Interfacial studies of protective layers on multi-absorber structures for photoelectrochemical solar fuel production

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Abstract

Artificial leaves based on III−V semiconductor tandem devices currently represent the highest solar-to-fuel conversion efficiencies [1-3]. However, the practical use of these materials in photoelectrochemical (PEC) cells is strongly limited by their chemical degradation under operating conditions, particularly in acidic electrolytes that are preferred for efficient hydrogen evolution reaction (HER) kinetics. Therefore, they require suitable layers for chemical and electronic passivation. Atomic layer deposited (ALD) TiO_2 has been widely applied as a protective layer, protecting the functional III-V layers, such as absorber layers and charge carrier selective contacts, at the solid-liquid interface from corrosion while enabling charge carrier transport to the surface. Although TiO_2 can suppress corrosion, so far long-term operational stability under HER conditions remains a critical challenge. Degradation is commonly initiated by catalyst detachment, followed by electrolyte penetration through structural defects and pinholes into the passivation layer and III-V layers underneath, leading to progressive dissolution of the layers [4].

TiO_2/(Al)InP (100) heterointerface studies showed that P-rich and In-rich surfaces both lead to abrupt type-II alignment, favorable for efficient charge carrier separation [5,6]. However, the native oxide layer on AlInP slows TiO_2 growth and may affect charge carrier transport and interfacial defect evolution depending on the oxide species at the interface. In contrast, GaN can form chemically robust and oxygen-free interfaces with the underlying III-V layers enabling efficient charge carrier transport [7]. We compared the stability and interfacial chemistry of PE-ALD-grown GaN with ALD-grown TiO_2 on III-V-based photocathodes. Photocathodes and the stability was evaluated under illumination using stepwise photoelectrochemical measurements to monitor degradation processes. Changes in surface chemistry and material dissolution were analyzed by X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma mass spectrometry (ICP-MS). Morphological changes were examined using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Photocathodes employing TiO_2 protection exhibited rapid performance decay during operation, with devices losing functionality within an hour. Post-characterization analyses showed that this degradation was initiated by early catalyst detachment, followed by progressive breakdown of the passivation layer and corrosion of the underlying III-V absorber. AFM measurements showed an increased surface roughness and the formation of nanoscale pits in the TiO_2 layers, indicating localized defects that likely act as initiation sites for electrolyte penetration and degradation. In contrast, GaN-coated photocathodes demonstrated significantly improved stability under identical conditions. GaN maintained a

smoother surface morphology, preserved catalysts, and reduced material dissolution. AFM analysis of as- prepared samples indicates that the GaN layers form a smoother and closed surface in contrast to TiO_2, suggesting a much reduced density of nanoscale defects and pinholes.

The enhanced performance is attributed to the chemically favorable GaN interface and the suppression of oxygen-related interfacial degradation pathways. Our results highlight the limitations of TiO_2 protection layers for III-V PEC photocathodes and demonstrate that GaN is a promising alternative to TiO_2 for improving the long-term stability of III-V-based artificial leaves in acidic PEC environments.

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