

## Band Edge Engineering of GaInP<sub>2</sub> for Photoelectrochemical Water Splitting

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Much research is being performed to find ways to efficiently split water with sunlight using semiconductor electrodes in a photoelectrochemical cell. P-type GaInP<sub>2</sub> is a good prospect as an electrode material because of its favorable bandgap and photovoltaic properties. However, its band edges do not overlap the water redox potentials, so that without modification the material cannot be used to split water (1). In this work various metalloporphyrins were applied to the GaInP<sub>2</sub> surface in an effort to shift the band edges into a favorable position for water splitting (2). The metal centers of the molecules were also chosen to help catalyze charge transfer from the semiconductor to the electrolyte.

Over 30 different metalloporphyrins have been tested by our group as surface treatments for GaInP<sub>2</sub>. In this paper six different porphyrins were evaluated carefully for their effect as a function of treatment procedure and electrolyte pH.

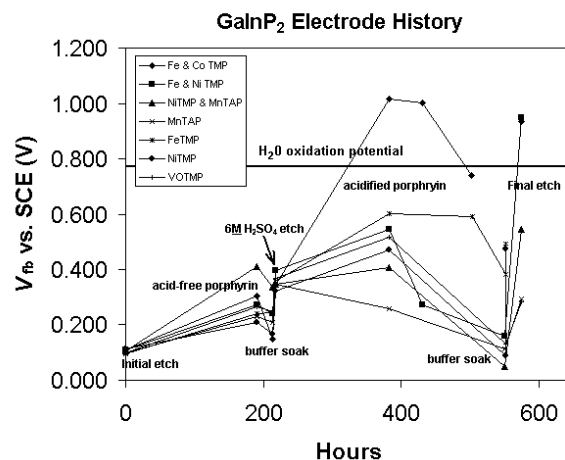
One  $\mu\text{m}$  thick epilayers of zinc doped p-type Ga<sub>0.51</sub>In<sub>0.49</sub>P (abbreviated GaInP<sub>2</sub>) were produced by atmospheric pressure metal organic chemical vapor deposition. The acceptor concentration in the GaInP<sub>2</sub> was about  $8 \times 10^{16} \text{ cm}^{-3}$ . The back surface of the wafer was coated with gold and attached with silver colloidal paint to a copper coil. The wafer was encased in nonconducting epoxy and attached to a glass tube to form an electrode with only the GaInP<sub>2</sub> surface in contact with the solution.

Figure 1 shows the flat band potential  $V_{\text{fb}}$  as a function of time during a series of porphyrin treatments and H<sub>2</sub>SO<sub>4</sub> acid etches. The  $V_{\text{fb}}$  values were determined by Mott-Schottky analysis at 10 kHz with a 10 mV rms AC voltage. The electrodes were exposed to a series of different acid and porphyrin treatments and buffer soaks, with periodic tests to monitor the  $V_{\text{fb}}$ . From this series of tests it was determined that 6 M H<sub>2</sub>SO<sub>4</sub> does not return the GaInP<sub>2</sub> surface to a pristine state. Concentrated H<sub>2</sub>SO<sub>4</sub> had previously been shown to restore the surface (3), but the final etch in this experiment was ineffective, apparently due to electrode damage after several weeks of treatment. Adding a small amount of H<sub>2</sub>SO<sub>4</sub> to the porphyrin solution enhances the shift in  $V_{\text{fb}}$ . Soaking the electrode in pH 7 buffer for extended periods decreases  $V_{\text{fb}}$ . Although several of the samples show a  $V_{\text{fb}}$  sufficiently high to split water, no water splitting was observed.

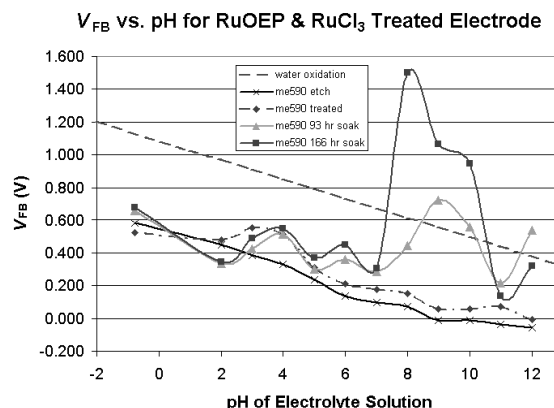
Figure 2 shows  $V_{\text{fb}}$  as a function of pH for GaInP<sub>2</sub> electrodes treated with ruthenium octaethylporphyrin (RuOEP) and RuCl<sub>3</sub> as follows. Immediately after etching for 10 s with concentrated H<sub>2</sub>SO<sub>4</sub> and rinsing in deionized water for 30 s, 3 drops of the 0.10 mM RuOEP in dichloroethane solvent are sequentially applied and allowed to evaporate. The electrode is then soaked in a 0.010 M solution of RuCl<sub>3</sub> for 60 s. An enhancement of  $V_{\text{fb}}$  in pH 3 and pH 4 buffers is seen, in agreement with earlier studies (4). However, the effect is not as large as previously observed, probably due to differences in

application procedures. In addition, after an extended soak in the buffer solutions the  $V_{\text{fb}}$  tends to decrease for low pH buffers and increase for high pH buffers. We do not have a satisfactory explanation for this phenomenon at this time. Since pH 2-4 are phthalate buffers, pH 5-8 are phosphate buffers, and pH 9-12 are carbonate buffers, the different observed effects in each pH range are likely due to reactions between the buffer salts and the metals that form insoluble surface species.

Electrodes for which  $V_{\text{fb}}$  exceeds the water oxidation potential ought to have band edges suitably positioned to split water. However, under illumination at pH 8-10 the electrodes show insufficient electrode-electrolyte potentials and no water splitting is observed. The reasons for this are unclear at this time.



**Figure 1** History of the flat band potential of one set of GaInP<sub>2</sub> electrodes treated with various porphyrins.



**Figure 2** Flat band potential for various buffer soak times of GaInP<sub>2</sub> electrodes treated with RuOEP and RuCl<sub>3</sub> as a function of the pH of the electrolyte solution.

### REFERENCES

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