Formation of stable surface oxides at n-GaP(100) photoanodes with increased durability for photoelectrochemical applications

Waqas Saddique, Gerhard Lilienkamp, Winfried Daum

Institute of Energy Research and Physical Technologies, Leibnizstr. 4,
38678 Clausthal-Zellerfeld, Germany
E-mail: wsa15@tu-clausthal.de

Theoretically, water splitting is possible with a potential of 1 V vs Ag/AgCl, but practically a potential of 1.5 V vs Ag/AgCl is required due to overpotentials. III-V semiconductors with suitable band gaps are candidates for photoelectrochemical (PEC) water splitting but they are prone to corrosion under PEC conditions and suffer from corrosion-related decrease of efficiency. Gallium phosphide (GaP) has an indirect band gap of 2.26 eV. As this band gap covers both the hydrogen and oxygen evolution potentials, GaP can in principle be used as both photocathode and photoanode, respectively. A comprehensive study was conducted on n-GaP(100) photoanodes to understand the effects of different PEC variables, i.e. pH of electrolyte, photoelectrode potential and illuminating light intensity, on surface corrosion. After PEC treatment, scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) were used for surface characterization of n-GaP(100) photoanodes.

Upon room light (fluorescent tube light) illumination, a 4 nm thin stable, oxide film was formed at the surface of an n-GaP(100) photoanode in 0.02 M HCl under specific PEC conditions and after subsequently hydrogenating the surface to passivate the defects in the oxide film. By AES we identified the stable surface layer as a Ga surface oxide, which inhibits corrosion while allowing the light and the charge carriers to pass through the oxide film for the completion of the PEC process. This photoanode surface was tested for durability for 15 days. During this period a constant photocurrent was recorded from the photoelectrode. No other prior surface treatments or catalysts were required for this process. An open-circuit potential (Voc) of 0.8 V vs Ag/AgCl was determined.

Under room light illumination, photocurrents in the range of µA were generated. To increase both Voc and photocurrents from n-GaP(100) photoanodes, light with higher intensity and a broader spectrum which also includes a UV contribution was used for illumination of the photoanode. After attaining stable PEC surface conditions, photocurrents in the range of mA were measured and an increase of Voc to 1.1 V vs Ag/AgCl was observed.

Illumination of n-GaP(100) at high anodic potentials causes an increase of surface roughness, as has also been observed by Vanmaekelbergh et al.[1] , and a notable increase of the photocurrent. Presumably, the increased surface area of the roughened surface leads to the observed increase of the photocurrent by a factor of 3. However, anodically modified n-GaP(100) photoanodes with a rough surface showed a decrease of Voc from 1.1 V to 0.95 V. The i-V measurement of a rough n-GaP(100) photoanode is shown in Fig. 1. At 0.5 V vs Ag/AgCl, at maximum photocurrent, gas formation at both the n-GaP(100) photoanode and the platinum cathode was observed. The stable n-GaP(100) photoanode supports gas formation. Except for a slight initial decrease, a constant photocurrent from the stabilized photoanode was observed over the course of 3 days after which the experiment was terminated. During the stability test experiments, the n-GaP(100) photoanode was removed from the PEC cell and

exposed to ambient atmosphere for 8-10 hours. This treatment did not markedly affect the surface oxide except for slight changes in i-V measurements.

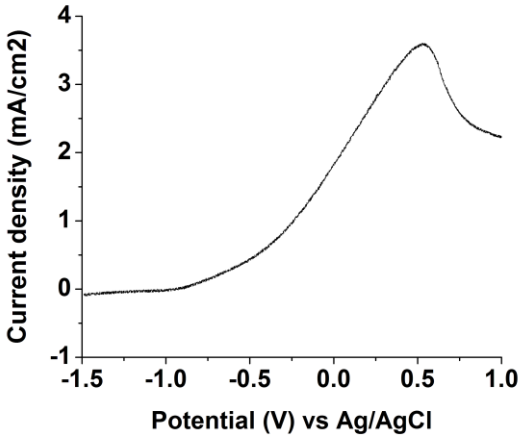

Figure 1: i-V measurement of an n-GaP(100) photoanode in 0.02 M HCl under high intensity light illumination

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References:

[1] D. Vanmaekelbergh et al., Electrochim. Act. 40 (1995) 689-698.