

630-mV open circuit voltage, 12% efficient *n*-Si liquid junction

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We report the first experimental observation of a semiconductor/liquid junction whose open circuit voltage V_{oc} is controlled by bulk diffusion/recombination processes. Variation in temperature, minority-carrier diffusion length, and/or in majority-carrier concentration produces changes in the V_{oc} of the *n*-Si/CH₃OH interface in accord with bulk recombination/diffusion theory. Under AM2 irradiation conditions, the extrapolated intercept at 0 K of V_{oc} vs T plots yields activation energies for the dominant recombination process of 1.1–1.2 eV, in accord with the 1.12-eV band gap of Si. A crucial factor in achieving optimum performance of the *n*-Si/CH₃OH interface is assigned to photoelectrochemical oxide formation, which passivates surface recombination sites at the *n*-Si/CH₃OH interface and minimizes deleterious effects of pinning of the Fermi level at the Si/CH₃OH junction. Controlled Si oxide growth, combined with optimization of bulk crystal parameters in accord with diffusion theory, is found to yield improved photoelectrode output parameters, with $12.0 \pm 1.5\%$ AM2 efficiencies and AM1 V_{oc} values of 632–640 mV for 0.2- Ω cm Si materials.

We recently reported results on the *n*-Si/(1-hydroxyethyl)ferrocene^{+/0}/CH₃OH interface which indicate that open circuit voltages V_{oc} in excess of 0.52 V and photoelectrode efficiencies (AM2 irradiation) in excess of 10% can be attained.¹ However, there still remains a question as to whether the interface parameters in such semiconductor/liquid junctions are controlled by surface states which pin the Fermi level. Fermi level pinning effects on the Schottky barrier height are common for Si-metal systems,² and analogous effects have been proposed to limit the available photovoltage at Si/liquid junctions.³ We report here measurements of the variation in V_{oc} at the *n*-Si/CH₃OH junction with changes in majority-carrier concentration, in minority-carrier diffusion length, and in cell temperature. These data are consistent with the notion that the bulk diffusion/recombination process in the semiconductor is the dominant recombination mechanism for this system. Notably, these studies represent the first experimental demonstration with any semiconductor/liquid junction that the bulk recombination limit on V_{oc} can be attained in an operating semiconductor/liquid cell. Furthermore, these data imply that after photoelectrochemical oxide growth is performed, surface pinning limitations on the photovoltage are minimal.

Consistent with our previous studies of the *n*-Si/CH₃OH junction,^{1,4} ELH type irradiation (3350-K color temperature tungsten halogen bulb) of mirror-finished *n*-Si electrodes [1.5- Ω cm resistivity, (100) oriented, 10-s etch in 48% HF followed by a CH₃OH rinse] in 0.20 M dimethylferrocene [(CH₃)₂Fc]/0.010 M (CH₃)₂Fc⁺/1.5 M LiClO₄/CH₃OH solutions yield V_{oc} values of 0.55–0.56 V at photocurrent densities of 20 mA/cm². We have subsequently investigated the recombination processes in this system, and find that use of Si crystals with different bulk properties leads to reproducible, systematic changes in V_{oc} (photocurrent density = 20 mA/cm²). As depicted in Table I, variation in majority-carrier concentration while holding L_p relatively constant (between 170–200 μ m) yields large variations in V_{oc} , with a change in V_{oc} of ≈ 60 mV per dec-

ade change in N_D . Additionally, degradation of the hole lifetime (Au diffusion at 700–1000 °C) results in substantial decreases in V_{oc} (Table I).⁵ Such changes in V_{oc} with variation in bulk properties would not be expected if surface effects such as thermionic emission over a pinned surface barrier, or leakage through chemical imperfections in the surface junction, provided the dominant recombination mechanism for these Si/liquid interfaces.

The observed dependence of V_{oc} on both N_D and L_p is in excellent agreement with bulk recombination/diffusion control of V_{oc} , as expressed by Eq. (1).^{6,7}

$$V_{oc} \cong (kT/q) \ln(J_{ph} L_p N_D / q D_p n_i^2). \quad (1)$$

Table I depicts the accord between the measured V_{oc} and the theoretically calculated V_{oc} , based on the known values of n_i and D_p (Ref. 7) and on the independent determination of N_D and L_p for these samples. Clearly, bulk recombination/dif-

TABLE I. Variation in open circuit voltage of *n*-Si/CH₃OH junctions.

Resistivity ρ (Ω cm)	Wafer thickness W (μ m)	Hole diffusion length L_p (μ m)	V_{oc} (theory) ^a (V)	V_{oc} (exptl) ^b (V)
0.20	315	195	0.630	0.630
0.60	370	165	0.589	0.593
1.50	390	190	0.566	0.568
1.95	330	85	0.540	0.550
1.70	240	45	0.528	0.523
1.70	240	12	0.492	0.495
1.70	240	8.0	0.482	0.470
1.70	240	5.0	0.470	0.462

^a Values are calculated from Eq. (1), taking $n_i = 1.45 \times 10^{10} \text{ cm}^{-3}$.⁷ We have assumed a large back surface recombination velocity. When $L_p > W/2$, the true L_p might exceed W ; if this is the case, assumption of a large back surface recombination velocity leads to theoretical V_{oc} values 15–20 mV greater than calculated.

^b Open circuit photovoltages relative to a Pt foil counterelectrode. Variation in V_{oc} is typically ± 5 mV from sample to sample. For samples with $\rho > 7 \Omega$ cm, we observe higher V_{oc} than predicted by Eq. (1), due to the onset of high level injection. All V_{oc} values were measured with ELH irradiation sufficient to provide short circuit photocurrent densities of 20 mA/cm² on each sample.

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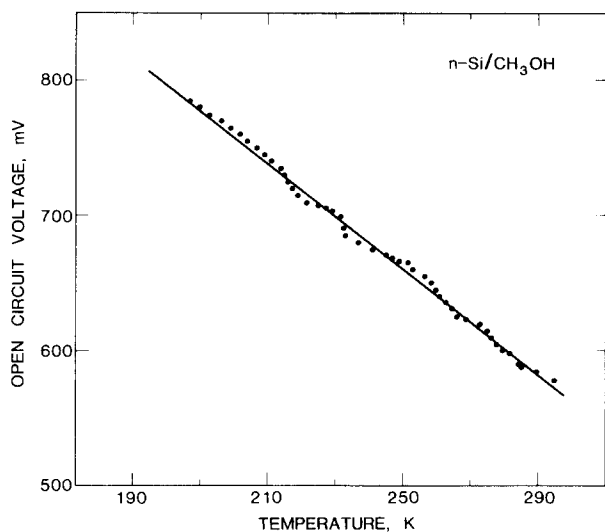


FIG. 1. Temperature dependence of the open circuit photovoltage between a 1.5- Ω cm resistivity *n*-type Si electrode and a Pt foil counterelectrode. The solution is 50 mM $(\text{CH}_3)_2\text{Fc}/10 \text{ mM } (\text{CH}_3)_2\text{Fc}^+ / 0.1 \text{ M LiClO}_4/\text{CH}_3\text{OH}$, and the incident light intensity (ELH-type tungsten halogen irradiation) is sufficient to provide a photocurrent density of 20 mA/cm² at 298 K. Typical intercepts at 0 K are 1.1–1.2 eV, and typical slopes are 1.8–2.1 mV/K. Correlation coefficients of a linear least-squares fit to the data exceed 0.995.

fusion effects dominate the V_{oc} of the *n*-Si/ CH_3OH interface at AM2 photocurrent densities.

The temperature dependence of V_{oc} further confirms the application of Eq. (1) to the *n*-Si/ $(\text{CH}_3)_2\text{Fc}^+ / 0 / \text{CH}_3\text{OH}$ system. Measurement of V_{oc} at a constant photocurrent density (20 mA/cm²) on a number of 1.5- Ω cm *n*-Si samples in CH_3OH solvent with variation in cell temperature (from 300 to 190 K) yields linear plots of V_{oc} vs T (Fig. 1), with typical slopes of 1.8–2.1 mV/K and extrapolated intercepts at 0 K of 1.1–1.2 eV. Rewriting Eq. (1) in terms of an explicit temperature dependence, it is seen that the intercept of a V_{oc} vs T plot should be approximately equal to E_g/q , as described by Eq. (2),⁷

$$V_{oc} = \frac{E_g}{q} + \frac{kT}{q} \ln \frac{J_{ph} L_p N_D}{D_p N_c N_v}. \quad (2)$$

The kinetic data in Fig. 1 are thus consistent with an activation energy for the dominant recombination process in the *n*-Si/ CH_3OH system of 1.1–1.2 eV, as would be expected if Eqs. (1) and (2) are applied to the *n*-Si/ CH_3OH semiconductor/liquid junction ($E_g = 1.12 \text{ eV}$ for Si at 298 K, and 1.17 eV at a 0 K).⁸

We have also obtained additional evidence to support a previous hypothesis from both liquid and Schottky barrier studies,¹ that photoelectrochemical Si oxide growth is the major chemical factor in obtaining efficient *n*-Si/ CH_3OH interfaces.¹ As displayed in Fig. 2(a), the initial photocurrent-voltage properties of *n*-Si anodes in very dry $(\text{CH}_3)_2\text{Fc}/\text{CH}_3\text{OH}$ solution (dried over activated 3A sieves) are poor, with modest V_{oc} values and low fill factors. The lower initial V_{oc} in $(\text{CH}_3)_2\text{Fc}/\text{CH}_3\text{OH}$ solutions relative to that observed previously in (1-hydroxyethyl)ferrocene/ CH_3OH solutions¹ is consistent with the more negative E^0 of $(\text{CH}_3)_2\text{Fc}$, and reflects the expected increase in surface recombination for the *n*-Si/ $(\text{CH}_3)_2\text{Fc}/\text{CH}_3\text{OH}$ interface. However, in the *n*-Si/ $(\text{CH}_3)_2\text{Fc}/\text{CH}_3\text{OH}$ system, constant potential oxidation at

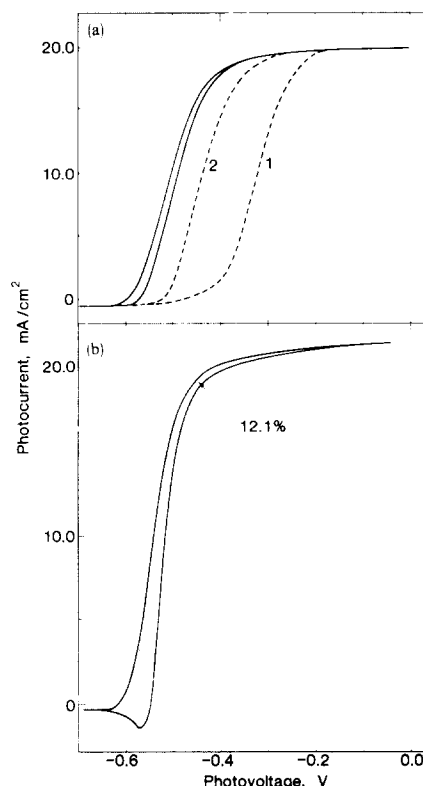


FIG. 2. Current-voltage characteristics (sweep rate 50 mV/s) of *n*-Si/1.5 M $\text{LiClO}_4/\text{CH}_3\text{OH}$ junctions under 70 mW/cm² of ELH-type irradiation. The curves are photoelectrode efficiencies measured under potentiostatic control of the working Si photoanode. (a) Improvement in illuminated J - V characteristics of a 0.2- Ω cm resistivity, (100) oriented, *n*-Si anode. The mirror-finished electrode surface has been etched for 10 s with 48% aqueous HF, and rinsed with CH_3OH ; the redox couple is 0.2 M $(\text{CH}_3)_2\text{Fc}/0.5 \text{ mM } (\text{CH}_3)_2\text{Fc}^+$. Numbers on dashed curves refer to J - V scan sequence from the initial scan in the positive voltage direction. After initial oxide growth (3–10 scans), a stable current-voltage characteristic is obtained (solid lines). The substantial increase in voltage and improvement in fill factor indicate the passivation of surface recombination by chemical modification (oxide growth) of the *n*-Si/ CH_3OH interface. (b) Light J - V characteristics at 296 K of 0.2- Ω cm resistivity, (100) oriented, matte-textured (see Ref. 1) *n*-Si anodes in a stirred 0.2 M (1-hydroxyethyl)Fc/0.5 mM (1-hydroxyethyl)Fc⁺ / 1.5 M $\text{LiClO}_4/\text{CH}_3\text{OH}$ solution.

short circuit for 5–30 s (or merely obtaining a few steady state I - V scans) yields dramatic improvements in the current-voltage behavior (Fig. 2). After such oxide growth has proceeded, the steady state current-voltage curves undergo essentially no change for several thousands of coulombs of charge passed through the interface, with the long-term stability of the photocurrent determined primarily by the water content of the electrolyte.¹ The role of Si oxide in passivating surface recombination in this system is consistent with the chemical model advanced by Heller,⁹ which states that strong chemical bonds at the semiconductor/liquid interface can prevent gap states from acting as effective recombination sites. Our system demonstrates that such chemical modification can be so effective on *n*-Si/ CH_3OH interfaces that at AM2 photocurrent densities, it allows formation of junctions which are limited only by the bulk-diffusion recombination inherent to the semiconductor itself.

Optimization of bulk Si properties, combined with photoelectrochemical oxide growth, has also lead to improved photocurrent-voltage behavior under solar illumination.

Use of long lifetime, low resistivity (float zone growth) 0.2- Ω cm Si wafers in the n -Si/0.2 M (1-hydroxyethyl)Fc/0.5 mM (1-hydroxyethyl)Fc⁺/1.5 M LiClO₄/CH₃OH junction yields photoelectrode efficiencies of 10.0% \pm 1.0% for mirror-finished electrodes (V_{oc} = 0.62–0.63 V, J_{sc} = 19–20 mA/cm²), while matte-textured surfaces¹ yield 12.0% \pm 1.5% efficiency (V_{sc} = 0.62–0.64 V, J_{sc} = 22–24 mA/cm²) under either 70 mW/cm² of ELH-type irradiation [Fig. 2(b)] or 70 mW/cm² of direct insolation.¹⁰ The major power losses in the present cell design can be attributed to residual uncompensated series resistance losses in our potentiostatically controlled (three-electrode) system,^{1,10} and to concentration overpotential losses at the working electrode. Consistently, the fill factor of the n -Si/CH₃OH system improves somewhat with addition of more (1-hydroxyethyl)Fc⁺ to the electrolyte. However, such changes do not improve the photoelectrode efficiency because of the compromise between improved fill factors and lower photocurrents [$\epsilon \approx 450$ M⁻¹ cm⁻¹ at 618 nm for (1-hydroxyethyl)Fc⁺] in the present cell design. Thus, even further improvements in efficiency for these liquid junction systems might be expected if a simultaneous reduction in these remaining losses can be attained.

A comparison to diffused Si p - n junction cells indicates that the n -Si/CH₃OH system exhibits V_{oc} values which are the highest for any n -Si based photovoltaic system, and are amongst the highest values for any type of Si junction cells fabricated to date.^{7,11} V_{oc} values at AM1 for NASA secondary standard cells are typically 0.57 V, and p -type Si MIS junctions with a 0.2- Ω cm resistivity Si base have demonstrated V_{oc} of 643 mV under 100 mW/cm² of ELH-type irradiation.^{1,11} For comparison, a 0.2- Ω cm n -Si photoelectrode under 100 mW/cm² of ELH irradiation yields V_{oc} = 0.632–0.640 V. Additionally, the short circuit spectral response in dilute (10 mM) (CH₃)₂Fc/CH₃OH solution exhibits negligible decline in external quantum efficiency for λ as short as 400 nm, indicating that liquid systems need not possess the “dead layer” observed in conventional diffused p - n homojunction Si cells. Our data on the n -Si/CH₃OH system clearly indicate that liquid junction systems can exhibit output parameters comparable to or better than conventional diffused p - n junction systems. Furthermore, it is clear that the Fermi level pinned interface behavior common to metal-silicon Schottky interfaces does not limit the photovoltage at photoelectrochemically oxidized n -Si/CH₃OH liquid junctions, and that bulk recombination diffusion is the

dominant recombination mechanism in this system under AM2 irradiation conditions. Extension of our photoelectrochemical oxide growth techniques to control the behavior of Si-metal interfaces, as well as further investigation of the recombination processes in the n -Si/CH₃OH photoelectrode system, is presently underway.

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