Metalloporphyrin/polysiloxane modified n-GaAs surfaces: effect on photoelectrochemical efficiency and surface stability

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Abstract

Tetra(-4-pyridyl)porphyrinatomanganese(III)sulfate (as an $Mn^{III} + Mn^{II}$ ion mixture) was embedded into a polysiloxane polymer matrix and attached to the surfaces of the n-GaAs electrode. The n-GaAs/polymer/MnP system was annealed under nitrogen and used for a photoelectrochemical study in a water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system. The values of short-circuit currents, measured after minutes of illumination, were significantly enhanced by modification. The modified electrode surfaces were more stable to degradation, in the dark and under illumination, than the unmodified ones. Furthermore, the modified electrodes showed higher light-to-electricity conversion efficiency than the unmodified ones. The methodology described here is advantageous in the sense that the semiconductor electrode properties can be enhanced in more than one aspect at the same time. © 2002 Elsevier Science B.V. All rights reserved.
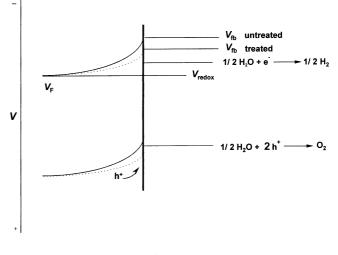
Keywords: n-GaAs; Stability; Metalloporphyrin; Efficiency; Short-circuit current; Photoelectrochemistry

1. Introduction

n-GaAs is one of the extensively studied semiconducting (SC) materials. This is due to the average value of the band gap of ~ 1.4 eV, and the very high electron mobility [1,2]. Despite the wide applications of n-GaAs in device manufacturing, its photoelectrochemical (PEC) applications are limited by its instability under aqueous PEC conditions and its narrow band gap [2].

It is often desirable to control the properties of semiconductors. In earlier studies, we modified n-GaAs with porphyrinatomanganese complexes (MnP) at a sub-monolayer coverage level. This was done by chemically binding MnP with the SC surface through an anchoring ligand via a quaternization reaction [3]. The resulting positive charges shifted the positions of the SC flat-band edges towards more positive values. Despite the unsuitability of n-GaAs for many PEC processes, such as light-driven water splitting, the repositioning of other semiconductor band edges is important for such purposes. n-GaInP$_2$ (with a band gap of ~ 1.8 eV) is a good candidate for water splitting processes, if its valence band edge is positively shifted by about 300 mV,

Scheme 1. Therefore, the results described in our preceding work [3], where n-GaAs was employed only as a model semiconductor, are relevant, exemplifying how the band edges may easily be repositioned as desired. In spite of these findings, the surface monolayer coverage did not stabilize the n-GaAs surface to degradation. In other reports, n-GaInP$_2$ surfaces have been modified with other species, such as 8-quinolinol and cupferron,

Scheme 1.

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and flat-band positive shifts were observed [4,5] but the surface stability difficulties were not overcome. To stabilize the SC surface, conjugated organic polymers were attached to semiconductor surfaces [6–14]. Frank and co-workers [7,8,10,11] and Noufi et al. [9] attached conjugated polymers to different SC surfaces. In the case of n-GaAs, the conjugated polymer matrix significantly stabilized the surface to photodegradation, but the short-circuit current was lowered [11]. In the case of n-CdS, a Schottky barrier resulted at the SC|conjugated polymer interface [11,13].

Therefore, it is important to modify semiconductor surfaces in a technique that can satisfy more than one objective at the same time, namely shifting the band-edges, stabilizing the surface and enhancing the light-conversion efficiency. In an earlier report [15,16], we described how attachment of metalloporphyrins, embedded inside polysiloxane matrices, shifted the positions of the flat-band potentials for n-GaAs at the solid|liquid interface. We now report on how such a technique enhances surface stability and light-conversion efficiency of n-GaAs. The choice of n-GaAs here was not arbitrary. It was used as a model unstable semiconducting material in order to evaluate the technique.

2. Experimental

2.1. Materials

$LiClO_4$, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, and the 5,10,15,20-tetra(-4-pyridyl)-21H,23H-porphine (H$_2$TPyP) were purchased from Aldrich, Ltd. The MnP complex mixture was prepared from H$_2$TPyP as described in the literature [17,18]. The mixture contained complexes of both Mn^{II} and Mn^{III} ions as depicted from the electronic absorption spectra in the visible region. Monocrystalline single surface mirror polished Si-doped (3.2×10^{17} cm^{-3} for the front and 9.9×10^{17} cm^{-3} for the tail) n-GaAs wafers (Crystal Specialties, Int.) were used. The monocrystalline plates, 50 mm round-shaped, were 0.4 mm thick with $\langle 100 \rangle$ orientation. The mobility was 2.8×10^3 cm^2 V^{-1} s^{-1} in the front and 2.3×10^3 cm^2 V^{-1} s^{-1} in the tail. The wafer was cut into smaller wafers. The indium metal back contact was made as thin uniform layers. The wafers were then annealed at 350 °C under a clean nitrogen atmosphere. The SC electrodes were fabricated as follows: a small square n-GaAs wafer (~ 0.1 cm^2) was mounted onto a copper plate (with a copper wire welded to it) using a thin layer of Ga–In eutectic. The backside and the edges of the electrode, together with the copper wire, were then insulated with a pressure-sealing material and allowed to dry overnight under nitrogen. The dried sealed electrodes were then rinsed repeatedly with

methanol to remove away any possible oily solvent contaminants. Etching was conducted using $Br_2 +$ methanol (1.0% V/V) as reported elsewhere [19].

2.2. Electrode modification

The etched SC electrode surface was modified as follows: a dilute solution of commercial (R.T.V.) polysiloxane $(-O-SiR_2-O-)_n$ as a paste in acetic acid, was prepared by dissolving 0.05 g of the paste in 100 ml of dichloromethane. Similarly, methanol solutions of MnP (0.1 g, 1.38×10^{-4} mol in 10 ml) were prepared. The MnP/polysiloxane solutions were prepared by adding the MnP solution to the polysiloxane solution, in a 1:4 V/V ratio, respectively. The stock solution (0.1 ml containing 4×10^{-5} g polysiloxane and 2×10^{-4} g MnP) was sprayed onto the n-GaAs electrode polished surface. The organic solvents were then allowed to evaporate, leaving a transparent thin layer of the MnP/polysiloxane matrix, with a relatively high concentration of MnP in the polysiloxane film (6.9 mmol cm^{-3}). The polymer matrix was calculated to be 4.0 μm thick, containing 2.0×10^{-4} g of MnP. With thicker films, the polymer matrix acted as an insulator and no current was measured. Therefore, unless otherwise stated, all experiments were conducted using the polymer thickness shown above.

The MnP/polysiloxane resistance, measured for a 4-μm thick film between indium tin oxide (ITO) and Ga–In eutectic electrodes, with a 1.0 cm^2 cross-section, was measured at 12 Ω, and the resistivity was calculated to be 3.0×10^4 Ω cm.

2.3. Equipment

Solid-state electronic absorption spectra were measured in a Shimadzu UV-1601 spectrophotometer, as solid thin films of MnP/polysiloxane on quartz slides. Current–potential measurements were performed using a Princeton Applied Research (PAR) Model 263A computer-controlled potentiostat.

2.4. Current density versus potential measurements

All current density versus potential (j–V) measurements were conducted in a thermostatted one-compartment three-electrode electrochemical cell with a standard calomel (SCE) reference electrode, a platinum counter electrode and the SC working electrode. LiClO$_4$ (0.10 M) was used as a supporting electrolyte, and Fe(CN)$_6^{3-/4-}$ (0.05 M K$_3$Fe(CN)$_6$ and 0.05 M K$_4$Fe(CN)$_6$) as the redox couple in freshly distilled water (pH 6.5). Magnetic stirring, with nitrogen bubbling was used to dissolve the solutes. Prior to measurement, stirring was stopped, and the nitrogen gas was kept flowing above the solution, throughout the experi-

ment, to minimize contamination with air. Illumination was carried out using a solar simulator 50 W xenon lamp, equipped with a concentrating lens, placed at a defined distance from the working electrode. A 10-mm thick water filter was placed between the lamp and the electrode. The light intensity at the electrode surface was measured by a pre-correlated light meter and was 0.1013 W cm^{-2}.

2.5. Cyclic-voltammetric measurements

Cyclic voltammetry was measured in a PAR 263A potentiostat, in a one-compartment cell using platinum electrodes and an SCE reference electrode, in water + LiClO$_4$ under a nitrogen atmosphere with a scanning rate of 100 mV s^{-1}. Thin films of MnP/polymer were cast onto a pre-cleaned platinum gauze and on ITO. The films were then used as working electrodes in order to measure the cyclic voltammograms of the MnP. An oxidation peak at (-100 mV) and a reduction peak at (-230 mV), against SCE, were observed.

2.6. Stability testing

Experiments were conducted using the same electrochemical cell with the same electrolyte and redox couple. The electrode was kept under a relatively high intensity illumination, 1400 lx (0.103 W cm^{-2}) for prolonged times using 0.00 V applied potential (vs. SCE). The short-circuit current I_{sc} was measured with time throughout the experiment. The cell power, at a given time, was calculated by multiplying the value of the short-circuit current (measured at that time) by the value of the open-circuit potential (V_{oc}) for the cell.

3. Results and discussion

The modification method described here is technically advantageous over other earlier methods [7–14,19–24]. In earlier reports [6–14], the SC surface was modified with conjugated polymeric matrices. The polymer layers were found to peel off. Efforts have been made to improve the adherence of the polymer to the electrode. Some researchers used to scratch the polished electrode surfaces to prevent the matrix peeling. In this work, the polymer matrix adhered well to the polished n-GaAs surface without any need for scratching. When the n-GaAs/MnP/polysiloxane system was annealed at 100 °C, the adherence was enhanced and a clear robust glassy uniform solid layer appeared on the surface. The nature of the interaction between the polysiloxane and the semiconductor surface has not been studied yet. Annealing would affect the physical and chemical characteristics of the polymer matrix, by increasing the cross-linkage patterns between the polysiloxane chains.

This yields a more robust three-dimensional polymer framework. When thick MnP/polysiloxane matrices were used (more than 4 μm), the j–V plots showed very low current density readings, indicating that the matrix conductivity was low. Therefore, thin matrices were made to lower the resistance. The maximum matrix thickness used was 4.0 μm. With such a thickness, well-defined uniform j–V plots were obtained. A study of the nature of the interaction between the semiconductor surface and the polysiloxane will be conducted in the future, employing very thin matrices sprayed by more advanced spray techniques.

Solid-state electronic absorption spectra were measured for MnP/polysiloxane matrices attached to quartz walls. This was to measure the extent of light intensity loss due to the matrix. Within the working range of the Xe lamp, $\sim$450–800 nm, the light intensity loss was less than 25% except at the three absorption bands characteristic for the MnP complex, at $\sim$455, 584 and 626 nm. The loss in the light intensity was compensated for by the enhanced cell efficiency of the modified electrode, and is not a shortcoming of the technique.

The effects of n-GaAs surface modification on its characteristics are presented.

3.1. j–V plots and electrode stability

n-GaAs surfaces are highly unstable in aqueous solutions when exposed to applied potentials. The water/ LiClO$_4$/Fe^{2+}/Fe^{3+} systems are not the best choice and give poorly defined j–V plots, in the dark and under illumination. The stability can be improved by using suitable redox couples. Conventionally, researchers use alternative systems for the j–V measurements of n-GaAs in water. Se^{2-}/Se$_2^{2-}$ redox couples are known to give better j–V plots for n-GaAs electrodes. Nevertheless, the water/LiClO$_4$/Fe^{2+}/Fe^{3+} system was intentionally employed in this work, so as to see if modification affects the quality of the n-GaAs j–V plots. Fig. 1 shows that the j–V plots of the n-GaAs electrode, measured in the dark, were poorly defined. This is not unexpected and is due to the oxide layers existing at the SC surface, which inhibit the dark current. On the other hand, Fig. 1 shows that attachment of the MnP/polysiloxane matrix to the n-GaAs surface significantly enhanced the quality of the dark j–V plots while using the Fe^{2+}/Fe^{3+} redox couple system in water. This is due to the extra protection of the SC surface, by MnP/polysiloxane. Exposure to traces of oxygen would, therefore, oxidize the Mn^{II}P instead of the n-GaAs surface itself.

No hydrogen gas bubbles, accompanying the dark current, were observed. This indicates that the majority carriers were transported to the redox couple rather than bringing about the hydrogen reduction.
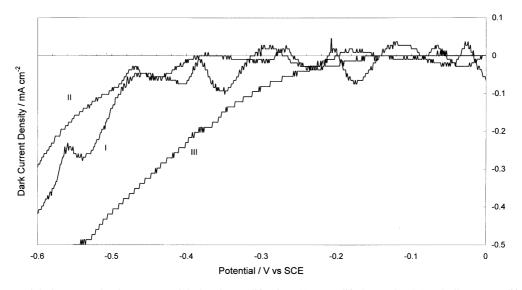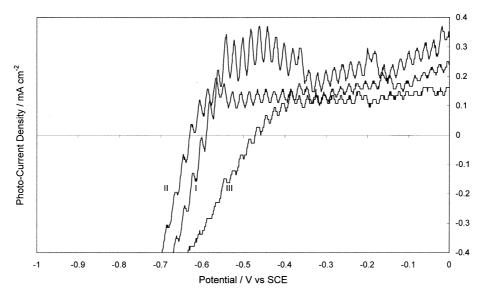
Fig. 1. Enhancement of dark current density vs. potential plots by modification: (I) unmodified n-GaAs; (II) polysiloxane-modified n-GaAs; and (III) MnP/polysiloxane-modified n-GaAs electrodes. All measurements were conducted using the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system in the dark at 25 °C.

Fig. 2. Enhancement of photocurrent density vs. potential plots by modification: (I) unmodified n-GaAs; (II) polysiloxane-modified n-GaAs; and (III) Mn/polysiloxane-modified n-GaAs electrodes. All measurements were conducted under illumination using a Xe lamp (illumination intensity at the electrode surface 0.1013 W cm^{-2}) in the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system at 25 °C.

The j–V plots were measured for the modified and unmodified n-GaAs surfaces under high intensity polychromatic illumination with a Xe lamp, in the unfavorable water/LiClO$_4$/Fe^{2+}/Fe^{3+} system described above. Fig. 2 shows that for the n-GaAs/MnP/polysiloxane electrodes, the photocurrent density versus potential plots were enhanced in shape, as compared to unmodified surfaces. The poorly defined j–V plots, measured for the unmodified electrodes under illumination, are a good indication of electrode photodegradation. The MnP/polysiloxane modified electrode showed enhanced j–V plots as shown in Fig. 2. This indicates that the matrix stabilizes the SC surface to such degradation

processes. The mechanism of such stabilization will be discussed in the later sections. The 120 mV lowering in the value of the V_{oc} is a good indication of a lowering in the value of the V_{fb}, as was described in earlier reports [15,16].

Note that the power outputs of the electrodes in Fig. 2 are relatively low. Continued exposure of the electrodes to light, as will be shown later, significantly enhances short-circuit current density with time. Light attenuation by the MnP/polymer is a possibility, since the MnP shows three absorption bands as discussed above. Furthermore, the MnP/polymer matrix showed relatively high resistivity, as was discussed above. De-

spite these facts, the ability of the matrix to behave as a charge-transfer catalyst compensates for these difficulties and enhances the current, as compared to the unmodified electrode, vide infra.

The MnP/polysiloxane-modified electrodes were tested for reuse. The electrodes were recovered and reused for $j–V$ measurements several times. The characteristics were retained and no damage in $j–V$ plots was observed after reuse for up to four times.

3.2. Capacitance and electrode stability

Capacitance (C) versus potential (V) plots were recorded in the water/LiClO$_4$/Fe^{2+}/Fe^{3+} systems in the dark and under illumination. Mott–Schottky (M–S) plots of C^{-2} verus V were constructed in order to measure the flat-band potential, V_{fb}, values directly, as described in the literature [22]. The Mott–Schottky plots, measured here for the MnP/polysiloxane modified and unmodified electrodes, indicated two important features. Firstly, there was a significant shift in the value of V_{fb} for the MnP/polysiloxane modified electrodes. Such an effect has already been shown in earlier communications [15,16]. Fig. 3 shows that the value, of V_{fb} for the MnP/polymer modified electrode, was shifted towards a more positive value [15,16]. Secondly, the values of the doping density (DD) calculated

from the Mott–Schottky plots for the n-GaAs/MnP/ polysiloxane electrodes were more accurate than the values measured for the unmodified electrodes.

Table 1 shows the values of the DD measured for the modified and unmodified electrodes in the dark. The DD value measured for the MnP/polysiloxane modified electrode resembled the authentic value provided by the vendor, that is 3.27×10^{17} cm^{-1}. The unmodified electrodes gave less accurate values for the DD, due to their instability. The MnP/polysiloxane modified electrode showed more accurate values due to its extra stability.

M–S plots were measured for the modified and unmodified n-GaAs surfaces in the water/LiClO$_4$/Fe^{2+}/ Fe^{3+} system under illumination. The effect of n-GaAs surface modification was more pronounced. The instability of the unmodified n-GaAs surface made it difficult to record the M–S plots under illumination. No linear M–S plots could be constructed for the unmodified surface. Annealing of the modified electrodes enhanced the M–S plots measured under room light illumination.

The polysiloxane-modified surface was also not stable enough to show linear plots. Only for annealed n-GaAs/MnP/polysiloxane were good linear M–S plots obtained under illumination with room light, Fig. 4 [15,16]. The non-annealed modified surface showed lin-
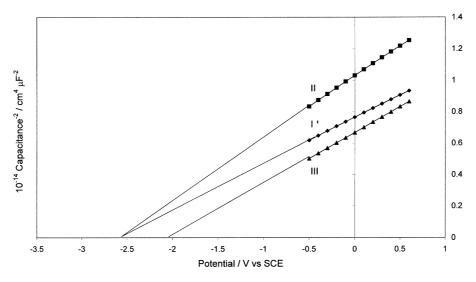

Fig. 3. Mott–Schottky plots for the: (I) untreated; (II) polysiloxane-treated; and (III) MnP/polysiloxane-treated n-GaAs electrodes measured in the dark, using 20 000 Hz frequency in the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system at 25 °C [15].

Table 1
Values of the doping density (DD) for n-GaAs electrodes measured from Mott–Schottky plots

Electrode	Naked	Polysiloxane modified	MnP/polysiloxane modified	Authentic value [a]
10^{-17} DD/cm^{-3}	5.24	5.0	3.26	3.26

Measurements were conducted in the dark using the water/LiClO$_4$/Fe(CN)$^{3-}$/Fe(CN)$^{4-}$ system at 25 °C.
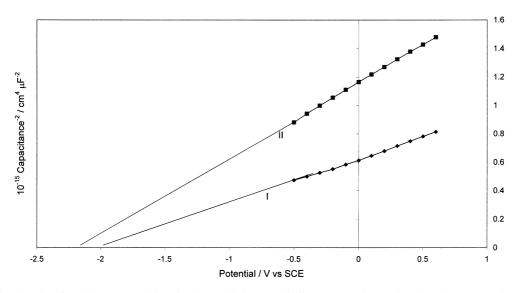[a] Authentic DD value provided by the vendor.

Fig. 4. Mott–Schottky plots for: (I) non-annealed and (II) annealed MnP/polysiloxane-treated n-GaAs electrodes measured under room light, using 20 000 Hz frequency in the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system at 25 °C [15].

ear M–S plots, as discussed earlier, but to a lesser extent [15,16].

3.3. Electrode stability with time

Researchers reported that attachment of organic polymer matrices to n-type SC surfaces enhanced the electrode stability but lowered the short-circuit current density, I_{sc} [6–14]. This is not favorable in PEC research, because the outcome would be a lowering in the PEC cell efficiency.

The effect of modification on stabilizing the n-GaAs surface was studied here while using the unfavorable aqueous LiClO$_4$/Fe^{2+}/Fe^{3+} system under constant high intensity illumination with a Xe lamp (light intensity at the electrode surface 1400 lx, equivalent to 0.103 W cm^{-2}) under 0.00 V applied potential (vs. SCE). A nitrogen atmosphere without magnetic stirring was used to minimize contamination with air. The I_{sc} value was enhanced by modification with MnP/polysiloxane.

In the absence of the MnP ions, surface stabilization by the polysiloxane, was observed but to a lesser extent. Fig. 5 shows that, with exposure time, the modified n-GaAs surfaces gave higher I_{sc} values than the unmodified surfaces. At 25 °C, Fig. 5a, the polysiloxane-modified surface has a value of I_{sc} four times that for the unmodified surface, when measured after 80 min exposure time. The n-GaAs/MnP/polysiloxane showed a rather higher I_{sc}, with about eight times that of the unmodified surface. At 35 °C the unmodified n-GaAs surface completely degraded after 200 min of exposure time. The n-GaAs/MnP/polysiloxane electrode showed a higher stability to photo-degradation, showing higher I_{sc} readings for longer times, Fig. 5b. The stabilizing effect of the MnP/polysiloxane is pronounced at tem-

peratures of 35 °C or lower. At higher temperatures, 45 °C, the modified and the unmodified surfaces showed a greater tendency to degrade than at lower temperature, as shown in Fig. 5c.

The stabilizing effect of the MnP/polysiloxane matrix is presumably due to two factors. Firstly, we speculate that the MnP/polysiloxane matrix prevents air oxidation of the semiconductor surface. The polymer film possibly lowers the water activity at the n-GaAs surface, thus slowing down the rate of photo-oxidative corrosion at the surface. This accounts for the fact that the MnP-free polymer matrix stabilizes the surface. Secondly, the MnP ions stabilize the surface as charge-transfer catalysts. The presence of the MnP, in both its Mn^{II}/Mn^{III} forms, furnishes an additional redox couple in close proximity with the SC surface. Cyclic voltammetry of MnP anchored to indium tin oxide and Pt electrodes, indicated that the MnP has an oxidation potential of -0.10 V and a reduction potential of -0.22 V (SCE, using pH range 6.5–7.0 under the same experimental conditions). The oxidation potential for the MnP couple is less positive (more negative) than that for the holes generated in the valence band (-0.1 V for the unmodified n-GaAs, and $+0.1$ V for the modified n-GaAs surface, vs. SCE, pH 7) [21]. Therefore, the holes will move upwards to oxidize the Mn^{II}P to Mn^{III}P$^+$. The Mn^{III}P$^+$ species will in turn convey the positive charge to another solution Fe(CN)$_6^{4-}$ ion to produce Mn^{II}P and Fe(CN)$_6^{3-}$.

The oxidation process, taking place by the holes coming from the valence band (VB), is accompanied by a reduction reaction taking place by the electrons coming from the conduction band (CB), where the Fe(CN)$_6^{3-}$ is reduced to Fe(CN)$_6^{4-}$. Eqs. (1)–(3) summarize all the reactions taking place at the solid | liquid
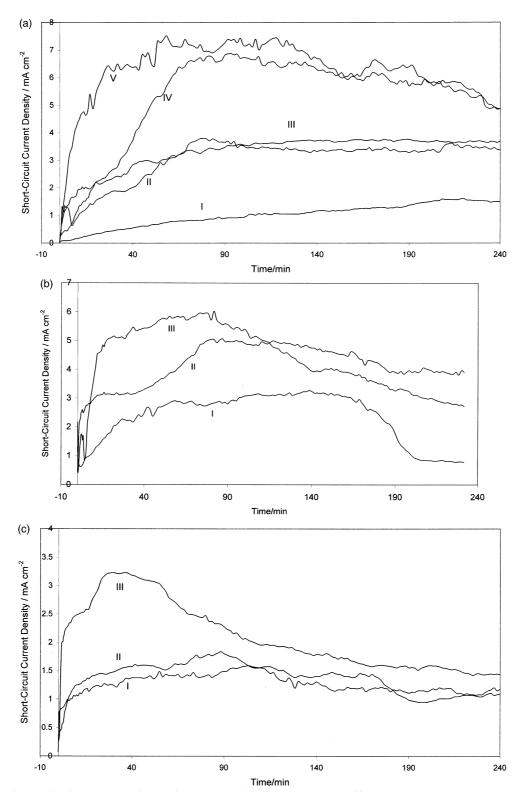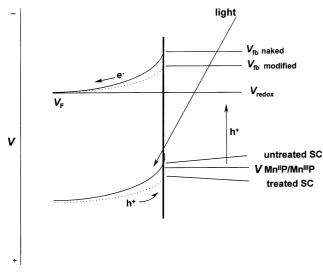
Fig. 5. (a) Plots of short-circuit current density vs. time measured for n-GaAs: (I) unmodified electrode; (II) non-annealed polymer-modified electrode; (III) annealed polymer-modified electrode; (IV) non-annealed MnP/polymer-modified electrode; and (V) annealed MnP/polymer-modified electrode. All measurements were conducted at 25 °C in the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system under illumination with a Xe lamp (illumination intensity at the electrode surface 0.1013 W cm^{-2}). (b) Plots of short-circuit current density vs. time measured for n-GaAs: (I) unmodified electrode; (II) polymer-modified electrode; and (III) MnP/polymer-modified electrode. All measurements were conducted at 35 °C in the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system under illumination with a Xe lamp (illumination intensity at the electrode surface 0.1013 W cm^{-2}). (c) Plots of short-circuit current density vs. time measured for n-GaAs: (I) unmodified electrode; (II) polymer-modified electrode; and (III) MnP/polymer-modified electrode. All measurements were conducted at 45 °C in the water/LiClO$_4$/Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ system under illumination with a Xe lamp (illumination intensity at the electrode surface 0.1013 W cm^{-2}).

Scheme 2.

that the attachment of ferrocene to n-Si surfaces stabilized them to photo-degradation in aqueous $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ systems. The ferrocene is considered as a mediator that kinetically favors the charge transfer to the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox couple rather than to the SC surface.

It should be noted here that the MnP redox couple itself is stable under the applied potential ranges used throughout this work. Cyclic voltammetric plots have been measured for the solid state and solution phases of the MnP complex, and these indicated that it is stable in the ranges -0.7 to $+0.7$ V or wider [3,15,16]. Exposure of the MnP/polysiloxane-modified electrodes, to high-intensity illumination of 0.1013 W cm^{-2}, for up to 4 h, indicated no change in the MnP/polysiloxane matrix. Exposure for longer times, under high-intensity illumination, indicated that the matrix suffered some degradation. This was accompanied by a color change in the matrix, with green spots appearing. This was attributed to possible permeation of the aqueous phase inside the matrix, which causes degradation of the n-GaAs surface. This is presumably the reason for the lowering in the electrode efficiency of the electrodes, as shown in Fig. 5a–c. This indicates that the n-GaAs surface experienced photo-degradation, as the aqueous phase reached the semiconductor surface.

3.4. Cell efficiency

Despite the lowering in the values of V_{oc}, the light-to-current conversion efficiency of the electrode was enhanced by modification. The measured maximum cell power [short-circuit current density (A cm^{-2}) × potential (V)], measured in W cm^{-2}, was calculated at different times of exposure to illumination. The cell efficiency [measured power (W cm^{-2})/incident power (W cm^{-2}) × 100%] was then calculated for the modified and unmodified n-GaAs surfaces under different times of exposure. Table 2 shows values of cell efficiencies for different electrodes measured at different times of exposure. The results indicate that with time the efficiency for the MnP/polysiloxane modified electrode is en-

interface. The positive charges created in the bulk of the MnP/polysiloxane matrix (Eq. (1)) will be accompanied by ClO_4^- counter anions, coming from the solution. On the other hand, the additional negative charges created by Eq. (3) will be equilibrated by the remaining excess solution cations (Li$^+$). Therefore, there is no net imbalance in the cation or anion species. The only overall result of Eqs. (1)–(3) is electric current flow.

$$[Mn^{II}P] + h^+ \rightarrow [Mn^{III}P]^+ \tag{1}$$

$$[Mn^{III}P]^+ + [Fe(CN)_6]^{4-} \rightarrow [Mn^{II}P] + [Fe(CN)_6]^{3-} \tag{2}$$

$$[Fe(CN)_6]^{3+} + e^- \rightarrow [Fe(CN)_6]^{4-} \tag{3}$$

In this respect, the MnP behaves as a charge-transfer catalyst that would speed up hole transfer to oxidize $Fe(CN)_6^{4-}$. The enhanced transfer of holes from the accumulation region is a key factor for the MnP role in stabilizing the SC surface. This explains why the MnP enhances both the I_{sc} and the stability of n-GaAs as depicted in Fig. 5a–c. Scheme 2 summarizes these discussions. Similar proposals have been suggested for other semiconductor surfaces. The literature [24] shows

Table 2
Values of cell conversion efficiency for different n-GaAs electrodes

Electrode [a]	Cell efficiency/% at different times/min					
	40	80	120	160	200	240
Naked n-GaAs	0.31	0.5	0.61	0.72	0.86	0.87
n-GaAs/polymer	1.24	2.35	2.12	2.08	2.10	2.08
n-GaAs/MnP/polymer	1.74	3.15	2.97	2.81	2.72	2.26

[a] All measurements were conducted in the water/LiClO$_4$/Fe(CN)$^{3-}$/Fe(CN)$^{4-}$ system at 35 °C using a 50 W Xe lamp, with a 0.1013 W cm^{-2} measured light-power intensity at the electrode surface. Cell maximum output power was calculated approximately by multiplying the measured I_{sc} (at 0.0 V) by the corresponding V value for the same electrode. The conversion efficiency was calculated by dividing the maximum output power by illumination intensity.

hanced. Up to a five-fold enhancement in cell efficiency was observed after 80 min of exposure. This enhancement of the efficiency is due to the photocurrent enhancement discussed earlier for the modified electrode. The lowering in the value of the V_{oc}, which should lower the value of the measured output power by about 30%, was compensated for by an eight-fold increase in the value of the short-circuit current density. As a net result, the cell efficiency was highly enhanced by modification with Mn/polysiloxane. The polysiloxane modified n-GaAs also showed some enhancement in cell efficiency, but to a lesser extent, Table 2.

4. Conclusions

Modification of n-GaAs surfaces with MnP/polysiloxane has improved the SC characteristics at the solid | liquid interface in PEC experiments in many aspects. n-GaAs wafers, modified with MnP/polysiloxane matrices, showed higher stability to degradation under PEC conditions (both in the dark and under illumination) without sacrificing the value of the short-circuit current density. The cell efficiency was significantly enhanced by modification. The lowering in the value of V_{fb} of the modified semiconductor was compensated for by the enhancement of the short-circuit current densities. The polymer layer adhered perfectly to the semiconductor surface without peeling off. Annealing the modified n-GaAs surface added further enhancement to its characteristics.

Additional work is underway, in this laboratory, using CdS, CdSe, GaInP$_2$ and other PEC photocatalyst materials, known to be good candidates for PEC processes, such as water splitting.

Acknowledgements

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