Studies of silicon photoelectrochemical cells under high injection conditions

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The behavior of Si/CH_3OH-dimethylferrocene$^{+/0}$ junctions has been investigated under high injection conditions. Open circuit voltages of (626 ± 5) mV were obtained at short circuit photocurrent densities of 20 mA/cm^2 for samples with an n^+-diffused back region, point contacts on the back surface, and with a base of thickness 390 μm and a 1 ms hole lifetime. The diode quality factor and recombination current density were 1.8 ± 0.1 and $(2.6 \pm 1.5) \times 10^{-8}$ A/cm^2, respectively. These data are consistent with recombination dominated by the base and back contact regions, and not at the Si/CH_3OH interface.

We have previously shown that n-Si/CH_3OH interfaces are of remarkable electronic quality, and exhibit open circuit voltages that are superior to those obtained from Si/metal junctions and from conventional Si p-n homojunctions.[1-3] Over a range of Si dopant densities and diffusion lengths, the open circuit voltage (V_{oc}) for n-Si/ CH_3OH-dimethylferrocene (Me_2Fc)$^{+/0}$ junctions follows the Shockley diode equation,[2,3] as expected for a junction in which interfacial recombination losses are negligible compared to the minority-carrier bulk diffusion/ recombination process.[4] Since these previous systems were operated under low-level injection conditions, the trade-off between high donor densities (N_d) and maximum minority-carrier diffusion lengths (L_p) resulted in maximum n-Si/CH_3OH V_{oc} values of 635 mV (light-limited photocurrent density, $J_{ph} = 20$ mA/cm^2, 298 K) for $N_d = 3.2 \times 10^{16}$ cm^{-3} n-Si with $L_p = 195$ μm, while higher V_{oc} values of 670 mV ($J_{ph} = 20$ mA/cm^2, 298 K) for $N_d = 1.8 \times 10^{17}$ cm^{-3} n-Si were only achieved with a concurrent degradation of base lifetime ($L_p = 20$ μm).[3] An alternative design exploited recently in solid-state Si photovoltaics to preserve high base lifetimes is to operate the base region under field-free, high injection conditions.[5] This approach has allowed fabrication of high efficiency ($> 22\%$) photovoltaic cells displaying air mass 1.0 V_{oc} values as high as 705 mV.[6] We now report studies of n-Si/ liquid junctions operated under high injection conditions. These cells take advantage of the electronic quality of the Si/CH_3OH interface, and have resulted in 630 mV V_{oc} values (on unoptimized base/back contact combinations) with no processing steps performed on the liquid side of the Si base region. In addition to advancing our basic knowledge of the electronic properties of semiconductor/liquid junctions, these Si/liquid systems might be useful for simple, nondestructive, spatially resolved diagnostics of Si base quality.

Figure 1 depicts the liquid junction cell. The semiconductor photoelectrode (typically squares of edge dimension 6-8 mm) consisted of an intrinsic Si layer (390 μm thick, $N_d = 1.3 \times 10^{13}$ cm^{-3}; low-level hole lifetime = 1 ms), with an n^+-type diffused layer (sheet resistivity = 40

$\Omega/\square$) on the back side of the wafer. Contact to the n^+ layer was achieved by an array of metal points (5 μm $\times$ 5 μm squares) covering 2% of the active device area. The remaining back surface area of the wafer was covered by a high quality thermally grown SiO_2 layer. This structure is similar to the processing used in high efficiency p-i-n solid-state concentrator cells,[5,6] and reduces parasitic recombination losses in the diffused region and at the back surface. For use in the liquid junction arrangement, no processing or diffusion steps were performed on the front surface; the Si samples were merely etched in 49% HF(aq) and were rinsed with H_2O and CH_3OH before use in a conventional photoelectrochemical cell arrangement.[3,7] For comparison purposes, a complete p-i-n cell was evaluated in parallel with the Si/liquid junctions. This p-i-n cell was not fabricated in the identical batch process as the structures examined in the liquid junction, but it nominally had the same back contact and base characteristics, with a front emitter consisting of an 80 $\Omega/\square$ p^+ region with point contacts, oxide passivation, and a textured front surface for light trapping purposes. The p-i-n test cell behavior was typical of such devices, although optimized cells with higher hole lifetimes and thinner bases have been reported to display slightly larger V_{oc} values.[6]

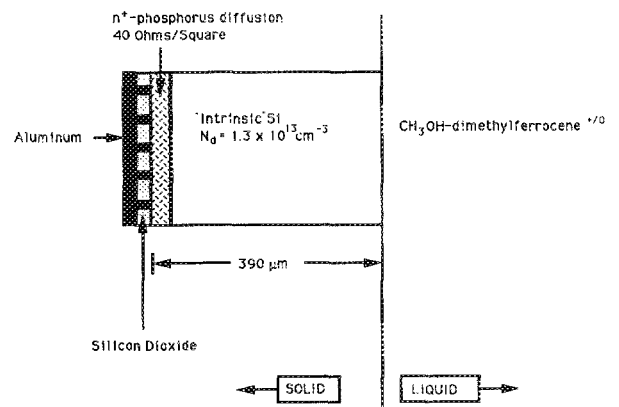Figure 2 displays the current-voltage (I-V) behavior at

FIG. 1. Schematic diagram of photoelectrode used in this study. Contact to the electrode was made through the Al back, and the electrode edges and back surface were encapsulated in epoxy to expose 0.4-0.6 cm^2 of active area to the electrolyte.

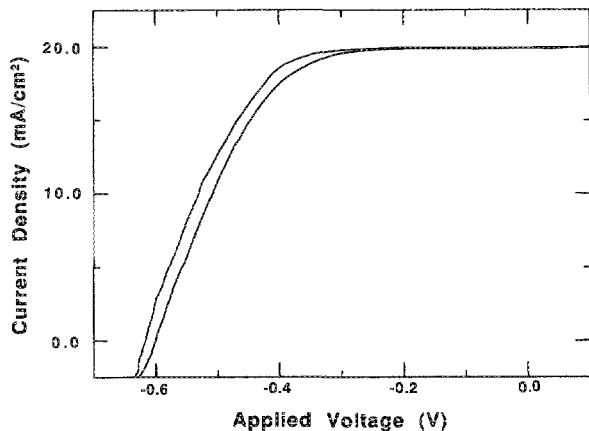[a] Address correspondence to this author.

FIG. 2. Potentiostatic three-electrode current-voltage (I-V) property of high injection Si/CH$_3$OH-Me$_2$Fc$^{+/0}$ photoelectrochemical cell. The reference electrode was a Pt wire in a Luggin capillary placed 0.2 mm from the photoelectrode surface. The counter electrode was a large area (> 3 cm^2) Pt foil. The poor fill factor is due to the concentration overpotential and to the large residual uncompensated resistance of the solution in this unoptimized semiconductor/liquid cell configuration.

298 K of the Si photoelectrode in contact with the CH$_3$OH-1.0 M LiClO$_4$-0.20 M dimethylferrocene (Me$_2$Fc)-0.010 M Me$_2$Fc$^+$ electrolyte. The Me$_2$Fc$^{+/0}$ redox system established the Fermi level of the liquid phase, and insured a high degree of equilibrium band bending in the Si base while maintaining electrode stability to photocorrosion.[7,8] The Si surface in the liquid junction was not optimized for light trapping or for minimization of optical reflection losses; thus, to facilitate comparison of electrical properties with the solid-state p-i-n test cell, the light intensity was adjusted to provide short circuit photocurrent densities (J_{ph}) of 20.0 mA/cm^2. Under these conditions, the V_{oc} of 626±5 mV obtained from the liquid junctions compares closely to the V_{oc} of 625 mV measured for the p-i-n device at $J_{ph} = 20$ mA/cm^2. This indicates that the ratio of minority-carrier collection to majority-carrier recombination is similar in the two systems, and underscores the high electronic quality of the HF-etched Si/CH$_3$OH junction. The V_{oc} values reported for the liquid junctions are statistically averaged results from 3 different Si samples used in a total of 11 separate Si/CH$_3$OH cells. The Si/CH$_3$OH junction in Fig. 2 is clearly operating in high-level injection, because the low-level injection bulk recombination/diffusion V_{oc} value for $N_d = 1.3 \times 10^{13}$ cm^{-3} Si with an effective minority-carrier diffusion length of 400 μm is only 473 mV at $J_{ph} = 20$ mA/cm^2.[4] Under these conditions, a V_{oc} higher than this 473 mV value can only be achieved if the injected majority-carrier density exceeds the equilibrium majority-carrier density, implying that the high injection condition has indeed been obtained. The poor fill factor in Fig. 2 results from the uncompensated resistance losses and concentration overpotentials that are inherent to an unoptimized liquid junction cell design. The V_{oc} values for such systems are still useful, because use of a thin layer cell configuration has been shown to minimize these cell-based losses while still pre-
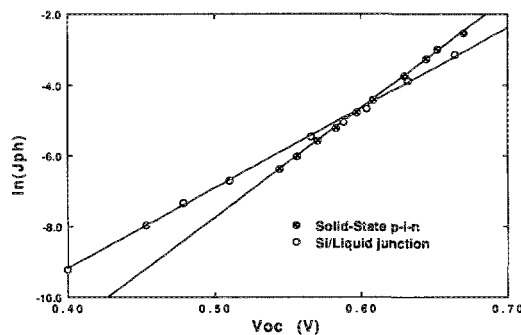

FIG. 3. ln(J_{ph}) vs V_{oc} for the solid-state p-i-n cell (dark circles) and for the photoelectrochemical cell (light circles). In this figure the ordinate is the natural logarithm of J_{ph} measured in A/cm^2. The V_{oc} for the liquid junction cell becomes greater than that for the p-i-n cell at high current densities.

serving the V_{oc} determined in the unoptimized cell arrangement used in Fig. 2.[9]

Plots of the dependence of V_{oc} on the light-limited photocurrent density for $J_{ph} = 0.10$–50 mA/cm^2 are presented in Fig. 3 for both the n-Si/CH$_3$OH junction and the p-i-n test cell. Analysis of the data using the standard diode relationship[4]

$$V_{oc} = (AkT/q)\ln(J_{ph}/J_0),\qquad(1)$$

(where A is the diode quality factor, kT/q is the thermal voltage, J_{ph} is the light-limited photocurrent density, and J_0 is the magnitude of the recombination current density) yielded values of $J_0 = 7.9 \times 10^{-11}$ A/cm^2 and $A = 1.2$ for the p-i-n cell, and $J_0 = (2.8 \pm 1.6) \times 10^{-8}$ A/cm^2 and $A = 1.8 \pm 0.1$ for the liquid junction. The dominant recombination mechanism for the p-i-n test cell has been assigned previously to recombination in the diffused regions of the device, leading to the observed A and J_0 values for the solid-state system.[5] In contrast, the liquid junction has no front diffused region, but consists of a high quality Si/liquid interface. The higher A value in the Si/liquid cell reflects this lack of front emitter recombination loss. For the relatively thick Si base (390 μm) with a 1 ms minority-carrier lifetime, recombination in the base region is expected to determine the device properties provided that the front emitter recombination can be suppressed. This is in accord with the observed A and J_0 values of the Si/CH$_3$OH junction. At high light intensities, use of the liquid contact to eliminate front emitter recombination results in higher V_{oc} values for the n-Si/CH$_3$OH junction than for the test p-i-n cell. Variation in processing to achieve further reductions in base recombination, such as using longer lifetime Si samples with thinner base regions, might allow air mass 1.0 V_{oc} values of Si/CH$_3$OH junctions to be competitive with the 705 mV values obtained from optimized p-i-n structures.

Considering the high concentration of both electron donors (Me$_2$Fc) and acceptors (Me$_2$Fc$^+$) in the liquid phase, it is remarkable that the n-Si/CH$_3$OH cell displays such large V_{oc} values under high injection conditions. The spectral response behavior, displayed in Fig. 4, underscores
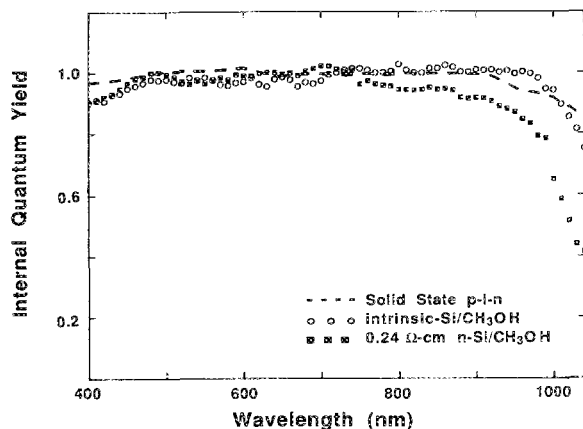
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FIG. 4. Internal short circuit quantum yield vs wavelength for the *p-i-n* cell (dashed line, last part of Ref. 5), the intrinsic Si liquid junction (light circles), and for a $N_d = 3.2 \times 10^{16}$ cm^{-3}, float zone grown, *n*-Si sample ($L_p = 195 \ \mu m$). The concentrations of redox ions for the liquid junctions were 0.001 M Me$_2$Fc and 0.0001 M Me$_2$Fc$^+$.

the excellent hole collection properties of this junction. Figure 4 compares the internal quantum yield of the *n*-Si/ CH$_3$OH interface using $N_d = 1.3 \times 10^{13}$ cm^{-3} and $N_d = 3.2 \times 10^{16}$ cm^{-3} Si samples to that for a typical $N_d = 1.3 \times 10^{13}$ cm^{-3} base *p-i-n* cell. In the long-wavelength region, the internal quantum efficiency of the $N_d = 1.3 \times 10^{13}$ cm^{-3} *n*-Si/CH$_3$OH junction is substantially higher than that of the $N_d = 3.2 \times 10^{16}$ cm^{-3} sample[3] and is comparable to the response of the *p-i-n* Si test cell. This behavior correlates with the larger effective minority-carrier diffusion length in the low-doped Si samples. For the mirror-finished Si surfaces used in contact with liquids, the maximum absolute external quantum yield of the *n*-Si/ CH$_3$OH interface was 0.75–0.80; however, it has been shown that surface texturizing etches can yield improvements in maximum external quantum yield to greater than 0.95 for $N_d = 3.2 \times 10^{16}$ cm^{-3} *n*-Si/CH$_3$OH junctions.[1,7,10] Thus, despite the potential for interfacial recombination at the Si/liquid interface, the achievable quantum yields are comparable to maximum external quantum yields achievable in optimized *p-i-n* devices.[5,6]

We have also investigated the dependence of V_{oc} on the concentration of donors and acceptors in the liquid phase. The concentration of Me$_2$Fc was varied from 0.005 to 0.20 M, the concentration of Me$_2$Fc$^+$ was varied from 0.0001 to 0.10 M, and the [Me$_2$Fc$^+$]/[Me$_2$Fc] ratio was varied from 20 to 5.0×10^{-4}. For all combinations studied, and over a range of J_{ph} from 2.0 to 20 mA/cm^2, V_{oc} did not change (± 10 mV) when the redox concentrations were varied. This is somewhat surprising, because under high injection conditions, carrier transport in the intrinsic layer should be purely diffusional. With no electric field to repel majority carriers, conventional electron transfer theories[11,12] predict that the highly exoergic electron capture by Me$_2$Fc$^+$ should be more kinetically facile than the less exoergic hole capture by Me$_2$Fc. The independence of V_{oc} with changes in redox concentrations, and the excellent majority-carrier rejection indicated by the spectral response data, both indicate that the rate-limiting recombination step for majority carriers does not involve bimolecular interfacial recombination with the dissolved redox

ions. The present data cannot address whether the underlying cause of the high (minority/majority) carrier collection ratio is due to a failure of the conventional Marcus–Gerischer electron transfer theory[11,12] in this system or is due to strong surface inversion induced by the CH$_3$OH-Me$_2$Fc$^{+/0}$ contact. The latter situation would result in *in situ* formation of a p^+-doped layer at the Si/CH$_3$OH interface, making the *p-i-n* cell and the Si/liquid cell very similar in device properties. Experiments designed to distinguish between these alternatives are currently in progress; however, the present data clearly show that the collection properties of the *n*-Si/CH$_3$OH interface can approach those of the best known solid-state Si photovoltaic systems.

Although the *n*-Si/CH$_3$OH interface yielded V_{oc} values that were higher than those in the *p-i-n* test cell used in this work, this requires operation under high light concentration, where the efficiency performance of a liquid junction suffers relative to solid-state systems. Even in thin (10 μm) electrolyte layers, mass transport limitations on the supply of redox couple to the Si interface lead to declines in power conversion efficiency at current densities higher than 50 mA/cm^2,[2,9] which is the range in which the high injection *p-i-n* devices exhibit superior efficiency performance.[6] The liquid junction behavior under high injection conditions is valuable, however, in advancing our understanding of carrier transport and recombination at solid/liquid boundaries. It is encouraging to note that the performance of such single-crystal Si/CH$_3$OH interfaces can approach that of the most technologically advanced photovoltaic systems, and that these semiconductor/liquid systems can afford relatively stable junction performance from simple, available chemicals and liquids.

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