Semiconductor Electrodes

XLII. Evidence for Fermi Level Pinning from Shifts in the Flatband Potential of p-Type Silicon in Acetonitrile Solutions with Different Redox Couples

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ABSTRACT

The flatband potential, V_{FB}, of p-Si electrodes in acetonitrile solutions containing various redox couples was determined by measurement of the cell impedance. V_{FB} was found to depend strongly on the redox potential of the solution, indicating the occurrence of Fermi level pinning. The shift of V_{FB} did not depend upon the nature (cationic or anionic) of the redox couples; thus it cannot be attributed to specific adsorption. The shift in V_{FB} was also found with redox couples (such as oxazine and benzoquinone) which have energy levels located below the middle of the gap, implying that inversion does not occur in these cases.

The concept of Fermi level pinning (FLP) was recently suggested to explain the relative independence of the open-circuit photopotential (V_{oc}) at the semiconductor electrode in the presence of redox couples whose standard potentials span a range of potentials greater than the bandgap, E_g (1-4). This behavior is different from that expected for the ideal semiconductor/electrolyte junction, where $V_{oc} = V_{redox} - V_{FB}$ (V_{redox} is the potential of the solution redox couple and V_{FB} is the flatband potential of the semiconductor in the absence of redox couple). Such behavior has been observed with several semiconductors, *e.g.*, Si (3, 4), GaAs (2), and CdTe (5). FLP occurs when a sufficient density of surface states exists in the bandgap that their equilibration with the solution redox couple causes a change in the surface charge and hence in the potential drop across the Helmholtz layer. Under these conditions V_{FB} shifts with V_{redox}. This behavior is very similar to that found at some metal/semiconductor (Schottky) junctions, where the photovoltage is independent of the metal work function (6-8). We sought to obtain independent evidence of FLP, as well as further insight into the conditions under which it occurs, by examining the shift of V_{FB}, as obtained from capacitance measurements, with various redox couples for p-Si in acetonitrile (MeCN) solutions.

Experimental

The solvent, MeCN, and the redox couples were purified following the procedures reported in earlier publications (9-11). The single crystals of p-Si (doping density, 2.05×10^{15} cm^{-3}), obtained from Texas Instruments, had the (100) face exposed to the solution and were provided with ohmic contacts by electrodepositing a layer of gold on the back-side. A copper wire lead for electrical contact was attached to the gold-coated side with silver conductive paint (Allied Product Corporation, New Haven, Connecticut) and was subsequently covered with 5 min epoxy cement. The entire assembly was mounted into 6 mm diam glass tubing and was held in position with silicone rubber sealant (Dow Corning Corporation, Midland, Michigan) which also served as an effective seal against seepage of electrolyte solution to the rear of the semiconductor electrode. The exposed area of p-Si was 0.1 cm^2. The surface of the electrode was etched before use for 30 sec with HNO_3:CH_3COOH:HF, 3:1:3, containing a drop of bromine, followed by a pure HF etch (5 sec), and then rinsed thoroughly with distilled water and dried.

A two-compartment electrochemical cell was used. The counterelectrode for coulometric generation was a platinum gauze separated from the test compartment by a medium porosity glass frit. An aqueous saturated calomel electrode (SCE) was used as a reference electrode. A large area (> 40 cm^2) Pt gauze, immersed in the same compartment as the working electrode, was used as a counterelectrode in impedance measurements.

A PAR Model 173 potentiostat and a PAR Model 175 Universal programmer (Princeton Applied Research Corporatioin, Princeton, New Jersey) equipped with a Model 2000 X-Y recorder (Houston Instruments, Austin, Texas) were used to obtain the cyclic voltammograms as well as for impedance measurements. In these latter experiments, a lock-in amplifier technique, which yields the in-phase and the 90° quadrature component of an a-c signal superimposed on a triangular sweep, was used (12, 13). The a-c signal (10 mV peak-to-peak) at different frequencies and its components were obtained by using a PAR Model HR-8 lock-in amplifier equipped with an internal oscillator.

All compounds and the solvent, MeCN, were stored inside a helium-filled Vacuum Atmospheres Corporation (Hawthorne, California) glove box. Polarographic grade tetra-n-butylammonium perchlorate (TBAP), dissolved and recrystallized from ethanol three times and dried under vacuum (< 10^{-5} Torr) for 3 days, was used as supporting electrolyte. All of the solutions were prepared and the cell filled and sealed in the glove box and removed for experiments. Prepurified nitrogen was bubbled through the solution for 30 min after the cell was opened to introduce the SCE reference electrode.

Results

The determination of V_{FB} from capacitance (C)-potential (V) data, *e.g.*, via Mott-Schottky (M-S) plots of $1/C^2$ *vs.* V, Eq. [1]

$$1/C^2 = \frac{2}{e\,\epsilon\epsilon_0 N_A}(V - V_{FB} - 0.025) \qquad [1]$$

is well documented (where C = capacitance per unit area, $e = 1.6 \times 10^{-19}$ C, = dielectric constant, $\epsilon_0 = 8.85 \times 10^{-14}$ μf/cm, N_A = acceptor density cm^{-3}, V = applied d-c bias, and V_{FB} = flatband potential). The determination of V_{FB} from the C-V data via S-M plots is based on the assumption that C can be taken to be the space-charge capacitance, C_{sc}, and that at the frequency used in the measurement, f, the surface states do not contribute to the measured value of C. This will be the case when the time constant associated with filling or emptying the surface states is long with respect to $1/f$ (*i.e.*, $1/f$ is short compared to the rate of charge exchange between the surface states and the bulk semiconductor). Under these conditions, $C \simeq C_{sc}$ and the surface states do not affect the measured capacitance, even when they are effective in pinning the

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Key words: cell impedance, redox potential, pinning.

Fermi level when they equilibrate with the solution redox species. The required frequency range for the measurement can be found from a plot of C *vs.* f (Fig. 1). Note that for the p-Si electrode in MeCN, 0.1*M* TBAP at 0.1V *vs.* SCE, C is essentially independent of f for $f \gtrsim 4$ kHz. In measurements used to determine V_{FB} in our studies, $f = 5$ kHz was employed. Although, in some cases, determination of V_{FB} from the intercept of the M-S plot involves some ambiguity (14), generally V_{FB} can be estimated to within 0.1V, and shifts in V_{FB} can be determined quite readily, even directly from the C-V plots themselves. The experiments here involved determination of C in the presence of various redox couples. The solution concentration and potential range was selected so that negligible faradaic currents were obtained. In the dark and at the frequencies chosen for measurement of C (1-10 kHz), any faradaic processes were assumed to make a negligible contribution to the measured impedance.

Consider the effect of adding nitrobenzene ($PhNO_2$) and then generation of its radical anion, $PhNO_2^-$ to the *C-V* behavior and the measured V_{FB}-value. The *C-V* plot of p-Si in the background solution alone, denoted p-Si/TBAP, MeCN, is shown in Fig. 2a, and the M-S plot for potentials in the depletion region is given in Fig. 3a. If it is assumed that the measured capacitance is purely space charge capacitance (13), the voltage-axis intercept of the M-S plot yields V_{FB} of p-Si in the background solution with no added redox couple of +0.15V *vs.* SCE. From the value of the acceptor density (N_A), the energy of the valence band (VB) edge is computed to be 0.05 eV below V_{FB}. By taking the E_g value of p-Si, 1.1 eV, and the VB edge energy, we can locate the bandedge positions under flatband conditions (Fig. 4). The associated V_{redox} values for various redox couples employed in these studies are also shown in Fig. 4. When $PhNO_2$ (30 mM) is added to the solution, the C-V curve is essentially the same as that in the background solution (Fig. 2b). However, coulometric generation of the reduced form, $PhNO_2^-$ (10 mM) causes a large shift of the C-V curve toward negative potentials (Fig. 2c) with V_{FB} obtained from the M-S plot (Fig. 3b) now at −0.5V.

Similar shifts in the C-V curves and M-S plots are found when other redox couples, *e.g.*, benzoquinone (BQ), anthraquinone (AQ), and oxazine (OX) are added to the solution and the reduced forms generated. The shift in V_{FB} in the presence of these couples is related to the redox potential, V_{redox} of the system (Fig. 5).

The shifts in V_{FB} upon generation of the reduced form of the redox couple are consistent with FLP, as

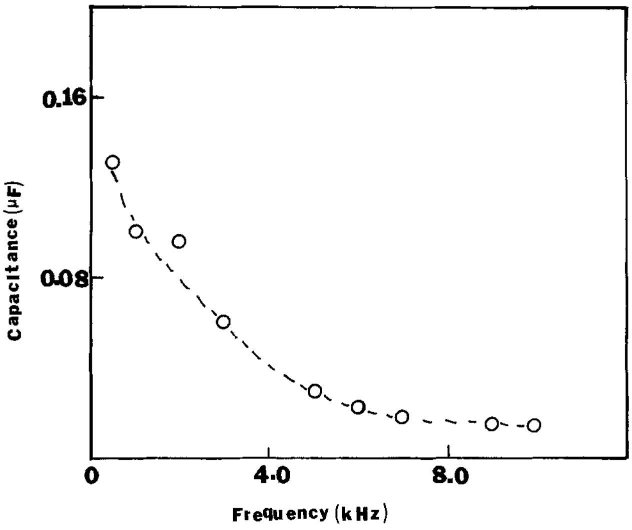

Fig. 1. Plot of variation of capacitance at 0.1V *vs.* SCE, with frequency, for p-Si/MeCN, TBAP (0.1*M*) interface.

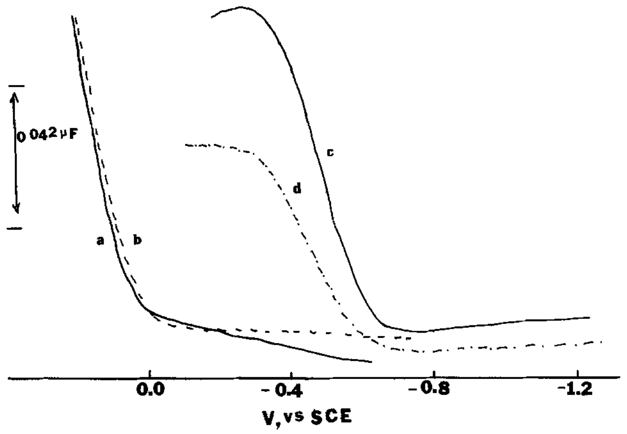

Fig. 2. Capacitance-potential (*C-V*) plots for the p-Si/MeCN, TBAP interface: (a) absence of redox couples, (b) with $PhNO_2$ (30 mM), (c) with $PhNO_2$ (30 mM) + $PhNO_2^-$ (10 mM), (d) $Ru(bpy)_3^{2+}$ (0.5 mM) + $Ru(bpy)_3^+$ (0.5 mM).

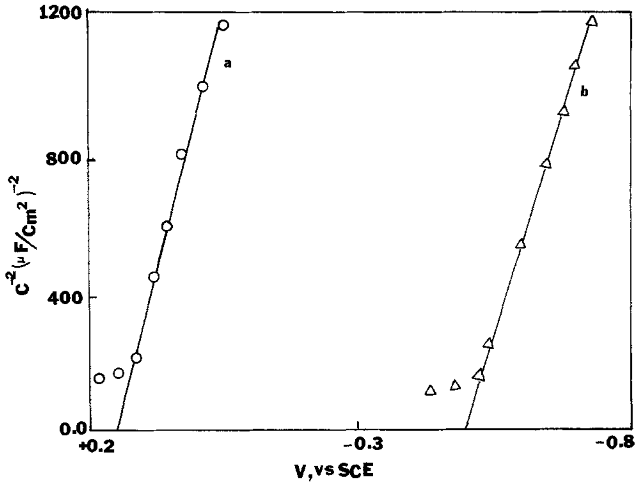

Fig. 3. Mott-Schottky plots of p-Si/MeCN, TBAP: (a) absence of redox couples, (b) with $PhNO_2$ (30 mM) + $PhNO_2^-$ (10 mM).

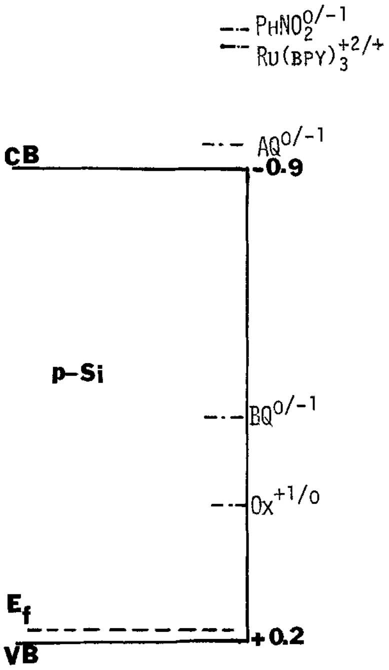

Fig. 4. Schematic diagram of p-Si/MeCN, TBAP interface under flatband conditions in the absence of added redox couples and the redox potentials of various couples investigated in this work.

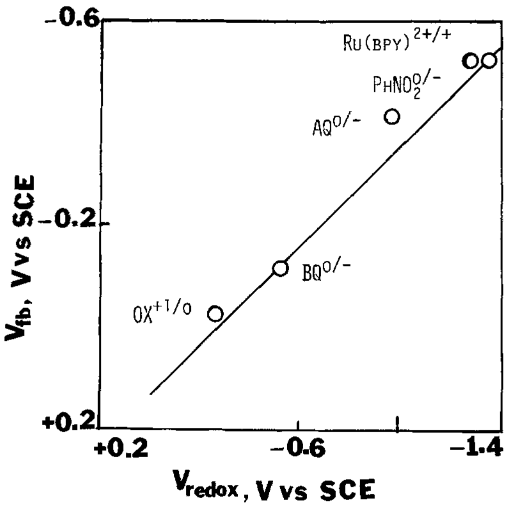

Fig. 5. Flatband potential, V_{FB}, of p-Si in MeCN as a function of redox potential, V_{redox}, of added solution couples: (a) oxazine (+1/0), (b) benzoquinone (0/−1), (c) anthraquinone (0/−1), (d) $Ru(bpy)_3^{2+/+}$, (e) nitrobenzene (0/−1).

discussed further below. However, since all of these reduced forms are also anionic, it is possible that the shift could be ascribed to the specific adsorption of the negative species on the p-Si surface. To test this possibility, C-V measurements were made in the presence of the $Ru(bpy)_3^{2+/+}$ couple (bpy = 2,2′-bipyridine), which is characterized by a redox potential near that of $PhNO_2^-$. The shift in C-V curve (Fig. 2d) and V_{FB} follows the same correlation as that observed with couples with anionic reduced forms.

The effect of a high density of surface states has been compared to that of a thin layer of metal on the electrode surface (1, 15). This effect has been investigated by vacuum deposition of a thin (<50Å) film of silver on the p-Si surface. The C-V curves in the absence and presence of a redox couple are shown in Fig. 6. Again, addition of the redox couple with a negative V_{redox} promotes a negative shift in V_{FB}.

Discussion

The shift in V_{FB} can be associated with the transfer of electrons from reduced forms in solution to surface states on the electrode (Fermi level pinning) (1) as shown schematically in Fig. 7. Initially, equilibration between partially filled surface states and the bulk semiconductor causes some band-bending (V_{sc}) (Fig. 7a). Addition of only the oxidized form of the redox couple (A) does not cause a shift of V_{FB} in the dark because this species cannot donate electrons to the surface states. Under irradiation, however, a shift in V_{FB} toward more negative potentials can occur, since photogenerated electrons in the CB or photogenerated A^-, can populate unfilled surface state levels. In the presence of A^-, a shift of V_{FB} is observed, even in the dark (Fig. 7b). Although V_{FB} shifts monotonically with V_{redox}, as shown in Fig. 5, the slope of the curve is less than unity as would be expected for a sufficiently high density of surface states (1). For the p-Si material employed here, addition of the A/A^- couple apparently causes a change in both the charge in the surface states and the space charge. Thus the presence of the A/A^- couple produces some additional band-bending as well as an increased potential drop across the Helmholtz layer. The relative variation of the potential drop across the space charge region and that across the Helmholtz layer depends upon C_{sc} and the density of surface states. We refer to the case shown in Fig. 7 as partial Fermi level pinning.

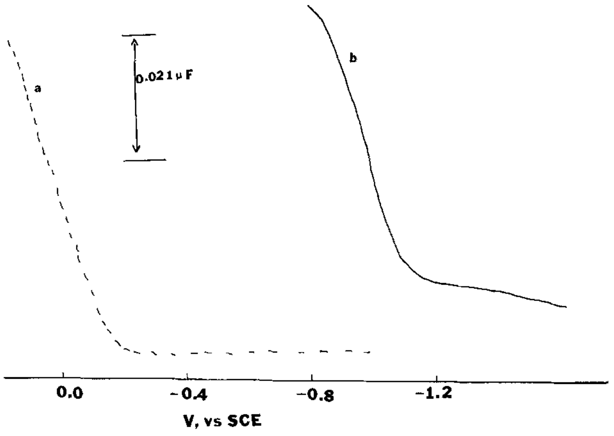

Fig. 6. C-V plots for the interface p-Si/Ag (<50Å)/MeCN, TBAP: (a) with no added redox couple, (b) with $PhNO_2$ (30 mM) and $PhNO_2^{-}$ (10 mM).

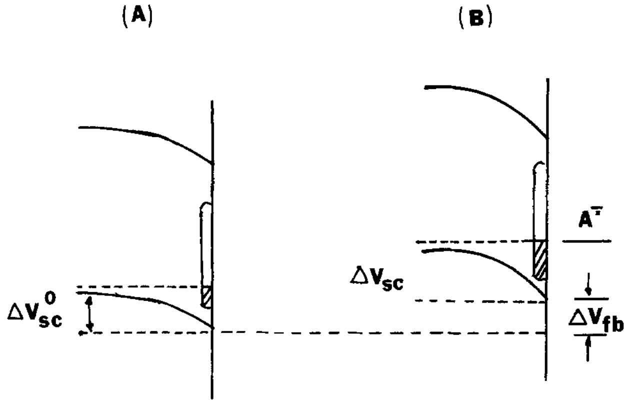

Fig. 7. Schematic representation of Fermi level pinning by injection of electrons to surface states from reductants in solution causing a shift of the bandedges to more negative values. (A) Before the addition of reduced form (A^-). (B) After the addition of A^-.

Shifts in V_{FB} can also be ascribed to the onset of inversion when couples at potentials representing energy levels above the middle of the bandgap are present (16-18). Note, however, that shifts in V_{FB} were found in this study with oxazine (+1, 0) and benzoquinone (0/−1), both of which have energy levels located below the middle of the gap (Fig. 4). Thus the shift in V_{FB} (and the location of the bandedges), at least in these cases, cannot be ascribed to inversion.

The further negative shift of V_{FB} by a thin Ag overlayer on p-Si as compared with a bare electrode in the same solution suggests that the thin Ag layer might act as or induce a set of "extrinsic" surface states of high density within the bandgap on p-Si. The extent of FLP will also depend on such factors as the nature of the solvent and electrolyte as well as the surface pretreatment (15). The effect of different etching procedures and chemical surface treatments is currently under investigation.

Conclusions

These measurements of the flatband potential of p-Si in MeCN via capacitance-potential plots provide clear evidence of the Fermi level pinning model previously proposed. The shifts in the flatband potential clearly parallel the shifts in the potential for the onset of the photocurrent and the observed cyclic voltammetric behavior for p-Si in CH_3CN obtained in earlier studies (3, 4). If only the oxidized form of the couple is present, the dark C-V behavior is similar to that for a solution in the absence of redox couples. When the reduced form of the couple is electrochemically generated, V_{FB} shifts to more negative values. The extent of the shift varies monotonically with V_{redox} (see Fig. 5).

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Technical Notes

The Specific Conductance of Molten Carbonate Fuel Cell Tiles

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Estimates have indicated that one-third to one-half of the observed polarization in molten carbonate fuel cells is due to *IR* losses in the electrolyte layer (1), yet the specific conductance of this component is not accurately known. The electrolyte layer, usually referred to as the tile, consists of a non-conducting porous lithium aluminate matrix with a conducting lithium/potassium carbonate eutectic enclosed in its pores. The purpose of this study was to evaluate the specific conductance of typical tile samples independent of fuel cell hardware.

Two well-characterized samples of tile were chosen for testing, an electrophoretic deposition (ED) tile,[1] and a tile commonly used in GE fuel cell tests, the hot-pressed (HP) tile.[2] These tiles are typically 45% by weight $LiAlO_2$ and 55% by weight 62/38 mol ratio lithium/potassium carbonate. The carbonates are standard analytical grade chemicals. The lithium aluminate powder has a particle diameter of 0.1-0.3 microns (15-20 m^2/g). The HP tiles are prepared by blending the $LiAlO_2$ powder with the carbonate and pressing this mixture in a die near the melting point of the carbonate (2). The ED tiles are prepared by suspending the $LiAlO_2$ powder in isopropanol and electrophoretically depositing (4) the $LiAlO_2$ on a mandrel. The deposits are removed from the mandrel and heat-treated to improve rigidity. They are then filled by melting a measured quantity of carbonate into the $LiAlO_2$ (3). The ED process allows one to measure the pore volume and pore size distribution of the $LiAlO_2$ matrix before it is impregnated with carbonate. The ED samples chosen for this study were found to be 51% porous with a mean pore size of 0.25 microns by mercury porosimetry (American Standard Company, Model No. 5721B). The appropriate amount of carbonate was added to the ED structure so that the tiles were completely filled. These two samples were designed to be similar. However, structural differences between these two samples must exist since the two preparation procedures are so different.

Experimental

The specific conductance of the tile was measured with a four-probe a-c impedance technique. The impedance was measured with a Wayne-Kerr a-c bridge. The four-probe technique was used to eliminate the lead resistance. The a-c signal was supplied by a PAR lock-in amplifier (Model 124A). The tuned receiver portion of the lock-in amplifier was used as the detector. The null was observed by monitoring the mixed monitor output of the amplifier with an oscilloscope. This system was capable of measuring the real and imaginary parts of the impedance from 1 to 50 kHz. This is not a particularly wide frequency range; however, enough information was obtained to spawn a reasonable level of confidence in the data. The real part of the impedance varied only 2% over this range of frequency.

The conductivity experiment was scaled to a size that optimized the accuracy of the resistance measure-

Key words: resistivity, fused salt, separator, energy storage.

[1] The electrophoretic deposition tile was prepared at General Electric Corporate Research and Development, Schenectady, New York (2).

[2] The hot-pressed (HP) tile was prepared by General Electric Direct Energy Conversion Programs in Wilmington, Massachusetts (3).