Behavior of n-Type and p-Type Silicon in Anhydrous Liquid Ammonia. Solvated Electron Generation: A Suprband-Edge Reaction

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The behavior of n-type and p-type silicon electrodes (single crystal (100)) is studied in anhydrous basic liquid ammonia with variable solvated electron concentration. In dilute medium, Fermi level pinning on the surface states occurs and the photoelectrochemical cell p-Si/NH3 + KBr (0.1 mol dm−3) + NH4+ (2 × 10−2 mol dm−3) + e−/counterelectrode delivers a large Veq (more than 0.5 V). In concentrated medium ([e−]) > 2 × 10−3 mol dm−3) the strong interaction of e− species toward the SC surface creates a thin conductive layer on the surface which gives a new interface state distribution. Then no photoeffects occur at n-Si or p-Si electrodes.

Numerous papers concern the behavior of n-type or p-type silicon in aqueous or nonaqueous electrolytes. The nonaqueous solvents were used to avoid water or oxygen traces which allow the growth of SiO2 or SiO4− thin layer on the silicon. This layer seems to play an important part in the redox charge transfer process at the interface, in this way, different results obtained with n-type and p-type silicon were explained by either partial or complete Fermi level pinning, an inversion mechanism, or interface states arising from the oxide layer.

Using oxide-free silicon electrodes in anhydrous medium, we were able to show the influence of pH on the flat-band potential of the semiconductor. This pH influence was recently observed...
in water with a suitable etching agent which continuously eliminated SiO₂ and SiO₃⁻.  

In this paper we report electrochemical and photoelectrochemical studies of oxide-free n-type and p-type silicon in an absolutely anhydrous solvent: we chose liquid ammonia which can be easily dehydrated and used etchings of Si under a controlled atmosphere to avoid the oxide formation. We analyze the influence of solvated electrons in solution on the photoelectrochemical behavior of Si/electrolyte junctions. 

Few experiments in this solvent concern the generation of solvated electrons and the behavior of semiconductor electrodes in the presence of solvated electrons. Using p-type Si as a photocathode the following photoelectrochemical cell (PEC) has been formed consisting of p-Si/NH₃ + KI (0.1 mol dm⁻³) + e⁻ (3 × 10⁻⁴ mol dm⁻³)/Pt. This PEC worked for more than 2 h. At the same time we formed an equivalent PEC (where KBr took the place of KI) and we tried to optimize the performance of this cell by increasing the e⁻ concentration. But if [e⁻] > 2 × 10⁻³ mol dm⁻³ then the photocurrent was not observed: neither photocurrent nor photocurrent could be obtained. 

The understanding of this unexpected behavior led us to the study of the n-type and p-type Si/solvated electron in ammonia junctions from a fundamental point of view, and we attempt here to explain the different key points concerning this particular behavior.

**Experimental Section**

The n-type and p-type Si single crystals (100 orientation) were purchased from LAAS (CNRS, Toulouse, France). They were provided with ohmic contacts and mounted as described previously. The samples of low resistivity (ρ = 1.5 Ω cm corresponding to a doping concentration N_A (p-type) = 10¹⁶ cm⁻³ and N_D (n-type) = 2 × 10¹⁵ cm⁻³) were received polished to a high mirror finish. 

The usual pretreatment for each electrode involved etching for 20 s in concentrated HF (40%) rather than in HF–HNO₃ mixtures because no difference in the electrode behavior has been observed after this etching, drying with blotting paper and, setting in the cell under an argon or a nitrogen stream, after the solution has been prepared. 

The ammonia was purified by double distillation from potassium amide. KBr (0.1 mol dm⁻³) was used as a supporting electrolyte after drying under vacuum at 350 K. Before any distillation, the cells were pumped for 24 h. 

In liquid ammonia, the existence of "stable" solvated electrons implies that the solvent is basic since the e⁻ species react with solvated protons NH₄⁺ giving NH₃ dissociation. Consequently, we have used basic ammonia solutions ([NH₃] = 2 × 10⁻² mol dm⁻³). The solvated electron solutions were stable for a few hours; the e⁻ disappeared slowly by reaction with the solvent: 

$$e^- + NH_3 \rightarrow NH_2^- + 1/2H_2$$

Potassium amide solutions were prepared "in situ" by addition of weighed amounts of potassium in the cell in the presence of a platinumized platinum wire. 

Solvated electron solutions were obtained similarly in the absence of any catalyst. We shall talk independently about the e⁻/H₂ redox couple or the K⁺/K redox couple. We shall consider the total solvated electron concentration including ion pair formation and dimerization. 

For experiments concerning the rest potential measurements, solvated electrons were generated by coulometry directly in solution. In this case two platinum foils were added in the cell, one in the solution as a working electrode, and the other in a separated compartment containing dissolved potassium as a counter electrode. The two-compartment cell has been described previously.

The reference electrode was either an Ag wire reference electrode or a Pt wire reference electrode. Potentials are generally reported vs. the Ag/Ag⁺ (5 × 10⁻³ mol dm⁻³) reference electrode (denoted silver reference electrode (SRE), V_SRE = +0.27 V vs. NHE in water) but in the presence of solvated electrons, a smooth Pt wire reference electrode in contact with K solution (0.1 mol dm⁻³) (denoted potassium reference electrode (PRE), V_PRE = –2.6 V vs. SRE) was used. Its potential remains constant for a few hours. For simplicity, all the potentials will be referred to SRE.

The interface was investigated by using classical electrochemical techniques: current–voltage characteristics (cyclic voltammetry), capacitance–voltage characteristics (impedance measurements), and photocurrent–voltage characteristics under white light illumination. Current–voltage characteristics were obtained with a PRT 20X type Tacussel potentiosat without positive feedback resistance compensation. 

The impedance of the semiconductor–electrolyte junction was obtained in the dark by measurement of the cell response to a low sinusoidal perturbing signal for a large range of frequencies (100 Hz < F < 150 kHz). See Appendix.

**Results**

(a) **Vollammograms in the Dark.** The current–voltage characteristics for carefully etched n-Si and p-Si are presented in Figure 1. The n-Si electrode, a cathodic current is observed if V < –2.3 V vs. SRE. It corresponds to the generation of solvated electrons as observed at a Pt electrode, because a uniform blue coloration is perceptible near the SC surface. 

On the reverse scan, after a few seconds at V = –2.5 V vs. SRE, a reoxidation peak appears, due to the reoxidation of the e⁻ species. 

Below V = –1.2 V vs. SRE, a limited cathodic current exists at the first scan. It seems to correspond to a reduction of etching products because this current was not observed in basic ammonia at a Pt electrode.

(ii) At the p-Si electrode, a cathodic current is observed if V < –2.3 V vs. SRE, as at n-Si or Pt electrodes, but this current remains smaller. It corresponds to the generation of solvated electrons. 

This behavior was investigated with p-Si materials of different doping concentrations (N_D = 10¹⁶, 10¹⁷, 10¹⁸ cm⁻³) and always the current flowed for applied cathodic voltages (V < –2.3 V vs. SRE) provided that the samples were carefully etched. With nonetched materials only small cathodic currents (I < 20 μA cm⁻²) were observed at very cathodic voltages: –4.5 V vs. SRE. This last behavior was already obtained with p-Si in ammonia.

On the reverse scan the reoxidation of e⁻ species is observed but the peak is wider than at the n-Si electrode.

(b) **Vollammograms under White Light Illumination.** (i) At the n-Si electrode, no photocurrent exists in the potential range corresponding to the solvated electron generation. 

(ii) At the p-Si electrode, a photocurrent starts at V_on = –1.95 V vs. SRE (see Figure 2). It corresponds to the photo-generation of solvated electrons. Under chopped white light illumination, the reoxidation current of the e⁻ species is observed during the dark intervals.

(c) **Mott–Schottky Plots.** The flat-band potential was estimated from Mott–Schottky plots deduced from impedance measurements in the dark. The C⁻¹–V curves are linear over a large potential

range if a depletion layer is formed at the SC/electrolyte interface.

Results at the n-Si electrode are presented in Figure 3 and at the p-Si electrode in Figure 4. With p-Si electrodes Mott-Schottky curves were not very reproducible. Nevertheless we achieved quite satisfying results with electrodes which were used just after the etching procedure and without any previous cathodic bias. At each frequency the \( C^{-2} V \) curves are linear but the slopes increase as the measurement frequencies increase even at high frequencies \( (F > 50 \text{ kHz}) \); however, the frequency dispersion is reduced if \( F > 80 \text{ kHz} \). This frequency dispersion is not observed in neutral or acidic liquid ammonia in which the residual water concentration is larger than \( 5 \times 10^{-4} \text{ mol dm}^{-3} \). The slope at very high frequency \( (F > 100 \text{ kHz}) \) gives a correct value of the number of majority carriers. Nevertheless all the curves converge to a common point on the \( V \) axis. This common point is assumed to be the flat-band potential \( V_{FB} \). The results are reported in Table I.

When the relations

\[
V_{CB}(n) = V_{FB}(n) + \frac{kT}{e} \ln \frac{N_D}{N_C} \tag{2}
\]

and

\[
V_{VB}(p) = V_{FB}(p) - \frac{kT}{e} \ln \frac{N_A}{N_V} \]

are used, it is possible to calculate the band-edge position at the surface: \( V_{CB}(n) \), \( V_{VB}(n) \), \( V_{CB}(p) \), and \( V_{VB}(p) \). Silicon in basic liquid ammonia obeys the relations \( V_{CB}(n) = V_{FB}(n) \) and \( V_{VB}(p) = V_{VB}(p) \).

(2) Behavior of Si in the Presence of Solvated Electrons. (a) Voltammograms in the Dark. The current–voltage characteristics are very similar (see Figure 5) for n-Si and p-Si. The rest potential of both types of Si corresponds to the redox potential of the \( e^- \) solution (when \( [e^-] > 2 \times 10^{-9} \text{ mol dm}^{-3} \)).

If the solution is stirred, then an anodic current appears above \( V = -2.3 \text{ V vs. SRE} \), the \( I-V \) curve being parallel to the \( V \) axis. Its plateau height is proportional to the \( e^- \) concentration. Thus the \( I-V \) curves are similar to those obtained at a Pt electrode. The n-Si/ and p-Si/electrolyte junctions present a quasimetallic behavior.

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**Table I: Flat-Band Potentials \( V_{FB} \) (V vs. SRE) in Basic Liquid Ammonia at \( T = 230 \text{ K} \)**

<table>
<thead>
<tr>
<th>Material</th>
<th>( \text{NH}_2^- )</th>
<th>( \text{NH}_2^- + e^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Si</td>
<td>-1.5 ( \pm 0.1 )</td>
<td>-2.6 ( \pm 0.2 )</td>
</tr>
<tr>
<td>p-Si</td>
<td>-0.9 ( \pm 0.1 )</td>
<td>-2.6 ( \pm 0.2 )</td>
</tr>
</tbody>
</table>

\( \text{[NH}_2^- \text{]} = 2 \times 10^{-2} \text{ mol dm}^{-3} \), \( \text{[NH}_2^- \text{]} = 2 \times 10^{-2} \text{ mol dm}^{-3} \); \( [e^-] = 3 \times 10^{-3} \text{ mol dm}^{-3} \). SRE corresponds to the Ag/Ag\(^+\) (5 \( \times 10^{-2} \text{ mol dm}^{-3} \)) reference electrode. The \( V_{FB} \) values obtained with p-Si electrodes are quite different from those published in ref 16. It is important to note that the experimental conditions were very different: in this reference we used a neutral medium with pH 16; the sample orientation was quite different (111); finally, the presence of a thin oxide layer on the surface due to bad etching shifted the apparent flat-band potentials toward positive potentials.

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Figure 3. Mott–Schottky plots at n-Si in basic liquid ammonia with carefully etched material (T = 233 K): A = 0.10 cm².

Figure 4. Mott–Schottky plots at p-Si in basic liquid ammonia with carefully etched material (T = 233 K): A = 0.05 cm².

(b) Voltammograms under White Light Illumination. Because of the great absorption of incident light by the e⁻ solution, the geometry of the cell had to be modified to minimize the width of the solution to be crossed by light. We could verify that the electrode surface was correctly illuminated.

If [e⁻] > 2 × 10⁻⁴ mol dm⁻³, then no photocurrent occurs at the n-Si/ and p-Si/electrolyte junctions. Illumination has no effect and I–V curves are the same as in the dark.

(c) Photoelectrochemical Cell under White Light Illumination. We determined the characteristics of the following PEC: Si/NH₃ + KBr (0.1 mol dm⁻³) + NH₂⁻ (2 × 10⁻² mol dm⁻³) + e⁻/Me, where Me is Au or Pt, when varying the e⁻ concentration.

(i) At the n-Si photoanode an open-circuit photovoltage \( V_{OC} \) = 0.1 V can be obtained if the e⁻ concentration is in the range 2 × 10⁻⁴ to 5 × 10⁻⁴ mol dm⁻³. No \( V_{OC} \) is observed if [e⁻] > 2 × 10⁻³ mol dm⁻³.

(ii) At the p-Si photocathode a \( V_{OC} \) = 0.6 V can be obtained in the range 2 × 10⁻⁴ mol dm⁻³ < [e⁻] < 10⁻³ mol dm⁻³. This value is close to that already published. The photocurrent–photovoltage curve is shown in Figure 6; with an 1-kΩ value of load resistance, the PEC gives its optimal efficiency corresponding to a fill factor FF = 0.4.

If [e⁻] > 2 × 10⁻³ mol dm⁻³, then no \( V_{OC} \) is observed. So the e⁻ concentration has a great influence on the PEC efficiency.

In order to understand this behavior we decided to measure the rest potentials of the various electrodes in relation to the e⁻ concentration.

(d) Rest Potential Measurements. For these experiments the solvated electrons were generated by coulometry directly in the cell (see Experimental Section).

We measured the rest potentials of Pt and p-Si electrodes in the dark and under white light illumination, while increasing the...
Figure 5. Cyclic voltammograms in the dark in the presence of solvated electrons \((3 \times 10^{-3} \text{ mol dm}^{-3}; [\text{NH}_3^-] = 2 \times 10^{-2} \text{ mol dm}^{-3}; T = 233 \text{ K}; \text{scan rate} = 0.1 \text{ V s}^{-1})\): (1) n-Si, \(A = 0.16 \text{ cm}^2\); (2) p-Si, \(A = 0.08 \text{ cm}^2\).

Figure 6. Current-voltage curve of the photoelectrochemical cell p-Si/NH_3\(^+\)/KBr (0.1 mol dm\(^{-3}\) + NH_3\(^-\) \((2 \times 10^{-2} \text{ mol dm}^{-3}) + e^- \((5 \times 10^{-4} \text{ mol dm}^{-3})/\text{Pt at 233 K}.\) Si area = 0.08 cm\(^2\). Illumination under white light (order of magnitude 0.1 W cm\(^{-2}\)). Illumination time < 5 min. If \([e^-]\) < \(10^{-3} \text{ mol dm}^{-3}\), then the rest potentials of Pt and p-Si do not correspond to the Nernstian potential of solvated electrons. Moreover, the p-Si rest potential remains more positive than the Pt rest potential. If the \(e^-\) concentration increases, then this difference vanishes and becomes close to zero (if \([e^-]\) > \(2 \times 10^{-3} \text{ mol dm}^{-3}\)).

If \([e^-]\) < \(10^{-3} \text{ mol dm}^{-3}\), then the illumination shifts the p-Si rest potential more than 0.5 V. The photoeffects become negligible when \([e^-]\) > \(2 \times 10^{-3} \text{ mol dm}^{-3}\) and disappear when \([e^-]\) increases more.

\(e^-\) concentration in solution (see Figure 7).

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(e) Mott–Schottky Plots. (i) At the n-Si electrode the Mott–Schottky plots were about the same as in basic medium but were shifted toward negative potentials. A frequency dispersion

Figure 7. Rest potential measurements in relation to the total solvated electron concentration \((T = 233 \text{ K})\): (1) Pt, \(A = 1.5 \text{ cm}^2\); (2) p-Si in the dark, \(A = 0.08 \text{ cm}^2\); (3) p-Si under white light illumination.

is observed but the different \(C^2-V\) lines converge to the \(V_{FB}\) value on the \(V\) axis: \(V_{FB} = -2.6 \text{ V vs. SRE}\) (see Table I).

After solvated electron disappearance, the calculated \(V_{FB}\) is shifted toward a positive value and becomes again equal to that obtained in the corresponding basic medium. If \(e^-\) are introduced again then \(V_{FB}\) is shifted again toward negative potentials. Thus, the shift of \(V_{FB}\) in the solvated electron presence is a reversible phenomenon.

(ii) At the p-Si electrode, if \([e^-]\) > \(2 \times 10^{-3} \text{ mol dm}^{-3}\), impedance measurements were difficult to perform because the depletion layer seems to exist at very negative potentials \((V < -2.6 \text{ V vs. SRE})\). In this potential range a large cathodic current flowed and the impedance measurements were not so accurate. Nevertheless it is possible to show that the flat-band potential is shifted toward negative potentials: \(V_{FB} \approx -2.6 \text{ V vs. SRE}\). These results show a similar behavior for p-Si/ and n-Si/e\(^-\) junctions. Both semiconductors have a flat-band potential lying near the \(e^-\) redox potential.

Discussion

(1) Absence of Solvated Electrons. At n-Si and p-Si electrodes the cathodic reaction in the dark corresponds to solvated electron generation because of the characteristic blue color around the
n-Type and p-Type Si in Anhydrous Liquid Ammonia

electrode. A similar behavior was observed with Ge and GaAs semiconductors\textsuperscript{29,30} in neutral liquid ammonia.

The standard redox potential, \( E^{\circ}_{\text{redox}} = -2.6 \) V vs. SRE in supporting KBr electrolyte, corresponds to the following reaction:

\[
\text{NH}_3 + e^{-} \rightleftharpoons e^{-} (\text{NH}_3)
\]

or

\[
K^+ + e^{-} \rightleftharpoons K
\]

After an injection of \( e^{-} \) in solution, the reoxidation of the excess species near the electrode surface may be obtained at the n-Si and p-Si electrodes.

At n-Si, the voltammetry "waves" are very similar to those obtained at a Pt electrode. They are independent of illumination.

At p-Si, the reduction current remains smaller and the reoxidation peak smaller corresponding to slow redox reactions.

Whatever the model used to explain the different current flows observed at semiconductor electrodes, i.e., to specify the charge transfer process, it is necessary to know the energy band location in relation to the redox energy level position. The location of the band-edge energy is given from the flat-band potential position \( V_{FB} \).

The \( V_{FB} \) values reported in Table I correspond to the extrapolation to the \( V \) axis of the experimental Mott–Schottky plots at n-Si and p-Si electrodes.

At n-Si and p-Si in basic liquid ammonia (pH \( \approx 30 \)), the band edges have been found in the position \( V_{CB} = -1.95 \) V (±0.1 V) and \( V_{VB} = -0.85 \) V (±0.1 V) vs. SRE. This position depends on the pH of the medium,\textsuperscript{15} showing the existence of an acid–base equilibrium on the SC surface.

It is possible to obtain the density \( N_{SS} \) and the distribution of the SS within the band gap from the impedance measurements at various frequencies (see Appendix). These states are distributed in energy within the band gap with an average density of \( N_{SS} \approx 2 \times 10^{11} \) eV\(^{-1}\) cm\(^{-2}\).

Thus Gerischer's model,\textsuperscript{38} based on an ideal SC/electrolyte interface (no significant SS density), is unusable. A model accounting for the presence of SS, as partial or complete Fermi level pinning,\textsuperscript{7-10} has to be considered. However, whatever the model used, a quasi-metallic behavior of n-Si toward solvated electron species is expected. As a matter of fact, the contact of a n-SC with a redox couple having a Fermi level in the conduction band makes the interface behave like a metal,\textsuperscript{15} because of an extremely high density of charges accumulated on the surface. Under such a condition the cyclic voltammograms are expected to be very similar to those observed at a Pt electrode and no photocurrent is observed.

(b) p-Si Behavior. According to the relative position of the band edges and the reduction current onset potential, all reduction processes are assumed to occur via the conduction band.

The presence of SS is demonstrated from impedance measurements in the same manner as at the n-Si electrode. These states are very fast SS, distributed in energy within the band gap with an average density of \( N_{SS} \approx 10^{11} \) eV\(^{-1}\) cm\(^{-2}\). In this case the SC Fermi level can be pinned to these SS, as often invoked by Bard,\textsuperscript{29,39} Wrighton,\textsuperscript{4} and other authors to explain the behavior of p-Si in liquid ammonia and acetonitrile.

The dark cathodic current may be explained if the SS are present. Although the band bending is sufficient to induce an inversion layer at the p-Si surface, it seems too small to generate a breakdown phenomenon as an avalanche multiplication or a tunnel effect through the space charge layer. However, charge transfer can occur via the SS: in this case the limiting rate step is the transfer between the SC and the SS, which is lower than the charge transfer between the SS and the energy level in the electrolyte.

Under white light illumination the injection of \( e^{-} \) in liquid ammonia is easier than in the dark. The injection current onset potential is 0.4 V more positive; this value can be related to the band bending in the dark due to the pinning of the Fermi level to the SS.

(2) Presence of Solvated Electrons. All the experimental results lead us to consider two cases according to the \( e^{-} \) concentration: if \( [e^{-}] < 10^{-6} \) mol dm\(^{-3}\) and if \( [e^{-}] > 2 \times 10^{-3} \) mol dm\(^{-3}\).

(a) \( [e^{-}] < 10^{-6} \) mol dm\(^{-3}\). In order to understand the influence of \( [e^{-}] \), we found it interesting to analyze the rest potential measurements (see Figure 7).

The curves obtained at the Pt electrode show that the solution does not follow the Nernst law when the solvated electrons are too dilute; the solution redox potential is not the one of K/K\(^+\) system but a mixed potential. This is not really surprising because a small ground reduction current is always obtained on a smooth Pt electrode in ammonia-amide solution and it has to be compensated by the solvated electron reoxidation current before this species gives its Nernstian potential to the solution.

Moreover the solvated electron does not give its mixed potential to the p-Si electrode. This behavior is not well understood but it is important to note that, if SS are present, the SC rest potential may be quite different from the redox potential of the solution.

The difference between the rest potential under illumination and in the dark at the p-Si electrode, which is close to the open-circuit photovoltage of the PEC (see Results,2c), remains greater than 0.5 V in a \( e^{-} \) concentration range, i.e., in a solution redox potential range. The maximum (0.6 V) is reached when \( [e^{-}] \) is about 5 \( \times \) \( 10^{-4} \) mol dm\(^{-3}\). This effect shows that Fermi level pinning occurs, with no modification in the distribution of SS.

At the n-Si electrode the same phenomenon occurs but the rest potential differences obtained under illumination remain small (about 0.1 V) and become smaller if \( [e^{-}] > 5 \times 10^{-4} \) mol dm\(^{-3}\).

(b) \( [e^{-}] > 2 \times 10^{-3} \) mol dm\(^{-3}\). It is worth noting that only the low \( [e^{-}] \) concentration in the vicinity of the SC surface is significant, so that the Si behavior is expected to be the same in concentrated \( e^{-} \) medium and in basic medium when an excess of \( e^{-} \) exists near the surface after an electrochemical generation of this species at very cathodic potentials.

In this concentration range, the rest potential measurements show that the Nernst law is followed at Pt, n-Si, and p-Si electrodes.

No photoeffects occur at p-Si and n-Si electrodes, indicating that there is no Fermi level pinning to SS. The p-Si and n-Si have a quasi-metallic behavior. Thus a new phenomenon is present at the Si/solvated electron interface.

This behavior was not observed by Bard and Wrighton\textsuperscript{2,3,37,38} on Si, InP, or GaAs electrodes which seem to obey the Fermi level pinning concept. Indeed when Fermi level pinning occurs, it is independent of the redox species concentration. But in these works \textsuperscript{38} G. Nagasubramanian, B. L. Wheeler, F. R. F. Fan, and A. J. Bard, "Processes of the Symposium on PEC Processes for Photoelectrochemical Solar Cells", The Electrochemical Society, Pennington, NJ, Extended Abstracts, Vol. 82–3, 1983, p 372.

the authors do not take into account the possibility of a strong interaction between the redox species and the SS at the SC surface. Now the solvated electrons are active species which slowly destroy the oxide layer of unetched silicon\(^{13}\) and interact strongly with the surface atoms.

The effect of alkaline metal atoms covering a clean-cleaved silicon surface is well-known: it induces a positive energy shift of the silicon band edges. So, the negative shifts of \(V_{FB}\) observed at n-Si and p-Si in the presence of sufficiently concentrated \(e^-\) (see Table I) led us to consider the presence of potassium atoms deposited on the Si surface.

In the presence of \(e^-\) \((C > 2 \times 10^3 \text{ mol dm}^{-3})\) potassium cations are reduced to metal atoms at the SC surface and these species create a new interface state distribution and form a thin interfacial conductive layer. So the rest potential of all electrodes corresponds to the redox potential and presents a Nernstian behavior.

This interfacial conductive layer is only formed (and reversely destroyed) if a large amount of \(e^-\) is present because in this case the rest potential of Si is sufficiently negative, so that the negative charge present on the surface can reduce the neighboring potassium cations to metal adatoms. If the bulk solution concentration of \(e^-\) decreases, the metal adatoms are reversely dissolved by ammonia and the Si behavior becomes again as in dilute \(e^-\) solution.

The influence of surface chemistry and derivatization to modify strongly the interfacial charge transfer kinetics is well-known. For the Si/solvated electron interface, the surface modification occurs without any outside intervention because the interfacial potassium layer appears reversely when the solvated electrons are sufficiently concentrated.

When this model is used the observed experimental results concerning the Si/solvated electron interface can be explained: the presence of a conductive layer induces the existence of a high density of the interface state between \(E_CB\) and \(E_{VB}\) and leads to a very similar behavior for n-Si, p-Si, and Pt electrodes as observed. Due to the strong interaction of potassium adatoms toward the Si surface, the band edges of Si have shifted so that the band bending remains slow. So the n-type and p-type Si do not have the same positions of \(E_CB\) and \(E_{VB}\) in this case because their rest potentials are the same.

The Mott–Schottky curves have a quasi-linear behavior with the slope giving the order of magnitude of \(N_A \) or \(N_D\). This indicates that the charging of the space charge capacitance with applied voltage has been correctly deduced from the total impedance. So the extrapolated \(V_{FB}\) values on the \(V\) axis are assumed to be the flat-band potentials. These values for n-type and p-type silicon correspond to the redox potential of the solution because both electrodes have a quasi-metallic behavior.

The shift of \(V_{FB}\) observed in a concentrated \(e^-\) medium compared to the basic medium corresponds to the high interface charge stored in the conductive layer. This shift can be related to the stored charge by the relation\(^{45}\) \(\Delta V_{FB} = Q_{CL}/C_{CL}\), where \(Q_{CL}\) and \(C_{CL}\) are respectively the charge and the capacity of the conductive layer.

Conclusion

The understanding of the unexpected behavior of the PEC p-Si/NH\(_3\) + NH\(_3\) + \(e^-\)/counter electrode when the solvated electrons are sufficiently concentrated—the photoeffects vanish—led us to study the n- and p-Si/Pt/solvated electron in basic liquid ammonia interfaces when \(e^-\) varies.

The n- and p-Si band edges are fixed in the position \(E_CB = -1.95 \text{ V vs. SRE}\) and \(E_{VB} = -0.85 \text{ V vs. SRE}\) in basic liquid ammonia (pH \(\approx 30\)).

tances, we made the capacitance measurements at high frequency ($F > 50$ Hz). This technique is a fruitful method for investigating the impedance of the SC/electrolyte junctions and also heterojunctions (MOS, EOS, ...).

In the presence of surface states the impedance model in Figure 8 is no longer usable and needs some improvements\(^\text{52-55}\) as shown in Figure 9.

After correction of $\text{Re}$ (obtained by extrapolation of the impedance to infinite frequency), it is easy to separate the diverse contributions in the total impedance by investigation of the complex admittance $Y$.

$$\frac{1}{Z - \text{Re}} = Y = G + jH$$

with

$$G = \frac{1}{R} + \frac{\omega^2 C_{SS} \tau_{SS}}{1 + \omega^2 \tau_{SS}} = G_{SC} + G_{SS}$$

$$H = \omega C = \left[ \frac{C_{SC}}{1 + \omega^2 \tau_{SS}^2} \right] \frac{C_{SS}}{1 + \omega^2 \tau_{SS}^2}$$

$\tau_{SS} = R_{SS} C_{SS}$ is the time constant.

The surface states density is directly deduced from the $C_{SS}$ value: $N_{SS} = C_{SS}/\varepsilon$.

Registry No. Si, 7440-21-3; NH$_3$, 7664-41-7; NH$_4^+$, 17655-31-1; KBr, 7758-02-3.


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Applications of Metal–Ammonia Solutions to Secondary Batteries

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It is shown that solutions of alkali metals in liquid ammonia can be used as negative electrodes in a battery, the positive electrode being a concentrated solution of sulfur in liquid ammonia. The negative electrode can be a ternary system such as K–KI–NH$_3$ or a saturated solution of lithium in liquid ammonia. With a negative electrode such as K–KI–NH$_3$, the positive electrode can be an intercalation compound such as, for instance, NiPS$_3$. The potential interest and the problems of these batteries are discussed.

Introduction

Many advanced studies are presently being made for obtaining reversible electrochemical batteries for electrical energy storage.\(^1\) The batteries to be studied have to associate light elements with electronegativities as different as possible. In this field, the sodium–sulfur battery using $\beta$-alumina as an ionic conductor has been studied in many aspects and in many places.\(^6\) Let us recall that it requires a temperature of about 350 °C, so that liquid sulfur is used between S and Na$_2$S$_2$. Since 1980, the use of concentrated metal–ammonia solutions as negative electrodes for electrochemical batteries has been examined by our group. Participants of Colloque Weyl VI know very well that concentrated solutions of alkali metals in liquid ammonia are liquids down to rather low temperatures\(^3\) (the eutectic temperature of the lithium–ammonia
