# Suppression of Band Edge Migration at the p-GaInP<sub>2</sub>/H<sub>2</sub>O Interface under Illumination via Catalysis

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The band edges of p-GaInP<sub>2</sub> are observed to migrate toward negative potentials during current flow under illumination in solutions with pH ranging from 1 to 14.5. The migration is not caused by a change in the pH of the semiconductor microenvironment but is a result of accumulation of photogenerated electrons at the p-GaInP<sub>2</sub>/water interface due to poor interfacial kinetics. This less than optimal interfacial charge-transfer rate can be catalyzed by treating the surface with transition-metal ions (e.g., Ru<sup>III</sup>, Rh<sup>III</sup>, Co<sup>III</sup>, Os<sup>III</sup>) which results in a suppression of band edge migration. As compared to an unmodified p-GaInP<sub>2</sub> surface, the metal-ion treatment does not induce any appreciable band edge shift in the dark but effectively suppresses the band edge migration under illumination. Ru<sup>III</sup> and Rh<sup>III</sup> are found to act as better hydrogen-evolution catalysts than electrodeposited Pt.

## Introduction

Photoelectrochemical splitting of water to produce hydrogen and oxygen using sunlight is a promising application of semiconductor electrochemistry, with increasing relevance in the present times of heightened environmental consciousness. To obtain a stable and efficient practical semiconductor based system, four criteria must be simultaneously satisfied. The band gap of the semiconductor must be greater than 1.7 eV, the band edges of the semiconductor must overlap the H<sub>2</sub>/H<sub>2</sub>O and O<sub>2</sub>/ H<sub>2</sub>O redox potentials *under*  $H_2/O_2$  *evolution condition*, and charge transfer across the semiconductor-liquid interface should be fast (Figure 1). In addition, the semiconductor surface should be chemically stable in the aqueous media.

Although p-type GaInP<sub>2</sub> with a band gap of 1.8-1.9 eV has been identified as a promising photocathode for water splitting, its band edges are 0.2-0.4 V too negative to effect photoelectrolysis.<sup>1-3</sup> Electrochemical investigations of GaInP<sub>2</sub> in aqueous media have found that the semiconductor surface is unstable and susceptible to corrosion.<sup>4</sup> Furthermore, it is not known if the charge-transfer rate from p-GaInP<sub>2</sub> to water under illumination is sufficiently high or if this rate can be further catalyzed.

Previously, Kocha et al. carried out surface modification of GaInP<sub>2</sub> to shift the semiconductor band edges positive.<sup>2,3</sup> Capacitance–voltage (C-V) measurements in the dark and current–voltage (I-V) measurements under illumination indicated that the GaInP<sub>2</sub> band edges could be shifted up to 0.3 V positive by adsorbing 8-quinolinol to the GaInP<sub>2</sub> surface. However, their attempts to split water with the quinolinol-modified surface proved unsuccessful. It was speculated that further treatment with a catalyst was necessary to lower the hydrogen and oxygen evolution overpotentials before photoelectrolysis of water could be achieved. That work implicitly assumed that during hydrogen evolution under illumination, the band edges of GaInP<sub>2</sub> remained in the same energetic position as in the dark.

At present, however, there is no information on the energetics (position) of the band edges or on the kinetics of charge transfer at the p-GaInP<sub>2</sub>/water interface under illumination, i.e., under conditions of H<sub>2</sub> evolution. Several impedance measurements in the literature have previously reported that band edges of semiconductors are not fixed with respect to the reference in the solution and are prone to migration under illumination.<sup>5–15</sup> These changes in flatband potential under illumination have been interpreted to indicate evidence of surface effects such as charge trapping, adsorption, or changes in the surface chemistry. The band edge positions are also known to be strongly affected by interfacial kinetics under illumination.9,11 Increased band edge migration as a result of illumination has been observed for interfaces with poor interfacial charge-transfer ability, and this migration has been suppressed by treating the semiconductor surfaces with transition-metal catalysts.<sup>10,16</sup>

In this paper we describe our work on evaluating the effect of interfacial kinetics on the energetics of the p-GaInP<sub>2</sub>/water interface by determining the band edge positions of bare p-GaInP<sub>2</sub> surfaces under illumination, i.e., under conditions of H<sub>2</sub> evolution. Capacitance-voltage (C-V) and current-voltage (I-V) measurements were done under various levels of illumination, in aqueous solutions of various pH to evaluate the extent of band edge migration. In addition, we describe the results of C-V and I-V measurements on p-GaInP<sub>2</sub> surfaces modified with transition-metal ions to evaluate their effectiveness as reagents for inducing band edge shifts in the dark and as electrocatalysts for suppressing band edge migration under illumination. In this study, the flow of photogenerated cathodic current at the semiconductor surface under illumination corresponds to generation of hydrogen from photoelectrolysis of water.

Note: A semiconductor surface treatment, such as the adsorption of a transition-metal ion, can have two distinct effects on the energetics of the interface as described below. Because of change of net charge in the Helmholtz layer, adsorption of a transition metal as a charged species (ion) on the semiconductor surface can change the band edge position relative to the band edge position for an underivatized surface—the band edge

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ECB



**Figure 1.** (a) Band gap criteria: The band gap of the semiconductor must be greater than 1.7 eV.  $\eta_a$  and  $\eta_c$  indicate anodic and cathodic overpotentials for electrode reactions, respectively. (b) Band edge overlap criteria: The band edges of the semiconductor must overlap the H<sub>2</sub>/H<sub>2</sub>O and O<sub>2</sub>/H<sub>2</sub>O redox potentials under H<sub>2</sub>/O<sub>2</sub> evolution condition. (c) Fast kinetics criteria: Charge transfer across the semiconductor—liquid interface must be fast. For a successful hydrogen-producing PEC system, all three criteria must be simultaneously satisfied.

positions for both the derivatized and the underivatized surfaces being compared vs a solution reference in the dark. This effect is referred to as band edge "shift" or flatband "shift" in this paper. On the other hand, the measured band edge position vs a solution reference can also move as a result of illumination due to accumulation of photogenerated charges at the interface. This movement is not due to a change in the charge in the Helmholtz layer. Its extent is determined by the level of illumination at the semiconductor surface and the interfacial charge-transfer kinetics. This movement can be suppressed if the transition-metal species acts as an electrocatalyst and catalyzes charge transfer across the interface, thereby reducing the accumulation of charge at the interface. In this paper, the movement of band edges due to photoelectron accumulation is referred to as "migration". In measuring the "migration" effect, the band edge position of a surface under a given level of illumination is compared with the band edge position for *the same surface* in the dark. Although both of these effects have been individually described in the literature as "shifts" of band edges,<sup>5–15</sup> we have used the terms "shift" and "migration" in this paper to distinguish between the two.

## **Experimental Section**

**Materials.** The zinc-doped 3  $\mu$ m thick p-type Ga<sub>0.51</sub>In<sub>0.49</sub>P epilayers, henceforth referred to as the p-GaInP<sub>2</sub> epilayers, were grown by atmospheric-pressure organometallic vapor-phase epitaxy on approximately 350 µm thick Zn-doped GaAs substrates misoriented from the (100) surface by 2° toward (110). A growth temperature of 700 °C, growth rate of 4  $\mu$ m/h, and phosphine pressure of 4.5 Torr were used.<sup>17</sup> The carrier concentration in the GaInP<sub>2</sub> layer was  $(6-12) \times 10^{16}$  cm<sup>-3</sup>. Ohmic contacts were made by electrochemically depositing gold onto the unpolished backsides of the substrate. The wafers were then cut into small pieces and were attached to a wire using electrically conductive silver epoxy (H-31, Epoxy Technology Inc.). After curing the Ag epoxy in an oven at 80 °C for a few hours, the backside and edges of the electrode were sealed with a nonconducting epoxy (Hysol 9462, Dexter Corp.), leaving only the polished surface  $(0.1-0.2 \text{ cm}^2)$  of the crystal exposed. All electrodes were etched in concentrated H<sub>2</sub>SO<sub>4</sub> for durations between 5 and 60 s before electrochemical measurements.

**Chemicals.** KOH (J. T. Baker), concentrated  $H_2SO_4$  (J. T. Baker), and  $K_2SO_4$  (Aldrich) were used as received. Phthalate (pH 4), phosphate (pH 7), and carbonate (pH 10) buffer solutions were obtained from Beckman. OsCl<sub>3</sub>, RuCl<sub>3</sub>, RhCl<sub>3</sub>, Co(NH<sub>3</sub>)<sub>6</sub>-Cl<sub>3</sub>, and K<sub>2</sub>PtCl<sub>6</sub> were obtained from Strem and used as received. All metal-ion solutions were made with house deionized water.

Metal-Ion Treatment. For metal-ion chemisorption, 0.010 M solutions of OsCl<sub>3</sub>, RuCl<sub>3</sub>, and RhCl<sub>3</sub> were made from dilute HCl (pH 1.5), while a 0.010 M solution of Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> was made in 0.010 M KOH(aq) (pH 12.0). A pH 1.5 solution was made of 7.7 mM K<sub>2</sub>PtCl<sub>6</sub> using H<sub>2</sub>SO<sub>4</sub>. In a typical metal-ion (Ru<sup>III</sup>, Rh<sup>III</sup>, Os<sup>III</sup>, Co<sup>III</sup>) treatment, a p-GaInP<sub>2</sub> electrode was etched in concentrated H<sub>2</sub>SO<sub>4</sub> for 60 s, dried in a stream of nitrogen, and was immediately immersed in a metal-ion solution. After 60 s, the electrode was emmersed, rinsed with housedistilled water, and blown dry under a stream of nitrogen. Upon immersion of these electrodes in 3 M KOH solution for electrochemical measurements, some metal-ion compound was observed to desorb off the epoxy and into the solution. Fresh 3 M KOH solution was used for each experiment to avoid any trace metal cross-contamination. Pt was electrodeposited by electrochemically biasing the p-GaInP<sub>2</sub> electrode in the K<sub>2</sub>PtCl<sub>6</sub> solution at -1.0 V vs SCE for approximately 15 s under illumination, corresponding to a reductive current density of  $\sim 1 \text{ mA/cm}^2$ . No hydrogen bubbles were seen to evolve during Pt deposition. The p-GaInP<sub>2</sub> surfaces, which were only etched and were not immersed in any metal-ion solution, are referred to as "untreated" surfaces.

**Electrochemical Measurements.** Capacitance–voltage (C–V) and current–voltage (I–V) measurements were performed in a conventional three-electrode setup to deconvolute the effects of counter electrode kinetics from those of the semiconductor electrode. The setup consisted of a p-GaInP<sub>2</sub> working electrode (~0.08–0.13 cm<sup>2</sup>), Pt gauze (~2 cm<sup>2</sup>) counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The samples were illuminated with a fiber optic illuminator housing an EKE type 150 W tungsten–halogen lamp. Data were collected using a Solartron 1286 Electrochemical Interface connected to a Solartron SI 1260 Impedance/Gain-Phase

## **SCHEME 1**



Analyzer. Simultaneous C-V and I-V measurements were made at a frequency of 10 kHz with a 20 mV p-p ac amplitude and a scan rate of 20 mV/s. For measurements in the dark, data were usually collected in a potential window of ~1.3 V. The limits of this window with respect to SCE depended upon the pH of the solution and ranged from -1.7 to +0.3 V vs SCE. The negative end of the scan window was extended up to -2.5V, as necessary, for collecting data under illumination. Since the instrument measured the ac and the dc current signals across the same resistor, the current sensitivity of the setup had to be adjusted as necessary for higher light intensities, and therefore the C-V data for higher light intensities are less accurate than those at lower light intensities or in the dark.

**Impedance Data Analysis.** A detailed impedance analysis of the p-GaInP<sub>2</sub>/water system in the dark has been previously reported, in which capacitance data in the frequency range 500  $\leq f \leq 10^5$  Hz, were attributed to the space charge layer of the semiconductor.<sup>3</sup> For the purpose of this study the series *RC* circuit (Scheme 1), where  $R_s$  is the series resistance of the circuit and  $C_{sc}$  is the capacitance of the space charge region, was deemed as the simplest circuit that could adequately describe the trends in the movement of the flatband potential under illumination.<sup>18</sup> The slope and *x*-axis intercept of the Mott–Schottky plots were used to determine dopant density and the flatband potentials, respectively.

#### Results

**Flatband Potentials of Etched p-GaInP<sub>2</sub>/Water Interfaces.** Figure 2 shows three representative Mott–Schottky plots for etched p-GaInP<sub>2</sub> electrodes immersed in 0.20 M K<sub>2</sub>SO<sub>4</sub> solutions of pH 1, 7, and 13. Data collected at each pH in the dark and under illumination show a negative migration of the flatband potential with increasing levels of light intensity. Figure 3a shows the corresponding flatband potentials calculated from similar Mott–Schottky plots for five different pH values. The curves for pH 1 and 13 were measured in unbuffered solutions of 0.20 M K<sub>2</sub>SO<sub>4</sub>, which were made acidic or basic using the necessary amount of H<sub>2</sub>SO<sub>4</sub> or KOH, respectively. The curves for pH 4, 7, and 10 were measured in commercial phthalate (pH 4), phosphate (pH 7), and carbonate (pH 10) buffer solutions.

Figure 3b shows the same data as the net migration of the flatband potentials measured vs the values observed in the dark. It is seen that even at low levels of illumination, e.g.,  $\sim 0.1 \text{ mA/cm}^2$ , the GaInP<sub>2</sub> flatband potentials (band edges) move up to 0.3 V negative as compared to their positions in the dark. As the level of illumination is increased, the negative migration of the band edges becomes more pronounced, with values reaching almost 1.0 V for current densities around 10 mA/cm<sup>2</sup>.

Effect of Transition-Metal Ions on the Flatband Potential of the p-GaInP<sub>2</sub>/Water Interface in the Dark. Figure 4 shows the flatband potentials of p-GaInP<sub>2</sub> electrodes, measured in 3 M KOH solutions in the dark, which have been exposed to four different transition-metal-ion solutions before immersion in the KOH solution. In addition, data are also included for photoelectrochemically deposited Pt for comparison. No significant shifts in measured flatband potentials were observed in the dark as a result of treatment with the five transition metals. The maximum shift exhibited by the metal-ion-treated surface is  $\sim 0.05$  V.



Applied Potential, V vs. SCE

Figure 2. Mott–Schottky plots of p-GaInP<sub>2</sub> electrodes immersed in pH 1, 7, and 13, measured in the dark and under varying levels of illumination.

**Effect of Transition-Metal Ions on the Flatband Potential** of the p-GaInP<sub>2</sub>/Water Interface under Illumination. Figure 5 shows Mott-Schottky plots for an untreated and a Ru<sup>III</sup>-treated p-GaInP2 surface, measured in the dark and under illumination in 3 M KOH solution. Figure 6a shows the corresponding flatband potentials calculated from similar Mott-Schottky plots of etched and metal-ion-treated p-GaInP2 electrodes in the 3 M KOH solution. In addition, the figure also shows flatband potentials measured with a GaInP2 electrode modified with electrodeposited platinum. Figure 6b shows the same data as migration of the flatband potentials measured vs the values observed in the dark. While the etched only (untreated) surface exhibits significant migration of the flatband potential under illumination, the migration is significantly suppressed for the metal-ion-treated surfaces. Whereas, corresponding to a hydrogen evolution current density of 0.7-1.0 mA/cm<sup>2</sup>, the underivatized surface showed a -0.34 V migration in flatband potential with respect to its position in the dark and the Pt-coated electrode shows a -0.24 mV migration, the Rh<sup>III</sup>- and Ru<sup>III</sup>-treated surfaces showed only 0.08-0.09 V migration under similar conditions. Table 1 lists the flatband potentials  $(V_{\rm fb})$  observed for the underivatized and the metal-ion-treated surfaces in the dark and under illumination. The "light" data reported corresponds to a current density of 0.7-1.0 mA/cm<sup>2</sup>.

Effect of Transition-Metal Ions on the I-V Properties of the p-GaInP<sub>2</sub>/Water Interface. Figure 7 shows the effect of metal-ion treatment on the current–voltage properties of the



**Figure 3.** (a) Flatband potentials of etched p-GaInP<sub>2</sub> electrodes, measured vs SCE, at five different pH values for varying levels of illumination. (b) Migration of flatband potentials vs the  $V_{\rm fb}$  values observed in the dark ( $V_{\rm fb,light} - V_{\rm fb,dark}$ ) in solutions of five different pH.



Figure 4. Flatband potentials of untreated (etched only) and metalion-treated p-GaInP<sub>2</sub> electrodes in the dark in 3 M KOH solution.

untreated (etched only) and metal-ion-treated p-GaInP<sub>2</sub> electrodes in 3 M KOH solution. The metal-ion-treated surfaces exhibit improved fill factors and decreased hysteresis as compared to the untreated surface. The open circuit voltages ( $V_{oc}$ ) observed for the metal-ion-treated surfaces were generally more positive than the untreated surface. Table 1 lists the  $V_{oc}$  values observed for the underivatized and the metal-ion-treated surfaces for the positive and the negative going scans and corresponds to a current density of 0.7–1.0 mA/cm<sup>2</sup>.



**Figure 5.** Mott–Schottky plots for (a) an untreated and (b) a  $Ru^{III}$ -treated p-GaInP<sub>2</sub> surface, measured in the dark and under illumination in 3 M KOH solution.

## Discussion

A practical single semiconductor photoelectrochemical system for water splitting requires that the three conditions of band gap, band edge overlap, and fast kinetics must be simultaneously satisfied (Figure 1). The first two conditions are determined, respectively, by the energetics of the semiconductor and the semiconductor/liquid junction, while the third condition is determined by the kinetics of the reaction of interest at the interface. In the present case, the reaction of interest is generation of hydrogen from photoelectrolysis of water. From the above description it would seem that in a p-type semiconductor/liquid junction cell, the first two conditions would be the only necessary and sufficient conditions for H<sub>2</sub> evolution at the semiconductor interface. However, we have shown here that fast interfacial kinetics is also a necessary condition for any significant amount of hydrogen evolution. The kinetics of interfacial charge transfer strongly affects the energetics of a semiconductor/liquid junction. Furthermore, we have shown (as also have others  $\hat{7}^{-15,\tilde{19}-21}$ ) that it is erroneous to assume that the band edge positions of the semiconductors remain in the same position during current flow under illumination as in the dark, except perhaps for interfaces with extremely fast interfacial charge-transfer rates. This realization is significant for GaInP<sub>2</sub> because it implies that any surface modification that is applied to shift semiconductor band edges to achieve band edge overlap must also not compromise interfacial kinetics or else any band edge shifts could be nullified by band edge migration under illumination.<sup>2,3</sup>

Mott-Schottky measurements described above show that the band edges (flatband potentials) of p-GaInP<sub>2</sub> migrate toward negative potentials, under illumination. We attribute this migration to the accumulation of photogenerated electrons at the p-GaInP<sub>2</sub>/water interface due to poor interfacial charge-transfer



Flatband Potential Migration, V

**Figure 6.** (a) Flatband potentials of untreated (etched only) and metalion-treated p-GaInP<sub>2</sub> electrodes under illumination in the 3 M KOH solution. (b) Migration of flatband potentials vs the  $V_{\rm fb}$  values observed in the dark ( $V_{\rm fb,light} - V_{\rm fb,dark}$ ) in 3 M KOH solution.

 TABLE 1: Capacitance–Voltage and Current–Voltage

 Measurements on Untreated and Metal-Treated p-GaInP2

 Surfaces in 3 M KOH Solution

	V <sub>fb,dark</sub> , V vs SCE	V <sub>fb,light</sub> , <sup>a</sup> V vs SCE	$\Delta V_{ m fb}$ , <sup>b</sup> V	$V_{\rm oc,p}$ , <sup>c</sup> V vs SCE	V <sub>oc,n</sub> , <sup>c</sup> V vs SCE
untreated	-0.19	-0.53	-0.34	-0.88	-0.52
Pt treated	-0.15	-0.39	-0.24	-0.67	-0.40
Ru <sup>III</sup> treated	-0.15	-0.24	-0.09	-0.67	-0.41
Os <sup>III</sup> treated	-0.14	-0.44	-0.30	-0.88	-0.37
Co <sup>III</sup> treated	-0.15	-0.38	-0.23	-0.77	-0.43
Rh <sup>III</sup> treated	-0.18	-0.26	-0.08	-0.64	-0.54

 $^a$   $V_{\rm fb}$  values measured at an illumination level corresponding to a current density of 0.7–1.0 mA/cm<sup>2</sup>.  $^b$  Band edge migration under illumination ( $V_{\rm fb,light}-V_{\rm fb,dark}$ ).  $^c$   $V_{\rm oc}$  values observed for positive (p) and negative (n) going scans corresponding to a current density of 0.7–1.0 mA/cm<sup>2</sup>.

kinetics.<sup>9,11,13–15,19–21</sup> At higher light intensities, as more current is forced through the interface, a greater equilibrium concentration of electrons is required to maintain that current and, hence, the band edge migration increases with light intensity.

Alternatively, at least some of the negative movement of the flatband potential observed under illumination could also be attributed to a change in the pH of the microenvironment of the semiconductor electrode surface.<sup>22</sup> At a p-type semiconductor, hydrogen evolution at the interface under illumination is accompanied by the generation of OH<sup>-</sup> (or consumption of H<sup>+</sup>). The reaction at the interface can be represented as

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$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-(base)$$
 (1)

$$\mathrm{H}^{+} + \mathrm{e}^{-} \rightarrow \frac{1}{2}\mathrm{H}_{2}(\mathrm{acid}) \tag{2}$$

Increased basicity (decreased acidity) of the semiconductor electrode microenvironment can manifest itself as a negative movement of flatband potentials when measured against a pH insensitive electrode like the SCE.<sup>8,22</sup>

Both electron accumulation and OH<sup>-</sup> formation (H<sup>+</sup> consumption) can cause a negative movement in the position of the semiconductor band edges and this movement is exacerbated for both processes by increasing light intensity (Figure 8). Fortunately, the two effects can be distinguished. As shown in Figure 8a, a pH change displaces the semiconductor band edges and the H<sub>2</sub>/H<sub>2</sub>O and O<sub>2</sub>/H<sub>2</sub>O redox potentials in the same direction and roughly by the same amount for a pH sensitive semiconductor surface like p-GaInP2.1 In contrast, as shown in Figure 8b, electron accumulation at the surface displaces only the semiconductor band edges negative and does not move the solution redox potentials. In other words, while a pH change does not move the band edge position with respect to the hydrogen and oxygen evolution potentials, accumulation of photogenerated electrons does. Differentiating between the two is important because if, as a result of surface modification, the "band edge overlap condition" can be achieved in the dark, then it will not be affected when the interfacial pH changes as a result of illumination (Figure 8a), whereas it will be affected by electron accumulation (due to poor interfacial charge-transfer kinetics) under illumination (Figure 8b).

To minimize the effects of pH change of the semiconductor microenvironment in our study, the experiments were done either in highly acidic or basic solutions or in buffered solutions. It is expected that at extreme pH values, the change in pH due to generation of base via reaction 1 or consumption of acid via reaction 2 would be minimal due to the high buffering capacity arising from high concentrations of  $OH^-$  and  $H^+$  ions in the solution, respectively. Hence, at these extreme pH values, the displacement of the band edge due to illumination can be attributed primarily to poor rate of charge transfer across the GaInP<sub>2</sub>/water interface. For the intermediate pH region, both phenomena can be significant. Therefore, for intermediate pH values buffered solutions were used to maintain the pH of the electrode microenvironment at values similar to the pH of the bulk solution.

Figures 2 and 3 show that the band edge positions of p-GaInP<sub>2</sub> in water are highly dependent on the level of illumination of the electrode irrespective of the pH of the solution. Even at low short circuit current densities  $(J_{sc})$  corresponding to low light intensities, where the change in the pH of the electrode microenvironment can be considered negligible, a negative migration of the flatband potential of up to 0.3 V is observed as compared to its value in the dark. This migration is further enhanced by as much as 1.0 V at higher  $J_{sc}$  values, suggesting strong accumulation of photogenerated electrons at the interface.<sup>9,11,13–15,19–21</sup> Another point of note is that the migration of flatband potential is greater for pH 13 than for pH 1 (Figure 3b). This difference in the extent of migration is not unexpected, as the charge-transfer reaction here corresponds to hydrogen production and it is well-known that hydrogen production is more facile in acidic solutions than in basic solutions of similar concentrations, especially at an uncatalyzed surface.

Further proof that these displacements of flatband potentials are not due to changes in the pH of the electrode microenvironment comes from data in Figures 5 and 6. Negative



Figure 7. Current–voltage (I-V) curves observed for untreated and metal-ion-treated p-GaInP<sub>2</sub> electrodes in 3 M KOH solution.



**Figure 8.** (a) A pH change displaces the semiconductor band edges and the  $H_2/H_2O$  and  $O_2/H_2O$  redox potentials in the same direction and roughly by the same amount for a pH sensitive semiconductor surface (e.g., p-GaInP<sub>2</sub>). (b) Electron accumulation at the surface moves only the semiconductor band edges negative and does not move the solution redox potentials. Both sides of each figure are shown at the same band bending (capacitance). The dashed line indicates the potential of a pH insensitive reference electrode (e.g., SCE).

migrations of flatband potential are also seen for the etched p-GaInP<sub>2</sub> surface in the highly basic 3 M KOH solutions (Figure 6, open circles), where one would not expect any further basification of the electrode microenvironment as a result of

OH<sup>-</sup> production via reaction 1.<sup>22</sup> The suppressed migration observed on ruthenium- and rhodium-treated surfaces (Figure 6) further supports the argument that the primary cause of band edge migration here is electron accumulation and not a change in the interfacial pH.<sup>10</sup> Note that in addition to the arguments presented above, when data from the metal-ion-treated surfaces are compared with the data obtained from the untreated surface in the same solution and at the same photocurrent density, any residual effects of surface pH change are further nullified. This truly allows us to attribute any band edge migration effects to poor interfacial charge-transfer kinetics. These results clearly indicate that the charge-transfer rate from etched p-GaInP<sub>2</sub> to water is significantly less than optimal and must be further catalyzed. In fact, these results underscore the necessity of catalyzing charge transfer across the p-GaInP<sub>2</sub>/water interface in order to suppress the undesired migration of the band edges under illumination.

It is well-known that metal ions deposited onto semiconductor electrodes act as effective catalysts for transferring charges across a semiconductor/liquid interface.<sup>10,16,23-39</sup> Transition-metal-ion treatment has been shown to increase the charge-transfer rate at the InP/water interface,<sup>16,24-27</sup> CdTe/Sn<sup>2+/4+</sup> interface,<sup>28-31</sup> GaP/water interface,<sup>32-34</sup> and the GaAs/Se<sup>-/2-</sup> (aq) interface.<sup>10,35-39</sup> Figures 5–7 show that this catalytic behavior is applicable to the p-GaInP<sub>2</sub>/water interface also. In fact, all four metal ions used in this study were found capable of electrocatalysis, albeit to different extents, as evident by the decrease in the band edge migration under illumination.

Since electrodeposited platinum has been widely used as a hydrogen evolution catalyst in the literature,  $^{16,26,34,40-44}$  we compared its effectiveness with the four transition-metal ions evaluated in this study. It was observed (Figure 6) that ruthenium and rhodium deposited in an electroless manner exhibited the greatest catalytic effect, even greater than electrochemically deposited platinum. The catalytic effect of the metal-ion treatment was also apparent as the improvement in the fill factors and a decrease in hysteresis of the *I*–*V* curves in Figure 7.<sup>10,37,39</sup>

The flat-band potential and, therefore, the energetics of the band edges of any semiconductor/electrolyte system are controlled by the charge in the Helmholtz inner layer. Any change in the charge in that layer changes the measured flat-band potential and subsequently the energetics of the band edges. The variation of the semiconductor flat-band potential with pH is due to the change in the adsorbed charge ( $H^+$  and  $OH^-$ ) on the electrode surface. Adding negative charge (such as  $OH^-$  ions) shifts the bands to more negative potentials, whereas adsorption of a positive charge (such as  $H^+$  ions) shifts the bands positive.

Transition-metal ions can also shift the flatband potential and, therefore, the band edge positions by adsorption of ionic charges at the semiconductor surface (within the Helmholtz layer).<sup>10</sup> In contrast to significant catalytic effects (vide supra), the metalion treatment in our experiments did not exhibit any significant band edge shifts in our study. The maximum shift exhibited by the metal-ion-treated surface in the dark was ~0.05 V, which is significantly less than the 0.2–0.4 V required for unassisted photoelectrolysis (Figure 4, Table 1). The ~0.05 V shift is within the experimental error and indicates that the metal-ion treatment described here cannot be used to affect band edge shift at the GaInP<sub>2</sub> electrodes to achieve the "band edge overlap" condition required for unassisted photoelectrolysis (Figure 1b).

The nature and amount of the catalyst at a semiconductor/ electrolyte interface is very important in determining the activity of the electrocatalyst. The coverage should be high enough to affect a high rate of hydrogen production and yet should not be so high as to impede light absorption by the semiconductor. Although the exact nature and the amount of the transitionmetal species adsorbed on the p-GaInP<sub>2</sub> surface is presently unknown, a previous study on a similar substrate (GaAs) suggests that the metal ions may be deposited as complexes, in submonolayer to a few monolayers amounts, via a redox reaction with the surface semiconductor atoms.<sup>38</sup> In any case, the lack of flatband shifts in the dark upon metal-ion treatment suggests that the metal complexes are present as overall neutral species on the GaInP<sub>2</sub> surface. If precious metals are to be used as catalysts for photoelectrochemical hydrogen evolution, it is important that the absolute minimum amount required for the highest catalysis be determined. Although the amount of catalyst deposited on the semiconductor surface has not been controlled or optimized in this study, it is clear that significant catalysis can be obtained even with near monolayer amounts of transitionmetal ions.

## Conclusions

This work shows that the p-GaInP<sub>2</sub> band edges migrate negatively under illumination in solutions with pH ranging from 1 to 14.5. The displacement is not due to a change in the pH of the semiconductor microenvironment but is caused by the accumulation of photogenerated electrons at the interface due to poor interfacial charge-transfer kinetics. Differentiating between the two is important for developing appropriate surface modification strategies to realize an effective water-photoelectrolysis system. From the experiments described above, it becomes imperative that any surface modification scheme used to achieve the "band edge overlap condition" must not compromise the charge-transfer kinetics at the interface. Our observations indicate a less than optimal rate of charge transfer across the p-GaInP<sub>2</sub>/water interface and underscore the necessity of catalysis at the p-GaInP<sub>2</sub>/water interface.

Treatment with transition-metal ions is found to effectively electrocatalyze transfer of photogenerated electrons from the semiconductor to the liquid and to arrest the undesired band edge migration under illumination. p-GaInP<sub>2</sub> electrodes treated with Ru<sup>III</sup>, Rh<sup>III</sup>, Co<sup>III</sup>, and Os<sup>III</sup> ions exhibit improved fill factors

and small positive increases in the  $V_{oc}$ . Light-limited current levels are reached at lower applied voltages. Ru<sup>III</sup> and Rh<sup>III</sup> treatments are found to suppress band edge migration better than electrochemically deposited platinum treatment, which is widely used as a hydrogen evolution catalyst in the literature. The observation that even the best catalysts of this study (Ru<sup>III</sup> and Rh<sup>III</sup>) show ~0.25 V band edge migration at a current density of ~10 mA/cm<sup>2</sup> suggests that other catalysts can be identified that can support higher currents through the interface without causing appreciable band edge migration. Details of such work will be reported shortly.

Although the metal-ion treatment does not shift the band edges of p-GaInP<sub>2</sub> positive enough to affect unassisted photoelectrolysis, nevertheless, it can be applied to tandem cell designs where it can reduce the voltage assistance required by the p-GaInP<sub>2</sub> top layer to split water, thereby increasing the efficiency (by decreasing the energy input required) of assisted hydrogen production.<sup>44</sup> Work in this area is currently in progress.

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