n-type GaAs photoanodes in acetonitrile: Design of a 10.0% efficient photoelectrode

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n-type GaAs semiconductor/liquid junctions have been studied in acetonitrile (ACN) solvent with the ferrocene/ferricenium redox couple. Previously reported inefficiencies in this system are demonstrated to be due to bulk electron-hole recombination and not to recombination at the junction. Increases in minority-carrier collection length lead to increases in short circuit current of the n-GaAs/ferrocene/ferricenium cell in ACN, with photocurrent densities in excess of 21 mA/cm^2 at 88 mW/cm^2 of ELH-type tungsten-halogen irradiation. Properly prepared n-GaAs samples yield photoelectrode efficiencies of 10.0% $\pm$ 0.5% for conversion of natural sunlight (65 mW/cm^2) to electricity, with open circuit voltages V_{oc} of 0.70–0.72 V, short circuit currents of 16–17 mA/cm^2, and fill factors of 0.52–0.56, when measured relative to the potential of a reversible reference electrode in the same solvent/redox couple/electrolyte solution.

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Nonaqueous electrolytes present advantages for photoelectrochemical cells such as a wide range of solution redox couples and stable electrode materials. However, very few efficient nonaqueous electrolyte systems have been reported to date. We recently disclosed results on nonaqueous semiconductor/liquid junctions from anodes of the type n-$GaAs_{1-x}P_x$.[1] We find a solar to electrical conversion efficiency for n-$GaAs_{0.72}P_{0.28}$ in acetonitrile (ACN) solvent of 13%, the highest solar conversion efficiency for any nonaqueous photoelectrode reported to date. During this study, we noted that the solar efficiency[2,3] and short circuit photocurrent density[2] reported for the n-GaAs system was anomalously low in nonaqueous solvents compared to values obtained for n-GaAs anodes in aqueous systems.[4] In addition, we observed that n-GaAs, with an optimum terrestrial band gap of 1.4 eV, has a lower reported photoelectrode efficiency than n-$GaAs_{0.72}P_{0.28}$.[1]

Thus, in order to understand these apparent discrepancies, we have investigated the photoelectrochemistry of n-GaAs in ACN. We observe that important variables in this system are the minority-carrier collection length in the semiconductor and the chemistry at the semiconductor/liquid interface. We report here results for the n-GaAs/0.1 M ferrocene (Fc)/0.5 mM ferricenium (Fc^+)/acetonitrile/1.0 M $[(C_2H_5)_4N][BF_4]$ system which display improvements in open circuit voltage V_{oc}, short circuit current I_{sc}, and fill factor of this photoelectrode. These improvements have produced increases in photoelectrode solar conversion efficiency to the 10.0% level, making the solar efficiency for the n-GaAs nonaqueous system competitive with the best semiconductor/liquid junctions reported to date.

Highly doped n-GaAs anodes have been previously reported[5] to have modest quantum yields of 0.3–0.4 with 632.8-nm light, and to yield an I_{sc} of 9 mA/cm^2 at 75 mW/cm^2 of sunlight.[2] However, increases in minority-carrier collection length can lead to a dramatic increase in I_{sc}. Figure 1(a) depicts the short circuit current density under tungsten-halogen ELH source irradiation (88 mW/cm^2) in 0.1 M Fc/0.5 mM Fc^+/ACN as a function of the donor density of a series of n-GaAs samples. All of the n-GaAs samples, (100) oriented, were mounted in a conventional cell and etched to a shiny finish with stirred 1:1 H_2O_2/H_2SO_4 solutions.[4(b)] Typical sample areas were 0.05–0.10 cm^2. The ELH lamp is a well-known solar simulator,[6] and we consistently find less than 10% difference in photoelectrode efficiency measurements in our cell configuration between our calibrated ELH source and actual sunlight. Current-voltage curves have been measured versus a Pt reference electrode through a 0.2-mm-diam Luggin capillary. The counterelectrode is a 2-cm^2 Pt foil, and the solutions are magnetically stirred during the measurement. We note that the ohmic resistance losses ($\sim 50\,\Omega$) which were uncompensated in our cell design make our photoelectrode efficiencies conservative by approximately 20% over what could be achieved in a sufficiently conductive electrolyte solution.

We attribute the increased values of I_{sc} to the increase in minority-carrier collection length at the lower doping levels in our series of samples. High doping levels in short diffusion length material (commonly used in studies of semiconductor/liquid junctions) lead to inefficient charge separation, resulting in poor quantum efficiencies.[7,8] This is verified by the poor wavelength response spectrum of our highly doped samples relative to samples with longer hole collection lengths [Fig. 1(b)]. Increases in carrier collection due to sufficient diffusion lengths and/or increases in depletion region thicknesses yield higher currents, and we find that epitaxial layers of GaAs with $N_d = 1\times10^{15}\ cm^{-3}$ yield short circuit currents of over 19 mA/cm^2 at 88 mW/cm^2 of incident ELH irradiation. Similar improvements would be expected for other semiconductor/liquid junctions where dopant densities and carrier lifetimes have not been investigated.

Elimination of bulk electron-hole recombination yields substantially improved efficiency parameters for the n-GaAs/ACN/Fc/Fc^+ interface. We consistently find that a matte etched (stagnant 1:1 H_2SO_4/H_2O_2)[4(b)] single crystal sample of (100) oriented, Si-doped n-GaAs ($N_d = 8.0\times10^{15}$ carriers/cm^3) yields the current-voltage characteristics in

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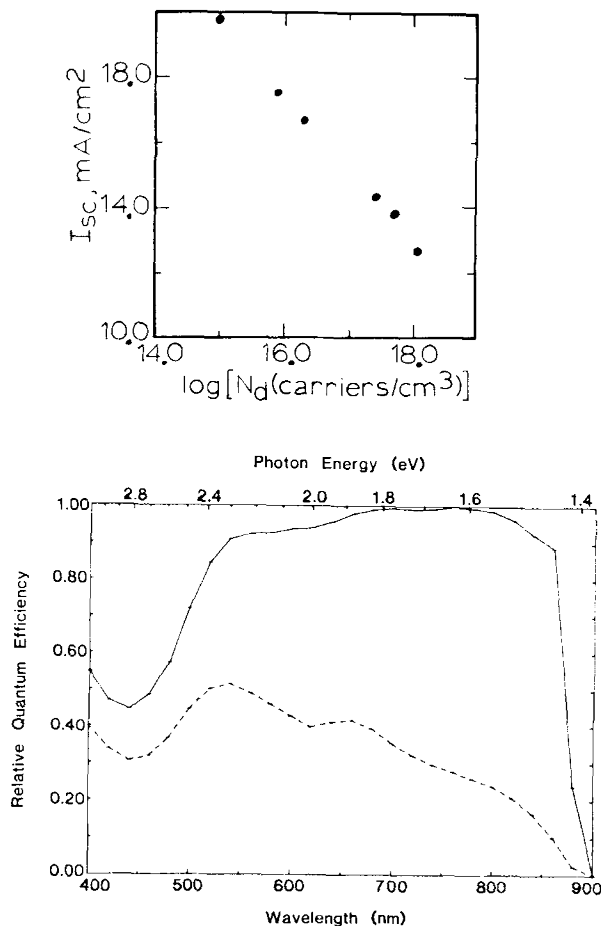

FIG. 1. (a) Plot of short circuit photocurrent density vs dopant density of the GaAs/ACN/0.1 M Fc/0.5 mM Fc^+ cell. Light source is ELH-type tungsten halogen illumination at 88 mW/cm^2, and all n-GaAs samples are (100) oriented and etched to a shiny finish with 1:1 H_2O_2/H_2SO_4. Linearity of plot is fortuitous, and reflects the compromise between carrier lifetimes and dopant densities of the particular samples chosen for study. (b) Plot of short circuit quantum yield for electron flow vs wavelength of excitation source for n-GaAs samples in 0.1 M Fc/0.5 mM Fc^+/ACN solution. The photoelectrodes are maintained at short circuit vs a Pt counterelectrode, and the incident light intensity is approximately 1 mW/cm^2. (—) Matte-etched (stagnant 1:1 H_2SO_4/H_2O_2) [Ref. 4(b)] sample of $N_d = 8.0\times10^{15}$ cm^{-3}, Si-doped, n-GaAs; response is normalized to unity at maximum value. (---) Response for shiny (stirred 1:1 H_2SO_4/H_2O_2) [Ref. 4(b)] $N_d = 1\times10^{18}$ cm^{-3} n-GaAs sample on same scale, showing low quantum efficiency and poor long wavelength response due to low minority-carrier collection length.

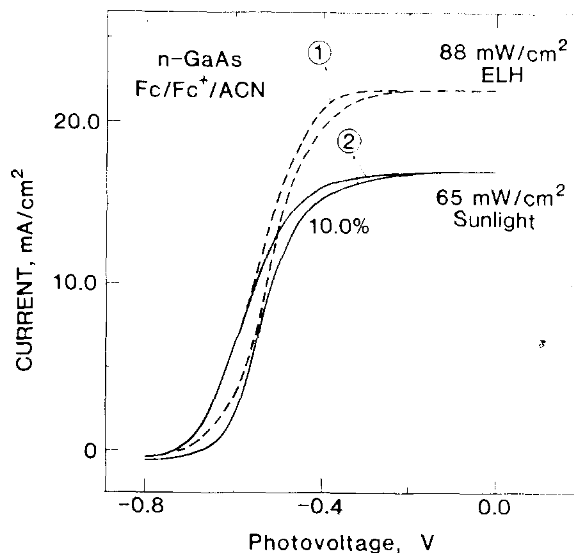

FIG. 2. Photocurrent voltage characteristics (50 mV/s) of 8.0×10^{15} Si-doped (100) oriented, n-GaAs single crystal anodes in mechanically stirred 0.1 M Fc/0.5 mM Fc^+/1.0 M $(Et_4N)BF_4$/ACN. The electrode is etched to a matte finish with 1:1 H_2O_2/H_2SO_4, washed with H_2O, then with ACN, and air dried. The increase in efficiency from 88 mW/cm^2 ELH irradiation to 65 mW/cm^2 of sunlight is due to smaller series resistance losses at the lower photocurrent densities. The photoelectrode is potentiostatted in a three-electrode configuration vs a Pt reference electrode poised at the reversible potential of the solution.

Fig. 2. Under 88 mW/cm^2 of ELH-type irradiation, we find $V_{oc} = 0.70$–0.75 V, $I_{sc} = 20$–22 mA/cm^2, and fill factors of 0.50–0.52, resulting in $9.5\% \pm 0.5\%$ photoelectrode efficiency. In actual direct sunlight (Fig. 2), we observe similar behavior, and at irradiance levels of 65 mW/cm^2, we typically observe a V_{oc} of 0.70–0.72 V, I_{sc} of 16–17 mA/cm^2, fill factors of 0.52–0.56, and $10.0\% \pm 0.5\%$ photoelectrode efficiency. Other etches of the electrode surface yield analogous behavior (3:1:1 $H_2SO_4/H_2O_2/H_2O$, 12 M HCl, stirred 1:1 H_2SO_4/H_2O_2), except that the decreased reflectivity of the 1:1 H_2SO_4/H_2O_2 matte etch leads to higher values of I_{sc}. We note that these values are based on power incident onto the photoelectrochemical cell as determined by a calibrated Solarex Si secondary standard cell and an Eppley thermopile, and are not corrected for any optical reflection or electrolyte resistance losses. Elimination of residual solution absorption and resistance drops would result in photoelectrode efficiencies comparable to the 13% level previously observed for the n-$GaAs_{0.72}P_{0.28}$/ACN/Fc/Fc^+ system.[1] We emphasize that these values are *photoelectrode* efficiencies representing potentiostatic control of the semiconductor electrode relative to the reference, and cannot be directly compared to solar cell efficiencies in a two-electrode configuration without actual fabrication of such devices.

Reported parameters for n-GaAs anodes in nonaqueous solvents are characterized by low values of cell operating voltages. The barrier height[5] determined for n-GaAs in the ACN/Fc electrolyte system is 1.1 V, yet the operating voltage for a solar cell under conditions of maximum power[2] is only 0.2–0.3 V. This has been attributed to interface states which may yield poor fill factors and low operating voltages.[9] With optimally prepared n-GaAs electrodes, we find little evidence for poor fill factors or recombination sites. We note that the high values of the short circuit quantum yield, >0.75 when integrated over the entire spectral range above $E_g = 1.4$ eV,[10] indicate effective competition with recombination centers and efficient charge separation.

A striking feature of the n-GaAs/ACN system is that the value of V_{oc} obtained, 0.70–0.75 V, is larger than that typically found in direct n-GaAs/noble metal junctions. n-GaAs/Au junctions yield V_{oc} values of 0.45–0.50 V under AM1 conditions.[8,11] Lower than theoretical values of V_{oc} have been attributed to pinning of the semiconductor Fermi level by surface states in ACN solvent.[12,13] In addition, previous GaAs/ACN work suggested that the Fermi level of GaAs is pinned so severely by surface states that the addition of other barriers, either metal overlayers or liquids, would not alter the band bending in the resulting device.[9,13] It has

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been suggested that pinning of the n-GaAs Fermi level occurs upon deposition of noble metal overlayers,[14,15] and it is also possible to form Ga alloy junctions or change surface stoichiometry upon deposition of metal overlayers. In contrast, the n-GaAs/ACN liquid junction does not involve the formation of metal-GaAs contacts, and thus presents a significantly different chemical situation at the barrier forming interface. Immersion of n-GaAs in liquids may not lead to similar changes in surface chemistry, yielding the high values of V_{oc} observed in the n-GaAs/ACN/Fc/Fc^+ system.

It is possible that an intervening oxide formed in liquid systems might also lead to the improved V_{oc} values in ACN solvent. Increases in the V_{oc} of Schottky systems can occur with formation of metal-oxide-semiconductor type structures.[16,17] We have developed a simple test which would seem to rule out the presence of such oxide effects in our system. We expose a sample of n-GaAs to operation in the ACN/Fc/Fc^+ cell and verify that current-voltage properties are as depicted in Fig. 2. We then simultaneously evaporate a 150-Å Au Schottky barrier onto the photoelectrode material and onto an identical n-GaAs substrate which had been etched, but not exposed to the Fc/Fc^+/ACN cell. If oxide formation in ACN is responsible for the improved electrode properties, we would expect to observe current-voltage properties of the Schottky diode which are similar to the semiconductor/liquid junction interface. We reproducibly find no change ($< 5\%$) in current-voltage properties of such Au/n-GaAs diodes, and the V_{oc} of 0.47 V (100 mW/cm^2 ELH irradiation) agrees very closely with the reported values for n-GaAs/Au interfaces.[8,11] We cannot completely rule out pinholes and parallel junctions as the source of lower voltages with metal overlayers; however, we do not observe evidence for parallel junctions with liquid contacts, which should also be sensitive to any nonuniformity of oxide coverage. Irreversible chemical changes such as oxide formation would thus not appear to be responsible for the improved performance of the liquid junction systems.

Properly prepared n-GaAs anodes are thus capable of high photoelectrode conversion efficiencies for solar irradiation to electricity in nonaqueous solvents. Notably, despite observations that the Fermi level of n-GaAs is pinned in ACN to limit values of V_{oc} to 0.5–0.6 V, we find that appropriate electrode preparation can indeed produce higher values of V_{oc} (0.72 V), relatively large operating voltages, and efficient anodes. The large V_{oc} is not unique to the Fc/Fc^+ redox system, and we observe similar V_{oc} values of 0.70–0.75 V under 88 mW/cm^2 ELH irradiation for n-GaAs/ACN junctions derived from acetyl ferrocene$^{+/0}$ and N,N,N',N'-tetramethyl-phenylenediamine$^{+/0}$ redox couples. When compared to most aqueous electrolyte/anode systems, photoelectrode stability is much less of a problem in nonaqueous systems in the short term, and permits study of systems without extensive competition from photocorrosion or passivation processes. In particular, n-GaAs has been shown previously to exhibit stable photocurrents if water can be successfully excluded from the cell environment.[2] However, oxide formation due to residual water will passivate n-GaAs in nonaqueous systems, and these systems may not lead to practical photoelectrochemical cells with long-term stability approaching those reported in aqueous Se^{2-} solutions.[4] Nonaqueous solvents do provide a framework for study of photoelectrode processes with a number of redox species, and can yield insight into interfacial chemistry which might not be available in aqueous electrolytes. The attainment of 10.0% efficiencies with single crystal material is highly encouraging for development and study of efficient nonaqueous photoelectrodes from common semiconductor substrates. Studies of the interface chemistry of polycrystalline and thin-film materials in these systems are under way at present.

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