

In situ interfacial functionalization of III-V tandems for efficient water splitting

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Epitaxially prepared, monolithically integrated layer stacks have been demonstrated to display the highest performance in basically all optoelectronic device structures as in the field of solar energy conversion - in photovoltaics [1] as well as in direct solar-driven water splitting systems [2]. In the latter one, the entire device is exposed to the electrolyte and needs to be developed with regard to several interconnected challenges such as sun light exploitation, passivation, catalysis, solid-liquid interfaces, stability, etc. Regarding the design of a water-splitting architecture and the given equilibrium and kinetic energetic condition to split H_2O , only absorbers with large band gaps or tandem structures with a sufficient voltage, i.e. with sufficient splitting of the quasi-Fermi level, can efficiently produce H_2 .

Considering the Fermi energies of charge carriers in the absorber layers, the anodic and cathodic redox potentials and over-potentials, which provide the driving force for the solid-liquid interfacial reactions, the energy gap of a single junction photoelectrocatalytic cell needs to be clearly larger than 2eV . In such a cell, the maximum solar-to-hydrogen (STH) efficiency is limited to lower values than 15% at one sun AM1.5. When using tandem structures much higher STH efficiencies can be achieved, potentially up to 25%.

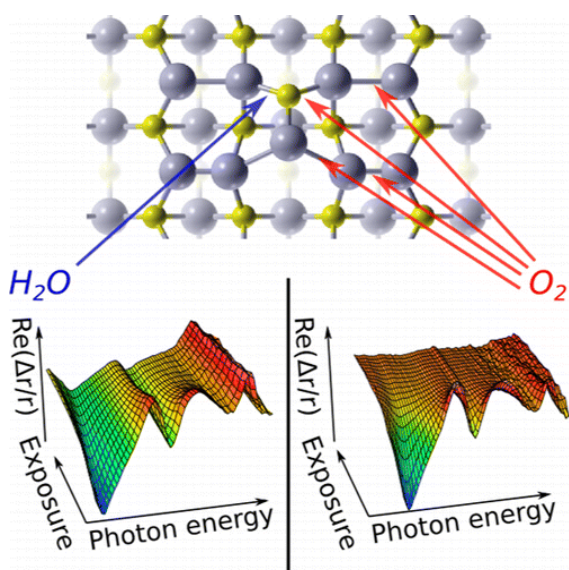


Fig.1: Reaction path, mechanisms and stability of well-defined surfaces treated with water and oxygen differ significantly with atomic surface reconstruction: the mixed-dimer In-rich surface exhibits dissociative water adsorption featuring In–O–P rather than unfavorable In–O–In bond topologies, the H-terminated, P-rich surface reconstruction is irreversibly removed.

In situ analysis: Oxygen exposure attacks the In-rich surface more efficiently and additionally modifies, unlike water exposure, bulk-related optical transitions. Hydroxyl is not observed, which suggests a dehydrogenation of adsorbed species already at ambient temperature.

The interface with the aqueous electrolyte and catalysts is crucial for its performance in direct solar water splitting and is not intrinsically stable against (photo)electrochemical corrosion, which also impedes the charge-transfer efficiency over the solid-liquid interface. Stability of light-driven water splitting structures can be addressed by interface functionalization and/or using passivation layers out of transition metal oxides, which can be produced by atomic layer deposition. In situ monitoring and control is an essential experimental strategy during critical surface-preparation processes with a high complexity. Based on surface chemistry considerations derived from model experiments in ultra-high vacuum [3], we developed an in situ surface-functionalization processing sequence for a $\text{Ga}_x\text{In}_{1-x}\text{P}/\text{Ga}_x\text{In}_{1-x}\text{As}$ tandem absorber. In situ functionalization, avoiding undesired exposure to atmospheric ambient, suppressing the creation of unfavorable oxide species, and in situ control during preparation, are elements towards a well-defined preparation, scalable processing routes, and to reduce recombination losses and degradation.

For that, we have studied interfacial chemistry and morphology by ultra-high vacuum (UHV)-based analysis as well as electron microscopy to identify scenarios for a specific modification of InP-based interfaces. We prepared well-defined III-V surfaces to explore different surface reconstructions on their initial interaction with water and oxygen in UHV. Optical in situ spectroscopy and interface sensitive benchmarking tools such as photoemission were employed to probe the adsorption on InP and GaP (100) surfaces identifying specific interfacial reactions for developing appropriate interfacial functionalization routes [4] and for comparison with theoretical modelling [5]. Photoelectrochemical benchmarking combined with photoemission show that chemical and electronic passivation can be controlled by photoelectrochemical surface modifications on a sub-nanometer scale, involving the formation of phosphate species. Here, we will present the performance-critical steps of the in situ functionalization in the scope of insights from photoelectron spectroscopy.

References

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