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Group III-nitride materials for high efficiency photoelectrochemical cells

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ABSTRACT

Two ternary alloys based on III-nitride semiconductor alloys are explored as potential components of photoelectrochemical cells (PECs) for the direct generation of hydrogen using solar energy. For $\text{In}_{1-x}\text{Ga}_x\text{N}$, it will be shown using prior measurements of band offsets that spontaneous water splitting can occur for x up to 0.2 and potentially higher. Flat band potential and photocurrent measurements from an n-type epilayer with $x = 0.37$ will be presented. This initial data appears to indicate that the flat band potential lies just below the H^+/H_2 from pH 0 – 14. In the case of $\text{GaAs}_x\text{N}_{1-x}$ we will demonstrate that the replacement of a few percent of As in N sublattice drives the bandgap down from the GaN value (3.4 eV) into a range that is attractive for PEC cells [1]. This band gap reduction is explained by the valence band anticrossing that pushes the valence band maximum up initially by 0.5 eV. From the point of view of a PEC cell, this reduces the gap (desirable for efficiency) without compromising the desired H^+/H_2 overpotential.

INTRODUCTION

Photoelectrochemical (PEC) cells, which use solar energy to split water into hydrogen and oxygen, were discovered in the early 1970's [2]. To date, prototype PEC cells have not been sufficiently efficient or durable for practical uses. However, this has been primarily due to materials limitations. It has been established that with better materials, PEC cells could be used as a method of large scale solar production of hydrogen and as a key component of a carbon-free economy based on renewable sources of energy [3,4]. Practical realization of technologies for direct photochemical production of hydrogen, whether based on organic (e.g. photosynthesis) or inorganic materials, depend critically on combining acceptable solar response and efficiency and sufficient service lifetime for energy payback. Most inorganic semiconductors which have the potential for efficient photo-electrochemical (PEC) hydrogen generation due to their favorable bandgaps have unacceptably high corrosion rates for practical purposes; GaInP is one example [5]. On the other hand, more stable materials, such as metal oxides (TiO_2), do not capture a sufficient portion of the solar spectrum and thus have rather low efficiencies [6].

In this context, two new ternary semiconductor alloys in the group III-nitride family— $\text{In}_{1-x}\text{Ga}_x\text{N}$ and $\text{GaAs}_x\text{N}_{1-x}$ —represent new opportunities for the development of inorganic photoelectrochemical (PEC) cells for water splitting and hydrogen generation. That is, they should satisfy three essential requirements for PEC use.

1. Their conduction and valence band edges can be made straddle the H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox potentials.
2. They can be made with the optimal bandgap of ~ 2.0 eV

3. They are expected to exhibit superior corrosion resistance compared to other semiconductors of similar energy gaps.

Initial electrochemical characterization results on $\text{In}_{1-x}\text{Ga}_x\text{N}$ will be presented and discussed here.

EXPERIMENTAL

$\text{In}_x\text{Ga}_{1-x}\text{N}$ films were grown on sapphire using GaN buffer layers by molecular beam epitaxy(MBE) methods described previously [7]. Growth of $\text{GaAs}_x\text{N}_{1-x}$ is described in ref. 1. Flat band potential and photocurrent measurements were performed with a Bio-Rad PN4300PC electrochemical C-V profiler. An indium dot pressed on the surface of the InGaN film adjacent to the area in contact with the electrolyte was used as a contact. Illumination was performed with a 150 W Xe lamp with an approximate intensity of 100 mW cm^{-2} at the sample surface.

RESULTS AND DISCUSSION

We start with the band diagram shown in Fig. 1, which is assembled from literature data for TiO_2 [4,6] and our prior optical measurements (absorption, photoluminescence, and modulated photoreflectance) on InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ [8,9,10] and for GaNAs [1]. A valence band offset of $1.05 \pm 0.25 \text{ eV}$ between InN and GaN was obtained from the experimental study of Martin *et al.*

Figure 1. Predicted valence band maxima (VBM) and conduction band minima (CBM) positions for InGaN and GaAsN. The water redox potentials are shown for pH = 1. For spontaneous water splitting to occur, the CBM must be above the H^+/H_2 level and the VBM must be below the $\text{O}_2/\text{H}_2\text{O}$ level. Notable compositions in the $\text{In}_{1-x}\text{Ga}_x\text{N}$ and $\text{GaAs}_x\text{N}_{1-x}$ that satisfy this condition and, thus, could split water efficiently in a PEC cell are noted. The VBM of $\text{GaAs}_x\text{N}_{1-x}$ rises rapidly at low values of x due to a strong band anticrossing effect (dotted line). This raises the VBM, which is desirable for producing high efficiency PEC cells.

Figure 2. Flat band potentials measured by the CV method for $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$. Data for n-GaN (squares) from ref. 12 are also shown.

[11]. It can be seen that the conduction band maximum of GaN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ for $x < 0.2$ is predicted to be above the H^+/H_2 redox potential for acidic conditions. Consistent with this analysis, spontaneous water splitting was demonstrated in n-GaN at both pH 0 and 14 n-GaN [12]. However, we note that there are uncertainties in the precise band alignments, making it desirable to investigate the electrochemical properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ directly.

A high quality, single-phase, n-type $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$ film ($E_g = 1.9$ eV, $n = 1.1 \times 10^{18} \text{ cm}^{-3}$, $\mu = 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) was investigated here. Typical diode-like behavior was observed in the dark IV curves over a wide range of pH (-0.1 to 14). Flat band potential measurements for this film are shown in Fig. 2. It appears that the flat band potential is somewhat below the H^+/H_2 redox potential over the pH range investigated. However, at pH 7, the measured potential is within experimental error of the H^+/H_2 redox potential and the difference at low pH is somewhat less than predicted by the data in Fig. 1. The variation of the GaN flat band potential is approximately Nernstian (59 meV/pH unit) [12]. Overall, the $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$ flat band potential appears to follow this trend, although the data at mid-pH deviate from it somewhat.

Under full lamp illumination, photocurrent under anodic bias was observed at all pH values. Reducing the light intensity by a factor of 10 suppressed the photocurrent and current-voltage (IV) curves similar to dark IVs were observed. Photocurrent data at selected pH values are shown in Fig. 3. The onset of measurable photocurrent varies from -0.2 V SCE at pH 14 to 0.6 V SCE at pH 2.4. It is interesting to compare these values to those observed previously in GaN: -1.5 V SCE for pH 14 and -0.5 V SCE for pH 0. While it will require more detailed work to

Figure 3. Anodic photocurrent measurements for a for $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$ under ca. 100 mW cm^{-2} illumination from a Xe arc lamp.

determine whether spontaneous water splitting can be achieved with the present alloy composition, it appear that is close to energetically possible. That is, with modest decreases in x (and correspondingly small increases in bandgap), it should be possible to find a optimal x that maximizes hydrogen production in this alloy system.

Finally, we note that the $\text{GaAs}_x\text{N}_{1-x}$ case also shows considerable promise. In this case, the alloying behavior is non-typical; this ternary is “high-mismatched” in that As is replaced by N, which has a much different electronegativity and atomic size. In materials of this type, the introduction of the alloying element causes a localized band to be formed, which then interacts with extended states that are close to it in energy [13]. In the case of GaN, the As localized level is located 0.6 eV above the valence band edge. When As is incorporated at the 2% - 6% level, the bandgap is reduced from the GaN value of 3.4 eV to 2.8 – 2.6 eV. As shown in Fig. 1, this band gap reduction (desirable for higher PEC efficiency) occurs primarily by a shift in the valence band. That is, the favorable position of the conduction band with respect to the H^+/H_2 redox potential is not strongly affected. Our calculations indicate that As could be incorporated at close to 20% before the conduction band is shifted below the H^+/H_2 redox potential (Fig. 1).

CONCLUSIONS

$\text{In}_{1-x}\text{Ga}_x\text{N}$ and $\text{GaAs}_x\text{N}_{1-x}$ alloys represent new opportunities for the development of inorganic PECs. More specifically, changing the alloy composition in these materials allows for independent adjustment of the energy band gaps and the location of the conduction and the valence band edges relative to the water redox potentials. Based on flat band potential

measurements, in n-type $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$ ($E_g = 1.9$ eV), the conduction band minimum appears to ca. 0.2 – 0.4 eV below the H^+/H_2 redox potential. Based on this finding, and our prior measurements of alloy bandgap bowing in this system, spontaneous water splitting should occur for $x \leq 0.2$.

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