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Experimental Measurement of Quasi-Fermi Levels at an Illuminated Semiconductor/Liquid Contact

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A novel electrode geometry and contacting procedure has allowed measurement of the quasi-Fermi levels, *i.e.*, the apparent electrochemical potentials, of electrons and holes at an illuminated semiconductor/liquid contact. The key feature of our experiments is the use of a lithographically patterned, high purity (100–400 Ω·cm n-type float zone material), low dopant density Si sample in contact with CH_3OH–dimethylferrocene$^{+/0}$ solutions. The photogenerated carriers can be collected at the back side of the Si sample through a series of diffused n^+ and p^+ points. The lifetime of photogenerated carriers approaches 2 ms in this sample, indicating that electron–hole recombination is minimized in the bulk of the semiconductor. Furthermore, surface recombination is minimized by use of low saturation current density, ohmic-selective contacts at the back of the sample. The solid/liquid contact also has a low recombination rate. Therefore, the potentials measured at the diffused points yield values for the quasi-Fermi levels of electrons and holes under illumination of the semiconductor/liquid contact. Transient photovoltage measurements have also been performed to confirm quantitatively that the quasi-Fermi levels are flat across the Si samples used in this work.

One of the key concepts in semiconductor photoelectrochemistry is the "quasi-Fermi level". This theoretical construct describes the thermodynamic tendency of the semiconductor carriers (electrons and holes) to react under nonequilibrium conditions.[1,2] Although quasi-Fermi level formalisms have been employed in numerous theories of semiconductor photoelectrochemistry, their usefulness and thermodynamic meaning have been debated in the past several years.[3–7] Furthermore, there has not yet been a direct measurement of the electron and hole quasi-Fermi levels at a semiconductor/liquid contact. Herein we describe experiments in which the apparent electrochemical potentials of electrons and holes can be monitored separately in the same sample, thus allowing us to validate the quasi-Fermi level concept experimentally.

We have utilized Si/CH_3OH interfaces for this work.[8–16] Such systems are stable to photocorrosion and have been well-documented to show "ideal" electrical junction behavior in the presence of a variety of redox species.[10,17] The 1,1′-dimethylferrocene $(Me_2Fc)^{+/0}$ redox couple is especially interesting because n-Si/CH_3OH–$Me_2Fc^{+/0}$ contacts exhibit open circuit voltages that are limited only by minority carrier injection processes and because the electrochemical potential of CH_3OH–$Me_2Fc^{+/0}$ solutions is close to the energy of the Si valence band edge.[10,11,13,17]

A key feature of our experiments is the use of a high purity (100–400 Ω·cm, n-type, 120 μm thick, float-zone grown), low dopant density Si sample (Figure 1).[18–20] The low dopant density and high carrier lifetime of the sample imply that, under moderate illumination levels, the density of the photogenerated carriers in the semiconductor will exceed the equilibrium donor concentration ($N_D = 3 \times 10^{13}$ cm^{-3}). The high concentration of photogenerated electrons and holes will minimize the built-in electric field at the semiconductor/liquid interface.[18,21,22] This ensures that the charge carrier motion is predominantly driven by diffusion, which simplifies the analysis of the photovoltage data, as described below.

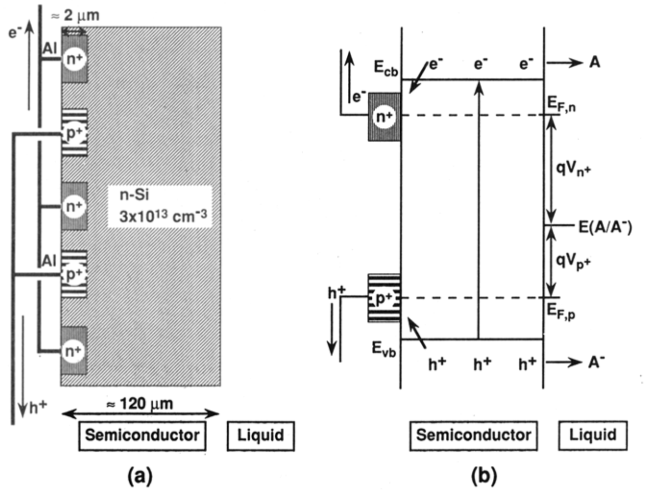

Figure 1. (a) Schematic diagram of the Si sample used in this study. The front surface of the sample was anisotropically etched and coated with TiO_2 to minimize optical reflection losses. The back contacts were encapsulated in epoxy to expose only 1.2 cm^2 of the front surface to the electrolyte. (b) Band diagram of the Si/CH_3OH interface under high-level injection conditions. $\mathbf{E_{cb}}$ and $\mathbf{E_{vb}}$ represent the conduction band edge and the valence band edge, respectively, and $\mathbf{E_{F,n}}$ and $\mathbf{E_{F,p}}$ are the electron and hole quasi-Fermi levels, respectively. qV_{n^+} is the energy difference measured between the n^+ point contacts and the solution electrochemical potential ($\mathbf{E}(A/A^-)$), while qV_{p^+} is the energy difference between the p^+ points and $\mathbf{E}(A/A^-)$. Under high level injection conditions, the electric field in the semiconductor is minimized, and the energy bands are essentially flat throughout the sample, except for the strong electric fields within and near the p^+ and n^+ points. As discussed in the text, under the uniform photogeneration conditions depicted, the gradient in quasi-Fermi levels is estimated to be <2 meV across this sample.

Another key feature of our sample is the use of low recombination, ohmic-selective contacts at the back surface. A series of diffused n^+ and p^+ points (2 μm in thickness; ≫10^3 Debye lengths between the metal and intrinsic regions), contacted by aluminum leads, was patterned on the back sides of the samples using standard lithographic methods.[23] In such samples, the electrons will be collected at the n^+ points and the holes will be collected at the p^+ points. Recombination at the back of the sample is minimized by use of the ohmic-selective contacts,[24] whose low saturation current density (≈10^{-12} A·cm^{-2})[18] and low areal coverage, in conjunction with the presence of a passivating SiO_2 layer over the remainder of the back surface, minimize "merging" of the quasi-Fermi levels near the back contact

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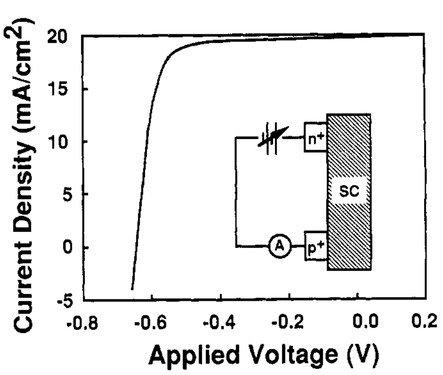

Figure 2. Current density–voltage (J–V) behavior of lithographically patterned Si in air, as measured between the n^+ and p^+ points on the back of the sample. The front of the sample was oxidized to minimize surface recombination.

region.[18,20] These contacts thus allow separation and simultaneous measurement of the potentials for each type of charge carrier. The apparent electrochemical potentials[1,2] of carriers, i.e., the quasi-Fermi levels, can thus be monitored through use of a voltmeter measuring the potential of either the n^+ or p^+ points relative to the solution potential.

Figure 2 depicts the current density–voltage (J–V) curves of a typical 1.1- × 1.1-cm sample in contact with air when voltage was applied, and current passed, between the n^+ points and p^+ points on the back of the Si. Due to the long carrier lifetime and field-free conditions, carriers that are created by illumination of the front of the sample are free to diffuse until they either recombine or are collected at the contact points. Facile transmission of electrons through the n^+ points (and transmission of holes through the p^+ points), combined with rejection of electrons through the p^+ points (and rejection of holes through the n^+ points), yields a highly rectifying J–V characteristic under these conditions. At an illumination intensity (ELH-type tungsten halogen lamp)[25] sufficient to provide a short circuit current density, J_{sc}, of 20 mA·cm^{-2}, the open circuit voltage (V_{oc}) was 630 ± 15 mV for several samples. In fact, the V_{oc} developed by this sample, which is a measure of the difference in quasi-Fermi levels of the electrons and holes at the back of the sample, is in accord with expectations that apply to the field-free, high-level injection conditions of this experiment[18] and is limited only by recombination within the semiconductor device.

Figure 3 depicts the J–V properties obtained when the passivating oxide overlayer and the TiO_2 antireflectance layer were removed from the front surface, and the Si sample was used as a working electrode in a three-electrode potentiostatic configuration. In this experiment, contact was made to either the n^+ points or p^+ points to produce the working electrode connection. The front surface of the Si was in contact with a CH_3OH–$LiClO_4$–$Me_2Fc^{+/0}$ solution, the counterelectrode was a Pt foil in the CH_3OH–$Me_2Fc^{+/0}$ solution, and the reference electrode was a Pt wire poised at the Nernstian solution potential, $E(A/A^-)$. At a light intensity sufficient to provide J_{sc} = 20 mA·cm^{-2}, an open circuit voltage of 580 ± 20 mV was measured between the reference electrode and the lead connected to the n^+ points.[26] Furthermore, the open circuit voltage between the p^+ points and $E(A/A^-)$ was 0 ± 5 mV under these conditions. Identical open circuit potentials were obtained on this illuminated Si sample in experiments where the potentials of the n^+ and p^+ points were independently, but simultaneously, measured through the use of two high impedance voltmeters that were separately connected to the n^+ and p^+ points and were each referenced to the solution potential.

The open circuit potentials measured in this experiment reflect the quasi-Fermi level positions of electrons and holes at the diffused back contacts. As a result of the minimal recombination in the bulk and at the back surface of our sample,[18] in combination with the low surface recombination velocity at the n-Si/CH_3OH–$Me_2Fc^{+/0}$ contact[27] and the high carrier diffusivity and small thickness of our specimen, the quasi-Fermi levels can be shown to be essentially flat throughout the semiconductor. This conclusion has been confirmed analytically by 3-dimensional modeling of the device physics[18] when the front surface of these samples is passivated with a low surface recombination velocity oxide overlayer. The 630 ± 15 mV V_{oc} value for our particular device in contact with air (Figure 2) corresponds to a total integrated carrier recombination velocity of 35 ± 10 cm·s^{-1}. A worst-case estimate of the gradient in the quasi-Fermi levels can be obtained by assuming that all of the recombination occurs at the front contact; even with this assumption, the quasi-Fermi level gradient would be <1 meV from the bulk to the front surface of the sample. This modeling must also apply when our samples are exposed to form n-Si/CH_3OH contacts, because the liquid contact and passivated solid-state overlayers display similar V_{oc} values and other device parameters are unchanged in the comparison. For example, the n^+-Si/liquid V_{oc} of 580 ± 20 mV corresponds to an integrated carrier recombination velocity of only (1.0 ± 0.3) × 10^2 cm·s^{-1}. Our set of voltage measurements therefore indicates that, in contact with the CH_3OH–$Me_2Fc^{+/0}$ solution, the quasi-Fermi level of electrons near the Si/liquid interface is well negative of the solution potential (qV_{n^+} = 0.58 eV) and the quasi-Fermi level of holes is very close to the electrochemical potential of the solution (qV_{p^+} = 0.00 eV). The position of the hole quasi-Fermi level suggests that the holes equilibrate with this redox solution, in agreement with the results obtained using normal, high dopant density, Si samples in the same solution.[17] The quasi-Fermi level separation in contact with the CH_3OH–$Me_2Fc^{+/0}$ solution is the sum of qV_{n^+} and qV_{p^+}, and this sum is similar to the quasi-Fermi level separation measured for this sample in contact with air (before etching and at the same value of J_{sc}) when electrons and holes were collected at the back point contacts (Figure 2). This result confirms that minimal surface recombination was present at the Si/CH_3OH–$Me_2Fc^{+/0}$ interface; otherwise, V_{oc} would be much lower for the semiconductor/liquid contact than the device-limited value obtained for the semiconductor sample in air.

To validate further the conclusion that the quasi-Fermi levels were flat throughout these samples under our conditions, transient measurements of the photovoltage were performed. Si/CH_3OH–$Me_2Fc^{+/0}$ contacts on a 1.1- × 1.1-cm sample were exposed to a 10-ns, 532-nm light pulse from a Nd:YAG laser, and the

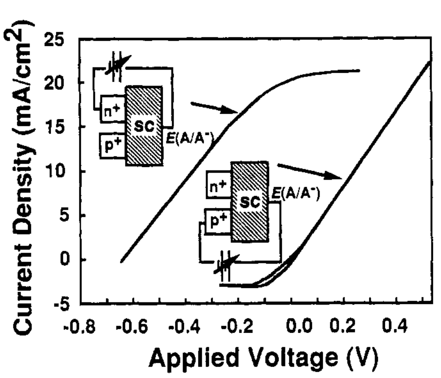

Figure 3. Current density–voltage behavior of Si/CH_3OH–1.0 M $LiClO_4$–0.11 M Me_2Fc–0.016 M Me_2FcBF_4 contacts under high level injection. The sample was etched in 48% HF for 6 min and in 2:5:15 HF:CH_3COOH:HNO_3(aq) for 60 s, followed by a 10-s etch in 48% HF(aq). This etch was used to remove the TiO_2 and oxide layers at the front surface and to remove 7 μm of the sample. This electrode was not run in an optimized cell configuration, so the relatively low fill factor results mainly from significant uncompensated resistance and concentration overpotential losses that can be minimized with optimal cell design (refs 8, 9, and 11). The J–V curve obtained between the p^+ points and the solution was not rectifying, with the cathodic current being limited by mass transport to the electrode surface. The light source was an ELH-type tungsten halogen bulb.

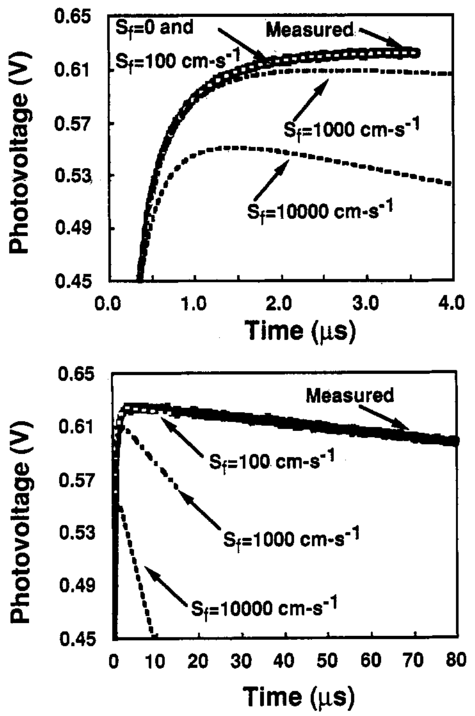

Figure 4. (a, top) Rise of the photovoltage of Si/CH_3OH–1.0 M $LiClO_4$–8.5 mM Me_2Fc–6.1 mM Me_2Fc^+ contacts as a function of time. The dashed lines (- - -) are the fits generated from the diffusional model. The simulated photovoltage rise assuming S_f = 0 cm·s^{-1} was identical to that calculated for S_f = 100 cm·s^{-1} on this time scale, but higher S_f values produced obvious deviations between the simulation and the data. The initial injection level (I_0) was taken as 2.9 × 10^{13} photons·cm^{-2}·$pulse^{-1}$, so that the maximum potential rise calculated from eq 3 agreed with the measured potential difference at 3.5 μs. The best fit simulation, with no other adjustable parameters, resulted in a thickness, d, of 113 μm, which was in excellent agreement with the calculated sample thickness of 113 μm resulting from etchant-induced removal of 7 μm from the 120 μm thick Si sample. (b, bottom) Photovoltage decay data for the junction of (a). The photovoltage decay time constant was 1.6 × 10^{-3} s. Simulations (dashed lines, - - -) showed that this decay time corresponded to a high level integrated recombination velocity of 1 × 10^2 cm·s^{-1}.

transient photovoltage between the n^+ and p^+ points was monitored with a 300-MHz bandwidth, 1-MΩ input impedance digital oscilloscope. The photovoltage transient was fit to an equation derived from a purely diffusional model for a sample of thickness d with an ambipolar diffusion coefficient, D, of 18 cm^2·s^{-1}.[18,28-30] The initial carrier distributions at time t = 0 ($n(x,0)$ and $p(x,0)$) were calculated using

$$n(x,0) = N_D + \alpha I_0 \exp(-\alpha x) \qquad (1)$$

$$p(x,0) = n_i^2/N_D + \alpha I_0 \exp(-\alpha x) \qquad (2)$$

with the absorption coefficient (α) for Si at 532 nm = 1.2 × 10^4 cm^{-1} [31] and I_0 equaling the injected carrier density per laser pulse. Recombination of carriers in the bulk was neglected because the carrier lifetime for this sample exceeds 1 ms, but a variety of surface recombination velocities were imposed for the boundary condition at the front surface. After computation of $n(x,t)$ and $p(x,t)$, the quasi-Fermi level separation at the back of the sample, $\Delta E_F(d,t) = |E_{F,n}(d,t) - E_{F,p}(d,t)|$, was calculated using the relation

$$n(d,t)\, p(d,t) = n_i^2\, [(\exp(\Delta E_F(d,t))/kT) - 1] \qquad (3)$$

As displayed in Figure 4a, the fit of the rising portion of the signal ($t \leq 3.5$ μs) to such a model with a high level front surface recombination velocity, S_f = (1.0 ± 0.3) × 10^2 cm·s^{-1} (which was indistinguishable from S_f = 0 on this time scale) was outstanding. The excellent agreement between theory and experiment in the rising portion of $\Delta E_F(d,t)$ indicates that carrier motion on these time scales is driven only by diffusion under our high injection conditions.

The quantitative agreement with $S_f \leq 1.0 \times 10^2$ cm·s^{-1} in Figure 4a is also important with respect to the conclusion that the quasi-Fermi levels are essentially flat througout our sample. The photovoltage transient data confirm earlier transient microwave and radio-frequency conductivity data[27] that yield $S_f < 10^3$ cm·s^{-1} at the Si/CH_3OH–$Me_2Fc^{+/0}$ contact, because the functional form of the photovoltage transient for $t \leq 3.5$ μs would be significantly different if $S_f > 1 \times 10^2$ cm·s^{-1} (Figure 4a). A one-dimensional device model incorporating carrier diffusion and front surface recombination with α = 1.2 × 10^4 cm^{-1} indicates that, for S_f = 1 × 10^3 cm·s^{-1}, the quasi-Fermi level positions in the bulk of the sample are only different by ≈14 meV (i.e., $<kT$) from those at the front surface, whereas $|E_{F,n}(d,\infty) - E_{F,n}(0,\infty)| < 2$ meV and $|E_{F,p}(d,\infty) - E_{F,p}(0,\infty)| < 2$ meV for S_f = 1 × 10^2 cm·s^{-1}. Thus, using S_f = 1 × 10^2 cm·s^{-1}, as opposed to the more stringent condition imposed by the measured value of S_f = 40 cm·s^{-1} for this solid/liquid interface,[27] the quasi-Fermi level positions at the back of the specimen are calculated, conservatively, to be within 2 meV of their values near the solid/liquid interface. This conclusion is further strengthened by the measured photovoltage decay time constant, which was (1.4 ± 0.3) × 10^{-3} s for the entire point contact Si/CH_3OH–$Me_2Fc^{+/0}$ junction (Figure 4b). The hypothesis that all of the recombination that produced this (1.4 ± 0.3) × 10^{-3} s decay time constant occurred at the front surface of the sample would yield the largest gradient in the quasi-Fermi levels, yet even this assumption only yields a high level surface recombination velocity of 1.0 × 10^2 cm·s^{-1} and a calculated gradient of <2 meV in $E_{F,n}$ or in $E_{F,p}$ between the bulk and surface of the specimen. Thus, the values measured at the point contacts in our device yield excellent approximations to the apparent electrochemical potentials of the charge carriers near the solid/liquid contact.

In conclusion, we have shown that the theoretically predicted quasi-Fermi levels can be directly measured at an illuminated semiconductor in contact with a liquid. The data indicate that the quasi-Fermi levels of electrons and holes for an operating semiconductor/liquid contact can be measured individually as apparent electrochemical potentials through n^+ and p^+ point contacts in the specially designed samples described herein. We have also shown that the photovoltage transients under high level injection conditions are well-modeled by diffusional processes and that the quasi-Fermi levels are essentially flat throughout our sample under our experimental conditions. This implies that the voltages measured at the back of the specimen yield good estimates to the quasi-Fermi level positions near the semiconductor/liquid interface. These field-free, long lifetime, lithographically patterned samples provide a unique opportunity to verify further aspects of the theory of semiconductor/liquid junctions, and such results will be presented in the future.

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