Semiconductor electrodes. 32. n- and p-gallium arsenide n- and p-silicon, and n-titanium dioxide in liquid ammonia

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Semiconductor Electrodes. 32. n- and p-GaAs, n- and p-Si, and n-TiO₂ in Liquid Ammonia

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Abstract: The behavior of several n- and p-type semiconductors in liquid ammonia with 0.1 M KI as supporting electrolyte was investigated. The flat-band potentials were estimated from Schottky-Mott plots, and the current-potential curves with several redox couples (e.g., benzophenone, naphthalene, nitrobenzene) in the dark and under illumination were obtained. Photoinjection of solvated electrons at p-GaAs and p-Si was demonstrated, and the results with these materials were shown to be consistent with those from the Fermi level pinning model. Solvated electron photovoltaic cells with these semiconductors were also constructed.

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<th>Table I. Semiconductor Materials</th>
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⁵ Heated in H₂ for 400 °C for 2 h.

Introduction

The behavior of semiconductor electrodes in nonaqueous solvents such as acetonitrile (MeCN) is often very different than that observed in aqueous solutions.¹⁻⁶ The smaller interaction of the solvent with the electrode material and its oxidation products frequently results in higher stability of the semiconductor under irradiation, which is important in the design of photoelectrochemical (PEC) cells. Moreover, the wide potential range over which the solvent is stable allows the investigation of redox processes not observable in aqueous systems. There have been a number of electrochemical studies at metal electrodes in liquid ammonia.⁷ Because the background limit of NH₃ is very negative and NH₂ has a low acidity, highly reduced species (e.g., radical anions, dianions) and solvated electrons are stable in this medium. In a recent study from this laboratory on the photoelectrochemical properties of p-GaAs in NH₃,⁸ we demonstrated that the photoinjection of solvated electrons at potentials ~0.9 V positive of the reversible potential for solvated electron production at a Pt electrode [−2.74 V vs. Ag/Ag⁺ (0.1 M)⁹] could be accomplished. Such photoinjection suggested either that the conduction band edge of GaAs was situated at very negative potentials compared to the location found in other solvents or that the photopotential originated from specific surface effects.

Recently, however, results from our group with p-GaAs,¹¹ as well as by Wrighton and co-workers for p-Si¹² have led to our proposing that with these materials in aqueous and MeCN solutions, Fermi level pinning occurs. This refers to the condition when the surface state density is sufficiently high that the accumulation of surface charge causes a shift in the location of the band edges; i.e., changes in the potential drop across the Helmholtz layer. More recent experiments have also suggested Fermi level pinning.


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pinning occurs with CdTe \textsuperscript{14} and molybdenum and tungsten dichalcogenides.\textsuperscript{15,16} Thus the photoinjection of electrons can be explained by the pinning of the Fermi level in the p-GaAs at a level near that of $e_T$.

We report here studies of n- and p-type GaAs and Si and n-TiO\textsubscript{2} in liquid NH\textsubscript{3}. Flat-band potentials ($V_b$) estimated from capacitance measurements (Schottky–Mott plots) are reported, and the behavior of several organic redox couples at these materials in the dark and under irradiation is described. The key points in the work described here include (a) demonstration of solvated electron injection from p-Si at considerable underpotentials, (b) construction of a regenerative (photovoltaic) PEC in which p-Si results in terms of the Fermi level pinning model. The results are of significance because solvated electrons represent the most reducing species thus far photogenerated at a semiconductor electrode. Their photoproduction raises a number of interesting synthetic possibilities for using light to promote reductions previously requiring alkali metals. The PEC cells with liquid NH\textsubscript{3} represent the lowest temperature PEC devices reported thus far. Several brief reports on the determination of $V_b$ for n- and p-type GaP,\textsuperscript{17} the behavior of cyclooctatetrenyl dianion at n-TiO\textsubscript{2},\textsuperscript{18} and electron injection processes from several semiconductors into liquid ammonia\textsuperscript{19} have appeared recently.

**Experimental Section**

The single-crystal semiconductors were provided with ohmic contacts (Table I) and mounted in glass tubes as described previously.\textsuperscript{1,2} The electrodes were polished with alumina and etched prior to use (Table I). The ammonia (Matheson Gas 99.9%) was purified by double distillation from sodium metal,\textsuperscript{8} and 0.1 M potassium iodide was used throughout as supporting electrolyte.

The two-compartment electrochemical cell was the same as that used previously,\textsuperscript{9} with a coiled Pt wire counter electrode, a silver wire reference electrode, and Pt disk and the semiconductor working electrodes. All potentials are reported vs. the Ag/AgNO\textsubscript{3} (0.1 M) reference electrode. The cell was cooled in a 2-propanol/CO\textsubscript{2} bath to approximately -50 °C.

Electrochemical measurements were carried out with a PAR 173 potentiostat, a PAR 175 Universal programmer (Princeton Applied Research Corp.), and i–V curves recorded on a Houston 2000 X-Y recorder (Houston Instruments, Austin, TX). The light source was a 275-W G.E. sunlamp, which provide a total (polychromatic) intensity of $\sim$80 mW cm\textsuperscript{-2} at the electrode.

Capacitance measurements were carried out in two ways. In method a a 5-mV sinusoidal signal (Wavetek VCG 114) was superimposed on the dc electrode potential and the output signals from the current and voltage followers of the potentiostat were amplified and resolved into their in-phase and quadrature components (PAR 5204 lock-in amplifier). The capacitance and resistance were computed as series circuit elements. In method b the charging currents of cyclic voltammograms were measured in a region where no faradaic reaction occurs, and the capacitance was calculated from these.\textsuperscript{7}

**Results and Discussion**

**Capacitance Measurements.** The flat-band potential in background electrolyte solution, $V_b$, which represents the potential at which no space-charge region exists within the semiconductor is often estimated by Schottky–Mott (S–M) plots.\textsuperscript{20} These are plotted according to eq 1, where $C_{sc}$ is the capacitance of the electrode at which no space-charge region exists within the semiconductor:

$$\frac{1}{C_{sc}^2} = \left( \frac{2}{\epsilon e_0 N} \right) \left( V - V_b - \frac{kT}{e} \right)$$

(1)

(14) Arushany, A.; Wrighton, M. S., private communication (submitted for publication).


(16) Schneemeyer, L. F.; Wrighton, M. S., private communication (submitted for publication).


conductors in a supporting electrolyte solution of 0.1 M KI, based on the S–M plots, are shown in Figure 2. Because of the frequency dispersion effects discussed above, the values of \( V_{fb} \) are probably only accurate to ±0.2 V.

**Voltammetric Studies.** Cyclic voltammetry (CV) at the semiconductor electrodes was carried out in the dark and under illumination in the absence and in the presence of a number of compounds that undergo reversible one-electron charge-transfer processes at Pt. Typically the couples utilized were benzophenone (BP), naphthalene (NP), and nitrobenzene (PhNO₂), whose behavior at metal electrodes in liquid NH₃ has been previously investigated. The reversible potentials of these are indicated in Figure 2. The most negative potential for the onset of anodic photocurrent for an n-type semiconductor and the most positive potential for the onset of cathodic photocurrent for a p-type semiconductor (\( V_{fb} \)) are often used in the estimation of the position of \( V_{fb} \), where \( V_{fb} \) is the flat-band potential found in the absence of a redox couple. Care must be taken in this identification, however, since surface changes or recombination processes can cause these onset potentials to differ from the true \( V_{fb} \) values. Moreover, \( V_{fb} \) may change upon specific adsorption of an ionic species or, as discussed below, on Fermi level pinning; these effects may yield \( V_{fb} \) values which are functions of the redox couple present in solution. The details of the voltammetric behavior of each semiconductor are discussed below.

**n-GaAs.** The background CV of n-GaAs in the dark at potentials negative of \( V_{fb} \) in 0.1 M KI was identical with that at Pt (Figure 3, inset) and showed a reversible wave beginning at ~2.4 V accompanied by the characteristic blue color for solvated electron (\( e_- \)) generation. On illumination a photoanodic current was observed at potentials positive of ~0.1 V (Figure 3). However, repeated scans in this potential region produced a decrease in current, suggesting that changes in the electrode surface, e.g., photooxidation of the GaAs lattice, were occurring. Similar behavior has been observed previously for n-GaAs electrodes in DMF. Species with \( V_{redox} \) values (as estimated from CV at Pt) negative of the conduction band edge (\( V_c \) = ~1.2 ± 0.2) would be expected to show essentially reversible behavior in the dark at n-type semiconductors, at potentials similar to those on Pt, due to the presence of an accumulation layer in the space-charge region. This behavior was observed for both \( e_- \) generation and for naphthalene (Figure 4). Reoxidation of NP on scan reversal occurred at the same potential as on Pt in the dark. However, under illumination, while the cathodic wave was unaffected, the anodic wave shifted toward slightly more positive potentials; the extent of this shift was a function of switching potential (\( V_s \)) (Figure 4). However, values of \( V_s \) negative of ~2.0 V produced anodic waves with \( V_{pe} \) values at more negative potentials than the cathodic wave.

**Benzophenone (BP) forms the radical anion, \( BP^- \), on reduction.** Since the redox potential of this couple is located near \( V_{fb} \) of n-GaAs, no photoeffect is expected for the oxidation reaction. BP produced an irreversible wave for reduction commencing just negative of \( V_{fb} \) in the dark and resulting in a broad peak with \( V_{pe} \) at ~1.9 V (Figure 5). However, illumination with chopped light gave a photooxidation peak with \( V_{pe} \) at ~1.6 V for reoxidation of the \( BP^- \) found on the negative scan. Thus as with NP, photoeffects were observed on n-GaAs at potentials well negative of the \( V_{fb} \) found in supporting electrolyte solution alone.

**p-GaAs.** The behavior of p-GaAs electrodes in the dark is shown in Figure 6. The onset of anodic current occurs at ~0.1 V (~\( V_{fb} \) from S–M plots) and, as with the anodic photocurrent at n-GaAs, decreased with repeated scanning, again suggesting surface changes upon oxidation of the semiconductor. Under illumination photogeneration of \( e_- \) was observed as reported previously.

The CV of NP on p-GaAs in the dark and on illumination is shown in Figure 7. In the dark only a small cathodic current was observed at potentials negative of \( V_{redox} \) (NP). On illumination, however, photoreduction of NP commenced at ~1.3 V with \( V_{pe} \) = ~1.6 V. Repeated scanning to a more positive switching potential, \( V_s \) (but still negative of ~0.9 V) caused a shift in the potential for current onset and \( V_{pe} \) toward more positive potentials to a limiting value for current onset, \( V_{on} \), of ~1.0 V. This represents an underpotential for the photoreduction of about 0.8 V which is similar to that observed for \( e_- \) photogeneration. When
the potential was scanned to values positive of $\sim 0.5$ V, the original CV (1 on Figure 7) was obtained on the return scan.

Benzophenone also showed photoeffects at p-GaAs electrodes. In the dark (Figure 8), only a slight increase in cathodic current was observed at $\sim -2.0$ V. For $E_r$ values negative of this potential, the reverse scan produced crossing of the $i-V$ curves (i.e., hysteresis), followed by a very small anodic peak whose location and magnitude depended on $E_r$. Coulometric generation of increasing amounts of BP$^-$ at a Pt electrode followed by positive-going potential scans from $-1.5$ V gave CV behavior at p-GaAs which was similar to that observed in the absence of excess BP$,^-$ suggesting that the small anodic peak is due to BP$^-$ oxidation produced in small amounts on the negative scans.

On pulsed illumination (Figure 8) photoreduction of benzophenone commenced at about $-0.4$ V with $E_{redo}$ being somewhat dependent on light intensity and with a $V_{redo}$ for the first wave of $-0.9$ V. During the dark periods at these potentials, an anodic current was observed due to the reoxidation of photogenerated BP$^-$.

Commencing at $-1.1$ V (the onset of BP reduction on Pt), a cathodic current was observed during the dark periods following the illumination pulses. The photoreduction of BP$^-$ occurred at $\sim -1.4$ V; some dark cathodic current following the light pulses was seen beginning at $-1.6$ V, a potential corresponding to the second BP reduction wave (BP$^-$ + $e^- \rightarrow$ BP$^{2-}$) on Pt. Photogeneration of $e^-_c$ commenced at $\sim -1.7$ V. The current observed during the dark periods was diffusion controlled and was fairly reproducible on cycling in the dark after illumination, provided that the potential remained negative of $\sim -0.8$ V. Cycling to 0 V gave the original dark CV.

The behavior of both n- and p-GaAs is generally consistent with the Fermi level pinning model$^{13}$ and with results previously found for this material in aqueous$^{11}$ and MeCN$^2$ solutions. Thus at p-GaAs photoreductions are observed for couples ($e^-_c$, NP$^{0^-}$, BP$^{2^-}$) lying at potentials appreciably more negative than the conduction band edge estimated from a S–M plot in background solution. The observed value of $V_{redo} = V_{redo}$ in all of these was...
Figure 8. Cyclic voltammogram of benzophenone on a Pt disk electrode (scan rate = 200 mV/s) and on p-GaAs in the dark and under pulsed illumination (scan rate = 50 mV/s).

Scheme I

Figure 9. Background cyclic voltammograms of a Pt disk electrode and p-Si in the dark and on illumination (scan rate = 200 mV/s).

layer forming a Schottky junction with the underlying semiconductor was proposed. To probe this possibility, X-ray spectra were taken of the surface of GaAs electrodes before use and after photogeneration of solvated electrons. Peaks at 41 and 44 eV were observed in the spectrum of both electrodes, consistent with As in GaAs and arsenic oxide (possibly As$_2$O$_3$), respectively.$^{21}$ The ratio of peak heights, however, changed significantly between electrodes, suggesting a thinner surface oxide film on the electrode at the potential of solvated electron photogeneration. The removal of oxide films from anodized GaAs, by etching with HCl or aqueous NH$_3$ solutions, has previously been shown to yield a surface rich in elemental As,$^{21}$ a semimetal or semiconductor of band gap 1.1 eV.$^{12}$ The Ga peaks in the XPS spectra of the two GaAs samples were also examined, but there was very little difference between the two electrodes. Clearly the chemical or molecular nature of the surface states and the effect of surface pretreatment of the semiconductor on its photoelectrochemical behavior are of importance.$^{23}$ Further studies on this system to elucidate these effects are contemplated.

n- and p-Si. The dark negative background CV for n-Si was identical with that on Pt. On illumination a photoanodic current was observed at $\sim$-0.4 V (Figure 3) just positive of $V_b^0$ from S-M plots as expected. The current decrease found on consecutive scans probably indicates a change in the nature of the electrode surface. The dark anodic background behavior of p-Si is shown in Figure 6. An anodic reaction commenced at +0.6 V in agreement with the value of $V_b^0$ from S-M plots. The negative background behavior is shown in Figure 9. In the dark, no current was observed even at potentials as negative as -4.0 V. On illumination, however, the photogeneration of $e_0^-$ occurred at $\sim$-1.8 V (the small prewave shown in Figure 9 was caused by impurities and was not always seen for p-Si/NH$_3$ systems). The photocurrent was directly proportional to light intensity with the decrease in current at potentials negative of -2.6 V being due to absorption of the light by $e_0^-$ generated near the electrode surface; similar effects were

Semiconductor Electrodes

Figure 10. Current, voltage, and power curves for the photoelectrochemical cell p-Si/e{sub}(-) (0.3 mM), 0.1 M KI, in NH{sub}3/Pt under illumination of ~80 mW cm{sup}-2.

seen with e{sup}- generation at p-GaAs.

A PEC photovoltaic cell was formed, as for p-GaAs, consisting of a p-Si photocathode and Pt anode in a solution containing e{sup}- (0.3 mM) generated coulometrically. An open-circuit potential, V{sub}oc, for this cell of +570 mV, was measured on a Keithley 600A electrometer (input resistance 10{sup}14 {ohm}) when the cell was illuminated with the sunlamp. The current, voltage, and power curves for different values of load resistance are shown in Figure 10. V{sub}oc was independent of the e{sup}- concentration and remained constant over a period of approximately 2 h. No attempts were made to optimize the performance of this PEC cell or study its long-term behavior. However, the ability to generate a photocurrent ~0.6 mA in a cell disconnected from any power sources clearly demonstrates the photoinjection of e{sup}- from p-Si into NH{sub}3 (with the collection of e{sup}+ at the Pt counter electrode). This cell, like the p-GaAs cell previously described, represents a rather unique electrochemical system where light "pumps" electrons through the solution as well as through the external circuit. Note that Krohn and Thompson have also reported the injection of e{sup}- from p-Si into NH{sub}3.

Benzophenone was also photoreduced on p-Si commencing at ~+1.0 V with a plateau at ~1.8 V just prior to e{sup}- generation. As with e{sup}- generation, no reoxidation of photogenerated BP{sup+} was observed.

The generation of e{sup}- at p-Si occurs at potentials well negative of the background solution conduction band edge of p-Si. Again a surface state Fermi level pinning model can account for this behavior. Wrighton and co-workers previously have shown pinning at p-Si electrodes and the equilibration of surface state levels, even with the very negative level associated with e{sup}- in ammonia, can account reasonably for the observed photoinjection of electrons.

n-TiO{sub}2. The dark background behavior of TiO{sub}2 on scanning to negative potentials again was identical with that on Pt. On illumination a photoanodic current was observed (Figure 3) commencing at ~0.8 V, which is about the value of V{sub}ph obtained from the low-frequency Schottky-Mott plots (Figure 1 C). The photocurrent was reproducible and light intensity dependent, suggesting that it was due to photooxidation of the supporting electrolyte (I{sup-}) or solvent. Species with V{sub}redox values negative of V{sub}ph (e.g., benzophenone) were reversibly reduced in the dark on TiO{sub}2 at potentials essentially the same as those on Pt, as expected for an n-type semiconductor in the absence of surface effects. Similarly e{sup}+ generation occurred essentially as on Pt. For species located in the band gap, e.g., nitrobenzene (PhNO{sub}2), irreversible dark reduction occurred at ~0.7 V; however, no photooxidation of the generated nitrobenzene radical anion (PhNO{sub}2{sup-}) was observed on illumination. Moreover, in the presence of PhNO{sub}2, the photooxidation of the background electrolyte disappeared.

The CV behavior, with the exception of the absence of the photooxidation in the presence of PhNO{sub}2, is essentially similar to the behavior of TiO{sub}2 in MeCN. The oxidation of the supporting electrolyte in liquid NH{sub}3 corresponds to energy levels in the band gap of TiO{sub}2 (+0.6 V). Therefore the background photooxidation of the electrolyte by holes generated in the valence band is far more favorable in NH{sub}3 than in MeCN, and the oxidation of species whose redox levels fall within the band-gap region will depend upon the relative rates of reaction of such species and background electrolyte or solvent with the photogenerated holes.

In general, the behavior of n-TiO{sub}2 in NH{sub}3 appears to follow the more "ideal" interface model, where V{sub}ph remains essentially fixed. This is also borne out by the carbanion photooxidation experiments of Fox and Kabir-ud-Din, whose estimate of V{sub}ph was very close to the one reported here. The behavior in the presence of PhNO{sub}2 under illumination is unusual, however. We have not previously observed such a quenching of the photocurrent by a solution species. We might note that Krohn and Thompson have reported no photocurrent at n-TiO{sub}2 in NH{sub}3 with NaCl, NH{sub}4Cl, or KNH{sub}2 as supporting electrolytes.

Finally, previous studies of n-TiO{sub}2 in MeCN or aqueous solutions provided evidence for surface states or an intermediate level located 1-1.2 eV below the conduction band edge. Since this corresponds to ~0.6 V vs. Ag/AgNO{sub}3 where background oxidation occurs, probing the region of more positive potentials to provide information about such levels will be difficult in NH{sub}3.

Conclusions

The behavior of semiconductors in liquid ammonia generally parallels that found with aprotic solvents and water. The results can be interpreted in terms of the ideal model for n-TiO{sub}2 and with the Fermi level pinning model for GaAs and Si. PEC photovoltaic cells can be constructed in this solvent system, and preliminary experiments suggest stable operation of GaAs and Si (although further experiments are necessary to establish the ultimate long-term stability and performance). Perhaps the most intriguing aspect of these experiments is the ability to photogenerate solvated electrons at p-Si and p-GaAs at potentials considerably less negative than the reversible potential for this species. This represents the photoproduction of the most negative (or reducing) species so far reported at a semiconductor and raises the possibility of utilizing such photoemitted electrons for synthetic purposes, e.g., a "Photo-Birch reduction".

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