Semiconductor electrodes. IV. Electrochemical behavior of n- and p-type silicon electrodes in acetonitrile solutions

Daniel Laser, and Allen J. Bard

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wavelength would be monotonically increasing or decreasing. Thus the spectra at intermediate times might be more accurately described as belonging to metastable intermediate configurations rather than to weighted sums of spectra from two extremes of shallow and deep traps. These intermediate configurations appear to be absent or very short lived in liquid ethanol near the freezing point. Baxendale and Wardman[9] observed an "end of pulse" (ca. 5 ns) spectrum in ethanol at 160 K which showed a minimum at about 1000 nm. Such a minimum is not indicated in ethanol glass at 77 K either in the work of Klassen[3] or in the present work.

Supplementary Material Available: an Appendix of experimental details (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. T. Richards and J. K. Thomas, *J. Chem. Phys.*, **53**, 218 (1970).
(2) (a) L. Kevan, *Chem. Phys. Lett.*, **11**, 140 (1971); (b) *J. Chem. Phys.*, **56**, 838 (1972).
(3) N. V. Klassen, H. A. Gillis, G. G. Teather, and L. Kevan, *J. Chem. Phys.*, **62**, 2474 (1975).
(4) J. R. Miller, *J. Phys. Chem.*, **79**, 1070 (1975).
(5) H. Hase, M. Noda, and T. Higashimura, *J. Chem. Phys.*, **54**, 2975 (1971).
(6) H. Hase, T. Wishimura, M. Noda, A. Namiki, and T. Higashimura, *J. Chem. Phys.*, **57**, 1039 (1972).
(7) T. Shida, S. Iwata, and T. Watandbe, *J. Phys. Chem.*, **76**, 3683 (1972).
(8) J. Miller, unpublished.
(9) J. H. Baxendale and P. Wordman, *J. Chem. Soc., Faraday Trans. 1*, **69**, 584 (1973).

Semiconductor Electrodes. IV. Electrochemical Behavior of n- and p-Type Silicon Electrodes in Acetonitrile Solutions

Daniel Laser and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 (Received August 27, 1975)

The behavior of n- and p-Si as electrodes for the reduction and oxidation of several redox systems (e.g., benzonitrile, 9,10-diphenylanthracene, anthraquinone, benzoquinone) in acetonitrile solutions in the dark and under illumination was investigated. The results were correlated with the relative energy levels of the valence and conduction bands of the semiconductor and those of the redox couples in solution, estimated by determination of the flat-band potential of the semiconductor–solution system by photopotential methods. The electrode behavior of Si strongly depended upon the electrode pretreatment and the absence of ideal semiconductor electrode behavior for this relatively small band gap material suggests the importance of surface states and breakdown phenomena for these electrodes. A unique electrogenerated chemiluminescence (ECL) experiment with a p-Si electrode is described.

Introduction

Although nonaqueous solutions offer many advantages in carrying out and understanding simple electrochemical processes (for example, an extended range of available potentials, the availability of numerous reversible one-electron transfer reactions without kinetic complications, and fewer difficulties with surface phenomena) only a few studies have been made with semiconductor electrodes in these media. Krotova and Pleskov[1] determined the capacitance of a Ge electrode in N,N-dimethylformamide (DMF), while Mark and Pons[2] qualitatively performed a reductive electrolysis at a Ge internal reflection plate. Acetonitrile (ACN) solutions were employed by Osa and Kuwana[3] with highly doped SnO_2 transparent electrodes and by Landsberg and coworkers[4] with n-type GaP. A previous paper in this series[5] dealt with the behavior of n-type TiO_2, a wide band gap semiconductor (sc), in ACN. This paper is concerned with the electrochemical properties of Si, a small band gap (1.1 eV) sc, and a comparison of the behavior of several redox systems at Pt, n-, and p-Si in ACN solutions, in the dark and under illumination.

General and detailed treatments of sc electrochemistry have been given by Myamlin and Pleskov[6] and Gerischer,[7,8] as well as in numerous papers on the properties of specific sc materials.[9-16] The picture which emerges for faradaic processes shows three main differences between metal and sc electrodes. These differences occur because for sc electrodes:

(a) The heterogeneous reaction rate (i.e., the exchange current) depends upon the relative energy (or redox potential) of the redox reaction and the energy levels of the sc bands. If a redox couple is represented by some Gaussian energy distribution function of electron acceptor levels (oxidized forms) and donor levels (reduced forms) in solution, equi-energetic charge transfer between the sc band at the surface and levels in solution requires a favorable overlap between these levels.[17] The exchange current depends upon this overall overlap, and thus on the relative position of the levels, the number of sc free carriers available for exchange, and the concentration of electroactive species in solution at the redox couple's equilibrium potential (thermodynamically independent of electrode material). For a

small band gap sc, there may be overlap of a redox couple with both the conduction and valence bands so that there may be contributions to the exchange current from both bands.[7] Experimentally a low exchange current will mean that even when the electrode potential is shifted from equilibrium the charge transfer reaction will still be slow and irreversible.

(b) The total applied overvoltage may not be effective in changing the potential drop between sc surface and solution. The kinetic stimulation of the electrochemical reaction by changing the activation energy of the preelectrode state in solution will be prevented, if the change in the applied potential does not change the value of the potential drop in the Helmholtz layer at the sc-electrolyte interface. In the case of a sc, unlike a metal, most of the applied overvoltage contributes to changes in the potential barrier in the space charge region and in the population of free carriers in it, so that the influence of the potential on electrode kinetics can be attributed to this effect. This is the usual situation at a sc unless a high density of surface states exists or a condition of high degeneracy prevails.[7]

(c) The current may be limited by the supply of free carriers. In contrast to metal electrodes, whenever minority carriers participate in the electrochemical process, the reaction rate may be limited by their rate of supply to the electrode–electrolyte interface. Minority carriers which are consumed may be resupplied to the surface by diffusion from the bulk through the quasineutral region,[6] generated in the space charge region[18] or at the surface,[19] usually leading, in a moderately doped sc, to very small currents. When mass transfer in solution is not a constraining factor, minority carrier participation in the electrochemical reaction will be characterized by a limiting current.

Other mechanisms of carrier production and transfer, such as intraband tunneling,[20] space charge region ionization,[21] and photogeneration must be considered as well. The organic systems employed allowed us to subject the Si electrodes to various conditions which are unacceptable in water so that its behavior could be interpreted according to the considerations discussed above. Electrode reactions involving the electrode material itself (i.e., anodic dissolution) were avoided, however.

Experimental Section

Si single crystals were mounted in a glass tube using silicone rubber adhesive (General Electric) which was found to be resistant to ACN and which insulated all electrode parts except the area exposed to solution. Electro deposited nickel provided ohmic contact to the n-material and thermally deposited gold (Hanovia Liquid Gold, Engelhard, N.Y.) was used for the p-type. Two samples of each type were used: 5 ohm cm (211 plane exposed to solution) and 1 ohm cm (100) for the n-type and 0.05 ohm cm (211) and $\simeq$ 5 to 10 ohm cm (111) for the p-type. The doping levels were all in the range of about 10^{15}–10^{18} cm^{-3}; the dopants were boron and phosphorous. Although the electrode surfaces were visually different, there was no difference between the sample of each type in the electrochemical behavior within the usual experimental reproducibility unless otherwise specified. The low resistance materials (n, 1 ohm cm; p, 0.05 ohm cm) (kindly donated by Texas Instruments, Dallas, Tx.) were received polished to a high mirror finish and were not wet by water. The other two samples had a hazy gray appearance, even after mechanical polishing. The usual pretreatment for the electrodes involved etching

them in an HF–HNO$_3$ mixture followed by drying in an oven prior to use. The n-type visually seemed to be little affected by a 2 min etching, while the p-type 5 ohm cm surface became somewhat duller and the 0.05 ohm cm p-type sample dissolved vigorously with black patches of amorphous Si[22] peeling off. Mechanical polishing with 0.3-μ alumina which was not followed by etching, although resulting in a visually smoother surface always led to a more active electrode. The behavior in this case resembled that of a metal electrode, especially when the sc was first used. Whenever changes in electrode behavior were observed during this work, the results obtained immediately after etching were taken to represent the electrode behavior, since these results were the most reproducible.

An Ag wire immersed in 0.01 M AgNO$_3$ in ACN, separated from the main solution by a porous Vycor (Corning) plug served as a reference electrode and all of the potentials are reported with respect to this reference. Its value vs. an aqueous SCE in ACN is about +0.3 V. This electrode was found to be very stable and reliable. No leakage of Ag$^+$ into the main solution was detected. A coiled platinum wire in a separate compartment was used as the auxiliary electrode.

All reagents and ACN were purified according to known procedures.[23] A vacuum-tight Pyrex cell equipped with a flat window facing the electrode surface contained the solution and electrode assembly. Solutions were prepared and the cell filled in a Vacuum Atmospheres Corporation drybox (Hawthorne, Calif.) under a helium atmosphere.

All measurements utilized the three-electrode potentiostatic mode, employing a Princeton Applied Research (PAR) Model 173 potentiostat, a PAR Model 175 programmer and a Model 2000 X–Y recorder (Houston Instrument Company, Austin, Tex.). To overcome the electrode bulk resistance and solution resistance, positive feedback resistance compensation was employed. In order not to overcompensate (e.g., because of the formation of a depletion layer, see Results) the amount of maximum compensation was determined either under a condition which led to sc degeneracy or when the electrode was illuminated, i.e., under conditions when the resistive element of the space charge region was minimized. Impedance measurements were performed by superimposing a 10-mV sine wave on a potential scan of 0.5 V/s. The in- and out-of-phase components of the current were separated by a PAR Model HR-8 lock-in amplifier. The instantaneous photopotential was measured with 0.5-ms strobe light pulses used for illumination.

The working electrode was biased against the auxiliary one with a power supply and its potential change vs. the reference electrode was displayed on an oscilloscope. A 500-W tungsten lamp equipped with an Esco 4811-0 3-mm red glass filter was used as the light source. For ecl measurements a photomultiplier detector was used, with its input filtered by an Esco-3-mm blue glass filter, so that the blue light could be detected in the presence of the red background illumination.

Results and Discussion

Useful Working Range. Figure 1 depicts most of the useful working range of the Si electrodes in ACN–0.1 M TBAP compared to the range of the same samples in aqueous (20% HF) solutions. This range in ACN extends over an interval twice as wide as the Si band gap; the flat band potential of the n-Si, as will be shown later, lies at about the mid-
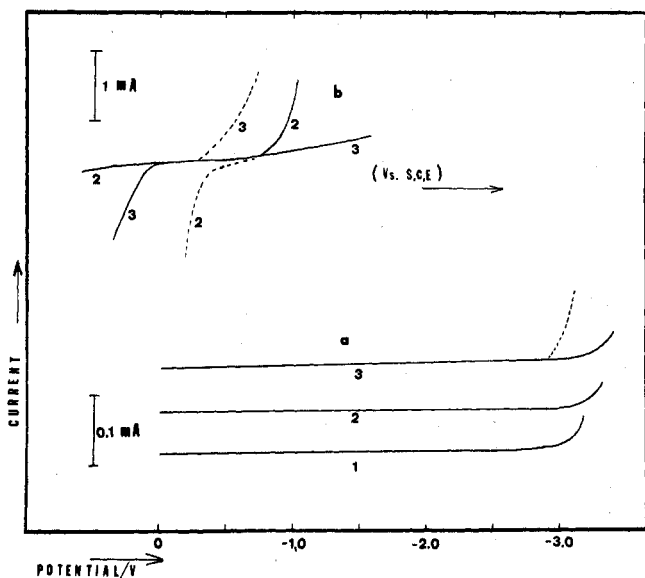
Figure 1. Background current. (a) ACN, 0.1 M TBAP (cathodic limit only); (b) aqueous, 20% HF. (1) Pt electrode; (2) n-Si, 5 ohm cm; (3) p-Si, 10 ohm cm. Dashed line shows effect of illumination.

dle of this range. Potentials positive of 0 V were avoided so as not to subject the electrodes to electrochemical conditions which might drastically change their surface properties (dissolution, passivation, etc.). Little difference was found between the n- and p-type samples and between both of them and Pt for the cathodic background reduction process (in the dark) compared to the clear difference seen in water. Under irradiation, the background current on p-Si was shifted to potentials positive of where background reduction occurs at a Pt electrode. The n-type electrode is unaffected by illumination in this potential region.

Flat Band Potential. The importance of this variable has been discussed elsewhere.[24] For an extrinsic sc the flat band potential, V_{fb}, closely represents the location of the majority carrier energy band in the bulk sc if the potential drop in the Helmholtz layer can be neglected. V_{fb} is needed so that the position of the sc bands and the energy levels in solution can be located with respect to one another on a common relative scale (e.g., with respect to a given reference electrode). Knowledge of the relative energy positions allows one to estimate the exchange current and to have an idea about which band will be involved in the charge transfer. Moreover, by knowing V_{fb} the "electrical state" of the sc (i.e., the carrier and potential distributions in the space charge region) at some other applied electrode potentials can be predicted.

Thus for an intrinsic sc the nature of its electrical states is symmetric with respect to V_{fb}, and for a small amount of band bending and in the absence of surface states, changes of applied potential hardly affect the potential drop in the Helmholtz layer. For a moderately doped sc (e.g., n-type) the electrical behavior is asymmetric with respect to V_{fb}. Degeneracy will occur following formation of a slight accumulation layer (e.g., upon negative polarization) when the concentration of majority carriers (e.g., electrons) in the space charge region approaches the effective density of states of the corresponding band (e.g., conduction band). On the other hand inversion and depletion layers[25] form over a much wider range of applied potentials (e.g., upon positive polarization). Hence a knowledge of V_{fb} is neces-

sary for an understanding of the effect of the imposed overpotential on electrode kinetics.

The flat band potentials were estimated by observing photoeffects caused by electrode illumination on electrode potentials and on electrode impedance. In the first method, the instantaneous perturbation in the equilibrium potential of the electrode due to illumination is minimized at the flat band position[26] (in the absence of fast surface states). The second method is based on the detection of the electrode potential at which a depletion layer begins to form when the sc bias (electrode potential) is increased in the appropriate direction from V_{fb}. Let us consider this second method in more detail. The sc impedance can be represented by a complex network of idealized passive elements.[27] The V_{fb} value can often be determined by measurement of the C_{sc}, the space charge capacitance as a function of potential (Shottky–Mott plot).[6] However our measurements of the dark in- and out-of-phase current components resulting from a 10-mV sine wave superimposed on a 0.5 V/s dc scan, could not be interpreted in a unique and meaningful way so as to obtain V_{fb}. However, we noticed that the resistive component of the impedance monotonically increases from a certain potential in the dark and is decreased to a constant level under electrode illumination (Figure 2). No faradaic current is detected at these potentials (even under electrode illumination), thus no shunting of the sc resistive elements is provided by the light. The capacitive component changes in a more complex way with electrode illumination but the relative magnitude of this change is much smaller. Although no arbitrary separation between the components is possible, we feel that the following interpretation of this effect allows estimation of V_{fb}. The monotonic increase of the resistive component with potential in the dark mainly reflects the formation of a depletion layer consisting of immobile charge in the space charge region. Electrode illumination, by forming free mobile carriers, eliminates this resistance. Thus the position of V_{fb} can be taken as the point where the dark resistive component deviates from that under illumination. Because all of the samples were fairly thick (1–2 mm), light effects that could arise at the ohmic metal–sc contact were avoided.

Since the resistive component varies approximately with the square root of potential in the dark, as expected from the variation of depletion layer width with potential,[28] and p- and n-type samples show symmetric behavior and yield an estimated band gap near the known value for Si, the above treatment is at least approximately correct. Moreover the n-type Si V_{fb} value coincides with that obtained by the photovoltage method. A related method which could provide similar information about the resistance variation under illumination involves surface conductivity measurements. Within the reproducibility of the measurement and the nature of the assumptions we place V_{fb} for n-type Si at -1.20 ± 0.15 V and that for p-type Si at -0.10 ± 0.15 V, independent of the doping level.

Relative sc–Solution Energy Levels. The energy levels in solution for a certain redox couple are identified closely with its standard electrode potential[17] and were determined by using cyclic voltammetry at a Pt electrode, where all couples showed reversible, one-electron waves. The midpoint between the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials was taken as the standard potential of the system.[29] Figure 3 is a schematic representation of the relative energy positions of the sc bands and the systems employed,
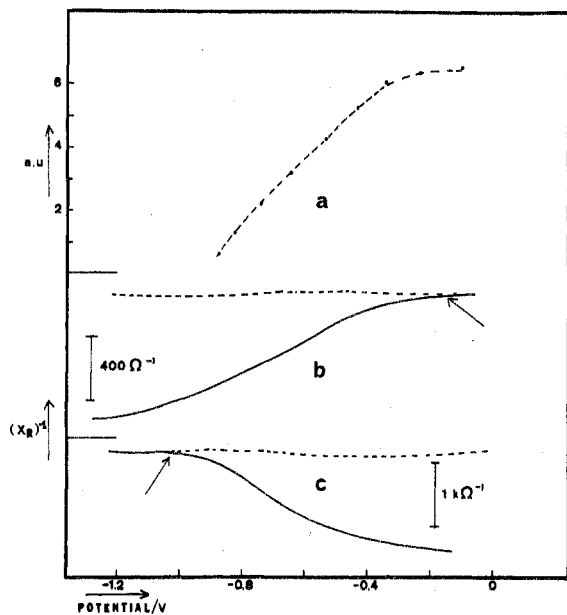
Figure 2. (a) Instantaneous photopotential at n-Si, 5 ohm cm; (b) resistive component of electrode impedance, p-Si 10 ohm cm; (c) resistive component of electrode impedance, n-Si, 5 ohm cm. For b and c dashed line, with electrode illumination; 4000 Hz, 10 mV sine wave; lock-in amplifier time constant, 1 ms. Arrows show estimated flat band potentials.
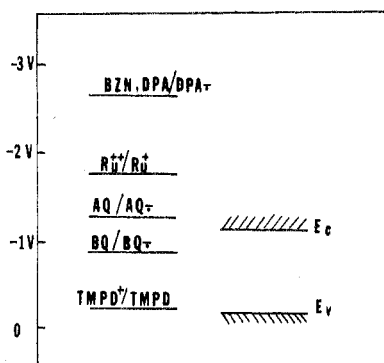

Figure 3. Schematic energy relation between Si bands and redox couples in ACN–0.1 M TBAP solution: TMPD, N,N,N',N'-tetramethyl-p-phenylenediamine; BQ, p-benzoquinone; AQ, 9,10-anthraquinone, Ru^{2+}, $Ru(bpy)_3(ClO_4)_2$; BZN, benzonitrile; DPA, 9,10-diphenylanthracene.

based on the measurements to be described. The acceptor (oxidized form) levels are supposed to have a Gaussian distribution of width λ which equals the difference in the oxidized and reduced form solvation energy, positioned $\lambda/2$ eV above the horizontal line representing the level, while the donor levels of the same shape are positioned $\lambda/2$ eV below.[17] Since λ, which is at least 0.5 to 1 eV, is comparable to the band gap of Si (1.1 eV), a fair amount of overlap is expected between the sc bands and levels in solution even for levels positioned in the gap region. Under these conditions contribution of both sc bands to the exchange current can occur.

n-Type Si. The system with the most negative standard potential, E_s, investigated was benzonitrile (BZN), which undergoes a reversible reduction at a Pt electrode in ACN. During the reduction of such a system, with an E_s so negative of V_{fb} that it is located well within the conduction band (cb), the sc properties of the n-type electrode are sup-

pressed. Degeneracy prevails and the Helmholtz potential drop at the sc–solution interface may be modulated so that metallic behavior is expected with only a small degree of irreversibility (Figure 4). Very similar behavior is exhibited by another negative system, DPA|DPA·⁻ (where DPA is 9,10-diphenylanthracene). For systems with somewhat more positive E_s values but those still negative of the n-Si V_{fb} one expects that both reduction and reoxidation of the reduced species will occur through the cb. The reduction will be stimulated by the applied overpotential either through electrons accumulating in the cb, yielding an apparent transfer coefficient of 1,[30] or, as before, through modulation of the Helmholtz potential because of degeneracy. For the concentrations (1–10 mM) employed here mass transfer in solution governs the reaction rate. The reoxidation, however, should be influenced less by a positive overvoltage, if the potential and population in the space charge region are modulated, because the number of free vacancies in the cb which accept electrons in the reoxidation process are nearly independent of potential. The three successive reductions and reoxidations of the chelate Ru-$(bpy)_3(ClO_4)_2$ (bpy = bipyridyl)[31] are an example of this case (Figure 5). The reason for the broadening of the third wave is unclear. The reoxidation of the +1 to the +2 species is sluggish and fails to produce a definite current peak. The cyclic voltammetry of anthraquinone (AQ) at Pt and n-Si is shown in Figure 6. The reduction to the radical anion, AQ·⁻, occurs at Pt at −1.3 V, a potential just slightly negative of V_{fb} of n-Si. Thus while the cb is almost certainly involved in the reduction process, there is also the possibility of some overlap between solution levels and the valence band (vb). The reduction of AQ at n-Si occurs with an E_{pc} 0.1–0.2 V more negative than that at Pt, suggesting that a slight accumulation layer must be formed in the space charge region before reduction occurs. Both cb and vb are candidates for the oxidation of AQ·⁻ but participation by the vb requires hole injection into solution and a rough calculation of the maximum supply of minority carriers based on estimated diffusion and hole generation rates predicts that this dark vb oxidation route is negligible. A small, but definite, oxidation current for AQ·⁻ is observed with some anodic overpotential compared to Pt; this anodic current increases significantly when the electrode is illuminated. Thus, in addition to an inefficient route for AQ·⁻ oxidation involving the cb or surface states near it, photosensitized oxidation via the vb is possible. In this case a sufficiently high electric field has to be formed in the space charge region (i.e., depletion layer formation) for the separation of the photogenerated carriers to occur, thus preventing electron–hole recombination. To observe the photoeffect the electrode potential must be sufficiently positive; thus the oxidation, even under illumination, occurs with some anodic overpotential.

p-Benzoquinone (BQ) shows similar behavior. The redox potential of this system at Pt is −0.85 V, positive of the n-Si V_{fb}. For this system a very pronounced negative overpotential is found compared to Pt, so that the reduction of BQ and AQ ($\simeq0.4$ V more negative on Pt) nearly coincide at n-Si. Indeed, the BQ reduction, if carried out via the cb, will not occur as long as the sc space charge region is in a depletion situation; only at an electrode potential where accumulation of electrons in the space charge region takes place, will BQ be reduced, and thermodynamically these potentials allow the reduction of AQ as well. As concerns the oxidation of BQ·⁻, again a photoeffect was found, thus
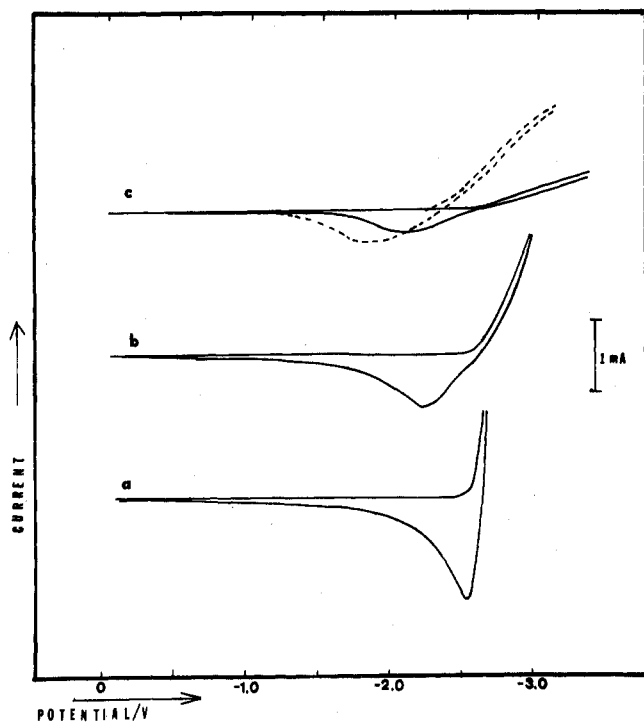
Figure 4. Current–voltage curve of 50 mM BZN in ACN–0.1 M TBAP: (a) Pt electrode; (b) n-Si, 5 ohm cm; (c) p-Si, 10 ohm cm. Dashed line, with electrode illumination. Potential scan rate, 50 mV/s.
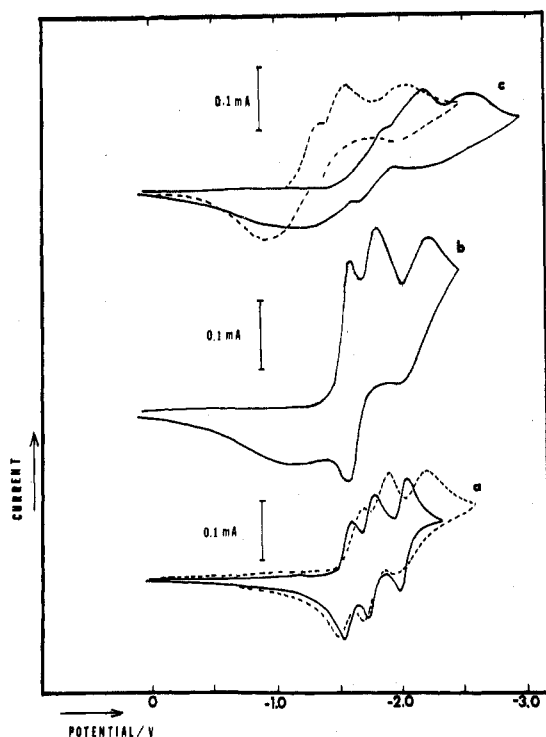

Figure 5. Cyclic voltammetry of 5 mM of Ru(bpy)$_3^{2+}$ in ACN–0.1 M TBAP: (a) Pt electrode; dashed line, "activated" p-Si 0.05 ohm cm (see text); (b) n-Si, 1 ohm cm; (c) p-Si, 10 ohm cm; dashed line, with electrode illumination. Potential scan rate, 50 mV/s.

demonstrating participation of the vb. In the dark, irreproducible behavior was found which was dependent on the electrode pretreatment. Sometimes no perceptible anodic current was observed and sometimes a small but definite
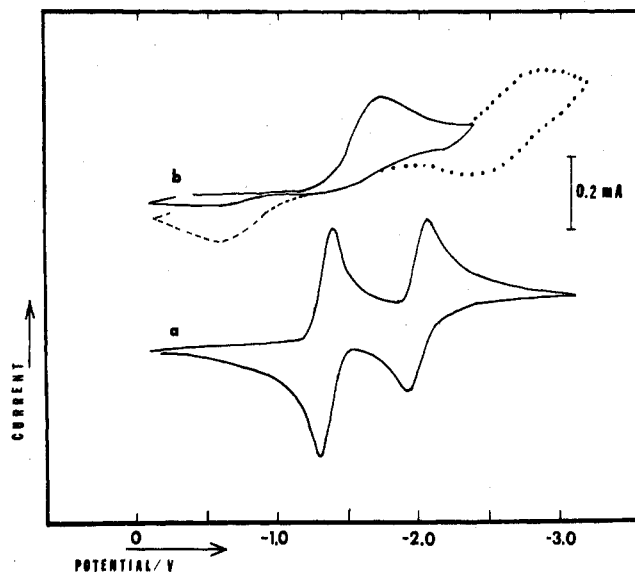

Figure 6. Cyclic voltammetry of 20 mM AQ in ACN–0.1 M TBAP: (a) Pt electrode; (b) n-Si, 5 ohm cm. Dotted line, scan continuation to more cathodic potentials; dashed line, with electrode illumination. Potential scan rate, 50 mV/s.

current, as for AQ.$^-$ oxidation, appeared. The energy distribution for BQ.$^-$ is less favorable for overlap with the cb, thus direct electron transfer to cb, as for AQ.$^-$, will probably be very ineffective. However, an indirect route for transferring an electron to the cb in the bulk via surface states (which will be positioned at this high surface band bending above the energy of the conduction band in bulk and hence will be capable of bringing trapped electrons from solution to the conduction band) may still be operative. The sensitivity of the electrode behavior to surface pretreatment implies such an involvement of surface states.

The most positive system investigated was TMPD.$^+$| TMPD (where TMPD is N,N,N',N'-tetramethyl-p-phenylenediamine). A solution containing TMPD and TMPD.$^+$ in equimolar amounts was prepared by bulk coulometric oxidation of TMPD at a Pt electrode. From its redox potential at a Pt electrode (Figure 7a) of -0.25 V compared with V_{fb} of n-Si, this sytem is expected to interact mainly with the vb, i.e., the solution energy level distribution of TMPD mostly overlaps with the vb while that of TMPD.$^+$ also overlaps the lower part of the band gap. Reduction of TMPD.$^+$ at n-Si (Figure 7b) occurs with E_{pc} of -0.7 V and shows only a very small associated anodic current on reversal. When the electrode is illuminated, however, a limiting anodic photocurrent, proportional to light intensity, is observed on scan reversal corresponding to TMPD oxidation, and the cathodic current is increased on the next scan because of the higher concentration of TMPD.$^+$ now in the vicinity of the electrode. A discussion of the mechanism of these redox reactions on n-Si will be given after the behavior of p-Si is described.

p-Type Si. Since the relative location of the energy levels in solution and for the p-Si should be essentially the same as for n-Si (as implied in Figure 3), all reductions which proceed primarily via the cb for n-Si (i.e., all compounds other than TMPD.$^+$) would be expected to occur also via the cb in p-Si and hence be limited by the minority carrier supply at the electrode surface. Under these circumstances very small cathodic currents might be expected. In
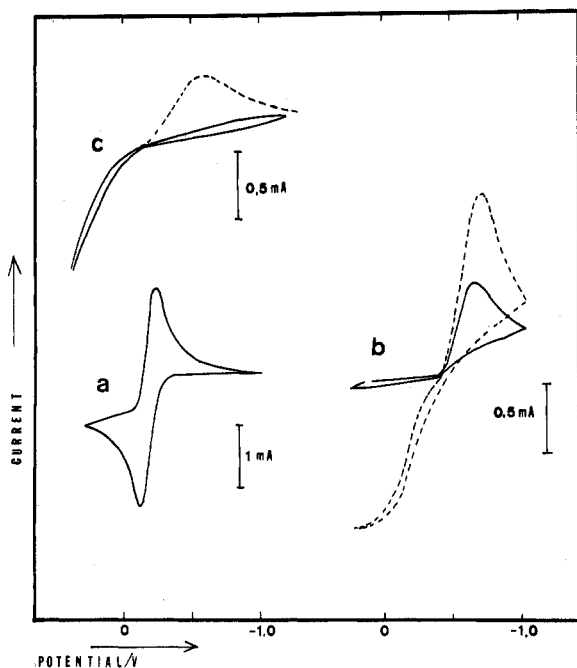
Figure 7. Cyclic voltammetry of TMPD·$^+$|TMPD mixture (ca. 1:1) in ACN–0.1 M TBAP: (a) Pt electrode; (b) n-Si, 5 ohm cm; dashed line, with electrode illumination; (c) p-type, 10 ohm cm; dashed line, with electrode illumination. Potential scan rate, 50 mV/s.

fact, however, all of the couples showed significant cathodic currents at p-Si with the i–E curves shifted toward negative potentials compared to the behavior on n-Si (Figures 1, 4, and 5). At electronic equilibrium the surface concentration of electrons in the p-Si should be the same as that for n-Si at the same electrode potential (e.g., E_s of Ru(bpy)$_3^{2+}$). Thus the exchange current for the reduction process, which depends upon surface concentrations of electrons and oxidized species, should be the same on both n- and p-type material.[8] However whereas for n-Si the electrons are the majority carrier and can be supplied by the usual conduction process in the sc, for p-Si the supply of electrons, the minority carriers, will be limited by their rate of supply to the surface. Neither diffusion of electrons through the quasineutral region[6] nor pair generation in the space charge region[18] seems to be sufficiently rapid to provide electrons at the milliamp current level. For these compounds the origin of electrons consumed in the reduction at the p-type electrode is the vb and we feel that the mechanism by which they arrive at the surface is related to the extreme band bending which occurs at this electrode under the reduction conditions. Consider, for example, the first reduction of Ru(bpy)$_3^{2+}$ observed at about −1.65 V (at Pt). When the electrode is subjected to this electrode potential, which is more than the band gap energy beyond the p-Si V_{fb} in the depletion direction, enormous band bending at the surface will take place. It is possible under these conditions that the band gap region, or even the edge of the cb, at the surface will be at the same or even below the energy of the vb in the bulk sc. Then, especially for the highly doped Si, where the potential barrier is narrow, direct transfer of electrons across the space charge region from the vb to a surface level in the gap or to the edge of the cb may be possible. Different mechanisms for a related phenomenon, the supply of holes (minority carriers) to the surface of an n-type sc, have been considered.[21] The intraband electron exchange on highly doped n-ZnO has also recently

been described.[32] Two experimental findings support this mechanism. (a) Reduction of these compounds at p-Si occurred at potentials very negative of V_{fb} so that large band bending and high potential barriers were established. BQ reduction on p-Si occurs at about the same potentials as at the n-type (ca. −1.4 V), quite negative of the potential at Pt (−0.85 V). For n-Si this overpotential probably arises from the necessity of forming an accumulation layer, in the space charge region, while for p-Si this overpotential represents the amount of band bending and surface field needed for this effect to occur. (b) After vigorous etching the 0.05 ohm cm p-type electrode sometimes behaved like an "activated electrode" whose surface consisted mainly of black patches of amorphous silicon[22] and whose behavior resembled that of a metal electrode for reductions much more than any of the n-type electrodes employed (Figure 5a). Indeed, tunneling and related phenomena are expected to be most pronounced for a heavily-doped electrode, because the depletion layer width, and hence the barrier width for tunneling, are inversely proportional to the square root of the majority carrier concentration in the bulk. In all cases the reductions are promoted by illumination of the p-Si electrode (Figures 1, 4, 5, 7). These photoeffects will be discussed in the next section. Oxidations of the reduced forms at p-Si show similar behavior to that found with n-Si for those compounds showing electron transfer mainly with the cb (BZN, Ru(bpy)$_3^{2+}$). For AQ and BQ oxidation can also occur in the dark at p-Si, since majority carrier (hole) injection is involved.

For the TMPD·$^+$|TMPD system, as discussed for n-Si, overlap is apparently mainly with the vb. For p-Si, where holes are available, oxidation of TMPD observed in the dark is enhanced by the applied potential either by hole accumulation in the space charge region or by changes in the Helmholtz potential drop in solution (Figure 7d). A small cathodic current is observed at p-Si for TMPD·$^+$ reduction in the dark, which is greatly enhanced under illumination. A reduction occurring via the vb should be relatively independent of potential if the potential drop in the Helmholtz layer remains unchanged. This behavior is found with p-Si (Figure 7d) but not with n-Si (Figure 7b). For the p-Si the reduction is occurring near its V_{fb}, while for n-Si the potential is quite positive of its V_{fb} so that large band bending occurs and perhaps results in a change in the potential drop in the Helmholtz layer. The reduction current peak obtained for the n-Si can also result from reduction via surface states. Such surface states, which have been shown to exist in the Si band gap,[15,33,34] are vacant at extreme anodic electrode potentials, but are gradually populated during a potential scan in a negative direction. These states may then transfer electrons to the reducible form. In this case, the potential dependence of the current will reflect the occupation statistics of these states. Such an effect was found for TiO$_2$,[5] a wide bandgap n-type sc for the reduction of systems located within the band gap region. A reduction of BQ limited by diffusion in solution and occurring with participation of the vb was also observed for the small band gap electrode, n-type Ge.[9]

Photoeffects at the p-Si Electrode. Illumination of p-Si with light of energy greater than that of the band gap (e.g., red light) excites electrons to the cb and promotes direct reduction through this band. Only some particular nuances of this well-known photoeffect,[35] i.e., those characteristic to this system, will be discussed here. The photoeffect was observed for all reducible couples employed. Even when the

reduction occurs via the vb (i.e., for TMPD·+) light provides more efficient reduction, although in this case the electrode is subjected to potentials only slightly negative of V_{fb}, so that a strong depletion layer has not formed and the "electrical state" of the sc is not very favorable for the observation of a photoeffect. The impossibility of an isoenergetic electron transfer directly from the cb to the TMPD·+ may require the existence of some energy states (e.g., surface states) within the gap which are filled by transfer from the cb before the transfer. Another possibility is that now, as in the dark, TMPD·+ reduction occurs exclusively via the vb, but that modulation of the Helmholtz potential drop in solution takes place at an illuminated sc electrode, because the extent of the sc surface band bending diminishes under illumination, as is observed in the usual photopotential effect,[35] and this enhances the reduction rate. The photoreduction occurs with an "underpotential" (Figures 1, 4, 5c), i.e., the reduction process takes place at the illuminated p-type Si electrode at less negative potentials than at a Pt electrode where its reduction is nernstian. This phenomenon has been observed at other sc electrodes[36-38] and very generally may be useful for utilizing light energy for driving an electrochemical reaction with a smaller (or no) electrical energy input. Under certain conditions the photoreduction appears to be selective, i.e., the potential sequence in which some of the consecutive photoreductions occur follows their order at a Pt electrode, although all are shifted in a positive direction (Table I). This is a special feature of the photoeffect at low band gap sc electrodes (whenever the background allows differentiation) in contrast to the nonselective photooxidations frequently observed at large band gap electrodes.[37]

Any oxidized form that at a certain electrode potential will be located at an energy position higher (more negative) than the sc cb in the bulk, where this relative energy location can be controlled by the applied potential in the same way as for a metal electrode, will not be reduced by a photogenerated electron in the cb. At a large band gap (e.g., 3 eV) sc, wherever the electrode potential enables the photoprocess to occur, more systems will be located within the bulk energy interval of the sc bandgap and they will all undergo photosensitized charge transfer at about the same potential, that where a sufficient depletion layer is established. Usually no limiting current proportional to light intensity is found. The reason for this seems to be that the reduction also proceeds in the dark via the breakdown mechanism discussed before. Thus a limiting current resulting from the rate of photogeneration of electrons will be partially masked by this dark background current. Moreover even if the breakdown phenomenon is greatly suppressed by light, because the establishment of high surface band bending is prevented in the presence of light, the concentration range employed (1–10 mM) is such that mass transfer limitation in solution occurs and indeed when a high concentration of BZN was used, a limiting photocurrent was found.

ECL at Si Electrodes. The medium employed in this work suggested the possibility of carrying out ECL[39,40] (electrogenerated chemiluminescence) at Si electrodes. Briefly, ECL is based on the mutual annihilation of appropriate electrogenerated radical cations with radical anions to give an excited state which emits light when decaying to the ground state. Especially interesting is the possibility of "up-conversion" of red light utilizing ECL at p-Si. Here one uses the features of photosensitized reduction at p-Si,

TABLE I: Photosensitized Potentials for Reductions at a p-Si Electrode Compared to a Pt Electrode for Several Compounds in ACN

Compound[a] reduced	Peak potential Pt, V	Peak potential[b] illuminated p-Si, V
TMPD·+	−0.25	−0.6
BQ	−0.85	−1.3 to −1.4
AQ	−1.30	−1.3
Ru(bpy)₃²⁺	−1.70	−1.4
DPA	−2.30	−1.95
BZN	−2.60[b]	−2.25[c]

[a] Concentration range, 1–10 mM. [b] This potential is not related to thermodynamic properties (e.g., the standard redox potential) as at Pt and is somewhat dependent upon the concentration employed. [c] No peak obtained, foot of the wave.
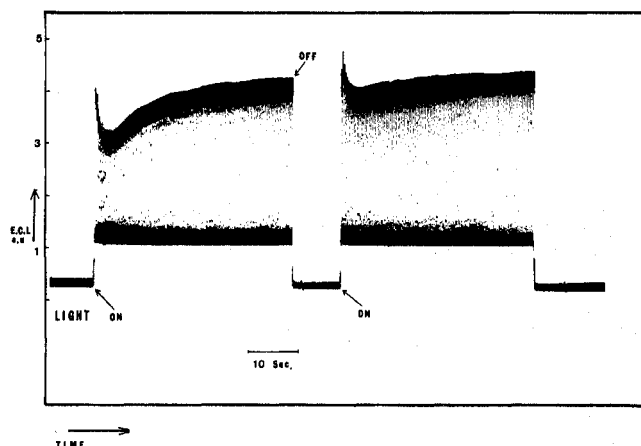

Figure 8. Pulsed ECL at a p-Si electrode with and without electrode illumination. Pulsing mode, −2.3 to −1.3 at 5 Hz; illumination, λ >650 nm, ECL emission at 450 nm. The solution contained 1 mM DPACl₂ and 0.1 M TBAP in ACN.

including the negative overpotential effect to carry out a photoinduced ECL process. DPACl₂ (9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene) is an especially useful compound for this experiment, since it produces blue ECL upon reduction.[41,42] By illuminating the p-Si with red light we initiated DPACl₂ reduction and obtained blue (420–450 nm) emission.[43] The conditions of the experiment were such that neither the electrical input alone (even at a Pt electrode) nor the illumination alone (i.e., a fluorescence experiment) were capable of producing the emission from this system, thus demonstrating the coupling of low photon energy with electrical energy to yield a more energetic photon. Figure 8 demonstrates this principle. Further details have been given elsewhere.[43] The p-Si electrode was subjected to pulses between −1.3 and −2.3 V at a frequency of 5 Hz. Blue ECL emission was observed whenever the p-Si was illuminated with red light, with the emission spacially limited to the area where the red light was impinging and ceasing when the illumination was stopped. Similar behavior has been observed in preliminary experiments with the small band gap sc electrodes p-GaAs and p-InP.

References and Notes

(1) M. D. Krotova and Yu. V. Pleskov, *Solid State Phys.*, **3**, 2119 (1963).
(2) H. B. Mark, Jr., and B. S. Pons, *Anal. Chem.*, **40**, 110 (1966).
(3) T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).
(4) R. Landsberg, P. Janletz, and R. Dehmlow, *Z. Chem.*, **15**, 38 (1975).
(5) S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, in press.
(6) V. A. Myamlin and Yu. V. Pleskov, "Electrochemistry of Semiconductors", Plenum Press, New York, N.Y., 1967.
(7) H. Gerischer in "Advances in Electrochemistry and Electrochemical Engineering", Vol. I, P. Delahay and C. W. Tobias, Ed., Interscience, New York, N.Y., 1961.
(8) H. Gerischer in "Physical Chemistry", Vol. IX A, H. Eyring, D. Henderson, and W. Yost, Ed., Academic Press, New York, N.Y., 1970.
(9) R. Memming and F. Möller, *Ber. Bunsenges. Phys. Chem.*, **76**, 609 (1972).
(10) R. Memming and F. Möller, *Ber. Bunsenges. Phys. Chem.*, **76**, 469 (1972).
(11) R. A. L. Vanden Berghe, V. P. Gomes, and F. Cardon, *Ber. Bunsenges. Phys. Chem.*, **77**, 289 (1973).
(12) B. Pettinger, H.-R. Schöppel, and H. Gerischer, *Ber. Bunsenges. Phys. Chem.*, **78**, 450 (1974).
(13) T. Ambridge, C. R. Elliot, and M. M. Faktor, *J. Appl. Electrochem.*, **3**, 1 (1973).
(14) R. Memming and G. Schwandt, *Electrochim. Acta*, **13**, 1299 (1968).
(15) R. Memming and G. Schwandt, *Surface Sci.*, **5**, 97 (1966).
(16) P. J. Boddy, *J. Electrochem. Soc.*, **115**, 199 (1968).
(17) H. Gerischer, *Photochem. Photobiol.*, **16**, 243 (1972).
(18) J. B. Flynn, *J. Electrochem. Soc.*, **105**, 715 (1958).
(19) Reference 6, pp 181, 182.
(20) A. Many, *J. Phys. Chem. Solids*, **26**, 587 (1965).

(21) R. L. Meek, *Surface Sci.*, **25**, 526 (1971).
(22) D. R. Turner in "The Surface Chemistry of Metals and Semiconductors", H. C. Gatos, Ed., Wiley, New York, N.Y., 1959.
(23) C. P. Keszthelyi and A. J. Bard, *J. Electrochem. Soc.*, **120**, 241 (1973).
(24) W. P. Gomes and F. Cardon, *Z. Physik. Chem. (Frankfurt am Main)*, **86**, 330 (1973).
(25) H. V. Harten, *Electrochim. Acta*, **13**, 1255 (1968).
(26) C. G. B. Garrett and W. H. Brattain, *Phys. Rev.*, **99**, 376 (1955).
(27) K. Lehovek and A. Slobodsky, *Solid State Electron.*, **7**, 59 (1964).
(28) W. W. Gärtner, *Phys. Rev.*, **116**, 84 (1959).
(29) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(30) Reference 6, p 164.
(31) N. E. Tokel-Takvoryan, R. E. Hemingway, and A. J. Bard, *J. Am. Chem. Soc.*, **95**, 6582 (1973).
(32) B. Pettinger, H.-R. Schöppel, T. Yokoyama, and H. Gerischer, *Ber. Bunsenges, Phys. Chem.*, **78**, 1024 (1974).
(33) B. F. Lewis and T. E. Fischer, *Surface Sci.*, **41**, 371 (1974).
(34) J. F. Dewald in "The Surface Chemistry of Metals and Semiconductors", H. C. Gatos, Ed., Wiley, New York, N.Y., 1959.
(35) H. Gerischer, *J. Electrochem. Soc.*, **113**, 1175 (1966).
(36) A. Fujishima and K. Honda, *Nature (London)*, **238**, 37 (1972).
(37) A. Fujishima and K. Honda, *J. Chem. Soc. Jpn.*, **74**, 355 (1971).
(38) M. D. Archer, *J. Appl. Electrochem.*, **5**, 17 (1975).
(39) A. J. Bard and L. R. Faulkner in "Electroanalytical Chemistry", A. J. Bard, Ed., Marcel Dekker, New York, N.Y., 1976.
(40) D. M. Hercules in "Physical Methods of Organic Chemistry", 4th ed, Part II, A. Weissberger and B. Rossitor, Ed., Academic Press, New York, N.Y., 1971.
(41) T. M. Siegal and H. B. Mark, Jr., *J. Am. Chem. Soc.*, **93**, 6281 (1971).
(42) K. Boto and A. J. Bard, *J. Electroanal. Chem.*, in press.
(43) D. Laser and A. J. Bard, *Chem. Phys. Lett.*, **34**, 605 (1975).

Aqueous Solutions of Azoniaspiroalkane Halides. II. Apparent Molal Volumes and Apparent Molal Heat Capacities

Wen-Yang Wen,* Antonio LoSurdo,

Jeppson Laboratory, Chemistry Department, Clark University, Worcester, Massachusetts 01610

Carmel Jolicoeur, and Jeanine Boileau

Department de Chimie, Universite de Sherbrooke, Sherbrooke, Quebec, Canada (Received July 14, 1975)

Densities and heat capacities of aqueous solution of azoniaspiroalkane bromides, $(CH_2)_n N^+ (CH_2)_n Br^-$ where $n = 4$, 5, and 6, have been measured at 25 °C using a flow densimeter and a flow microcalorimeter, respectively. Apparent molal volumes and apparent molal heat capacities obtained for these salts are compared with those of the corresponding tetraalkylammonium bromides. These comparisons show that the apparent molal volumes of the spiro ions are smaller, and the heat capacity of the water surrounding these ions is substantially reduced. Some indications are found for the flexibility of alkyl chains in the tetraalkylammonium ions when volume data for the two types of ions are compared. Forming closed rings from the alkyl chains in tetraalkylammonium ions seems to alter their solution properties greatly and weaken their hydrophobic character considerably.

Introduction

Earlier studies on the comparative solution properties of hydrophobic ions containing either linear or cyclic alkyl groups have shown some important differences among the properties of these two types of solutes.[1-3] The broad current interest toward the tetraalkylammonium ions as typical hydrophic species[4] has prompted us to study the solution behavior of their counterpart azoniaspiroalkane ions. The latter should provide information on the role of geometrical and dynamic configurational effects in the ther-

modynamic properties of alkyl-substituted quaternary ammonium ions.

In the first paper of this series (hereafter cited as paper I)[1] enthalpies of solution of azoniaspiroalkane halides, $(CH_2)_n N^+ (CH_2)_n X^-$, in H_2O and D_2O have been reported. Apparent molal heat contents and enthalpies of transfer from H_2O to D_2O obtained were compared with those of the corresponding tetraalkylammonium halides. The results showed that forming closed rings from the alkyl chains in tetraalkylammonium ions alter their enthalpic