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The Concept of Fermi Level Pinning at Semiconductor/Liquid Junctions. Consequences for Energy Conversion Efficiency and Selection of Useful Solution Redox Couples in Solar Devices

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Abstract: Fermi level pinning refers to a situation where the band bending in a semiconductor contacting a metal is essentially independent of the metal even for large variation in the work function of the metal. We find that a similar situation sometimes results for a semiconductor contacting liquid electrolyte solutions containing redox couples having very different electrochemical potentials. When Fermi level pinning obtains, illumination of the semiconductor can result in an output photovoltage which is independent of the solution potential. Fermi level pinning is brought about by semiconductor surface states resulting in a situation where the potential drop across the semiconductor (band bending) is essentially fixed and the potential drop across the Helmholtz layer in the solution is thus the variable. Recently, workers in the field of semiconductor photoelectrochemistry have emphasized a limiting case of the model of the semiconductor/liquid interface where the drop across the semiconductor depends on applied potential; at equilibrium with the solution, the band bending is generally regarded as varying with changes in the solution potential by virtue of changes in the redox couple or simply changing the ratio of oxidized and reduced material. Fermi level pinning results in semiconductor/liquid interfaces which can be viewed as analogous to a Schottky barrier photocell in series with an electrochemical cell in that the extent to which a given redox process can be driven uphill is independent of the potential of the redox couple. Quantitative considerations show that a surface state density as low as $\sim 10^{12}$ cm^{-2} is sufficient to result in Fermi level pinning. n-GaAs, p-GaAs, and p-Si are semiconductors that exhibit Fermi level pinning in liquid electrolyte solutions ($CH_3CN/[n\text{-}Bu_4N]ClO_4$) of redox reagents and these are among the materials known to exhibit Fermi level pinning when contacted by metals. Fermi level pinning has the disadvantage in practical terms of limiting photovoltage in optical energy conversion applications, but such a phenomenon allows the use of a very wide range of solution couples. Since Fermi level pinning results from surface states, changes in the surface brought about by deliberate surface chemistry may change the surface states and hence the photovoltage in solid-state and liquid-junction solar devices.

We and others have been actively engaged in the study of the chemistry resulting from illumination of semiconductor electrodes in electrochemical cells.[3-5] Such semiconductor-based photoelectrochemical cells have been demonstrated to be the best man-made chemical systems for the conversion of solar energy to chemical fuel or to electricity. In this article we wish to present a revised model of the semiconductor/liquid interface which provides new insight into the criteria for contriving new combinations of semiconductor and redox reagents that may be useful in solar energy conversion devices.

To date, the advances in efficiency and understanding of semiconductor-based photoelectrochemical cells have come from a realization that the interfacial charge transfer kinetics and energetics are crucial matters deserving considerable study. For example, n-type GaAs is the semiconductor providing the highest demonstrated solar efficiency,[6] but its use with any efficiency whatsoever depended on the discovery of a solution redox active material which could completely suppress the photoanodic destruction which is a ubiquitous problem for all nonoxide, n-type semiconductor photoelectrodes.[3-5] After the discovery that aqueous solutions of Se_2^{2-}/Se^{2-} are capable of yielding constant output from n-type GaAs-based cells,[7,8] further improvement resulted from surface treatment with $RuCl_3$ giving different interface charge-transfer properties.[6] The n-type GaAs is not unique, and there are now a number of systems in the several percent efficiency range whose operation depends on judicious choice of the solution reagents and careful treatment of the surface.[3-5]

Chemical derivatization of semiconductor photoelectrode surfaces using hydrolytically unstable redox reagents is another technique, arising from studies of solution redox reagents, that has been demonstrated to allow manipulation of interfacial charge-transfer processes.[9,10] For example, n-type Si derivatized with ferrocene reagents has been shown to be able to effect the photoanodic generation of I_3^- from I^- in aqueous solution under conditions where the nonderivatized n-type Si is too susceptible to photoanodic SiO_x growth to allow any sustained, or even reproducible, photoelectrochemistry.[11] Chemical derivatization may thus allow the design of photosensitive interfaces for light-driven processes of all kinds.

Recently, independent results from our two laboratories

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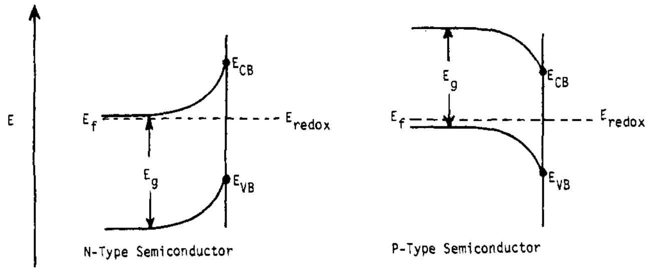
Scheme I. Interface Energetics for an Ideal n- or p-Type Semiconductor (No Surface States) Contacting a Liquid Electrolyte Solution



demand a new model for the semiconductor/liquid interface. Specifically, we are concerned about the hypotheses dealing with interface energetics that should allow prediction of the (1) redox reactions that can be light driven and (2) output voltage that could be expected from a solar cell based on a given solution redox couple. To explain some of our recent results we find it necessary to modify the usual model for the semiconductor/liquid junction interface to account for high densities of surface states that are situated between the top of the valence band, E_{VB}, and bottom of the conduction band, E_{CB}. We advance the concept of "Fermi level pinning" which is associated with solid-state semiconductor/metal interfaces (Schottky barriers). Our model is intended as an amplification of the treatment usually applied in which the band edges remain fixed with respect to solution levels.[12-15] The experimental results upon which our model is based already establish varying degrees of inconsistency with the ideal Schottky barrier treatment and lead to new expectations concerning what redox processes can be light driven and with what efficiency. Our model provides a framework within which to design new photoelectrochemical devices and improve overall energy conversion efficiency.

Semiconductor/Liquid Junction Energetics. Ideal Semiconductors

The present working model for the energetics at a semiconductor/liquid junction follows that for a semiconductor/metal (Schottky barrier) where the electrochemical potential of the solution, E_{redox}, is the equivalent of the Fermi level of the metal in the Schottky barrier.[12-15] Thus, for n- and p-type semiconductors at charge-transfer equilibrium with the solution, the situation drawn in Scheme I exists. In these diagrams E_g is the band gap, E_f is the Fermi level of the semiconductor, E_{VB} is the top of the valence band at the interface, and E_{CB} is the bottom of the conduction band at the interface. The essential points of the model are as follows: (1) the potential drop between bulk semiconductor and bulk solution is principally confined to a region of ~20-10 000 Å within the semiconductor (the space-charge region) depleted of majority charge carriers such that $\geqslant E_g$ irradiation absorbed in this region results in minority carriers (holes for n type, electons for p type) at the surface available for a charge-transfer event; (2) the maximum oxidizing power of photogenerated holes is E_{VB} and the maximum reducing power for excited electrons is E_{CB}; (3) the maximum open circuit photovoltage is equal to the amount of band bending or the barrier height.

The potential of the electrode with respect to a reference electrode in solution at which the bands are flat, i.e., at which a space charge is absent, is V_{fb}, the flat-band potential. The maximum open-circuit photovoltage, $(V_{oc})_{max}$, is given by the equation

$$(V_{oc})_{max} = |V_{fb} - V_{redox}| \qquad (1)$$

where V_{redox} corresponds to the redox potential of the solution couple ($V_{redox} = -E_{redox}/e$).

The same energetic diagrams as shown in Scheme I would be drawn for a semiconductor/metal Schottky barrier except that E_{redox} would be replaced by the Fermi level of the metal replacing the liquid solution. The metal contact differs in two other respects in that a metal has a dense continuum of states and the mechanism of conductivity is electronic, not ionic as for the liquid electrolyte solution. These latter distinctions give rise to differences in expectations for charge-transfer kinetics across the interface, but we shall not elaborate on this point here.

It is generally assumed that, when the species in solution do not interact with the semiconductor surface, changes in E_{redox} will give identical changes in the expected photovoltage. This prediction follows from the fact that E_{VB} and E_{CB} are fixed in such an instance and the band bending at equilibrium depends on the position of E_{redox} (see eq 1). Thus, variation in the ratio of oxidized to reduced material in solution can effect a change in E_{redox} to improve output voltage. A change in the nature of the redox material can result in even larger changes in E_{redox}. Assuming E_{VB} and E_{CB} to be fixed, E_{redox} more negative than E_{CB} for n-type semiconductors or more positive than E_{VB} for p-type semiconductors results in an interface having the property of no expected output photovoltage. For E_{redox} more positive than E_{VB} for n-type semiconductors or more negative than E_{CB} for p-type the photoeffects are also expected to be minimal. Therefore, only for E_{redox} situated between E_{VB} and E_{CB} do we expect useful photovoltaic junctions. The objective is to fix E_{redox} close to E_{VB} for n-type photoanodes and close to E_{CB} for p-type photocathodes to achieve optimum output photovoltages. In Schottky barrier devices the barrier height is again the maximum output photovoltage and variations in the barrier height are expected for a given semiconductor upon variation of the metal. For example, Al on n-type GaAs would be expected to give a smaller barrier height than Au on n-type GaAs. The view implied in this discussion and in Scheme I is that the output photovoltage can be varied intentionally and that certain redox couples would not be useful at all in a semiconductor/liquid junction solar device.

The positions of E_{VB} and E_{CB} at a semiconductor/liquid junction are measurable by determining the value of E_f corresponding to V_{fb}. The doping density gives the difference between E_{FB} and E_{CB} or E_{VB} and thus the interface energetics can be defined. When there is surface chemistry (i.e., specific adsorption or surface reactions) with solution species, the positions of E_{VB} and E_{CB} can be moved as reflected in differences in V_{fb}. For example, all semiconducting oxides exhibit surface chemistry in aqueous electrolyte solutions associated with proton-transfer equilibria such that V_{fb} moves more positive, ~59 mV/pH unit, as the acidity increases[16-18] Another example is with n-type CdS (and several other II-VI materials) exposed to S^{2-} in aqueous solution; V_{fb} for n-type CdS is ~ −0.9 V vs. SCE in H_2O without S^{2-} but is ~ −1.5 V vs. SCE in S^{2-}-containing media[19-21] Finally, note that V_{fb} for n-type MoS_2 is ~ +0.3 V vs. SCE in $H_2O/NaClO_4$ but ~ −0.2 V vs. SCE in the presence of 1 M I^-.[22] These effects of surface chemistry are explicable within the framework of the existing hypotheses, although large changes in expectations do result. For example, for a redox couple A^+/A whose formal potential is independent of pH, the output voltage for the oxide semiconductor-based cells can be manipulated by simply changing the pH. For species like I^- or S^{2-}, though, their absorption on n-type materials likely precludes direct hole reaction with solution species other than I^- or S^{2-}.

Fermi Level Pinning. Qualitative Considerations

Fermi level pinning for semiconductor/metal Schottky barriers refers to the phenomenon in which surface states of a semiconductor give rise to a fixed barrier height, independent of metal.[23-26] Some time ago, it was realized that semicon-

Table I. Semiconductor/Metal Interface Barrier Heights: "Fermi Level Pinning" at Solid-State Junctions[a]

semiconductor	metal	*T*, K	barrier height, V
n-GaAs	Au	300	0.95 ± 0.03
	Pt	300	0.94 ± 0.03
	Be	300	0.82
	Ag	300	0.93 ± 0.03
	Cu	300	0.87 ± 0.03
	Al	300	0.80 ± 0.02
	Al	77	0.88 ± 0.04
p-GaAs	Au	300	0.48 ± 0.01
	Au	77	0.46
	Pt	77	0.48
	Ag	77	0.44
	Cu	77	0.52 ± 0.02
	Al	300	0.63 ± 0.06
	Al	77	0.61 ± 0.05
n-CdTe	Au	300	0.71 ± 0.02
	Pt	300	0.76
	Ag	300	0.81
n-InP	Au	300	0.49 ± 0.05
	Au	77	0.56 ± 0.04
	Cu	77	0.5
	Ag	300	0.54
	Ag	77	0.50

[a] Data are from ref 24; barrier heights given are from capacitance measurements, but photoresponse measurements are consistent where both measurements were made. Materials such as $SrTiO_3$, SnO_2, or $KTaO_3$ give a change in the barrier height of ~1.0 V from Al to Au as the metal, for comparison.[25,26]

ductor/metal interfaces are not as predictable as suggested by the model above for ideal semiconductors. Indeed, for some semiconductors it has been determined that the Schottky barrier height is independent of the metal even for metals having very large differences in work function, Table I. Generally, more ionic semiconductors (e.g., large band gap oxides) give more ideal behavior in this connection than do the more covalent (e.g., GaAs) and elemental semiconductors (e.g., Si), Table II. Data over the years has been somewhat irreproducible owing, at least in part, to the difficulty of preparing Schottky barriers without intervening oxides or other materials which compromise the ideal interface model. However, it is now widely believed that there are certain semiconductors for which the barrier height is very insensitive to metal, while for other semiconductors the expected ordering of barrier heights does exist. For the situation where the barrier height does vary the Schottky barrier model above is said to apply. However, when the barrier height is "pinned" to a constant value, it is believed that surface states between E_{VB} and E_{CB} must be taken into account. The phenomenon of a metal-insensitive barrier height is referred to as *Fermi level pinning* and is believed to result from a significant density of surface states at a more or less defined potential to which the Fermi level becomes pinned independent of the overlaying metal. Fermi level pinning contributes to the difficulty in preparation of Schottky barrier solar cells which have high efficiency, since the output photovoltage is limited to a value determined by the surface states of the semiconductor.

We assert that Fermi level pinning obtains for certain semiconductor/liquid junctions, and as for Schottky barriers, we attribute the effect to a significant density of surface states more or less localized at a certain potential. We note a similar conclusion[22b] from the recent work on MX_2 (M = Mo, W; X = S, Se, Te) electrode materials. The experimental results which prompt our assertion are that (1) a number of different A^+/A systems with widely different values of E_{redox} give rise to nearly the same output photovoltage for a given semiconductor, and, perhaps more importantly, (2) certain solution A^+/A systems produce photoeffects and respectable output photovoltages when the ideal semiconductor/liquid junction model would suggest E_{redox} to be situated such that no photovoltage is expected. These findings are the liquid junction analogue of the metal-insensitive Schottky barrier height. We will detail and amplify the theoretical model and the experimental justification below, but first Fermi level pinning for the liquid junction will be elaborated.

Table II. Semiconductors That Do and Do Not Exhibit "Fermi Level Pinning" When Contacted by Metals[a]

exhibit fermi level pinning[b]	do not exhibit Fermi level pinning[c]
Si	$SrTiO_3$
Ge	ZnS
InP	SnO_2
GaAs	$KTaO_3$
InSb	ZnO

[a] Data from ref 25 and 26. [b] Barrier height essentially insensitive to metal. [c] Barrier height very sensitive to metal.

One way to view Fermi level pinning is to think of a metal, having a high density of states, which contacts an ideal semiconductor (no surface states) to form an ideal Schottky barrier. Once the Schottky barrier has been made additional overlayers of another metal or contacting the metal with an electrolyte solution will not change the barrier height. To illustrate, a Schottky barrier cell could be used to drive current through an electrolyte solution of A^+/A with driving force (potential) independent of the energetics of the A^+/A couple. Now consider an ideal semiconductor perturbed by having a high density of states near and at the surface. Depending on their distribution the surface states can result in band bending in a manner analogous to that resulting from contacting the ideal semiconductor by a metal to form the ideal Schottky barrier. Thus, the surface states play a role analogous to that of a metal and give a barrier as if a metal were contacting the ideal semiconductor. The density and energy distribution of surface states would determine their energy level or work function just as for a metal, and the result is a semiconductor whose amount of band bending (barrier height) is determined by the layer of surface states. When such is the case, the addition of a layer of metal, or contacting the surface with a liquid electrolyte, does not alter the band bending, just as would be expected if one takes an ideal Schottky barrier and puts on another metal or contacts an electrolyte solution. Scheme II illustrates the difference in interface energetics for one semiconductor that does and one that does not exhibit Fermi level pinning when contacting liquid electrolyte solutions of A^+/A and B^+/B where E_{redox} of the two solutions is different.

Thus, we can point to three extremes for the treatment of a semiconductor/liquid junction. First, there is the situation represented in Scheme I where surface states are essentially (never completely) absent and the barrier height depends, in a straightforward manner, on E_{redox}, eq 1. Even in such semiconductors (e.g., n-SnO_2 and n-$SrTiO_3$)[25,26] levels or surface states present at energies within the gap can affect their electrochemical properties; e.g., in n-type materials surface states facilitate dark reduction of couples with E_{redox} between E_{CB} and E_{VB} and promote recombination processes during irradiation.[27] Second, the other extreme is where there is a large number of states between the valence and conduction band and these extend throughout the semiconductor resulting in a continuum of states such that the semiconductor is metal-like in its behavior as an electrode and gives little photovoltage. Such materials are associated with so-called degenerate doping that provides so many charge carriers that a space-charge region inside the semiconductor is not possible. The behavior of such materials is metal-like. When electronic equilibrium occurs between electrode and solution, the potential drop occurs exclusively across the Helmholtz layer at

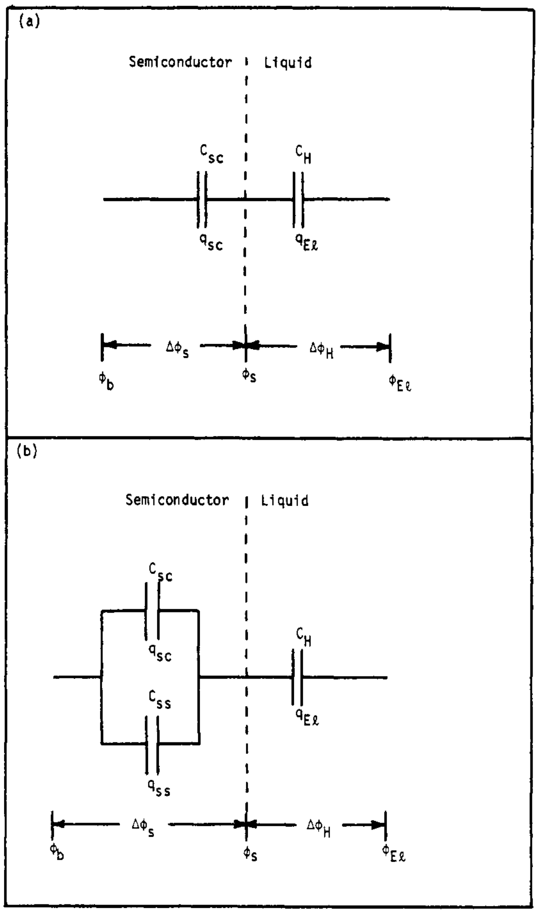
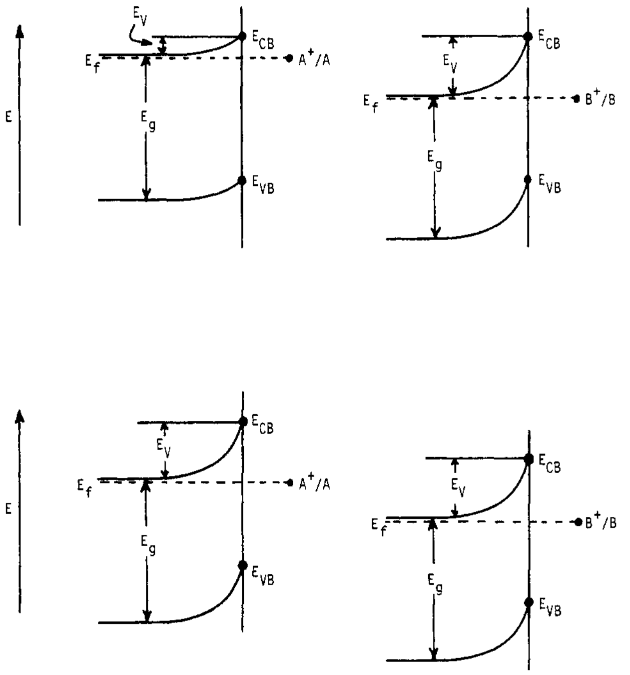


Figure 1. Approximate equivalent circuits for the semiconductor/liquid interface (a) in absence of surface states and (b) in presence of surface states (under assumption that the potential drop over the diffuse layer in solution is negligible). $\Delta\phi_s$ is the potential drop between bulk semiconductor and surface and $\Delta\phi_H$ is the potential drop across the Helmholtz layer attributable to semiconductor charge.

the interface. Variation of the potential between bulk semiconductor and solution results in changes of the potential drop across the Helmholtz layer and not within the low-resistance semiconductor. Third, we now suggest that semiconductors that have a significant density of surface states between E_{VB} and E_{CB} can exhibit Fermi level pinning when contacting a liquid electrolyte solution such that (1) many redox couples having different electrochemical potentials give the same output voltage, (2) two couples whose formal potentials are more widely spaced than the separation of E_{CB} and E_{VB} for a given semiconductor can be used and give comparable output photovoltage, and (3) surface modification aimed at changing the number and location of surface states may be an important way to improve the output characteristics of photoelectrochemical devices where Fermi level pinning obtains for the photoelectrode.

Before turning to quantitative considerations and experimental justification, it is appropriate to point out that, though Fermi level pinning may be observed for some redox couples, other couples may not yield a similar output photovoltage. There are at least two reasons why this may occur: (1) the solution species reacts with or absorbs onto the semiconductor in such a way that surface states are changed dramatically and/or (2) at some extreme values of E_{redox} and depending on the surface state density and distribution the redox couple may contact the semiconductor in a manner not unlike that for formation of a so-called "ohmic contact" between a metal and a semiconductor. In the latter situation essentially reversible electrochemical behavior will result, and may be due again to a dramatic change in the nature of the surface states. Finally, observing an output voltage equal to the barrier height is not always possible owing to the rate of recombination processes. Such effects depend on interfacial kinetics, perhaps controlled by surfaces states, that may preclude achievement of the maximum output voltage at even the highest light intensities.

Scheme II. Interface Energetics for an Ideal n-Type Semiconductor (Top) Contacting a Solution of A^+/A or B^+/B Showing Band Bending, E_V, Dependent on Position of E_{redox} While E_{VB} and E_{CB} Are Fixed. Interface Energetics for an n-Type Semiconductor Exhibiting Fermi Level Pinning (Bottom), Where E_V Is Independent of E_{redox} While E_{VB} and E_{CB} Shift Relative to Solution Levels



Quantitative Aspects of Fermi Level Pinning

Although the nature of the semiconductor/liquid interface in the absence and presence of surface states has been discussed frequently,[12,15] it seems worthwhile to indicate in a rather elementary way the conditions under which Fermi level pinning will occur. The basic concepts in this treatment follow closely those employed earlier in discussions of the semiconductor/metal junction.[23-26] Qualitatively Fermi level pinning will be important when the charge in the surface states (q_{ss}) becomes appreciably larger than that in the space charge region (q_{sc}). Under these conditions changes in potential between the bulk semiconductor and bulk solution will mainly affect the potential drop across the Helmholtz layer ($\Delta\phi_H$) rather than the drop within the semiconductor ($\Delta\phi_s$). In the absence of surface states the semiconductor/liquid system can be modeled as two capacitors in series (Figure 1a). (In all that follows, we assume that the electrolyte concentration is high and that the potential drop across the diffuse double layer in the liquid is negligible.) The Helmholtz layer capacitance, C_H, can be taken as

$$C_H = \epsilon_H\epsilon_0/d = q_{El}/\Delta\phi_H \tag{2}$$

where ϵ_H is the dielectric constant in the Helmholtz layer, ϵ_0 is the permittivity of free space, and d is the thickness of the Helmholtz layer. The total solution excess ionic charge, q_{El}, is assumed to be arrayed at a distance d from the electrode surface, and is equal in magnitude to the space charge, q_{sc}. We take $\Delta\phi_H$ to be the potential drop across the Helmholtz layer. The actual drop also includes a term attributable to the dipole layers at the interface but we assume that this term is independent of the charge distribution at the interface.[13] The space charge capacitor, C_{sc}, cannot be treated as parallel plate capacitor. However, the q_{sc} value can be calculated as a function of the carrier level, n_b, and $\Delta\phi_s$ with the equation[15]

$$q_{sc} = (2kTn_i\epsilon\epsilon_0)^{1/2}\,[F(\lambda,Y)] \tag{3}$$

$$F(\lambda,Y) = [\lambda(e^{-Y} - 1) + \lambda^{-1}(e^{Y} - 1) + (\lambda - \lambda^{-1})Y]^{1/2} \tag{4}$$

$$\lambda = n_i/n_b \qquad Y = e\Delta\phi_s/kT \tag{5}$$

where n_i is the intrinsic carrier density, k is the Boltzmann constant, and T is the temperature.[28] Calculation of $\Delta\phi_s$ and $\Delta\phi_H$ from these equations for moderately doped semiconductors leads to the finding that changes in potential between the bulk semiconductor and bulk solution $[\Delta(\phi_{El} - \phi_b)]$ mainly result in changes across the space charge region rather than across the Helmholtz layer and is the basis for the familiar model of the semiconductor/liquid interface where the band edges remain fixed with respect to solution redox levels.

In the presence of surface states the model that can be adopted is that of Figure 1b.[14] The relation between q_{sc} and $\Delta\phi_s$ follows eq 3. The form of the equation for the relation between q_{ss} and $\Delta\phi_s$ depends upon the nature of the distribution of surface state energies, i.e., whether the surface states are uniformly distributed in energy[23] or are localized at a single energy level.[12] For example, if a uniform distribution of acceptor surface states is assumed, centering around an energy E_0 (i.e., such that there is no net surface charge when the states are filled to an energy E_0), then q_{ss} can be given by[23]

$$q_{ss} \simeq eN_{ss}\frac{(E_0 - e\Delta\phi_s - E_F)}{E_0} \tag{6}$$

where N_{ss} is the total number of surface states per cm^2. (Note that, when $e\Delta\phi_s = E_0 - E_F$, $q_{ss} = 0$.) For the case more frequently considered, that of acceptor states at a single energy level, E_{ss},[12-15] the surface state charge is

$$q_{ss} \simeq eN_{ss}/\{1 + g_{ss}^{-1}\exp[-(E_{ss} - e\Delta\phi - E_F)/kT]\} \tag{7}$$

where g_{ss} is the degeneracy of the energy level. For simplicity we will assume in the calculations that the $\Delta\phi_s$ value is such that the states are half-occupied, so that $q_{ss} = eN_{ss}/2$. For the system in Figure 1b the total charge in the electrolyte is equal in magnitude to $q_{ss} + q_{sc}$ (with q_{sc} calculated by eq 3 and the corresponding value of $\Delta\phi_H$ calculated via eq 1). Fermi level pinning by surface states occurs when the q_{ss} becomes larger than q_{sc} at a given $\Delta\phi_s$. In this case even in the absence of electrolyte solution band bending within the semiconductor can occur ($q_{El} = 0$, $q_{sc} = -q_{ss}$).

To illustrate the conditions required for Fermi level pinning, the results of calculations of q_{sc} as a function of n_b and q_{ss} as a function of N_{ss} for n-GaAs (taking $n_i = 1.3 \times 10^6$ cm^{-3}, $\epsilon = 12$, and $kT = 0.0257$ eV) are shown in Figure 2. Note that, when N_{ss} becomes larger than ca. 10^{12} cm^{-2}, q_{ss} is greater than q_{sc} for any moderate doping level. It is under these conditions that variations of potential between the semiconductor and the solution lead to significant changes in the potential drop across the Helmholtz layer. Since the number of atoms on the surface is ~10^{15} cm^{-2}, surface states representing ~1% surface coverage will bring about Fermi level pinning. If the surface state density becomes very high, as discussed earlier by Green,[12,13] then the semiconductor behavior can approach that of a metal. This behavior is sometimes observed at moderately doped semiconductor electrodes following mechanical polishing or grinding of the surface.

Note that within the scope of this treatment no distinction can be drawn between surface states inherent to the semiconductor surface ("inside the semiconductor surface") attributable to dangling bonds, surface imperfections, etc. (Tamm[29] or Shockley[30] states), and those formed at the semiconductor surface by adsorption of electron acceptor or donor molecules or by surface modification by purposeful attachment of electroactive functionalities. However, ionizable surface groups (i.e., groups in which charge is produced by a chemical reaction such as deprotonation) or adsorbed ions can be treated separately, as pointed out by Gerischer.[14]

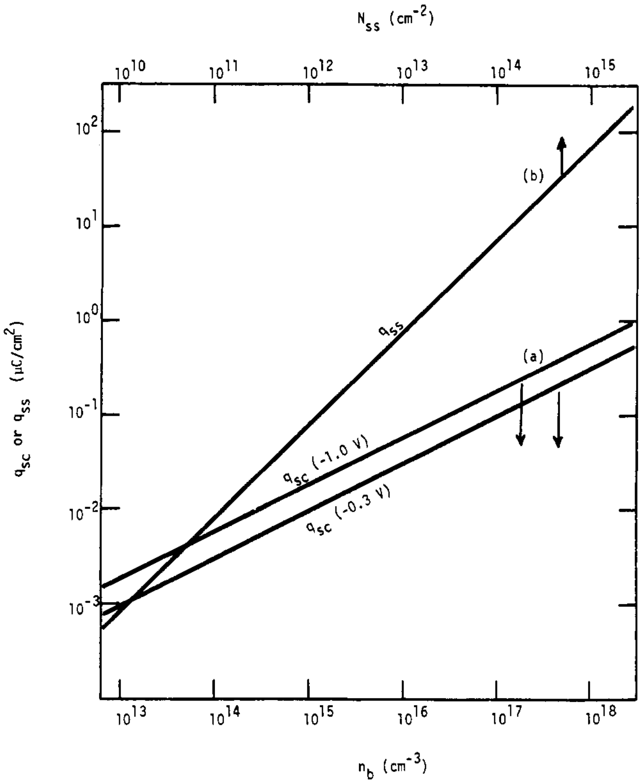


Figure 2. Surface charge in an n-type semiconductor: (a) space charge, q_{sc}, at various doping levels (n_b) at $\Delta\phi_s$ of -0.3 and -1.0 V; (b) surface state charge (q_{ss}) as a function of surface state density, N_{ss}, assuming half-occupancy. Potential drop across Helmholtz layer due to semiconductor charge can be calculated by eq 2, or with $\epsilon_H = 4$ and $d = 3$ Å, $\Delta\phi_H$ (V) $= 0.085q$ (μC/cm^2).

Experimental Justification for Invoking Fermi Level Pinning

The concept of Fermi level pinning can explain results of a number of studies of semiconductor electrodes. For example, the study of p-type GaAs in a number of aqueous solutions clearly shows that the open circuit photopotential is independent of the potential of the solution redox couple (see Table I in ref 31). Experiments at n- and p-type GaAs in CH_3CN solutions[32-34] similarly showed photoeffects for couples whose redox levels were located outside of the band-gap region as determined by measurements of V_{fb} in blank solutions in the absence of redox couples. Moreover, the potential range over which photoeffects were observed at n-GaAs in CH_3CN was at least 2.5 V,[32] which is considerably wider than the E_g value of 1.35 eV. Similar effects were noted with p-GaAs in CH_3CN. Some data are given in Table III. The model used in these papers[32,34] involved the formation of a Schottky junction (taken as analogous to a metal-semiconductor junction) upon reduction of the electrode surface, although conclusive evidence of changes in the nature of the surface could not be obtained by electron spectroscopy. The pinning by surface states (so that the "Schottky junction" is formed between the surface states and the bulk semiconductor) modifies this model so that observable chemical changes of the electrode surface are not expected. A particularly striking example of pinning is the photoinjection of electrons from p-GaAs into liquid ammonia.[35] In this case the photoprocess occurs at potentials more

Table III. Semiconductor/Liquid Interfaces Where "Fermi Level Pinning" Applies[a]

semiconductor (E_g, eV)	redox couple ($E°$, V vs. SCE)	photovoltage, V	ref
n-GaAs (1.35)	TMPD$^{+\cdot}$/TMPD (0.1)	0.52	32
	Ox-1$^{+\cdot}$/Ox-1 (−0.42)	0.56	
	BQ/BQ$^{-\cdot}$(−0.52)	0.46	
	AQ/AQ$^{-\cdot}$(−0.94	0.50	
	Ru(TPTZ)$_2^{3+/2+}$ (−0.81)	0.42	
	Ru(TPTZ)$_2^{2+/+}$ (−0.97)	0.41	
	Ru(TPTZ)$_2^{+/0}$ (−1.63)	0.29	
	Ru(TPTZ)$_2^{0/-}$ (−1.88)	0.24	
	Ru(bpy)$_3^{2+/+}$ (−1.30)	0.35	
	Ru(bpy)$_3^{+/0}$ (−1.49)	0.30	
	Ru(bpy)$_3^{0/-}$ (−1.73)	0.35	
	DPA/DPA$^{-\cdot}$(−1.84)	0.43	
	A/A$^{-\cdot}$(−1.94)	0.35	
p-GaAs (1.35)	TMPD$^{+\cdot}$/TMPD (0.1)	0.02	32
	Ox-1$^{+\cdot}$/Ox-1 (−0.42)	0.12	
	AQ/AQ$^{-\cdot}$(−0.94)	0.29	
	Ru(TPTZ)$_2^{3+/2+}$ (−0.81)	0.44	
	Ru(TPTZ)$_2^{2+/+}$ (−0.97	0.44	
	Ru(TPTZ)$_2^{+/10}$ (−1.63)	0.56	
	Ru(TPTZ)$_2^{0/-}$ (−1.88)	0.61	
	Ru(bpy)$_3^{2+/+}$ (−1.30)	0.58	
	Ru(bpy)$_3^{+/0}$ (−1.49)	0.64	
	Ru(bpy)$_3^{0/-}$ (−1.73)	0.65	
	DPA/DPA$^{-\cdot}$(−1.84)	0.25	
	A/A$^{-\cdot}$(−1.94)	0.34	
p-Si (1.1)	PQ^{2+}/PQ$^{+\cdot}$(−0.45)	0.39	38
	PO$^{+\cdot}$/PQ^0 (−0.85)	0.42	
	Ru(bpy)$_3^{2+/+}$ (−1.30)	0.42	
	Ru(bpy)$_3^{+/0}$ (−1.49)	0.42	
	Ru(bpy)$_3^{0/-}$ (−1.73)	0.38	

[a] All data are for $CH_3CN/[n\text{-}Bu_4N]ClO_4$ solutions of the given redox couple. Photovoltage is taken to be the difference in $E°$ and the peak of the photoanodic wave (n-type semiconductors) or the photocathodic wave (p-type semiconductors) in a cyclic voltammetry scan of the illuminated semiconductor under conditions where photocurrent is limited by diffusion of the redox reagent in the quiet solution. Experiments for a given semiconductor/redox couple are most reliable; e.g., p-GaAs/Ru(bpy)$_3^{2+/+/0}$. Data for p-Si are for one solution initially containing PQ^{2+} and Ru(bpy)$_3^{2+}$. Abbreviations: TMPD = *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine; Ox-1 = oxazine-1; BQ = benzoquinone; AQ = anthraquinone; bpy = 2,2′-bipyridine; TPTZ = 2,4,6-tripyridyl-*s*-triazine; DPA = 9,10-diphenylanthracene; A = anthracene; PQ^{2+} = *N,N′*-dimethyl-4,4′-bipyridinium.

than 1 V negative of V_{fb} (determined in blank solution by a Schottky-Mott plot),[36] with the surface state level moving to that of the solvated electron. This demonstrates how the solution redox couple can "lift" the energy level of the photogenerated carriers to levels not predictable by measurements of V_{fb}.

Experiments with n- and p-Si[37,38] are also best accommodated by invoking Fermi level pinning. Some data for p-Si in CH_3CN solution are included in Table III.[38] As for GaAs, significant photoeffects are found for redox couples whose formal potentials span a range exceeding the value of E_g, 1.1 eV for Si. Further, the five one-electron systems shown give evidence for a virtually constant amount of band bending over a wide range of solution potentials. At illuminated n-type semiconducting Si photoanodes two, one-electron waves for the oxidation of species such as bis(fulvene)diiron (BFD) can be observed in the cyclic voltammogram, rather than one, two-electron wave as would be expected in the absence of Fermi level pinning.[37] Again, it appears that a similar output photovoltage obtains for redox couples having very different formal potentials.

Recently, studies of the photovoltage for MX_2 (M = Mo, W; X = S, Se, Te) as a function of redox couple in solution have led to a conclusion similar to our own.[22b] For these systems it was found that the photovoltage did not obey eq 1 and a conclusion to the effect that surface states pin the Fermi level was drawn.

Undoubtedly, new examples of Fermi level pinning will be encountered in the study of semiconductor/liquid interfaces. Further, it will interesting to follow the extent to which expectations from semiconductor/metal interfaces will be realized.[25,26] But it is worth stressing that Fermi level pinning need not occur for *all* possible solution redox couples. For example, in Table III for p-type GaAs ten of the couples give rise to a significant photovoltage in the range 0.3–0.6 for a variation in $E°$ of about 1 V. However, the most positive couple, TMPD$^{+\cdot}$/TMPD, gives little photovoltage. Likewise, ferricenium can be photoreduced on p-Si,[38] but the photocathodic peak is not significantly positive of $E°$. These two illustrations reflect the fact that a given solution species may nearly form an "ohmic" contact to the semiconductor, the liquid junction analogue of an ohmic contact being reversible electrochemistry. Thus, though Fermi level pinning may result in a constant output photovoltage for many couples, the voltage range over which this is true may be limited.

The experimental justification for invoking Fermi level pinning a semiconductor/liquid junctions is quantitative and qualitative as for solid-state interfaces. The surface states of the semiconductor are crucial, and it may be that chemistry with the liquid solution will be useful in changing the nature of the surface states in such a way that output photovoltage can be improved. There are already adequate demonstrations of the importance of surface modifications.[6,9–11,38] Fermi level pinning provides a framework within which to design new experiments and devices based on surface modification.

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Semiconductor Electrodes. 24. Behavior and Photoelectrochemical Cells Based on p-Type GaAs in Aqueous Solutions

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Abstract: The electrochemical behavior of single-crystal p-type GaAs in aqueous solutions containing several redox couples (I_3^-/I^-, Fe(III)/Fe(II), Sn(IV)/Sn(II), Eu(III)/Eu(II)) in the dark and under irradiation is described. The observation that the difference in potential between that for the onset of photocurrent and the standard potential for the redox couple was 0.4–0.5 V, independent of the couple, leads to a revised model for semiconductor/electrolyte solution interface with semiconductors having a high density of surface states with energies within the band-gap region. In such a surface controlled system the Fermi level of the semiconductor is pinned at the surface state level. Several solar cells in which p-GaAs shows stable behavior are described. The cell p-GaAs/I_3^-(0.25 M),I^-(0.75 M)/Pt showed an open-circuit voltage of 0.20 V and a short-circuit current density of 30 mA/cm^2 under irradiation with 1.7-mW He-Ne laser. The quantum efficiency at the maximum photocurrent in this cell was about 95%.

Introduction

Considerable success has been realized recently[1-3] in converting visible light to electricity using n-type semiconductor-based photoelectrochemical (PEC) cells. In principle, p-type semiconductors should be useful as photocathodes in a PEC cell. Some p-type semiconductor electrodes studied to date, p-MoS$_2$, p-CdTe, p-GaAs, or p-GaP, seem to be stable when used as photocathodes.[4-8] Unfortunately, the onset photopotential for the PEC reaction on most p-type electrodes lies negative of the flat-band potential, V_{fb}, and close to the standard potential of the redox couple in the electrolyte. This limits the open-circuit photovoltage of p-type semiconductor-based PEC cells to relatively small values.

In this paper we describe PEC effects on p-GaAs electrodes. We show that the quantum efficiencies of these PEC cells are strongly dependent on the redox couples present in the solution and the "one-third rule" in semiconductor physics[9] is applicable to explain the present results. In addition, we demonstrate a p-GaAs based solar cell in an I^-/I_3^- system. The short-circuit quantum yields for electron flow of this cell approach 100%. Under short-term illumination with the full visible (longer than 590 nm and IR filtered) output from a 450-W Xe lamp focused onto the photocathode, the p-GaAs electrode was stable. To our knowledge this represents the first example of a single p-type semiconductor-based PEC cell in aqueous solution which shows near 100% short-circuit quantum efficiency under fairly strong light intensity with good stability.

Experimental Section

The semiconductors used are p-type GaAs single crystals obtained from Atomergic Chemicals (Long Island, N.Y.). The acceptor concentration was 3×10^{18} cm^{-3}. The ohmic contact was obtained by electroplating Au on the rear surface (which was polished first with sandpaper and then with 0.5-μm alumina on felt). A copper wire was then attached to the ohmic contact with conductive silver epoxy (Allied Products Corp., New Haven, Conn.) which was subsequently covered, along with the copper wire and the sides of the crystal, with silicone rubber sealant (Dow Corning Corp., Midland, Mich.). The semiconductor material was then mounted onto an 8 in. long piece of 7-mm diameter glass tubing, resulting in an exposed area of p-GaAs of 0.05 cm^2. Before use, the surface of the electrode was etched for 10–15 s in concentrated H_2SO_4/30% H_2O_2/H_2O (3:1:1) followed by 6 M HCl for 10–15 s.

A conventional three-electrode, single-compartment cell was used for the electrochemical measurements. The electrochemical cell (volume ~ 25 mL) which contained the Pt disk or semiconductor working electrode was fitted with a flat Pyrex window for illumination of the semiconductor. Removable air-tight Teflon joints were used with the Pt disk or semiconductor electrode. A platinum foil (~40 cm^2) was used as the counterelectrode and an aqueous saturated calomel electrode (SCE) as the reference electrode.

The cyclic voltammograms were obtained with a PAR 173 potentiostat, PAR 175 universal programmer, and PAR 179 current-to-voltage converter and recorded on a Houston Instruments Model 2000 X-Y recorder (Austin, Texas). In the solar cell measurements, current (i) and voltage (V) readings were taken between the working electrode and the platinum counterelectrode with no external power source. The photovoltage and the photocurrent as functions of the load resistance

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