

Semiconductor Electrodes. 20. Photogeneration of Solvated Electrons on p-Type GaAs Electrodes in Liquid Ammonia

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Abstract: The electrochemical behavior of p-type GaAs electrodes in liquid ammonia, in the dark and under illumination, has been investigated. Results show that it is possible to photogenerate solvated electrons (e_s^-) from the semiconductor at an underpotential of about 0.9 V compared to Pt, indicating an extremely negative flatband potential for p-GaAs in NH_3 compared to that found in other solvent systems. The dark collection (oxidation) of solvated electrons appears to occur via surface states at energies in the gap region. A regenerative photovoltaic cell based on the system p-GaAs/ NH_3 , e_s^- /Pt is also described.

Introduction

There has been much recent interest in the application of semiconductor electrodes in nonaqueous solvents (e.g., acetonitrile) to studies of the properties of the semiconductor materials and to photoassisted electrochemical processes.¹ Cells employing GaAs, which has a band-gap energy, E_g , of 1.35 eV and thus is suitable for optimal utilization of solar energy, have been described² and shown to be stable and yield good efficiencies in the production of electricity, paralleling earlier studies of aqueous solutions with stabilizing electrolytes. However, except for some preliminary studies by Thompson and Krohn³ on p-Si, no results have been reported for semiconductor electrodes in liquid ammonia. Liquid NH_3 is of interest, because its properties are very different from those of the aprotic solvents used previously. It has been used previously for numerous electrochemical studies where highly reduced species have been shown to be very stable,⁴ and because solvated electrons (e_s^-) are very stable in this medium.⁵ We report here a study of p-type GaAs in liquid NH_3 and demonstrate that photoemission of electrons to form e_s^- occurs with good efficiency showing that the conduction band edge is located at remarkably negative potentials.¹²

Experimental Section

The p-GaAs single crystal semiconductor (purchased from Atomergic Chemicals, Long Island, N.Y.) was provided with an ohmic contact⁶ and mounted in a glass tube as described previously.⁷ The back and sides of the crystal were insulated from the solution with Nordel (E. I. du Pont de Nemours, Inc., Wilmington, Del.), an ethylene-propylene copolymer, dissolved in Skelly B. This material was impervious to attack from either liquid NH_3 or solvated electrons. The semiconductor was polished prior to use with 0.5- μ m alumina and then etched in $H_2SO_4/H_2O_2/H_2O$ (3:1:1) for 5 s followed by 6 M HCl for 25 s.² The ammonia (Matheson Gas, 99.9%) was purified by double distillation from sodium metal.⁵ Potassium iodide was used for supporting electrolyte as in previous studies (0.1 M).⁵

A standard two-compartment cell was used with the coiled Pt wire counter electrode separated from the main compartment by a medium-porosity glass frit. The quasi-reference electrode was a silver wire immersed in the solution and separated from it by a fine-porosity glass frit. The main compartment also contained both a Pt disk and a large Pt foil electrode. All potentials are reported vs. the Ag/AgNO₃ (0.1 M) reference electrode. The cell was cooled in a 2-propanol/ CO_2 bath to approximately $-50^\circ C$.

Electrochemical measurements were carried out with a PAR 173 potentiostat and PAR 175 universal programmer (Princeton Applied Research Corp.) and the current-potential curves recorded on a Houston Model 2000 X-Y recorder (Houston Instruments, Austin, Texas). The light source was a 275-W G.E. sunlamp (maximum intensity ~ 80 mW cm^{-2}), a 1.7-mW He/Ne laser (Spectra Physics, Model 132), or a 650-W G.E. Quartzline lamp (maximum intensity ~ 1 W cm^{-2}).

Results

The cyclic voltammetric background current in liquid ammonia on the Pt disk electrode is shown in Figure 1a. The cathodic current, which starts at -2.4 V, represents the electrogeneration of solvated electrons (formal potential, $E^0(e_s^-) = -2.69$ V)⁵ and is accompanied by the appearance of the characteristic blue color at the electrode surface. A similar scan with a p-GaAs electrode in the dark shows no appreciable current for this process until potentials well negative of $E^0(e_s^-)$ (Figure 1b). Under constant illumination a cathodic photocurrent commencing at -1.5 V (Figure 1c) is observed at the p-GaAs electrode; the simultaneous blue coloration in the solution near the electrode surface indicates that this process is the generation of solvated electrons. The photocurrent reached a maximum at about -2.05 V before decreasing. When the light was pulsed (Figure 1d), a cathodic photocurrent was again produced during periods of illumination, while an anodic current was observed during the dark periods at potentials between -1.5 and -2.0 V. This latter represents the reoxidation of the solvated electrons generated on illumination. The decrease in the cathodic photocurrent at potentials negative of -2.05 V cannot be attributed to mass transfer effects but rather was caused by absorption of the light by solvated electrons generated on the electrode surface. This was shown by illuminating the surface with a He/Ne laser while maintaining the potential at -2.2 V, producing the current/time response shown in Figure 2. When the laser intensity was decreased with neutral density filters, a much smaller current decay with time was observed. The current was almost constant at low intensities, when the low concentration of solvated electrons near the electrode resulted in negligible absorption of the incident light. Moreover, correction of the measured currents (Figure 2), taking into account the absorption of light by the solvated electrons, gave a constant current/time relationship as shown in the dashed line in Figure 2. The correction was made by using the observed current density (Figure 2) to calculate the total amount of solvated electrons generated per unit area of electrode surface. From the molar absorptivity for e_s^- , 1.5×10^3 L mol⁻¹ cm⁻¹,^{8,9} the extent of absorption of the incident radiation by e_s^- was calculated and this was employed to determine the photocurrent per unit intensity at the electrode surface. This also indicates that the back reaction (reoxidation of solvated electrons) is not responsible for the decreasing photocurrent at these potentials.

The dependence of the initial laser-generated photocurrent on light intensity at -2.2 V is shown in Figure 3. The linear relationship indicates that the photogeneration of solvated electrons is a one-photon process. The quantum efficiency for the photogeneration at this potential, calculated from these

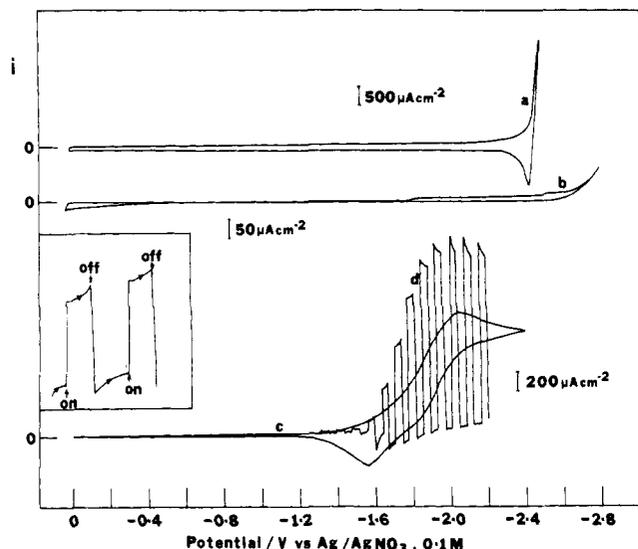


Figure 1. (a) Cyclic voltammetric background current for a Pt disk electrode in liquid NH_3 . Scan rate 200 mV s^{-1} . (b) A similar scan for p-GaAs in the dark. (c) p-GaAs under constant (sunlamp) illumination. Scan rate 100 mV s^{-1} . (d) p-GaAs under pulsed illumination (as inset). Scan rate 50 mV s^{-1} .

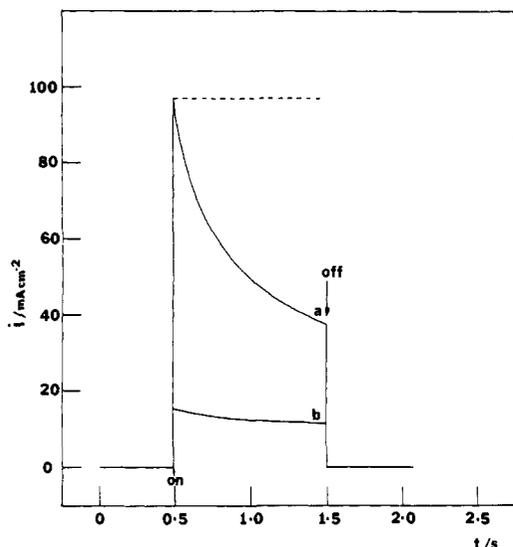


Figure 2. Current (per cm^2 illuminated)/time response of the cathodic photocurrent on illumination with a 1.7-mW He/Ne laser at -2.2 V . (a) Full laser intensity. (b) One-tenth laser intensity. ---: (a) after correction for absorption of incident light by e_s^- .

initial photocurrent values, was 0.6, independent of laser intensity.

The nature of the dark oxidation of e_s^- at p-GaAs was investigated by studying the cyclic voltammetry in a solution containing $0.3 \text{ mM } e_s^-$ produced by coulometric generation at a Pt electrode (Figure 4). The anodic current commences at about -2.2 V , i.e., at more negative potentials than the onset of photogeneration (-1.5 V). The anodic peak current occurred at -1.7 V . The peak height was proportional to the concentration of solvated electrons indicating diffusion-controlled oxidation of e_s^- .

A photocell was formed with a GaAs photocathode and a Pt foil anode in a 0.2 mM solution of solvated electrons (coulometrically generated): p-GaAs/ e_s^- , NH_3/Pt . The dependence of the open circuit potential, V_{oc} , on light intensity is shown in Figure 5; a limiting value of V_{oc} was $+700 \text{ mV}$ (with respect to the Pt electrode) as measured with a Keithley Model 600A electrometer. The current, voltage, and power curves for

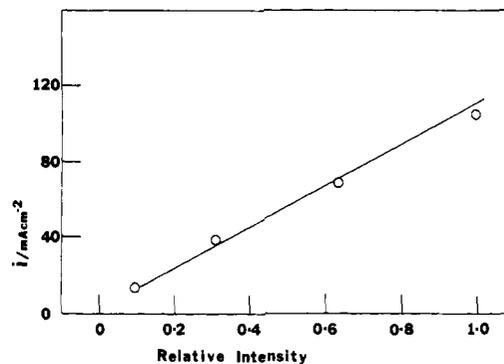


Figure 3. Dependence of the initial laser-generated photocurrent on light intensity at -2.2 V .

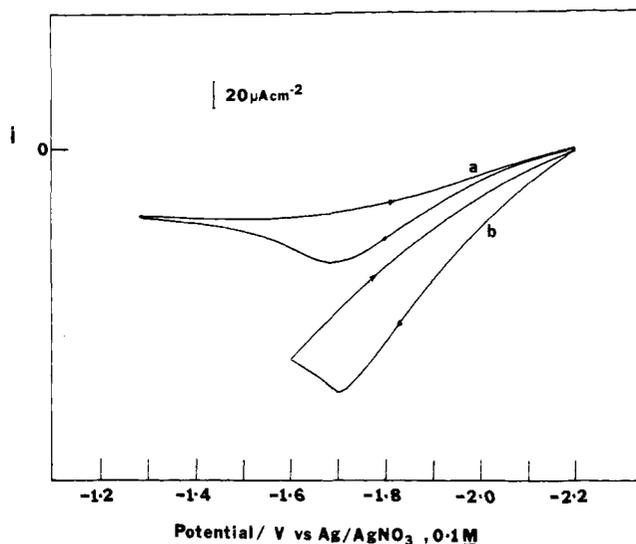


Figure 4. Cyclic voltammogram on a p-GaAs electrode in (a) 0.28 mM , (b) 0.61 mM solutions of solvated electrons. Initial scan positive. Scan rate 100 mV s^{-1} .

different values of load resistance at the maximum light (sunlamp) intensity are shown in Figure 6. The cell showed stable operation for about 2 h, which corresponds to the lifetime of the generated solvated electrons in the solution.⁵ To our knowledge this represents the first example of an electrochemical cell in which solvated electrons play the role of the redox couple and in which transport of electrons occurs in both the solution and external circuit.

Discussion

The results can be interpreted based on a diagram of the semiconductor energy levels as shown in Figure 7. Electrons, photoexcited from the valence band, are emitted from the conduction band into solution at potentials negative of the flatband potential (V_{fb}) because of the favorable downward band bending in the space-charge region of the semiconductor. The onset of photogeneration of solvated electrons thus indicates a flatband potential of -1.5 V . This value, combined with the band gap energy, E_g , of GaAs, 1.35 eV , places the conduction band edge at about -2.8 V , above that required for production of e_s^- . The oxidation of e_s^- then occurs at potentials corresponding to energies within the gap region (i.e., at potentials negative of V_{fb}). We suggest that this oxidation occurs via surface states or intermediate levels within the gap which mediate electron transfer and are filled by electrons from solution when the Fermi level drops below this level. An analogous explanation has been proposed to explain the reduction of species at n-type semiconductors at potentials in the gap region.^{1a}

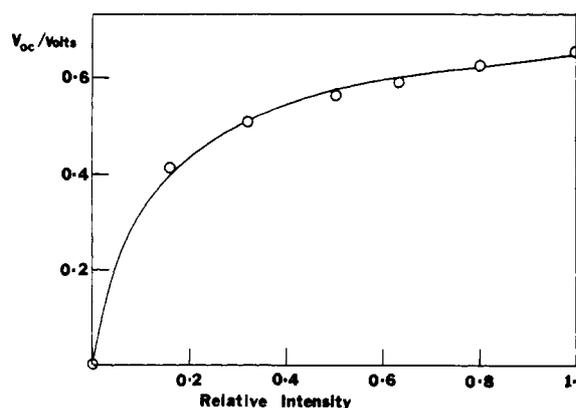


Figure 5. Dependence of the open-circuit potential (V_{oc}) of the p-GaAs/ NH_3, e_s^- /Pt photocell on light intensity (Quartzline lamp).

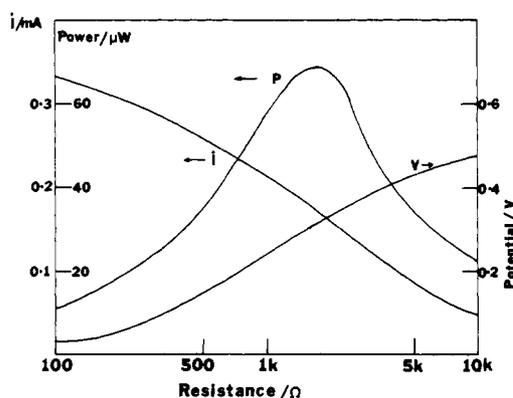


Figure 6. Current, voltage, and power curves for different values of load resistance at maximum light intensity (sunlamp) for the cell p-GaAs/ NH_3, e_s^- /Pt.

The position of the conduction band edge found in this study (based on a band gap of 1.35 eV) is compared to values found in other solvent systems in Table I. All potentials are referenced against the ferrocene/ferricenium couple in an attempt to place these on a common scale independent of shifts in the reference electrode potential in the different solvents.¹⁰ The GaAs conduction band energy falls at surprisingly negative values in liquid ammonia compared to the other solvents. The reason for this very negative shift is not clear. Studies of GaAs in aqueous solutions have demonstrated that V_{fb} is pH dependent¹¹ and one could argue that the negative value in NH_3 is attributable to the very basic nature of the solvent. Studies of GaAs in acetonitrile showed unexpected photoeffects on both p- and n-type material for couples with solution redox levels located above the conduction band edge.^{2a} The observed effects were explained by the formation of a surface layer creating a Schottky junction with the semiconductor.^{2a} Such a surface layer could also be present in liquid NH_3 , although the magnitude of the observed photoeffect is much larger than that found in acetonitrile and the observed shift in V_{fb} appears too large to explain in this way.¹²

In conclusion we have demonstrated the photoemission of solvated electrons in liquid NH_3 from a p-type semiconductor, at a large underpotential and good quantum efficiency. This finding gives rise to the possibility of using light energy (e.g., solar) to assist in the generation of solvated electrons which could then be used for synthetic purposes, for example, in the reduction of organic systems (a "photo-Birch reduction"). The utilization of this reaction in a particulate system, however, would require the existence of an irreversible oxidation reaction

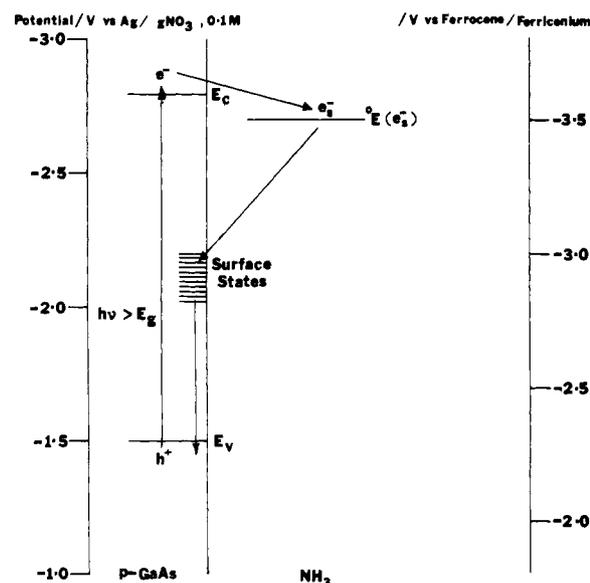


Figure 7. Energy diagram for GaAs in liquid ammonia.

Table I. Position of the Conduction Band of GaAs in Different Solvent Systems^a

solvent	conduction band position/V
liquid NH_3	-3.6
acetonitrile	-1.3 ²
aqueous (pH 7)	-0.75 ¹¹
aqueous (pH 12)	-1.0 ¹¹

^a Potentials vs. the ferrocene/ferricenium redox couple.¹⁰

at potentials more negative than the V_{fb} of p-GaAs. While the regenerative photocell operating at very low temperatures is probably impractical for most terrestrial applications, it could find application in the low-temperature environment of outer space.

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References and Notes

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- (12) NOTE ADDED IN PROOF. Further studies of both n- and p-type GaAs electrodes with several redox couples (benzophenone, nitrobenzene, naphthalene) indicate that the observed effects at p-GaAs are probably caused by formation of a surface layer on the electrode. Work is currently in progress to confirm this.