

Solar hydrogen production with epitaxial III-V tandem absorber structures

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Solar fuel generation by direct photoelectrolysis of water provides a possible solution for the energy storage and transportation needs of a sustainable energy economy. The initial observation of photoelectrochemical (PEC) water splitting [1] triggered the search for appropriate semiconductor materials sufficient for large-scale economic solar hydrogen production. In contrast to photovoltaic (PV) applications, where highest device power is a sufficient efficiency criterion, PEC devices must provide the threshold voltage to drive the water splitting reactions, while the solar-to-hydrogen conversion efficiency is directly proportional to the generated current.

Wide band gap materials may drive the water splitting reaction, but do not make use of a substantial portion of the solar spectrum. In contrast, most standard PV materials like silicon do not provide the thermodynamic threshold to split water [2]. Tandem absorber structures overcome this undesirable trade-off, featuring promising efficiency potentials. Subsequent absorption of different portions of the sunlight by two semiconductor materials with appropriate band gaps enables better utilization of the solar spectrum [Fig. 1], providing a sufficient combined voltage.

InGaP₂/GaAs tandem photoelectrodes have enabled world record solar to hydrogen conversion efficiencies of up to 12.4% [3], but are still susceptible to relatively fast degradation under operational conditions. Under illumination, destructive photocorrosion reactions occur at the InGaP₂ interface with the electrolyte, successively eroding the epitaxial layer and ultimately destroying the device. We explore the potential to improve both efficiency and durability of III-V tandem absorber structures aspiring to technologically and economically viable solar water-splitting devices.

Epitaxial InGaP₂ layers were grown by metalorganic vapor phase epitaxy (MOVPE) on GaAs(100) substrates. Undesirable surface roughness of the 4 μm thick InGaP₂ top absorber layers could be traced back to successive 4° faceting [4] during the growth process. The effect was controlled by utilization of GaAs(100) substrates with appropriate misorientation (of 4°), resulting in devices featuring both mirror-like

surfaces and improved performance. PEC characterization included incident photon-to-current efficiency (IPCE) and chopped-light voltammetry (J-V), as well as extended durability analysis under illumination, either under short-circuit or constant current (-10 mA/cm²) conditions, all conducted in 3M H₂SO₄.

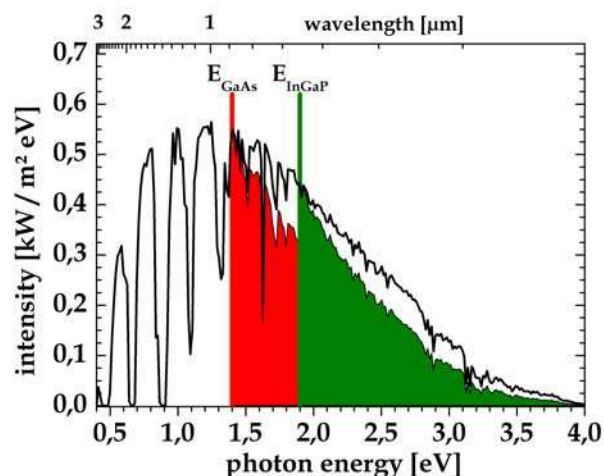


Figure 1. Standard solar spectrum (ASTM G-173-03) for terrestrial irradiance (AM1.5): Colored lines indicate the absorption edges of GaAs and InGaP₂, respectively; colored areas reflect an upper limit for the solar energy potentially captured in this tandem configuration.

Post-growth modifications of the epitaxial InGaP₂ surfaces are essential to achieve the desired device performance and durability in contact to the electrolyte. Metal co-catalyst deposition significantly reduces the overvoltage requirements for the hydrogen evolution reaction. Enhanced performance was achieved with sputtered metal nanoparticles in comparison to electrochemical Pt deposition.

In contact with an aqueous electrolyte, both pure III-N materials as well as classical III-V semiconductors with only dilute bulk nitrogen concentrations demonstrate inherently better stability than pure phosphides [5]. Hence, we have evaluated post-growth nitridation of the crucial InGaP₂ surface to form the interface with the electrolyte. As will be presented, low-energy N₂⁺ ion bombardment actually has led to greatly improved durability without significant impact on PEC performance. Both X-ray photoelectron spectroscopy (XPS) and synchrotron-based soft X-ray emission spectroscopy (XES) were applied to characterize the quantity and chemical configuration of implanted nitrogen in order to resolve its role in the effective protection on InGaP₂ surfaces against photocorrosion reactions.

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