

Preparing tandem structures for highly efficient water splitting

M.M. May^{1,2,3}, H.-J. Lewerenz^{2,4}, O. Supplie^{1,2,3}, R. van de Krol², F. Dimroth⁵, D. Lackner⁵, T. Hannappel^{1,2}

¹Ilmenau University of Technology, Institut für Physik, Gustav-Kirchhoff-Straße 5, D-98693 Ilmenau, Germany

²Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany

³Humboldt-Universität zu Berlin, Institut für Physik, Newtonstraße 15, D-12489 Berlin, Germany

⁴California Institute of Technology, Joint Center for Artificial Photosynthesis, 1200 East California Boulevard, Pasadena, CA 91125, USA

⁵Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany

Abstract

Solar-driven water splitting systems, which are entirely exposed to an electrolyte, need to be developed with regard to different complex challenges such as sun light exploitation, electronic and chemical passivation, catalysis, the interface to the electrolyte, robustness, etc. Also the costs of ingredients have to be considered. In the design of a water-splitting architecture all thermodynamic requirements of the system have to be considered, such as chemical potentials of electrons and holes in the semiconductor layer structure as well as redox potentials and over-potentials of anode and cathode, providing the driving force for the solid-liquid interfacial reactions. Bearing these points in mind, the conversion efficiency that could be achieved for a single junction structure is limited to less than 15% without light concentration and under standard conditions (AM1.5 spectrum). Significantly higher efficiencies could be achieved utilizing high-performance semiconductor tandem structures, which can potentially reach conversion efficiencies beyond 25%. In photovoltaics as well as in water splitting devices, tandem structures based on III-V compounds have been used in record devices.

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 fabricated by atomic layer deposition. In situ monitoring and control and in vacuo analysis are essential experimental strategies during critical surface-preparation processes with a high complexity. It provides the realization of layer structures and junctions, consisting of high-quality semiconductors for suitable devices with highest performance such as epitaxial III-V compound layer structures [1]. In a further development, appropriate III-V layers can be directly grown on silicon substrates [2]. Such a material is GaPN(As)/Si(100), exhibiting a perfect band gap combination and also being cost effective [2,3]. Furthermore, potential future device arrangements are suggested, such as silicon/III-V nanowire arrangements [3].

We show high-performance water-splitting device layer structures realized by preparing appropriate III-V-based tandem structures via metal organic chemical vapor deposition (MOCVD) [4], combined with an appropriate in situ surface-functionalization processing route enabling efficient, unassisted water splitting with current densities beyond 11 mA/cm² under

one sun (AM 1.5G) and resulting in solar-to-hydrogen efficiencies beyond 13% [4]. For that, we have utilized MOCVD-grown tandem absorbers with band gaps of around 1.8 and 1.3 eV being close to the maximum theoretical values for a water-splitting tandem device. Surface-functionalization involves an etching procedure and a (photo)electrochemical transformation of the interface followed by the deposition of rhodium as electrocatalyst.

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 a reduction of 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 successful surface-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 functionalisation routes [5] and for comparison with theoretical models [6].

References

- [1] B.E. Sagol, U. Seidel, N. Szabo, K. Schwarzburg, T. Hannappel, *Chimia* 61 (2007) 775; Dimroth et al., *Prog. Photovolt: Res. Appl.* 2014.
- [2] O. Supplie, M.M. May, H. Stange, C. Höhn, H.-J. Lewerenz, and T. Hannappel, *J. Appl. Phys.* 115, 113509 (2014); O. Supplie et al., *J. Phys. Chem. Lett* 6 (2015) 464
- [3] T. Hannappel, M.M. May, and H.-J. Lewerenz, in *Photoelectrochemical Water Splitting: Materials, Processes and Architectures*, The Royal Society of Chemistry (2013) pp. 223–265
- [4] M.M. May, H.-J. Lewerenz, D. Lackner, F. Dimroth, T. Hannappel, submitted.
- [5] M.M. May, H.-J. Lewerenz, and T. Hannappel, *J. Phys. Chem. C* 118 (2014) 19032; M.M. May et al., *New Journal of Physics* 15 (2013) 103003.
- [6] [4] B.C. Wood, E. Schwegler, W.I. Choi, and T. Ogitsu. *J. Phys. Chem. C* 118, (2014) 1062.; H. Atwater et al., *J. Phys. Chem. C* 116 (2012) 17604