky metal-insulator-semiconductor device, which yields decreased surface recombination and increased values of open-circuit voltage and short-circuit current. The n-Si system was shown to provide sustained photocurrent at air mass 2 levels (20 mA/cm²) for charge through the interface of >2,000 C/cm². The n-Si/MeOH system represents a liquid junction cell that has exceeded the 10% barrier for conversion of optical energy into electricity.

Nonaqueous solvent systems have been shown to be useful in suppressing electrode corrosion or passivation processes at semiconductor photoanodes (1–4). However, the efficiencies of most systems under solar irradiation conditions generally have been modest (<6%). This has been ascribed to the presence of states at the liquid/solid interface that act as recombination centers and can seriously limit the efficiency of such systems (4–7). Thus, although the use of nonaqueous solvents may improve the cell stability, such systems may not be useful unless they can be designed to produce acceptable conversion efficiencies under solar irradiation conditions.

In particular, n-type Si cells in ethanol are estimated to yield about 1% efficiency for conversion of sunlight into electricity (5). Because the bulk properties of the materials studied are essentially identical to those used in high-efficiency solid-state solar cells, we reasoned that the primary source of inefficiency in nonaqueous systems must be at the semiconductor/liquid interface. We therefore attempted to exploit chemical treatments that would be effective in changing the chemical and electronic nature of these interface states. We describe herein the results of such experiments, which have resulted in a 10-fold increase in the conversion efficiency of n-Si electrodes in nonaqueous solvents. Notably, our cells consistently yield 10.1% efficiency for conversion of light to electricity under air mass 2 (AM2) solar conditions—a Si-based liquid junction cell that is in excess of the 10% barrier for conversion of optical energy into electricity.

The interface energetics for an ideal semiconductor/liquid interface (8) at charge transfer equilibrium are presented in Fig.

1a. The presence of a depletion layer in the semiconductor results in the separation of photogenerated electron-hole pairs, with the electrons being driven into the bulk and the holes migrating to the solid/liquid interface. These holes are then consumed by a solution reductant, resulting in a flow of current. The voltage difference between the energy at the edge of the semiconductor conduction band and the redox potential of the solution determines the barrier height of the device. Fig. 1b depicts a possible situation for the interface energetics when recombination sites are present at the surface (9). Here, the fill factor and short-circuit quantum yield may be lower than optimal due to the presence of these states at the interface. Thus, one method of improving the efficiency of a given semiconductor/liquid junction may be to treat chemically the surface in order to eliminate the deleterious recombination sites.

Another commonly appreciated difficulty in surface barrier devices such as Schottky cells and solid/liquid junction cells is the large value of dark current arising from thermionic emission of carriers at the interface (10, 11). This large dark current leads to values of the open-circuit voltage (V_{oc}) at typical solar intensities which differ substantially from the barrier height of these types of devices. For example, for an ideal Si/Au Schottky barrier with a barrier height of 0.8 V, it can be shown that V_{oc} under AM1 conditions will be only 0.3 V (12). Clearly, methods of raising the values of V_{oc} in such systems would be highly desirable. A technique used in Schottky systems is to introduce a thin interfacial layer of oxide, creating a metal-insulator-semiconductor (MIS) type cell. This procedure can drastically reduce the dark bucking current (10, 12–16) and thus increase the V_{oc} and efficiency of these devices.

We have applied these concepts to the n-Si/liquid electrolyte system. The silicon surface in our studies has a native oxide after etching and exposure to atmosphere (17). The rectifying properties of this oxide should be sensitive to the etching procedure, liquid solvent, and other such factors. We find that n-Si photoelectrodes in MeOH solvent exhibit the high V_{oc} values and efficiencies characteristic of MIS devices, with no evidence of the declining fill factors or the poor quantum yields that have been observed in previous studies of n-Si junctions in nonaqueous solvents.

EXPERIMENTAL

The silicon electrodes were fashioned from polished wafers of 1.3–1.7 ohm·cm resistivity, phosphorus-doped, (100) oriented, single-crystal material obtained from Monsanto. Typical electrodes consisted of squares 4.0 mm on each side, which were rubbed on the unpolished side with Ga-In eutectic to form an

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Abbreviations: AM, air mass; V_{oc} , open-circuit voltage; SCE, standard calomel electrode; MIS, metal-insulator-semiconductor.

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FIG. 1. (a) Interfacial energetics at equilibrium for an ideal n-type semiconductor/liquid junction. The electric field in the semiconductor promotes spatial separation of photogenerated holes and electrons, providing for net current flow. (b) Interfacial energetics for a particular distribution of surface states at an n-type semiconductor/liquid junction. Photogenerated carriers are separated as in a; however, the presence of intermediate levels can promote recombination. This may lead to loss of photocurrent and photovoltage and may result in inefficient conversion of light into electricity.

ohmic contact (15). The electrode was then attached to a coil of Cu wire with Ag paint, and the Cu wire was passed through a glass tube to provide insulation from the solution. The exposed Cu and Ag were then sealed with ordinary epoxy cement to expose only the Si to the electrolyte solution. Shiny electrode surfaces were obtained by etching in concentrated (48%) aqueous HF for 20 sec followed by a MeOH rinse. Matte electrode surfaces were prepared by exposing unmounted Si to solar cell etchant type 200 (Transene, Rowley, MA) for 60 min at 80°C and were then mounted as for shiny surfaces. The matte electrodes were etched with 48% HF and rinsed with MeOH immediately before use.

Methanol was Baker reagent grade, and was distilled under nitrogen from Mg powder immediately before use. Dried solvent was obtained by storage over activated Linde 3A molecular sieves for 48 hr after distillation from Mg. LiClO₄ was obtained from Alfa-Ventron (Danvers, MA) and was used as received for most experiments. Dry LiClO₄ was obtained by fusion of this "anhydrous" LiClO₄ at 350°C for 24 hr under reduced pressure (0.01 mm Hg) and was stored in a dry box (Vacuum Atmospheres, Los Angeles) until used.

(1-Hydroxy)ethylferrocene, I, was prepared by reduction of acetylferrocene (Aldrich) with LiAlH₄ (18) and was dried *in vacuo* and stored under nitrogen until used. The ferricenium salt of this derivative was prepared by electrochemical oxidation in MeOH at +0.7 V [referenced to standard calomel electrode (SCE)] at a large-area Pt electrode.

Potential control was accomplished with a Princeton Applied Research model 363 potentiostat equipped with a model 175 voltage programmer. Traces were recorded on a Houston Instruments model 2000 X-Y recorder, and current-time measurements were recorded with a Linear model 555 strip chart recorder. A Luggin probe was fashioned from a borosilicate glass pipette and had a measured outer diameter of 0.2 mm. The reference electrode was an aqueous SCE and was connected to the cell via a salt bridge (1.0 M LiClO₄ in MeOH) to the Luggin probe. For stability experiments, this SCE was replaced with a Pt wire reference electrode connected directly into the cell compartment. The counterelectrode in all experiments was a large-area (>5 cm²) Pt electrode.

Conductivity measurements were performed with an Altex conductivity bridge at a frequency of 1.0 kHz. The cell constant was calibrated to be 1.01 and was verified by use of standard

solutions of aqueous KCl. The conductivity of 1.0 M LiClO₄ in MeOH solution was measured to be 38 mmho/cm. This contrasts with that of 0.1 M (n-Bu₄N) ClO₄ in EtOH, which is approximately an order of magnitude lower. The uncompensated ohmic resistance (≈50 ohms) present in our cell design in MeOH has not been eliminated or compensated for instrumentally and thus makes our present efficiency measurements conservative by 10–15%. Also, although the experiments described in this manuscript were performed in a three-electrode configuration, we expect that efficiencies actually would be higher in a two-electrode device of optimized cell geometry due to less light absorption by the solution.

Light sources were a 5.0-mW polarized He/Ne laser (632.8 nm), an ELH-type tungsten halogen bulb with a ground glass diffuser, or an ENH-type bulb with a ground glass diffuser (for stability runs). Intensity calibration was performed routinely with a Solarex secondary standard Si cell and was periodically verified to be within 10% of the value measured with an Eppley thermopile detector. Laser intensities were measured with a Newport Research (Fountain Valley, CA) model 815 photometer. For equilibrium current/voltage measurements, the laser beam was expanded with a 5X beam diffuser and collimator from Aerotech (Pittsburgh). The light intensity was varied by rotation of a Hoya polarizer in the path of the polarized laser beam.

Spectral response curves were obtained with a computer-controlled system at SERA Solar Corp. (Santa Clara, CA). This apparatus consisted of a Spex 1670 Minimate monochromator with a range of 400 to 1,100 nm and provided an average intensity of 1 mW/cm². The beam was chopped at 13 Hz and was referenced to a Si detector (United Detector Technologies, Culver City, CA). Data acquisition and plotting were performed with a Hewlett-Packard 9826 computer.

RESULTS

Photocurrent–Voltage Curves. n-Type Si electrodes exhibited high conversion efficiencies for optical energy to electrical power when used in methanol solvent. Tungsten-halogen irradiation at 70 mW/cm² of a polished n-type Si electrode in solution in 0.2 M I⁻/0.5 M I⁺ in MeOH containing 1.0 M LiClO₄ resulted in 7.8% efficiency for conversion of polychromatic light to electricity (Fig. 2). In this cell, the photoanode produced I⁺ which was reduced at the counterelectrode. Thus, there was no net chemical change in the cell, and the work produced by the nonspontaneous flow of current through the cell could be harnessed through a resistive load. We observed V_{oc} of 0.53 V, short-circuit currents of 17 mA/cm², and fill factors of 0.60 under these conditions.

The current–voltage characteristics in Fig. 2 indicate that the Si/MeOH interface is substantially free of the deleterious effects of surface states that have been observed previously (5). A sensitive test for the presence of recombination centers is the variation of the short-circuit quantum yield with light intensity. Recombination sites should be the dominant pathway for electron-hole pairs at low light intensities and should become less important as they become saturated at higher fluxes of electron-hole pairs. This should be reflected in low quantum yields for electron flow at low incident light intensity and correspondingly higher values at higher irradiance levels. We observed high values (>0.6) of the short-circuit quantum yield, which were essentially independent of the incident light intensity. The calculated values of the quantum yield in Table 1 are based upon current flow per photon incident on the cell and do not take into account the substantial reflection of light by the Si electrode surface, beaker reflection, or absorption of the excitation light by I⁺ (λ_{max} = 623; ε = 450 M⁻¹cm⁻¹). When these factors were

FIG. 2. Current-voltage characteristics (50 mV/sec) of (100) oriented n-type Si electrodes in 1.0 M LiClO₄/MeOH with 0.2 M I⁻, 0.5 mM I⁺. The light intensity was 70 mW/cm² from a calibrated solar simulator ELH-type tungsten-halogen source. The solution was magnetically stirred, and the equilibrium redox potential of the solution was +0.185 V (vs. SCE) as measured at a Pt indicator electrode. Polished (---) refers to electrode surfaces subjected to a 30-sec 48% HF etch followed by a MeOH rinse. Matte (—) refers to textured surfaces. (Texturing leads to decreased surface reflectivity and yielded 10.1% efficiency for conversion of light to electricity at the maximum power point, when referenced to the equilibrium potential of the solution.)

minimized (see below), we routinely observed quantum yields for electron flow in excess of 0.8. The main point here is that the high values of the quantum yield and the independence of these values with increases in light intensity is consistent with the idea that surface recombination has been substantially reduced in these n-Si/MeOH systems.

Consistently, the fill factor of the n-Si/MeOH cell remained relatively high even at solar irradiation intensities. We examined the equilibrium current-voltage characteristics under monochromatic 632.8-nm irradiation and observed similar behavior. Fig. 3 shows a set of such curves for a typical Si electrode in a MeOH solution containing 0.2 M I⁻ and 1.0 mM I⁺. The solution was stirred, and we verified, with metal electrodes, that the stir rate and concentration of reductant were sufficiently high that none of the currents were limited by mass transport of reductant to the electrode surface. Detailed analysis of these

FIG. 3. Equilibrium photocurrent voltage curves for n-Si in 1.0 M LiClO₄/MeOH with 0.2 M I⁻ and 1.0 mM I⁺ added. The solution was stirred, and the light source was a 5.0-mW He/Ne laser at 632.8 nm.

current-voltage curves is given in Table 1. We observed V_{oc} values ranging from 440 mV at low light intensities up to 520 mV at the highest intensity used, 20 mW/cm², with efficiencies for conversion of monochromatic 632.8 nm light of 9–10%. We also observed fill factors that were nearly independent of the incident light intensity. This would seem to rule out significant contributions from recombination centers to decrease the photocurrent at the Si/MeOH interface over the intensity range studied. Notably, we observed no saturation in quantum efficiency, even at incident light intensities >100 mW/cm² from the tungsten-halogen light source.

Surface Texturing. The energy conversion efficiency of the n-Si/MeOH/I system can be improved from the 7.8% level by texturing the electrode surface in order to decrease reflectivity losses. It is possible to preferentially etch a (100) oriented surface and leave the (111) planes exposed, creating 1- to 3- μ m hillocks. When this procedure was performed on n-Si electrodes irradiated under AM2 conditions, we observed an increase in the photocurrent of $\approx 50\%$, leading to short-circuit currents of 25 mA/cm² at 70 mW/cm² (Fig. 2). A detailed examination of the effect of a similar surface etch on the behavior of n-Si anodes in ethanol has been reported (19). However, difficulty in reproducing the etch procedure was mentioned, and the highest increase in photocurrent observed was 20% at low light intensity with little or no effect at higher irradiance levels.

We have repeated our experiments several times, with sample sizes ranging from 0.1 cm² to >1.5 cm² and consistently obtained the improvements depicted in Fig. 2. With the Transene etchant, properly textured samples displayed a velvety black appearance to the naked eye; this required 60 min of etching with our solutions in order to develop 1- to 3- μ m pyramids. In addition, the textured etch left a substantially different oxide on the silicon than is produced with a HF etch. We observed little or no improvement of photocurrent with the texture etch unless the Si is exposed to a fresh 30-sec HF etch and MeOH rinse after the texturing procedure. The importance of formation of the proper oxide is discussed in detail below.

Photocurrent-Spectral Response. The spectral response (photocurrent as a function of the wavelength of incident light)

Table 1. Representative conversion efficiencies for optical energy into electricity for n-Si in MeOH

Input,* mW/cm ²	Φ_{sc}	V_{oc}	$V_{pmax}^{\dagger}$	$\eta,^{\ddagger}\%$
2.20	0.70	0.44	0.34	9.6
3.76	0.65	0.46	0.36	9.9
7.53	0.60	0.48	0.34	8.9
11.1	0.63	0.50	0.34	9.5
15.1	0.62	0.51	0.34	9.2
18.1	0.64	0.52	0.34	9.7

* Input is at 632.8 nm from a beam-expanded (2.6 mm diameter) He/Ne laser.

[†] Voltage at maximum power point.

[‡] Maximal energy conversion efficiency for monochromatic light to electricity uncorrected for cell reflection losses or solution absorption. The potential of the cell was measured as +0.16 V (vs. SCE). These data correspond to curves presented in Fig. 3.

of this Si/MeOH cell is shown in Fig. 4. The average light intensity was approximately 1 mW/cm^2 , and the 1-cm^2 electrode was maintained at short circuit versus a Pt foil counterelectrode at $+0.157 \text{ V}$ (vs. SCE). The error in this measurement is estimated to be $\pm 10\%$ in photocurrent quantum yield. Note that the quantum efficiency (uncorrected for solution absorption and reflective losses at the air/glass interface) approaches 90% for matte etched samples for all excitation wavelengths above the band gap of the Si and below the absorption of the MeOH/I/I^+ electrolyte solution. This is in excellent agreement with the observed values of short-circuit currents for the matte samples with the polychromatic irradiation reported in Fig. 2. The value 25 mA/cm^2 at 70 mW/cm^2 is within 80% of the value expected for our solar simulator source if every photon above the band gap of Si were absorbed with unit quantum efficiency (20). We routinely observed these high values with the proper matte etch treatment.

For matte etched samples, at 70-mW/cm^2 incident light intensity we observed a V_{oc} of 530 mV, with 0.32 V and 22.2 mA/cm^2 at the maximum power point, for a conversion efficiency of AM2 simulated solar light into electricity of 10.1% (Fig. 2). For a range of samples and in several different test solutions, we observed an efficiency distribution of $10.0\% \pm 0.5\%$ with matte etched samples under these conditions. In actual direct sunlight, we observed similar parameters and found typical efficiencies of 9.5–10% under AM2 conditions. Notably, the 10.1% conversion efficiency displayed in Fig. 2 represents one of the highest values reported to date for any semiconductor/liquid junction cell (21, 22), as well as one of the highest efficiencies of any Si-based surface barrier type device for conversion of light to electricity (23).

DISCUSSION

A major factor in the improved performance of our system is the minimization of uncompensated ohmic resistance. We find that

FIG. 4. Quantum efficiency for electron flow vs. wavelength for n-Si in $1.0 \text{ M LiClO}_4/\text{MeOH}$ with 0.2 M I and 0.5 mM I^+ added. The solution was stirred and the electrode was potentiostated at $+0.16 \text{ V}$ (vs. SCE)—i.e., very close to short-circuit conditions. The average light intensity at each wavelength was approximately 1 mW/cm^2 . The electrode area was 1.0 cm^2 in each case. Textured surfaces ($\bullet$) show approximately 50% increase in quantum yield over shiny surfaces at all wavelengths measured. The quantum yields are shown uncorrected for solution absorption and electrode reflection and are based on light incident onto a reference Si photocell in the same plane of the photoelectrode. The error in absolute quantum yields determined by this method is $\pm 10\%$, due to inhomogeneity of the excitation beam and precision in sample placement; however, relative values of quantum yields vs. wavelength should be quite accurate.

excessive series resistance leads to parameters similar to those reported for n-Si (5). A striking feature of the performance of the n-Si/I/MeOH cells is the large value of V_{oc} under AM2 conditions. The values of $0.53\text{--}0.55 \text{ V}$ are significantly larger than the 0.30 V reported for n-Si Schottky barriers with metals such as Pt and Au (12, 24). Even the n-Si/EtOH/ferrocene system is reported to yield only $0.3\text{--}0.35 \text{ V}$ at these light intensities (5). The high values of V_{oc} observed in our cells resemble values reported for MIS-type devices with n-Si. In MIS systems, deliberate introduction of a thin oxide layer between the metal and semiconductor interface is found to result in substantial reduction of dark current and consequent increase of V_{oc} . The decreased recombination is thus reflected in increased short-circuit quantum yields and higher V_{oc} . It has been reported that an isopropanol rinse of n-Si and subsequent oxide growth before evaporation of an Al MIS Schottky barrier contact is effective in reducing the dark forward-bias current in these devices (13). It is attractive to conclude that a similar mechanism is at least partially responsible for the high efficiencies of the n-Si/MeOH/I system.

It is also possible that the role of the oxide in MIS structures is to relieve the strain at the metal/semiconductor interface and thereby reduce the density of gap states. Solid/liquid junction systems might also have this advantage; certainly the interfacial chemistry of a semiconductor exposed to a liquid contact will be substantially different from the situation in a simple Schottky barrier. In this regard, the similar chemistry of many noble metal/silicide interfaces has been suggested as a rationale for obtaining Fermi level pinning in Schottky systems (25). Use of a liquid contact might thus lead to design of systems with different interfacial reactions and improved cell parameters.

A demonstration of the importance of exposure of the Si to MeOH was obtained by examination of the behavior of n-Si/Pt Schottky barrier cells. If the improved V_{oc} of the semiconductor/liquid systems does not involve any chemical interaction between the solid and liquid phases (formation of extrinsic surface states or surface oxides, etc.), then the formation of a semiconductor-metal contact after exposure to the liquid should have no effect on the V_{oc} of the Schottky barrier. Fig. 5 compares the current-voltage characteristics of two n-Si/Pt Schottky barriers, one formed directly after a HF etch and MeOH rinse and the other formed after exposure to irradiation at 70 mW/cm^2 in the MeOH/I/I^+ cell for 3 min. The two Si samples were simultaneously contacted with the Pt; thus, both had equal, $50\text{-\AA}$ -thick Pt barrier contacts. The improvement in current-voltage characteristics of the Si/Pt interface after photoelectrochemical treatment was striking. We observed substantial improvement in V_{oc} and in short-circuit current. Note that the V_{oc} of this cell at 100 mW/cm^2 irradiation, 0.56 V , is close to the value observed for the Si/MeOH system. The improvement in short-circuit current is also significant in that it reflects a reduction in recombination processes which would compete with photocurrent flow. When corrected for the fact that the $50\text{-\AA}$ Pt overlayer reflects approximately 50% of the light, the liquid-treated n-Si/Pt interface yields current-voltage characteristics and efficiencies similar to those of the shiny Si/MeOH interface depicted in Fig. 2. The similarities in behavior of the Si/metal and Si/liquid interfaces strongly suggest that the surface chemistry upon irradiation in the MeOH/I/I^+ cell is responsible for the decreased recombination and increased performance of these systems. Given the similarities of these systems to metal/oxide/Si MIS structures, we propose that the formation of silicon oxides in MeOH/I/I^+ is important for the increased performance of our solid/liquid cells.

We have examined the photocurrent stability of the n-Si/MeOH/I/I⁺ cells under several different conditions. Even

FIG. 5. Photocurrent-voltage characteristics of n-Si/Pt Schottky diodes. The light intensity was 100 mW/cm^2 from an ELH-type lamp, and the area of the evaporated metal contact was 3.14 mm^2 . The Pt was evaporated to a 50-Å layer as indicated by an oscillator-type thickness monitor. ---, Si/Pt interface fabricated by a 30-sec HF etch, 10-sec MeOH rinse, air dried, and Pt evaporation; —, identical procedure except that the etched, MeOH-rinsed electrode was illuminated at short circuit for 3 min in $0.2 \text{ M I}^-/0.5 \text{ mM I}^+$ at 70 mW/cm^2 of tungsten-halogen (ELH) light, rinsed again with MeOH, and contacted with Pt. Note the increases in voltage and current of the photoelectrochemically treated sample as compared to the simple Si/Pt Schottky barrier.

with reagent grade MeOH solvent not deliberately dried and with continuous exposure to the atmosphere, we find photocurrent stability for short time periods (minutes) at current densities in excess of 40 mA/cm^2 . Use of low concentrations of I^- , deliberate injections of H_2O , or significantly higher current densities leads to noticeable decay of photocurrent after minutes of operation. However, the high solubility of I^- in alcohol solvents permits effective competition for photogenerated holes in deliberately dried MeOH solvent. At $0.5 \text{ M I}^-/10 \text{ mM I}^+$ in MeOH distilled from Mg and stored over 3A molecular sieves, we find stable photocurrents ($\pm 10\%$) at 20 mA/cm^2 for passage of $>2,000 \text{ C/cm}^2$ through the Si/MeOH interface. Extremely long-term stability is expected when the H_2O concentration is sufficiently low, as in thin-layer photoelectrochemical cell arrangement. At this time it is important to note that the photoelectrochemical properties of the n-Si/MeOH/ I^-/I^+ interface are certainly not simply transients and can be sustained at expected AM2 current densities for substantial periods under laboratory conditions.

It is interesting to compare the strategy used in the approach described here with other methods for stabilization of n-Si (in aqueous solutions). Recently, several systems have been described consisting of aqueous cells of n-Si coated with Pt, Au, $\text{In}_2\text{O}_3\text{-SnO}_2$, or other barrier-forming metal (26, 27). The advantages of these systems are that they can be of use in aqueous solutions, particularly in situations in which electrocatalysis will be required to form fuels. However, it is well known that a significant impediment in improving the efficiency of Si/metal

systems is the low value of V_{oc} obtained due to pinning of the Si Fermi level by metal silicide formation (25, 28). This often can occur even at submonolayer coverages of metal on the Si surface. The approach discussed here has the disadvantage of being limited to relatively H_2O -free nonaqueous systems and would not seem useful at present for the direct production of fuels such as chlorine or oxygen. The advantages of our system are the ability to avoid intermediate Schottky barrier-type steps in the formation of the junction and the ability to effect chemistry on surface states and grain boundaries via manipulation of the solution composition. Such chemistry has been shown herein to be effective in improving the performance of both liquid and metal contacts. The ability to effect chemistry directly on the semiconductor/liquid junction has been shown to be effective for thin-film GaAs systems as well (29). The presence of a stable, efficient, Si/liquid junction in MeOH/ I^-/I^+ should now allow application of these principles to the technologically important Si polycrystalline and thin-film systems.

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