(13) (a) Gerischer, H. *Adv. Electrochem. Eng.* **1961**, *1*, 139. (b) Gerischer, H. In "Physical Chemistry: An Advanced Treatise", Vol 9A; Eyring, H., Henderson, D., Jost, W., Eds.; Academic Press: New York, 1970; Vol. 9A.
(14) Kurtin, S.; Mead, C. A. *Phys. Rev. Lett.* **1969**, *22*, 1433.
(15) Kohl, P. A.; Bard, A. J. *J. Electrochem. Soc.* **1979**, *126*, 598.
(16) Bocarsly, A. B.; Bookbinder, D. C.; Dominey, R. N.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.*, following paper in this issue.
(17) (a) Gerischer, H. *J. Electroanal. Chem.* **1977**, *82*, 133. (b) Bard, A. J.; Wrighton, M. S. *J. Electrochem. Soc.* **1977**, *124*, 1706. (c) Park, S.-M., Barber, M. E. *J. Electroanal. Chem.* **1979**, *99*, 67.

Photoreduction at Illuminated p-Type Semiconducting Silicon Photoelectrodes. Evidence for Fermi Level Pinning

Andrew B. Bocarsly, Dana C. Bookbinder, Raymond N. Dominey, Nathan S. Lewis, and Mark S. Wrighton*

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received November 5, 1979*

Abstract: Studies of p- and n-type Si electrodes are reported which show that semiconducting Si electrode surfaces do not allow efficient H_2 evolution in the dark (n type) or upon illumination with band gap or greater energy light (p type). The key experiment is that *N,N′*-dimethyl-4,4′-bipyridinium (PQ^{2+}) is reversibly reduced at n-type Si in aqueous media at a pH where H_2 should be evolved at nearly the same potential, but no H_2 evolution current is observable. The $PQ^{2+/+\cdot}$ system may be useful as an electron-transfer mediator, since $PQ^{+}\cdot$ can be used to effect generation of H_2 from H_2O using a heterogeneous catalyst. The $PQ^{+}\cdot$ can be produced in an uphill sense by illumination of p-type Si in aqueous solutions. Studies of p-type Si in nonaqueous solvents show that PQ^{2+}, $PQ^{+}\cdot$, $Ru(bpy)_3{}^{2+}$, $Ru(bpy)_3{}^{+}$, and $Ru(bpy)_3{}^{0}$ are all reducible upon illumination of the p-type Si. Interestingly, each species can be photoreduced at a potential ~500 mV more positive than at a reversible electrode in the dark. This result reveals that a p-type Si-based photoelectrochemical cell based on $PQ^{2+/+\cdot}$, $PQ^{+/0}$, $Ru(bpy)_3{}^{2+/+}$, $Ru(bpy)_3{}^{+/0}$, or $Ru(bpy)_3{}^{0/-}$ would all yield a common output photovoltage, despite the fact that the formal potentials for these couples vary by more than the band gap (1.1 V) of the photocathode. These data support the notion that p-type Si exhibits Fermi level pinning under the conditions employed. Fermi level pinning refers to the fact that surface states pin the Fermi level to a given value such that band bending (barrier height) is fixed and any additional potential drop occurs across the Helmholtz layer of the electrolyte solution at charge-transfer equilibrium. Surface chemistry is shown to be able to effect changes in interface kinetics for electrodes exhibiting Fermi level pinning.

We recently communicated results[1] showing that illumination of a p-type Si photoelectrode could be used to effect sustained, uphill reduction of *N,N′*-dimethyl-4,4′-bipyridinium (PQ^{2+}):

$$PQ^{2+} \xrightarrow[\text{p-Si}]{\text{light, potential}} PQ^{+}\cdot \qquad (1)$$

The light energy required must be greater than the band gap, E_{BG}, of Si, 1.1 eV,[2] and the electrode potential, E_f, at which the reduction can be effected is ~0.5 V more positive than at a reversible electrode such as Pt. Part of the significance of these results is that reaction of $PQ^{+}\cdot$ according to the equation[3]

$$2PQ^{+}\cdot + 2H_2O \xrightarrow[\substack{\text{catalyst} \\ \text{pH} < 6}]{\Delta,\ 25\ ^\circ\text{C}} H_2(g) + 2OH^- + 2PQ^{2+} \qquad (2)$$

allows the light-driven evolution of H_2 from H_2O in an uphill sense. The ~0.5 V is the maximum contribution to the 1.23 V minimum needed[4] to split H_2O according to the equation

$$H_2O(\ell) \rightarrow H_2(g) + {}^1\!/_2O_2(g) \qquad (3)$$

Thus, a photoelectrochemical cell as sketched in Figure 1 can be used to effect the decomposition of H_2O according to eq 3 where the added electrical power supply in series in the external circuit provides as little as 0.73 V toward the driving force needed to drive the electrolysis.

In the cell depicted in Figure 1 the $PQ^{2+}/PQ^{+}\cdot$ system is necessary for efficient operation of the cell because the current density for direct H_2 production under the same conditions is very small. The apparent role, then, of the $PQ^{2+}/PQ^{+}\cdot$ system is to provide an oxidized material which is efficiently photoreduced, eq 1, and a reduction product which can be efficiently reacted with H_2O to evolve H_2, eq 2. The $PQ^{2+}/PQ^{+}\cdot$/catalyst system is said to be an electron-transfer catalyst system for H_2 evolution at the irradiated p-type Si photocathode; similar results obtain for p-GaAs.[5]

Our studies of p-Si[1] and n-Si[6] photoelectrodes have led to some unexpected findings within the framework of the model for an ideal semiconductor contacting a liquid electrolyte solution.[7] These results bear significantly on possible mechanisms for improving the efficiency of the process depicted in Figure 1, and in particular on the nature of semiconductor/liquid interface energetics in general. In the two preceding articles the concept of Fermi level pinning was described[8a] and experimental evidence for this was given for GaAs.[8b] In this article we amplify our findings of p-type Si/liquid junctions and provide strong experimental evidence for the conclusion that p-type Si contacting a liquid electrolyte solution can result in an output photovoltage that is independent of the electrochemical potential, E_{redox}, of the solution, contrary to our expectation based on the usual semiconductor/liquid interface model.[7] We show additional results indicating that derivatization of the surface with molecular reagents can influence the interfacial charge-transfer kinetics.

Results and Discussion

A. H_2 Evolution from Si Electrode Surfaces. The notion that H_2 evolution from Si has a large overpotential stems first from the observation that very few electrode materials yield a high exchange current density for the H_2O/H_2 redox couple. Various reasons exist for the general overpotential associated with H_2 evolution but the result is that more voltage than is thermodynamically needed is required to evolve H_2 at a given rate (current density). p-Type semiconductor photocathodes should be able to effect H_2 evolution under illumination for an

0002-7863/80/1502-3683$01.00/0

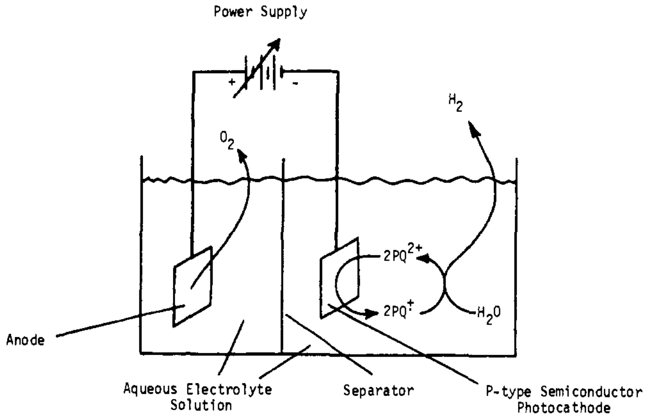
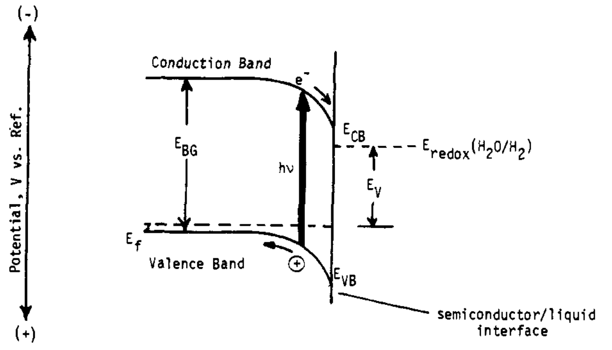


Figure 1. Sketch of p-type semiconductor based cell for the photoelectrolysis of H_2O to H_2 and O_2 using an electron-transfer catalyst system in the photocathode compartment.

Scheme I. Interface Energetics Suitable for Light-Driven Uphill H_2 Evolution from a p-Type Semiconductor



interfacial energetic situation where the bottom of the conduction band, E_{CB}, is more negative than the H_2O/H_2 potential, Scheme I, since the maximum reducing power of the excited electrons is E_{CB}. The difference between E_{CB} and $E_{redox}(H_2O/H_2)$ can be thought of as the excess driving force for evolving the H_2. The extent to which the H_2 can be evolved in an uphill sense, E_v, is given by the difference between $E_{redox}(H_2O/H_2)$ and the electrochemical potential of the p-type semiconductor, E_f, where H_2 is being generated. The band bending provides for the spatial separation of photogenerated electron-hole pairs such that the majority carrier (hole) is driven into the bulk and the minority carrier (electron) is driven to the interface to be available for a reduction process. Since electrons are unavailable in the dark, optical excitation is required to effect a reduction process. However, holes are the majority charge carrier and p-type electrodes can be used to effect dark anodic processes. Thus, p-type electrodes are photocathodes and dark anodes. By way of contrast, n-type semiconductors have electrons as the majority charge carrier and are dark cathodes but require light to generate holes to effect anodic processes.[9]

When contacting a common solution, it would be expected that an n-type semiconductor and a p-type semiconductor of the same material, e.g., Si, would have the same positions of E_{VB} and E_{CB}.[10] We can use this notion to illustrate the poor kinetics associated with H_2 evolution from the Si surface. Since n-type Si should serve as a dark cathode it should be capable of serving as an electrode for H_2 evolution in H_2O electrolyte solution when E_f is moved sufficiently negative. It has been claimed that E_{CB} is at ~−0.3 V vs. SCE for n-type Si in aqueous media;[11] thus, for pH values where $E_{redox}(H_2O/H_2)$ is more negative than this E_{CB} position we would expect facile H_2 evolution. However, as shown in Figure 2, at pH 5.5 the rate of H_2 evolution is very slow even for n-type Si electrode potentials that are as far negative as −1.4 V vs. SCE. Under the same conditions (pH, electrolyte) a material in the solution such as PQ^{2+} is easily reducible in the dark at n-type Si as evidenced by the cyclic voltammetry data included in Figure 2. The reduction of 2 mM PQ^{2+} appears to be essentially reversible at potentials where no H_2 evolution current is observable. The formal potential of the $PQ^{2+}/PQ^{+}\cdot$ system under the conditions used is −0.61 V vs. SCE as determined by cyclic voltammetry at a Pt electrode.[12]

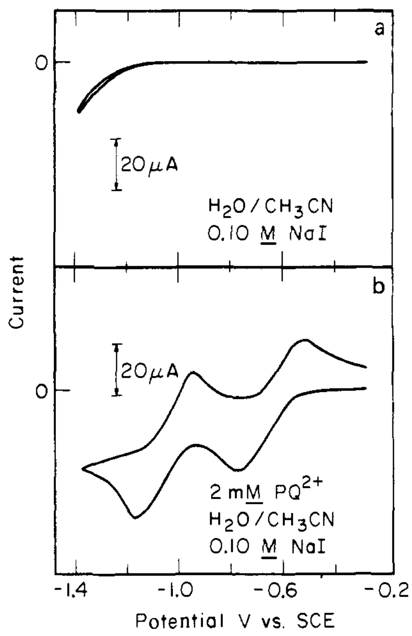


Figure 2. Cyclic voltammetry (100 mV/s) for n-Si. (a) In H_2O/CH_3CN (70/30) with 0.10 M NaI (pH 5.5). (b) Same solution with 2 mM PQ^{2+} added.

The data in Figure 2 show that H_2 evolution from n-type Si is slow under conditions where the generation of H_2 is energetically possible and where $E_{redox}(H_2O/H_2)$ is situated more negative than E_{CB} where a good reduction rate could be expected. A fast heterogeneous redox system, $PQ^{2+}/PQ^{+}\cdot$, is reversible under the same conditions. Thus, if *p-type* Si were to be considered as a photocathode material, the expectation is that H_2 evolution would be slow kinetically except for E_{CB} much more negative than $E_{redox}(H_2O/H_2)$ where the photogenerated electron may have the excess driving force to overcome a kinetically sluggish reduction process. But the facile reduction of PQ^{2+} suggests that the H_2 evolution could be subsequently effected according to eq 2.

B. Photoreduction of PQ^{2+} at p-Type Si. For the reasons outlined above we proposed the $PQ^{2+}/PQ^{+}\cdot$/catalyst system as a scheme for mediating the photoinduced evolution of H_2 from aqueous solution. Good results are found in the sense that efficient photoreduction of PQ^{2+} to $PQ^{+}\cdot$ does occur at an illuminated p-type Si photocathode.

Figure 3 shows a comparison of the cyclic voltammetry for PQ^{2+} at a reversible Pt electrode and for a p-type Si electrode in dry CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ solution. The data show that the PQ^{2+} can be reduced at either Pt or illuminated p-Si first to $PQ^{+}\cdot$ and then to PQ^0. However, the photocathodic processes each occur ~500 mV more positive than on the Pt electrode. Consistent with the discussion above, for p-type semiconductors, the cathodic process at p-Si can only be effected when the electrode is excited with $\geq E_{BG}$ light. The ~500 mV more positive reduction peaks are one measure of the extent to which light can be used to drive the reduction process uphill.

In our earlier communication,[1] we showed steady-state photocurrent-voltage curves in stirred, high-concentration

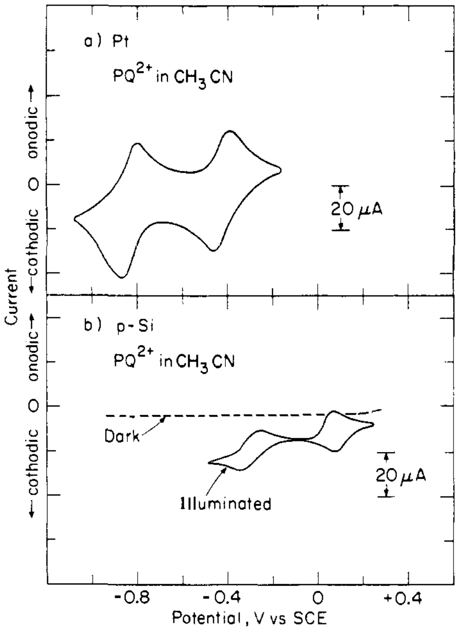


Figure 3. Cyclic voltammetry (100 mV/s) of 2 mM PQ^{2+} in CH_3CN with 0.10 M [*n*-Bu_4N]ClO_4. (a) Pt wire. (b) p-Si (i) dark; (ii) illuminated (632.8 nm, 50 mW/cm^2).

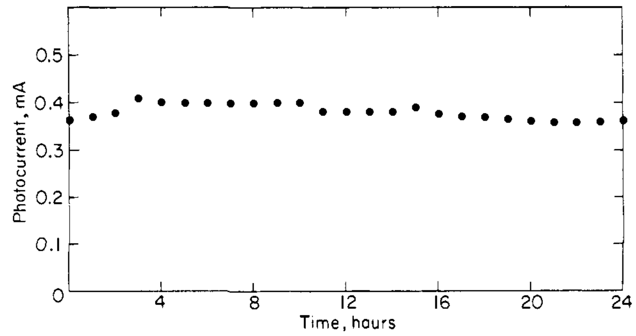
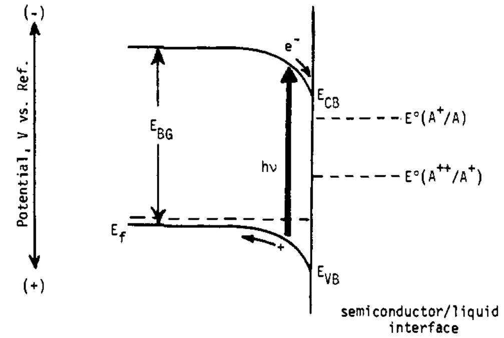


Figure 4. Plot of current vs. time for a p-Si (~0.10 cm^2) illuminated (632.8 nm, 50 mW/cm^2). The electrode was immersed in a stirred H_2O/CH_3CN (70/30) solution of 0.025 M PQ^{2+} and 0.10 M NaI. The electrode potential was fixed at −0.4 V vs. SCE.

Scheme II. Ideal Semiconductor/Liquid Interface Energetics for Sequential Two-Electron Photoreduction $A^{2+} \rightarrow A^{+} \rightarrow A$



PQ^{2+} solutions consistent with the cyclic voltammetry given in Figure 3. Short-circuit quantum yields exceeding 0.5 and maximum output voltages of ~500 mV gave photoelectrochemical conversion of visible light to electricity with an efficiency of several percent based on the $PQ^{2+}/PQ^{+}\cdot$ chemistry. Figure 4 illustrates that good photocurrent densities can be sustained for long periods of time without deterioration of the output properties of the p-type Si photocathode.

C. Discord between Theory and Experiment. Photoreduction of PQ^{2+} and Other Species at p-Type Si. The efficient photoreduction of PQ^{2+} at p-type Si is surprising, since the results in Figure 2 indicate that $E^0(PQ^{2+}/PQ^{+}\cdot)$ is more negative than E_{CB}. The model implied in Scheme I would suggest that for E_{redox} more negative than E_{CB} little or no photocurrent would be expected. The $E^0(PQ^{+}\cdot/PQ^0)$ is even ~400 mV more negative than $E^0(PQ^{2+}/PQ^{+}\cdot)$, and yet the photocathodic reduction of $PQ^{+}\cdot$ to PQ^0 can also be effected in an uphill sense to the extent of ~500 mV.

The fact that there are two one-electron waves for the overall $PQ^{2+} \rightarrow PQ^0$ process is another inconsistency with the model even if for some reason the positions for E_{CB} for n- and p-type Si are not the same. Scheme II shows the interfacial picture expected for a redox-active system having two well-separated and reversible one-electron processes where a photoeffect would be expected. When the two E^0's are situated between E_{CB} and E_{VB}, the ideal model leads to the expectation that there would be one, two-electron wave for the $A^{2+} \rightarrow A^0$ process at a p-type photocathode illuminated at sufficiently high light intensity. This follows from the fact that the excited electrons have sufficient reducing power (E_{CB}) to reduce either A^{2+} or A^{+}. Yet we see two one-electron waves at p-type Si for the $PQ^{2+} \rightarrow PQ^0$ even at high intensities available from an Ar ion laser; the separation of the waves for $PQ^{2+}/PQ^{+}\cdot$ and $PQ^{+}\cdot/PQ^0$ is insensitive to the light intensity for light intensities above the value that gives well-defined waves. Interestingly, the two waves on p-type Si are separated by an amount nearly identical with their spacing on a reversible electrode such as Pt (see Figure 3). Such a result was previously reported[13] for photoreduction of $Ru(bpy)_3{}^{2+}$ at p-GaAs.

In our studies[6] of two-electron photooxidations at illuminated n-type Si we found that two, one-electron waves are generally found for species such as *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) and bis(fulvene)diiron (BFD) for the processes TMPD → $TMPD^{+}\cdot$ → $TMPD^{2+}$ and BFD → $BFD^{+}\cdot$ → BFD^{2+}. In those cases we invoked an important role for surface states, electronic levels situated between E_{VB} and E_{CB}, that effectively allow a potential-dependent oxidizing power for the photoanode. If surface states are present and have sufficient density, they can effectively provide a mechanism for back electron transfer to the primary photooxidation product at electrode potentials E_f that are more positive than the flat-band potential. For p-type materials such as Si a similar argument could also be used to account for the two, one-electron reduction waves by invoking surface states to allow back reaction to preclude direct $PQ^{2+} \rightarrow PQ^0$ reduction at potentials more positive than a certain value. We do believe surface states to be very important, but their role goes beyond controlling recombination kinetics, as the following experiments show.

Thinking that the $PQ^{2+} \rightarrow PQ^{+}\cdot \rightarrow PQ^0$ photoreduction at p-type Si is unusual we decided to examine other solution redox reagents. Figure 5 shows a remarkable result: illumination of p-type Si photocathode can be used to effect the uphill reduction of ferricenium, PQ^{2+}, $PQ^{+}\cdot$, $Ru(bpy)_3{}^{2+}$, $Ru(bpy)_3{}^{+}$, and $Ru(bpy)_3{}^{0}$. The cyclic voltammetry at a Pt electrode for each of these species is shown for comparison. With the exception of the ferricenium/ferrocene system, each one-electron wave at the Pt electrode is seen at the p-type Si photocathode but shifted positive by ~440 mV. This indicates that illumination of p-Si can be used to effect the uphill, one-electron reduction of $Ru(bpy)_3{}^{0}$ to the extent of ~440 mV! The ferricenium system does not show a significant positive shift, but by using modulated optical excitation we find the onset potential for ferricenium photoreduction to be ~+0.9 V vs. SCE or ~400–500 mV more positive than the usual onset for a reversible electrode such as Pt. The positive potentials do lead to very facile oxidation processes involving SiO_x formation from traces of H_2O in the solvent, as well as the apparent ox-

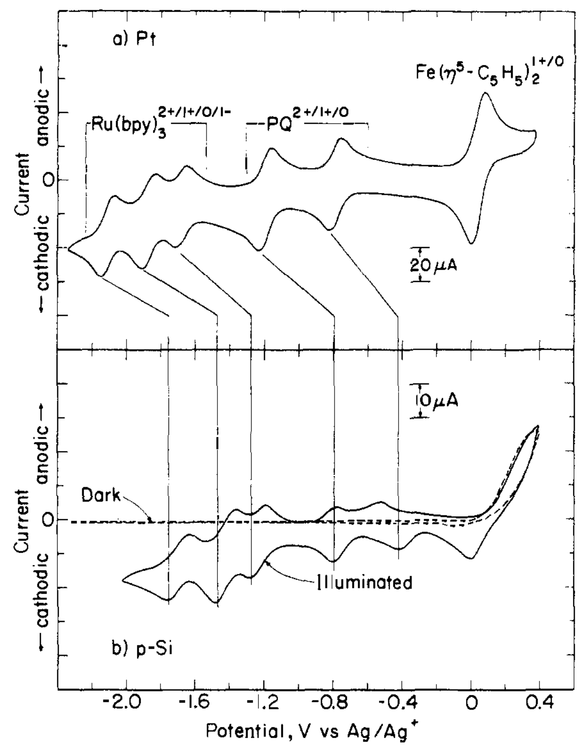


Figure 5. Cyclic voltammetry (100 mV/s) of a solution containing 2 mM $Fe(\eta^5\text{-}C_5H_5)_2$, 1 mM PQ^{2+}, and 1 mM $Ru(bpy)_3{}^{2+}$ in CH_3CN with 0.10 M $[n\text{-}Bu_4N]ClO_4$. (a) Pt wire. (b) p-Si (i) dark; (ii) illuminated (632.8 nm, 50 mW/cm^2).

idation of ferrocene at nearly the same potential as at Pt. However, no ferricenium reduction is found unless the p-Si is illuminated.

The main finding from Figure 5 is that for redox couples whose formal potentials span the range -1.75 to $+0.40$ V vs. SCE a large photocathodic current can be obtained at p-type Si. The range of potentials may be even greater, but the data allow us to conclude that for a series of couples whose $E°$'s are more widely spaced than the value of E_{BG} one can see a photocathodic effect. For Si the value of E_{BG} is 1.1 eV[2] and the $E°$'s are separated by ~2.1 eV! Such a situation is not expected within the framework of the ideal semiconductor/liquid interface model.

From the data in Figure 5 it is apparent that for a number of redox couples the output photovoltage is independent of $E°$ for the couple. For ferrocene the amount of band bending is also in the vicinity of 500 mV but the surface states provide fast oxidation kinetics for the ferrocene. On the basis of nearly constant output voltage for $E°$'s differing by greater than E_{BG} of the semiconductor we conclude that the surface states on the p-type Si pin the Fermi level such that the band bending (barrier height) is independent of the $E°$ of the couple in solution.[8a] In such an instance the band bending is the same at charge-transfer equilibrium for any couple and any additional drop in potential occurs across the Helmholz layer in the solution. The p-type Si is said to exhibit Fermi level pinning, and without specific adsorption or surface chemistry any redox couple in solution will give the same barrier height.[8a]

When Fermi level pinning exists, the photoelectrode can be thought of as equivalent to having a Schottky cell in series in the external circuit providing a constant driving force between the two electrodes. In the same sense that a Hg cathode only sluggishly yields H_2,[14] the p-type Si photocathode has poor kinetics for H_2 evolution also. But other redox reagents, Figure 5, are fast at p-type Si and a good output voltage and photocurrent can be realized.

D. Fermi Level Pinning and Mediated H_2 Generation. A large number of oxidized substances are capable of being photoreduced at p-type Si. However, with respect to mediated photogeneration of H_2, the objective remains to effect the uphill generation of a reductant capable of making H_2 and one that is generated at potentials substantially more positive than H_2 evolution at a reversible H_2O/H_2 electrode. For example, $Ru(bpy)_3{}^0$ can be photoreduced to $Ru(bpy)_3{}^-$ in an uphill sense, but the electrode potential at which the photoreduction can be effected is more negative than H_2 evolution even in strongly alkaline solution. The point is that Fermi level pinning allows photogeneration of very powerful reductants in an uphill sense, but whether such is useful to evolve H_2 depends on the energetics of the overall process. The ideals are (1) to generate a species, A, capable of producing H_2 where the formal potential of A^+/A is just slightly more negative than H_2O/H_2 under the same conditions, (2) to work with a semiconductor having a direct band gap of 1.4 eV, for optimum solar response, (3) to effect the reduction of A^+ to A in an uphill sense to an extent approaching the band gap of the semiconductor, and (4) to have a quantum yield approaching unity. To achieve good output photovoltage from semiconductor photoelectrodes exhibiting Fermi level pinning because of surface states it may be necessary to do surface chemistry to change kinetics and energetics. The final section below (F) gives some preliminary results in this area indicating that manipulations are at least possible.

E. Limits to Fermi Level Pinning. PQ^{2+} at n-Type Si and Ferrocene at p-Type Si. In contacting semiconductors with liquid electrolyte solutions containing redox reagents it may not be possible to obtain the output photovoltage that would be expected from the barrier height observed. The lack of a good photovoltage may reflect the fact that there are mechanisms for back electron transfer. Such seems to be the case for ferricenium photoreduction at p-type Si; a photoreduction onset at $+0.9$ V vs. SCE can be detected, but the ferrocene formed is easily reoxidized at potentials more positive than $+0.4$ V vs. SCE.

Similar situations at n-type materials may well exist. For example, reduction of PQ^{2+} and $PQ^{+}\cdot$ is reversible at n-type Si, and there is no detectable photoeffect on the oxidation of PQ^0 or $PQ^{+}\cdot$ under conditions where ferrocene can be photooxidized in an uphill sense to the extent of ~400 mV, Figure 6. The complete lack of a photoeffect on the PQ^0 or $PQ^{+}\cdot$ oxidation indicates that there is not a depletion layer in the semiconductor and that the Fermi level pinning does not apply. But for materials such as TMPD and BFD it would appear that Fermi level pinning does apply.

One final point is worth making. When preparing Schottky barriers (semiconductor/metal junctions) the contact between semiconductor/metal may be "ohmic". For our purposes here we can think of an ohmic contact as one involving little or no barrier and allowing uninhibited charge transfer (nonresistive) through it. Ohmic contacts can be made even for semiconductors which exhibit Fermi level pinning. In making ohmic contacts the rule of thumb would be that one must contact the valence band for p-type materials and the conduction band for n-type materials.[15]

In contacting semiconductors with liquid electrolyte solutions of redox reagents the analogue of an ohmic contact is reversible electron transfer in the dark. Again the rule of thumb would be to contact the conduction band for n-type and the valence band for p-type semiconductors. Thus, it would appear that only redox couples which are sufficiently negative will result in Fermi level pinning at p-type semiconductors and only those couples that are sufficiently positive will result in Fermi level pinning at n-type semiconductors. It would appear that $E°(PQ^{2+}/PQ^{+}\cdot)$ is sufficiently negative to make an "ohmic" contact to n-type Si and that $E°$(ferricenium/ferrocene) may come close to making an "ohmic" contact to p-type Si. By way of contrast, couples that are at very negative potentials, e.g.,

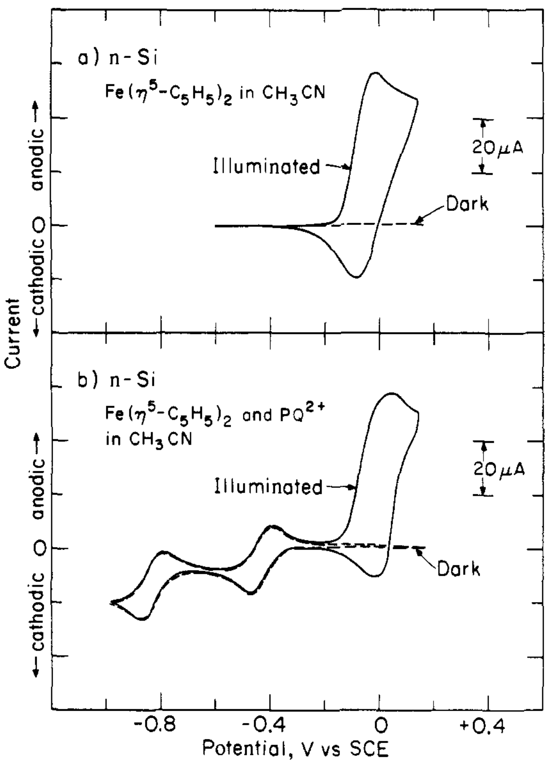


Figure 6. Cyclic voltammetry (100 mV/s) for an n-Si photoanode in CH_3CN with 0.10 M $[n\text{-}Bu_4N]ClO_4$. (a) 2 mM $Fe(\eta^5\text{-}C_5H_5)_2$ (i) dark; (ii) illuminated (632.8 nm, 50 mW/cm²). (b) 2 mM $Fe(\eta^5\text{-}C_5H_5)_2$ and 1 mM PQ^{2+} (i) dark; (ii) illuminated.

anthracene/anthracene$^-$· ($E°$ = −1.94 V vs. SCE), do not make an ohmic contact at n-GaAs.[13]

Thus, in addition to changes in the barrier height that might be brought about by specific adsorption and other surface chemistry, the barrier may be nonexistent for couples which are sufficiently negative at n-type or sufficiently positive at p-type semiconductors. Therefore, though Fermi level pinning may occur for a large number of couples, the range of redox potentials over which this can occur is not well defined and the mechanism for forming the "ohmic" contact is not clear. One real possibility is that redox reagents which do make an ohmic contact effect changes in surface chemistry which will alter the surface states. But this cannot be the only mechanism, since ferricenium/ferrocene behaves essentially the same at illuminated n-type Si independent of whether the PQ^{2+} is present.

F. Surface Chemistry and Interfacial Charge-Transfer Kinetics. The charge-transfer kinetics for oxidation and reduction of solution species is believed to be very sensitive to the nature of the surface. When Fermi level pinning occurs for the semiconductor/liquid junction, it is also possible that surface chemistry can have profound effects on the kinetics. In our studies of the electrochemistry of ferrocene at p-type Si we have discovered that whether there is an observable dark reduction of ferricenium depends on the pretreatment of the p-Si surface. Our usual pretreatment is etching the p-type Si with HF. The electrode can then be used in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ to effect a dark oxidation of ferrocene to ferricenium but the reduction of ferricenium requires illumination of the p-type semiconducting photocathode, Figure 5. However, if the same HF etch pretreatment is used and the electrochemistry is done in EtOH/0.1 M $[n\text{-}Bu_4N]ClO_4$, instead of the CH_3CN solution, both oxidation of ferrocene and reduction of ferricenium can be effected in the dark. Further, if the electrode is then taken from the EtOH solution and put back in the CH_3CN solution, the ferricenium reduction in the dark persists for a fairly long period of time (several cyclic voltammograms at 100 mV/s). It would appear that EtOH reacts with the surface in such a way that the ferricenium reduction becomes possible in the dark, presumably via EtOH-induced changes in the surface state distribution.

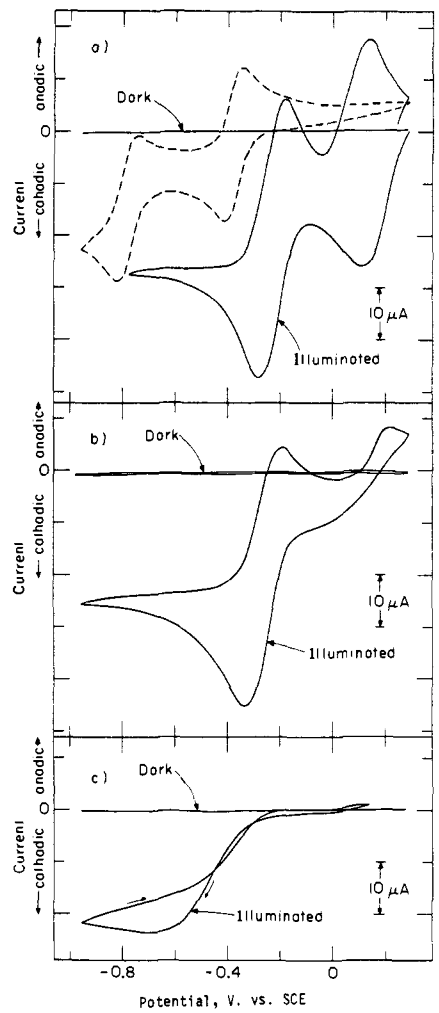


Figure 7. (a) Cyclic voltammetric characterization of Pt (---) and naked HF etched electrodes in a 1 mM $(PQ)(PF_6)_2$/0.1 M $[n\text{-}Bu_4N]ClO_4$/ACN solution at a scan rate of 100 mV/s. Illumination is from a He-Ne laser at 632.8 nm, ~4.5 mW over the entire surface (~10 mm²). (b) Cyclic voltammograms at 100 mV/s of the same p-Si electrode used in (a) after being derivatized with (1,1′-ferrocenediyl)dichlorosilane to a coverage of ~2.4×10^{-8} mol/cm². (c) Dark and illuminated cyclic voltammograms at 100 mV/s of the same p-Si electrode used in (a) and (b) after further derivatization to a coverage of ~1.1×10^{-7} mol/cm².

Another type of surface chemistry that may be important is in cases where electroactive materials are confined to the surface of the electrode. For example, confining ferrocene moieties to the surface of n-type Si via reaction with (1,1′-ferrocenediyl)dichlorosilane[16] results in a derivatized electrode which is essentially passive to the $PQ^{2+}/PQ^{+}\cdot/PQ^0$ system, whereas the "naked" (nonderivatized) electrode is reversible for the same redox system, Figure 2. n-Type Si electrodes having 1.9×10^{-8} to 2.1×10^{-7} mol of electroactive ferrocene per cm² of projected surface area show no evidence of well-defined PQ^{2+} or $PQ^{+}\cdot$ reduction waves. Electrodes having coverage as low as 4×10^{-9} mol/cm² show considerable attenuation of PQ^{2+} reduction waves. Derivatizing p-type Si with the same derivatizing reagent precludes its use in the uphill photoreduction of PQ^{2+} that can be effected at the naked surface, Figure 7. These illustrations of retarding electron transfer likely arise from the fact that the derivatizing layer is a neutral species in the reduced form and apparently cannot effect the reduction of PQ^{2+}. Effecting changes in the available "surface states" by molecular derivatization is one approach to change the effects resulting from Fermi level pinning arising from intrinsic surface states of the semiconductor.

It should be noted that our discussion of "surface states" here includes the electronic levels that are associated with the surface species present whether they be "intrinsic" or due to SiO_x/Si, Si/SiO_x/molecular reagent, etc. The comparison of a pure Si surface to our electrode surfaces exposed to solutions would be important but has not yet been the object of our studies.

Summary

p-Type Si can be used as a photocathode to drive the uphill reduction of a number of species. The extent to which substances can be reduced in an uphill sense is ~500 mV, independent of the formal potential of the redox couple. The redox potential independent output voltage indicates that p-type Si exhibits Fermi level pinning. Species that can be photoreduced in aqueous solution may be useful as mediators for H_2 evolution provided that the reduced form reacts (or can be catalyzed to react) with H_2O to yield H_2 and can be photogenerated at electrode potentials more positive than the H_2O/H_2 couple at a reversible electrode under the same conditions. Subtle changes from surface chemistry with solvent, e.g., CH_3CN vs. EtOH, can have a profound effect on the photoelectrochemical properties and designed changes by using molecular derivatizing reagents may be possible routes to improved photovoltages and interface kinetics.

Experimental Section

Materials. Single-crystal p-type Si wafers (0.35 mm thick, 111 face) doped with B and with a resistivity of 3-7 Ω cm were obtained from Monsanto Co., Electronics Division (Palo Alto, Calif.). Ohmic contact to the back side of the Si was made by first masking the polished side of the wafer with epoxy cement, then placing the wafer into an electroless Ni plating solution as reported by Sullivan and Eigler.[17] The epoxy was then dissolved in reagent-grade CH_2Cl_2 and the Si cut into pieces of an area ~0.2 cm^2. The Ni-plated surface was then rubbed with a Ga-In eutectic and secured to a coiled Cu wire with conducting silver epoxy. The Cu wire lead was passed through 4-mm glass tubing; then all surfaces were sealed with ordinary epoxy so as to leave only the front surface (111 face) of the p-Si single crystal semiconductor exposed.

Just prior to use, all electrodes were pretreated by etching at 298 K in concentrated HF for 60 s, rinsed with distilled water and then with acetone, and air dried.

Derivatized electrodes for study of attenuation of reversible electrochemistry of PQ^{2+} were prepared using (1,1′-ferrocenediyl)dichlorosilane[16] as the derivatizing reagent. Derivatization was carried out by dipping the Si electrode in 10 M NaOH at 25 °C for 60 s subsequent to the HF etch. The electrode was then immersed in an alkane solution of the derivatizing reagent under Ar and allowed to react for variable periods of time. Coverage of electroactive ferrocene material was determined by integration of cyclic voltammetry waves corresponding to redox of the confined ferrocene moieties. High-coverage (~10^{-7} mol/cm^2) derivatization was achieved by dropping alkane solutions of the reagent onto the surface under Ar and the surface was then "cured" in air at 25 °C.

Chemicals. Spectrograde CH_3CN was distilled from P_2O_5; [*n*-Bu_4N]ClO_4 (Southwestern Analytical Chemicals) was vacuum dried at 70 °C for 24 h. NaI or $NaClO_4$ was obtained from commercial sources and used without further purification. *N,N*′-Dimethyl-4,4′-bipyridinium iodide ($PQ^{2+}2I^-$) and $PQ^{2+}2PF_6^-$ salts were prepared as previously described.[18] Ferricenium tetrafluoroborate was recrystallized twice from EtOH/$(CH_3)_2CO$. $[Ru(bpy)_3]^{2+}$ (Baker) was used as the PF_6^- salt.

Electrochemical Equipment and General Procedures. All experiments employed solutions of CH_3CN/0.10 M [*n*-Bu_4N]ClO_4 (which were passed through anhydrous, neutral Al_2O_3 just prior to use to assure dryness) or solutions of distilled H_2O/CH_3CN (70/30 by volume) containing either 0.10 M NaI or $NaClO_4$. All solutions were degassed using an Ar purge and then kept under a positive pressure of Ar.

Cyclic voltammograms and steady-state current-voltage curves were obtained using a PAR Model 173 potentiostat equipped with a Model 175 programmer. Data were recorded on a Houston Instruments XY recorder, or, for current vs. time plots, on a Hewlett-Packard strip chart recorder. For cyclic voltammograms a single-compartment cell was used employing a standard three-electrode configuration with a Si photocathode, a Pt counterelectrode, and reference electrodes being either a saturated calomel electrode (SCE) or a silver wire immersed in 0.10 M $AgNO_3$/0.1 M [*n*-Bu_4N]ClO_4 in CH_3CN. Current vs. time experiments were carried out using the same type of cell except that a Hg pool counterelectrode was used in place of a Pt wire.

Electrodes were illuminated using a beam-expanded 632.8-nm He-Ne laser (Coherent Radiation) providing ~50 mW/cm^2 or an Ar ion laser (Spectra Physics Model 164) tuned to the 514-nm line. Laser intensity was varied using Corning colored glass filters and monitored using a beam splitter and a Tektronix J16 radiometer equipped with a J6502 probe. The laser beam was masked to match the size of the Si surface. The light intensity used was sufficiently high to ensure that photocurrent was controlled by diffusion of the redox reagents in the solution in the cyclic voltammetry experiments.

Electrodes were routinely checked by running current-voltage curves at different light intensities in a solution of 25 mM $PQ^{2+}2I^-$/0.1 M NaI in H_2O/CH_3CN (70/30) at 10 mV/s under illumination. Good electrodes show a photocurrent onset near 0.0 V vs. SCE, fill factors >0.6, and quantum yield for electron flow ⩾0.4 at −0.4 V vs. SCE.

Acknowledgment. We thank the National Aeronautics and Space Administration (support for A.B.B.) and the U.S. Department of Energy, Office of Basic Energy Sciences (support for R.N.D. and D.C.B.), for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar, 1975–1980, and N.S.L. acknowledges support as a John and Fannie Hertz Predoctoral Fellow, 1977–present.

References and Notes

(1) Bookbinder, D. C.; Lewis, N. S.; Bradley, M. G.; Bocarsly, A. B.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7721.

(2) Wolf, H. F. "Silicon Semiconductor Data"; Pergamon Press: Oxford, 1969; p 111.

(3) Krasna, A. I. *Photochem. Photobiol.* **1979**, *29*, 267.

(4) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, N.J., 1952.

(5) Fan, F.-R. F.; Reichman, B.; Bard, A. J. *J. Am. Chem. Soc.*, **1980**, *102*, 1488.

(6) Bocarsly, A. B.; Walton, E. G.; Bradley, M. G.; Wrighton, M. S. *J. Electroanal. Chem.* **1979**, *100*, 283.

(7) Gerischer, H. *J. Electroanal. Chem.* **1975**, *58*, 263.

(8) (a) Bard, A. J.; Bocarsly, A. B.; Fan, F.-R. F.; Walton, E. G.; Wrighton, M.S. *J. Am. Chem. Soc.*, accompanying paper in this issue. (b) Fan, F.-R. F.; Bard, A. J. *Ibid.*, preceding paper in this issue.

(9) Nozik, A. J. *Annu. Rev. Phys. Chem.* **1978**, *29*, 189.

(10) Laflere, W. H.; Cardon, F.; Gomes, W. P. *Surf. Sci.* **1974**, *44*, 541.

(11) Bocarsly, A. B.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.*, **1980**, *102*, 3390.

(12) Potentials in other media have been reported: Hunig, S.; Gross, J.; Schenk, W. *Justus Liebigs Ann. Chem.* **1973**, 324.

(13) Kohl, P. A.; Bard, A. J. *J. Electrochem. Soc.* **1979**, *126*, 59.

(14) Many electrode materials have large H_2 evolution overvoltage; see, for example, Skoog, D. A.; West, D. M. "Fundamentals of Analytical Chemistry"; Holt, Rinehart and Winston: New York, 1963; p 523.

(15) Smith, R. A. "Semiconductors"; Cambridge University Press: New York, 1964; p 287.

(16) (a) Bolts, J. M.; Bocarsly, A. B.; Palazzotto, M. C.; Walton, E. G.; Lewis, N. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1378. (b) Wrighton, M. S.; Palazzotto, M. C.; Bocarsly, A. B.; Bolts, J. M.; Fischer, A. B.; Nadjo, L. *Ibid.* **1978**, *100*, 7264.

(17) Sullivan, M. V.; Eigler, J. H. *J. Electrochem. Soc.* **1957**, *104*, 226–230.

(18) Luong, J. C.; Nadjo, L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 5790.