

## (Photo-)electrochemical reactions on semiconductor surfaces, part B: III-V surfaces—atomic and electronic structure

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### Abstract

III-V semiconductors provide the highest performance levels in optoelectronic applications, especially as thin film solar cells and photoelectrochemical cells. However, these performance levels are only reached using epitaxial layers and highly sophisticated contact formation recipes as no easy surface passivation route, as known for Si, has been identified yet. In order to address the surface and interface properties of III-V semiconductors in relation to their performance, we present in our contribution at first a short review of PV and PEC cells based on III-V single- and multi-junction cells. Next, the synthesis and properties of well-defined surfaces after MOVPE preparation, which are not affected by contact to the ambient, will be presented. In the following section, we discuss the essential considerations on the surface properties of III-V semiconductor/electrolyte contacts in relation to photoelectrochemical cells from a conceptual and from a theoretical modeling perspective,

assuming mostly idealized surface conditions. Next, we address the properties of III-phosphide surfaces exposed to ambient conditions and their modifications by chemical etching and vacuum cleaning procedures. Subsequently, experimental model experiments on the surface reactivity of III-phosphide and III-nitride surfaces to H<sub>2</sub>O exposure are presented. These different surface science approaches are then related to photoelectrochemical cells for H<sub>2</sub> evolution from H<sub>2</sub>O using different III-V based tandem cells, which provide highest conversion yields of up to 19% STH efficiency.

## Introduction

For III-V semiconductors, the chemical, crystalline, and electronic structure of the involved surfaces and interfaces play a dominant role in the performance of (opto-)electronic devices, especially if they are based on classical semiconductors, where the bulk properties are of high quality as is realized by using well-defined bulk or thin film materials. Also nontraditional semiconductors as oxides and novel compound semiconductors are affected by the defect chemistry on their surfaces and interfaces, but for these materials with not yet optimized bulk properties, the relative influence of bulk versus surface limitations can hardly be discriminated in a clear manner in many investigations. For this reason, we have concentrated our contribution, which is orientated on the fundamental electrochemical-related surface properties and related performances of semiconductor devices, to two semiconductor material classes: In part A we have addressed Si-based materials, whereas in this part we will address the specific (photo-)electrochemical surface properties of III-V semiconductors. In both contributions, the main application directions are related to optoelectronic applications, especially photoelectrochemical water-splitting cells. Therefore, the central part will cover the surface/interface properties and related challenges in surface passivation and engineering. Whereas for Si surfaces, passivation treatments such as forming SiO<sub>2</sub>, S-H or Si-R have already intensively been studied, similar surface passivation techniques for III-V semiconductors are only at the beginning of being explored due to the more complex surface chemistry of these compound semiconductors.<sup>1</sup>

III-V semiconductor compounds have a variety of properties which make them suitable candidates for the light-absorbing material in a photoelectrochemical cell. The epitaxial growth of ternary and higher-order III-V compounds by metalorganic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE) enables tunability of the band gap energy in combination with a well-defined and high material quality.<sup>2</sup> III-V semiconductor compounds with different band gap energies can be grown on top of each other to form multi-junction solar cells which absorb the majority of the solar spectrum and provide a sufficiently high photovoltage to drive the water splitting reaction. The versatility of the III-V semiconductor growth processes as well as the exceptional charge transport properties and the high light absorption coefficient of some III-V compounds (e.g., indium phosphide (InP) and gallium arsenide (GaAs)) are the reason that III-V materials hold record efficiencies for both single-junction and multi-junction solar cells<sup>3</sup> and also for photoelectrochemical cells.<sup>4–6</sup>

## Short survey of PV and PEC cells using III-V semiconductors

According to the current solar cell efficiency tables,<sup>3</sup> the record efficiency for a triple-junction solar cell under the global AM 1.5 spectrum of 37.9% is obtained for a stack of three III-V compounds: InGaP/GaAs/InGaAs. As often in efficient III-V multi-junction solar cells, Gallium indium phosphide (GaInP<sub>2</sub>) has been used as top cell material. Depending on its stoichiometry, Ga<sub>x</sub>In<sub>1-x</sub>P has an optical band gap between 1.35 eV (InP) and 2.26 eV (GaP),<sup>7</sup> which changes with increasing gallium content from a direct to an indirect band gap. With a gallium content of  $x \approx 0.5$ , the band gap is still direct and 1.8–1.9 eV wide, which allows conversion efficiencies over 30% with GaInP/GaAs tandem cells<sup>8</sup> and 20.8% for a single-junction solar cell.<sup>9</sup> Semiconductors with similar lattice parameters can be grown epitaxially on top of each other to form a multi-junction solar cell. The thermodynamic minimum energy for the water-splitting reaction is 1.23 eV per electron/reduced proton, which is not far off from the band gap of a single-junction solar cell near the maximum solar conversion efficiency according to the detailed balance limit by Shockley and Queisser.<sup>10</sup> However, for photoelectrochemical solar cells in practice, additional loss factors such as the hydrogen (HER) and oxygen evolution (OER) overvoltages as well as resistance losses increase the necessary voltage to drive the water-splitting reaction at sufficiently high rates for the production of hydrogen.<sup>11</sup> This leads to a minimum operational photovoltage of more than 1.7 V. From the binary III-V semiconductors, only the compounds aluminum phosphide (AlP,  $E_g = 2.48$  eV), gallium phosphide (GaP,  $E_g = 2.26$  eV), aluminum arsenide (AlAs,  $E_g = 2.15$  eV) and the nitrides GaN ( $E_g = 3.2$ – $3.4$  eV) and AlN ( $E_g = 5.2$  eV) have a band gap energy  $E_g$  above 1.7 eV.<sup>7</sup> Furthermore, the open-circuit voltage is generally smaller than the band gap of the solar cell.<sup>11</sup> Without light concentration, this leads to a reduction of at best 0.4 V, resulting in a minimum band gap energy of about 2.1 eV if a single semiconductor should be used as photoabsorber. Solar cell materials with band gap energies in this range only use a small amount of the solar spectrum and often have indirect band gaps as AlP and GaP, which lead to a poor light-to-electricity conversion efficiency. For these reasons, tandem solar cells have to be used if water splitting should be achieved with high efficiency.<sup>12</sup> They allow an efficient use of the solar spectrum if the right band gap energy combinations are chosen and supply sufficient voltage for a water-splitting device since the delivered voltage is the sum of the individual subcell voltages.<sup>2</sup>

A GaInP/GaAs photoabsorber combination was also used in one of the first high-efficiency water-splitting devices by Turner and coworkers, which achieved a long-time record solar to hydrogen conversion efficiency (STH) of 12.4% under illumination with a power density equivalent to 11 suns.<sup>13</sup> Nevertheless, more recent benchmarking protocols and the use of AM 1.5 solar irradiation lead to a correction of this value to  $\eta_{\text{STH}} = 9.3\%$ ,<sup>14</sup> which is still one of the highest STH efficiencies reported in the literature.<sup>4</sup> The versatility of the III-V growth process together with new approaches which permit epitaxial growth with a small lattice mismatch

(<1%) even make theoretical efficiencies >25% possible.<sup>15</sup> These values can be obtained with band gap combinations of 1.65–1.8 eV/0.95–1.15 eV.<sup>12</sup> Ternary III-V alloys like GaInP, AlGaAs and GaInAs allow the fabrication of devices that come close to the needed band gap energies. With a GaInP/GaInAs tandem absorber, the current (19.4%<sup>16</sup> from 2018) and the previous record STH efficiencies (16.2%<sup>15</sup> from 2017 and 14%<sup>1</sup> from 2015) for an integrated water-splitting device were achieved. The realization of these high efficiencies required to control the corrosion-induced formation of charge-carrier recombination centers for maintaining the minimum required photovoltage. In addition, the overall (electro-)chemical corrosion rate had to be reduced by several orders of magnitude, as the typical, untreated window layers—for instance AlInP—serving as the electronic passivation of the underlying light absorber only exhibit stabilities in the order of seconds under operating conditions.

The main reason for the high STH efficiencies which can be achieved with III-V semiconductors is the efficient conversion from solar to free energy achieved for optimized tandem cells. Another important reason is the often good alignment of the conduction and valence band edges of the material to the redox potentials in aqueous solutions. In particular, the conduction band minimum (CBM) of a photocathode should be above (more negative in potential than) the water reduction potential  $H^+/H_2$  and the valence band maximum (VBM) of a photoanode should be below (more positive in potential than) the water oxidation potential  $H_2O/O_2$  considering also potential band edge shifts due to surface trapping of charge carriers under operation conditions. Fig. 1 compares the band edge positions of different semiconductors at pH = 0. GaInP<sub>2</sub> is one of the few semiconductor materials which could straddle both of the water redox potentials. Nevertheless, the VBM of GaInP<sub>2</sub> is too negative to drive the water oxidation reaction without an externally applied bias voltage and as a consequence GaInP<sub>2</sub> is not an ideal photoanode material on its own. However, it should be noted that in multi-junction approaches the band alignment to the absolute positions of the redox levels as displayed in Fig. 1 is of limited validity for operational conditions. The band alignment with the redox couples will be affected by charge redistribution under illumination. This is similar to the development and measurement of a surface photovoltage, for instance by XPS: In that case, the Fermi level of the back-contact of the sample will align with the Fermi level of the spectrometer (ground) and the measured energy bands on the front will be then shifted by the photovoltage. For the illuminated multi-junction in contact with an electrolyte on both sides, the electrochemical potentials of electrons and holes (given by their quasi-Fermi levels, see also Fig. 2) will first align with the most active redox couple in the electrolyte, and then the photovoltage will develop from there, similar to the back-contacted vacuum case. Yet the complication of the activity- and related charge redistribution- of the less active redox couple in relation to the photogeneration current will slightly modify this picture.

Besides the efficiency, also the stability of the material is a crucial point for the choice of an absorber for a photoelectrochemical cell. If the photoabsorber is in direct contact with the electrolyte, the electrochemical reactions will take place at the semiconductor/electrolyte interface and the surface of the semiconductor is susceptible to photo-induced corrosion. In the case of a photocathode, photocorrosion becomes an issue if the quasi-Fermi energy of the photo-generated electrons is higher than the thermodynamic reduction potential  $\phi_{red}$  of the material.<sup>18</sup> Depending on the alignment of  $\phi_{red}$  relative to the water reduction potential  $\phi(H^+/H_2)$ , the electrons can reduce the water molecules or the photocathode itself. The cathode is stable against reduction if  $\phi_{red}$  lies within the conduction band or above  $\phi(H^+/H_2)$ . In the latter case, the stability depends on the kinetic rates of the reactions. The electron consumption rate of the water reduction reaction should be higher than the rate for the reduction of the material.<sup>19</sup> Similarly, a photoanode is stable against hole oxidation, if the thermodynamic potential  $\phi_{ox}$  is lower than either  $\phi(H_2O/O_2)$  or the VBM. The thermodynamic reduction and oxidation potentials are also plotted in Fig. 1. Like the examples in the graph,

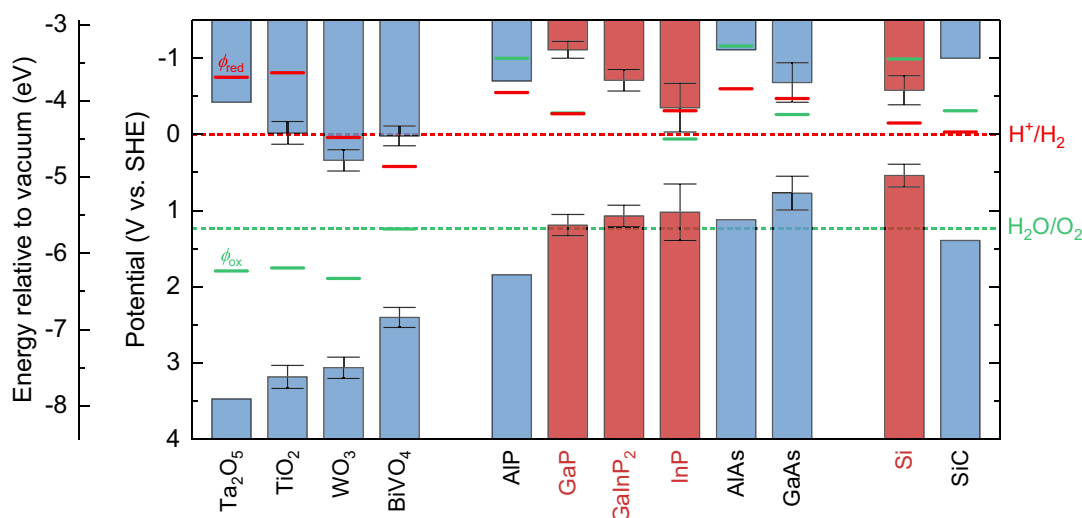


**Fig. 1** Band edge positions for various semiconductors relative to the redox potentials of water at pH = 0.<sup>17</sup> The positions are given relative to the standard hydrogen electrode potential (SHE) and relative to the vacuum level  $E_{vac}$ . The error bars represent the SD of different band edge positions in the references. The reduction potentials  $\phi_{red}$  (in red) and the oxidation potentials  $\phi_{ox}$  (in green) of the materials are also given. Adapted from Chen et al.<sup>18</sup> and complemented with additional literature values from Refs. 5,6.

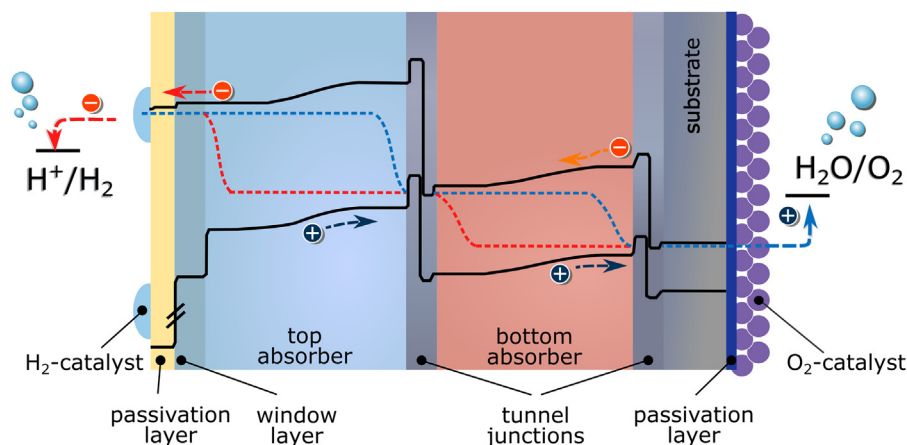


**Fig. 2** Scheme of an artificial leaf in a tandem device structure. The scheme is a combination of an energy band diagram in the interior with a schematic arrangement of the cocatalysts on the surfaces.

almost all nonoxide semiconductors are unstable against self-oxidation if they are used as photoanodes for the oxygen evolution reaction.<sup>20</sup> However, if they are used as photocathodes, all nonoxide semiconductors are resistant to photo-induced reduction.<sup>18</sup> In the cases of AlP, GaP, AlAs, Si and SiC the potential  $\phi_{\text{red}}$  is below  $\phi_{\text{ox}}$ , which implies that electron–hole pairs can be generated spontaneously without the help of a photon. These materials are therefore even unstable in the dark. The energetic position of the VBM and the CBM is given by the ionization potential and the electron affinity in contact with electrolyte components and can in principle be measured by using photoelectron spectroscopy if the right contact phases are applied.<sup>21,22</sup>

The stability of water-splitting devices has been recognized as the critical issue for their technical application for several decades.<sup>20,23,24</sup> In order to make efficient photoabsorber materials more stable under water-splitting conditions, surface engineering approaches can be considered.<sup>20,22</sup> A physical protection layer for the unstable absorber material may be applied. This layer of a dense and chemically stable material should protect the absorber from direct contact with the electrolyte. Also the application of a cocatalyst material that accelerates the desired water-splitting reactions is possible. This kinetic protection method can reduce unwanted surface charge recombination and self-oxidation or reduction of the semiconductor. The third pathway is the formation of a buried junction. In this approach, the photoabsorber is modified by charge-selective layers for efficient charge separation, sometimes erroneously referred to as ‘charge-separation by a built-in electric field’ as discussed in detail elsewhere.<sup>25</sup> Very often all three approaches must be used in parallel, which leads to buried junction photoelectrochemical cells with specifically engineered interfaces. Appropriate engineering strategies must be applied to prepare and adjust the different layers as the passivation and protection layers as well as the cocatalysts to the electrolyte solutions forming the electrochemical contact of the electrode. Designing working engineering strategies and their experimental realization by soft thin-film deposition technologies need a detailed knowledge of the involved surface compositions and related (opto-)electronic properties as is schematically shown in Fig. 2.

The III-V photoabsorbers are commonly grown by MOVPE, as it allows for high-purity semiconductor epitaxy on great quantities of large-area wafers in a single process. Unfortunately, monitoring via electron-based techniques is not yet possible with the needed surface control due to H<sub>2</sub> gas and high pressure in MOVPE reactors. Instead, optical, in situ techniques can be applied. One technique which is highly surface sensitive is reflection anisotropy spectroscopy (RAS, also called reflectance difference spectroscopy (RDS)).<sup>26</sup> RAS measures the difference in (complex) reflection along two orthogonal crystallographic directions  $x$  and  $y$  in the surface plane in near normal incidence geometry, normalized to their mean reflection,

$$\frac{\Delta r}{r} = 2 \frac{r_x - r_y}{r_x + r_y} \quad (1)$$

Commonly, the optical data are taken in the range of 1.5–5.0 eV photon energy. Here, RAS is aligned such that  $x = [01\bar{1}]$  and  $y = [011]$ . To compare RAS signals between different measurements, the amplitude of RA spectra should be calibrated to an oxidized Si(110) Ref. 26 This optical technique is highly sensitive for dimerized (001) surfaces of cubic crystals as their bulk contribution is optically isotropic. Thus, the main contribution of the RAS signal originates from the anisotropic geometrical structure of the (near-) surface. RAS can monitor changes in surface reconstruction, surface chemistry and surface states. However, other contributions might change the line-shape and amplitude of the RA spectra, as for example electric field (electro-optic effect) within the extended space charge layer in case of highly doped III-V semiconductors.<sup>27,28</sup> Thus, direct interpretation of RAS signals is not straightforward. To understand the origin of the RA spectra, they can be compared with theoretical calculations or the surfaces can be ‘benchmarked’ by various complementary optical or UHV-based surface science techniques. To avoid oxidation of the surfaces during transferring the samples from the MOVPE reactor to in vacuo techniques, a contamination-free mobile UHV shuttle<sup>29</sup> can be used. RAS is also applicable in UHV or to probe solid–liquid interface.<sup>30–34</sup> Once the microscopic origin of the RA spectra is understood, they can act as qualitative and/or quantitative fingerprints, which allows to prepare atomically well-ordered surfaces and interfaces.<sup>35</sup>

The binary semiconductors InP and GaP have been studied early on for hydrogen photoevolution. InP has a long history as an efficient photocathode for  $H_2$  evolution, however an external power supply must be added,<sup>36–39</sup> as its band gap of around 1.3 eV at room temperature is not enough to provide a sufficient photovoltage. InP has been shown to be unstable in aqueous electrolytes and susceptible to corrosion,<sup>40–42</sup> which in turn increases surface recombination.<sup>43</sup> A modification of the InP-based surfaces toward oxides and phosphates/phosphites can improve surface stability and charge carrier transfer to the electrolyte.<sup>1,43</sup> GaP on the other hand has been studied as a photocathode or photoanode less insensitively,<sup>44</sup> even though its use in solar water splitting dates back to 1977.<sup>45–47</sup> Its large band gap of about 2.3 eV at room temperature might provide enough photovoltage to drive the process of  $H_2$  evolution but the generated photovoltage is rather low, and, as InP, GaP is rather unstable in electrolytes, especially for the oxygen evolution reaction.<sup>48,49</sup> However, GaP benefits from its lattice constant, which is almost matched to Si. This fact renders it an ideal candidate for pseudomorphic virtual III-V-on-Si substrates for photoelectrochemical water splitting.<sup>50</sup>

## III-V surfaces after thin film preparation

### III-phosphide surfaces

In the discussion of the III-V surfaces, GaP(001) and InP(001) are of particular interest since they may serve as prototype surfaces regarding H-based MOVPE processing of phosphides, where hydrogen strongly affects the atomic surface structure compared to UHV preparation. When in contact with water, different atomic surface reconstructions of GaP(001) and InP(001) significantly affect the stability and the reaction path.<sup>30,51</sup> The accumulated knowledge in the surface preparation and surface band energy diagrams of the binary materials can be transferred to GaP and InP-based ternary compound semiconductors, such as GaInP or AlInP, which are used as top layers in highly efficient photoelectrochemical multi-junction cells.<sup>1,15</sup> Therefore in the following, a detailed understanding of the atomic and electronic surface structures of GaP(001) and InP(001) will be presented based on a combination of optical in situ spectroscopy, in-system UHV-based surface sensitive measurements techniques, and complementary density-functional theory (DFT) calculations.

### Atomically well-ordered surfaces of InP(001) and GaP(001)

#### Anisotropic fingerprint of different atomic structures

Regarding surface structure, reconstruction, and termination as well as MOVPE preparation conditions, GaP(001) and InP(001) are very similar. In H-based ambient, depending on the P chemical potential for given molar flow of the phosphorus precursor and surface temperature,<sup>52,53</sup> typically two surface reconstructions are possible for both GaP and InP: (i) A P-rich  $(2 \times 2)/c(2 \times 4)$  surface reconstruction which consists of buckled P dimers stabilized by one H atom each.<sup>52,53</sup> (ii) A  $(2 \times 4)$  mixed dimer surface (here referred to as either 'Ga-rich' or 'In-rich' surface) which is terminated by a mixed dimer formed by group-III and P atoms.<sup>54,55</sup> Each surface exhibits a characteristic RAS line-shape which can be regarded as a fingerprint. Fig. 3 compares the RA spectra (measured at 20 K) of P-rich and group-III-rich (a) GaP(001) and (b) InP(001) surfaces prepared in MOVPE reactor after a contamination-free transfer to UHV.<sup>29,58–60</sup>

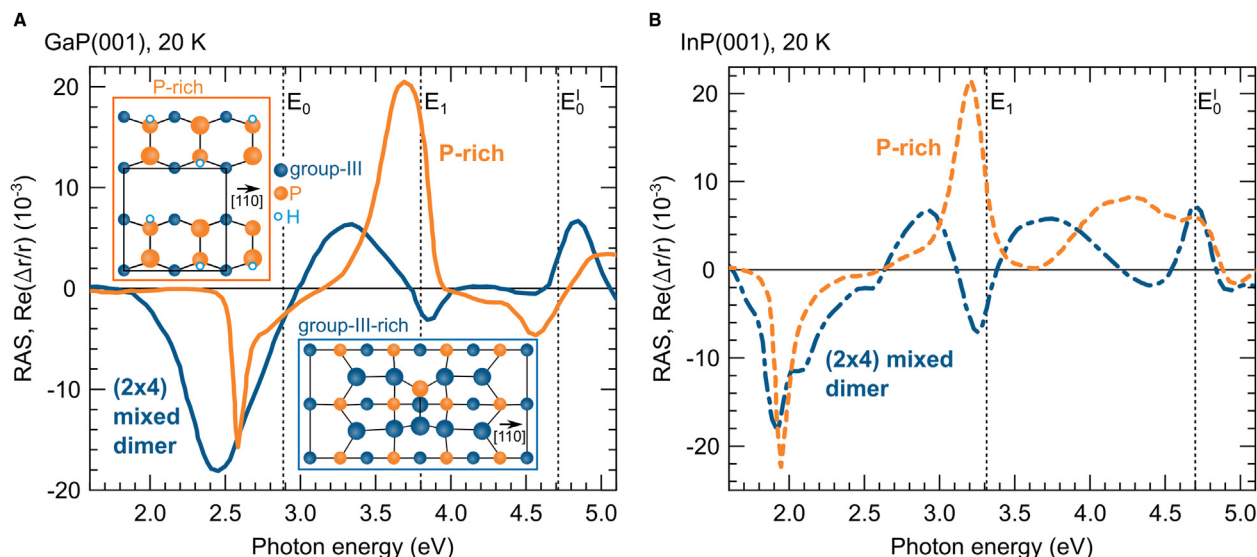


**Fig. 3** RAS of GaP(001) (A) and InP(001) (B) surfaces with P-rich  $2 \times 2$ -reconstruction (orange solid (A) and dashed (B) line) and Ga-rich (A, blue solid line) or In-rich (B, blue dash-dotted line)  $2 \times 4$ -reconstruction, data measured at 20 K from Refs. 29,56. Gray vertical lines indicate the critical interband transitions of GaP<sup>56</sup> and InP.<sup>57</sup> The ball-and-stick models in (A) depict surface reconstructions which correspond to the RA spectra of GaP(001) and InP(001).

The GaP(001) P-rich surface can be prepared at rather low temperatures or when stabilized with the P precursor after homoepitaxial growth. When the phosphorus precursor (tertbutylphosphine, TBP) supply is stopped at 420 °C, the surface is covered with excess P and precursor residuals, which can be desorbed by subsequent annealing without the precursor supply at the same temperature.<sup>59</sup> The Ga-rich surface is formed above 490 °C when P desorbs preferentially, with an almost direct transition from the P-rich to the Ga-rich surface.<sup>58,59</sup> The spectral differences between the P-rich and group-III-rich surfaces enable in situ identification of the different surface reconstruction. The RA spectrum of the P-rich surface (Fig. 3A, orange solid line) exhibits a characteristic minimum at about 2.6 eV and maximum at 3.7 eV slightly below the  $E_1$  interband transition, and a small local minimum and maximum near 4.5 and 5.0 eV, respectively. The RA spectrum of the Ga-rich GaP(001) surface (Fig. 3A, blue solid line) exhibits a characteristic minimum slightly below 2.5 eV, a local maximum at around 3.2 eV, a small local minimum close to the  $E_1$  interband transition, a shoulder at around 4.2 eV, and a local small maximum slightly above the  $E'_0$  interband transition. Fig. 3B shows RA spectra of the InP(001) surfaces. Compared to RAS of the GaP(001), the spectra are shifted to lower photon energy. The line-shape of the RA spectrum of the P-rich surface (Fig. 3B, orange dashed line) is very similar to the RAS of the P-rich GaP(001) surface. It also consists of a characteristic minimum around 1.9 eV and maximum at 3.3 eV slightly below the InP  $E_1$  interband transition. The line-shape of RAS of the In-rich surface (Fig. 3B, blue dash-dotted line) is also similar to the one of the Ga-rich GaP(001) surface but the minimum around 1.9 eV is sharper and has more features. In analogy to GaP(001), the P-rich InP(001) surface can be prepared by cooling under stabilization with the P precursor after homoepitaxial growth. By monitoring the intensity of the minimum near 1.9 eV along with a small shift toward lower photon energy, the atomic order of the surface can be in situ finetuned.<sup>61</sup> A cycle of heating to 360 °C without precursor supply and subsequent cooling to 300 °C in the presence of the P precursor increases the atomic order on the surface. The transformation from P-rich to In-rich surface, same as for GaP, was studied in situ with RAS in great detail and can occur via heating of the P-rich InP(001) surface above 370 °C without P stabilization, which results in enhanced P desorption, P depletion and a slow change toward the In-rich surface.<sup>59,62</sup> The different line-shapes of the anisotropic fingerprints of the two surfaces allows for in situ study of the initial interaction of the surfaces with water and oxygen<sup>30,51</sup> or hydrochloric acid and sulfuric acid,<sup>34</sup> as discussed in more detail in section 5.1 and 6.1, respectively.

The atomic structure of both III-rich and P-rich surfaces of InP(001) and GaP(001) substrates was experimentally investigated in great detail and the obtained results were compared to DFT calculations. The P-rich surface shows  $(2 \times 1)$  low-energy electron diffraction (LEED) pattern with streaks at half order in the  $\times 1$  direction.<sup>58,63</sup> As calculated<sup>52,53,64</sup> or directly observed by scanning tunneling microscopy (STM),<sup>52,65,66</sup> the top most buckled phosphorus dimers are stabilized by one hydrogen atom which saturates one of the dangling bonds of the dimer. At room temperature, a flip-flop motion of the dimer can be detected by STM as the H atom is mobile.<sup>65</sup> A phase shift of the periodicity of half a unit cell can take place in adjacent rows, and instead of  $(2 \times 2)$ , a  $c(4 \times 2)$  surface reconstruction is also formed. Thus, the randomly distributed two different domains show  $(2 \times 1)$ -like symmetry on the mesoscopic length scale. The presence of hydrogen on the P-rich surface was confirmed by Fourier transform infrared spectroscopy (FTIR).<sup>61</sup> The group-III-rich  $(2 \times 4)$  surface reconstruction of GaP(001) and InP(001) was also confirmed by LEED.<sup>59,64</sup>

#### Electronic structure of the surfaces and the origin of the RA spectral features

The obtained experimentally in situ RA spectra of GaP and InP surfaces can be compared with calculated spectra to identify the microscopic origin of their line-shapes. The ab initio DFT calculations of RAS of the P-rich surfaces show that the minimum at 2.6 eV for GaP (Fig. 3A, orange line), and at 1.9 eV for InP (Fig. 3B, orange dashed line), is related to optical transitions between occupied and unoccupied surface states induced by H termination of one H atom per P dimer.<sup>52,53</sup> The maximum at 3.7 eV for GaP (Fig. 3A, orange line), and at 3.2 eV for InP (Fig. 3B, orange dashed line), both close to the  $E_1$  interband transition, originate from surface-modified bulk transitions. The characteristic minima of the Ga-rich GaP(001) (Fig. 3A, blue solid line) and In-rich InP(001) (Fig. 3B, blue dash-dotted line) surfaces were attributed to a series of transitions between several occupied surface states close to the VBM and unoccupied surface resonances or unoccupied surface states in the conduction band related to the mixed  $(2 \times 4)$  reconstruction.<sup>54,67,68</sup> Several anisotropic optical transitions can explain the rather broad line-shape of these minima in comparison to the minima of the P-rich surfaces. In analogy to the P-rich surfaces, the RA spectral features close to the  $E_1$  interband transition stem from a surface-modified bulk transition.

The electronic structure of the here described surfaces can be investigated by in-system ultraviolet photoelectron spectroscopy (UPS) or time-resolved two-photon photoemission (*tr*-2PPE) spectroscopy. The advantage of the *tr*-2PPE over standard photoemission techniques is that it addresses both occupied and unoccupied electronic states, which however makes data interpretation more challenging. The excitation of electrons above the vacuum level occurs either in a direct coherent two-photon transition from occupied states or in a two-step process involving intermediate states above the Fermi level. In-system measurements by UPS<sup>69</sup> and with angular-resolved photoelectron spectroscopy with synchrotron radiation<sup>70</sup> were performed for P-rich and In-rich InP(001) surfaces. For both surfaces, surface states near the valence band maximum and surface resonances were observed and correlated with RAS and with ab initio calculations of the electronic surface structure. The presence of occupied and unoccupied surface state was also observed experimentally with in-system 2PPE on atomically well-ordered GaP(001) and InP(001) surfaces.<sup>2,71–74</sup> Fig. 4 depicts the positions of the occupied states in the VB ( $SS^O$ ) and the unoccupied states in the CB ( $SS^U$ ) relative to the CB and VB edges for P-rich and mixed  $(2 \times 4)$  reconstructed GaP(001) and InP(001) surfaces. For all surfaces, occupied surface states, approximately 0.2 eV for P-rich surfaces and 0.1 eV for mixed dimer surfaces below the VBM, were observed.<sup>2,74</sup> The position of the unoccupied states is different for each surface, and only for the P-rich GaP(001) surface they were not detected. These measurements can be well correlated with DFT calculations and the detected energies of the surface states complement the theoretical predictions. Moreover,

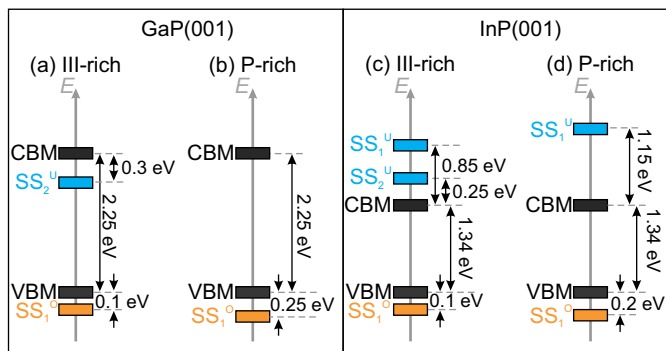


**Fig. 4** Energetic position of surface states ( $SS_{1,2}^{o,u}$ ) determined by 2PPE in relation to the conduction and valence band edges (CBM and VBM, respectively) for III-rich and P-rich InP(001) and GaP(001), after Ref. 2.

there is a good correlation between features in the RA spectra, and the energy spacings between states at the surface, which were detected with 2PPE.

#### Atomically well-ordered AlInP(001) and GaInP(001) surfaces

**Fig. 5** shows RAS of 200 nm thick AlInP(001) and 100 nm thick GaInP(001) surfaces, taken at 300 °C. Note that the RA spectra shown in **Fig. 3A** and **B** were measured at a much lower temperature of 20 K, at which the RA spectra are shifted toward higher photon energy.<sup>29</sup> Both epitaxial layers were grown at 600 °C on Ge(001) wafers, and the content of Al and Ga in the bulk of AlInP and GaInP, respectively, was adjusted to around 50% to match the lattice constant of the substrate.<sup>76</sup> The RA spectrum for GaInP(001) (black line) shows the characteristic line-shape of a P-rich  $(2 \times 2)/c(2 \times 4)$  reconstructed surface, confirmed by LEED<sup>76</sup> on a nearly ordered GaInP layer, typical for growth under these conditions.<sup>77,78</sup> Its line-shape is very similar to the RAS of P-rich GaP(001) and InP(001) surfaces and its photon energy is in between those two RA spectra. The minimum near 1.9 eV (at 300 °C) can be as well related to the P-dimerized surface reconstruction. It was shown that a gradual increase of Al content in the bulk of GaInP causes an increase in the anisotropy and a shift of the maximum near 3.1 eV for GaInP to higher photon energy.<sup>77</sup> This shift of the composition-dependent peak corresponds to the change in the AlGaInP bulk dielectric properties.<sup>79</sup> An RA spectrum of a P-rich AlInP(001) surface with 50% Al content in the bulk is shown in **Fig. 5** (black line). The P-rich  $(2 \times 2)/c(2 \times 4)$  surface reconstruction was confirmed by LEED combined with XPS measurements.<sup>75,76</sup> The inset shows XPS measurements of the P 2p core level with a fit of two spin-orbit pairs. The component shifted toward higher binding energy confirms presence of P–P dimers on the surface (blue line), and the one shifted toward lower binding energy is related to the bulk (green line).<sup>76</sup> Compared to GaInP, the maximum is shifted to around 3.3 eV, and is broader. The features below around 3.0 eV are related to Fabry-Perot oscillations. The amplitude of these oscillations is higher for AlInP(001) buffer compared to

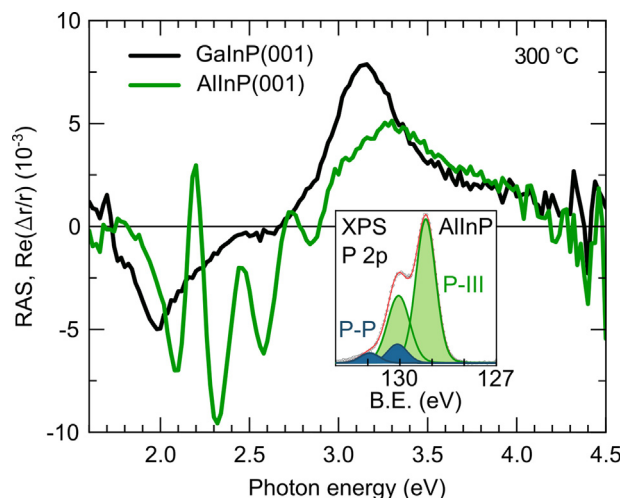


**Fig. 5** RAS of P-rich GaInP(001), black and AlInP(001), green, surfaces, measured at 300 °C. The lattice constant of both epitaxial layers is matched to GaAs(001) substrate, which corresponds to a ratio of around 1:1 of In to either Al or Ga in the bulk. The inset shows XPS measurement of P 2p core level of the corresponding AlInP(001) surface, including one surface, and one bulk component.<sup>75</sup>



### III-nitride surfaces after thin film preparation

III-nitrides including their ternary and quaternary alloys allow to tune their electronic properties, such as band gap, lattice constant, surface band bending, interface band offsets over a wide range. Since the III-nitrides have as a result a wide range of applications different growth methods have been applied including (PA)MBE, MOCVD/MOVPE, VPE, HVPE depending on the desired application and the resulting demands. For many applications, the understanding of surface/interface states and band bending is crucial. However, these properties depend on growth method, surface preparation, and intentional/unintentional doping and adsorbates. In the following we will concentrate on pure GaN and InN in their wurtzite crystal structure grown by PAMBE and characterized in vacuo directly after growth. Thereby GaN typically exhibits an upward<sup>81–83</sup> and InN by contrast a downward band bending.<sup>84</sup>

Exemplary, we refer to in vacuo studies on different GaN and InN thin films with different orientations ((0001), (000-1), (1-100) and (11-20) and surface reconstructions) grown by plasma enhanced molecular beam epitaxy (PAMBE). For a GaN(0001)-2x2 surface an upward band bending of 0.4 eV<sup>85</sup> and in case of InN an downward band bending of 0.5 eV for InN(000-1)-2x2 was observed (in line with the long time stated downward band bending as “universal feature” of InN<sup>84</sup>), while flat band condition could be validated for N-polar, m-plane and a-plane InN<sup>86</sup> – in line with other studies.

## The semiconductor/electrolyte contact of III-V semiconductors: Surface reactivity and surface/interface states

### Surface and interface properties needed for efficient PEC cells

Efficient photoelectrochemical cells should deliver photocurrent densities  $\geq 10 \text{ mA} \cdot \text{cm}^{-2}$  under normal terrestrial sunlight illumination. In general, strongly acidic ( $\text{pH} \leq 1$ ) or strongly alkaline electrolytes ( $\text{pH} \geq 13$ ) are used to provide sufficient conductivity to support these current densities without substantial resistance losses. Most semiconductors are, however, chemically unstable in such potentially corrosive electrolytes. In order to reach lifetimes of several years while maintaining efficiencies well over 10%, which are the conditions for the commercial deployability of photoelectrochemical devices,<sup>4</sup> the photoabsorber has to be protected from the electrolyte. Metal oxide semiconductors have been widely used as protection layers for photoelectrodes because of their relatively high intrinsic chemical stability and their minimal parasitic light absorption. Such oxides are usually already present on semiconductor surfaces after contact to ambient conditions. Whether such oxides, which form as a result of the self-oxidation of the unstable semiconductor materials, are suitable as protection layers must be investigated because they often hinder the efficient charge transport depending on their thickness.<sup>19</sup> The general requirements for the protective films are that they are electrically conductive, electrochemically stable, optically transparent and that they form a closed layer that prevents direct contact between the semiconductor and the electrolyte. An ideal protection layer would additionally be antireflective (or reflective if it is used to protect the bottom absorber), constitute a large energy barrier for the majority carriers and, at the same time, show a suitable band alignment for efficient charge transport of the minority carriers. Furthermore, an interface with a small trap state density should be formed.<sup>87</sup> Therefore, the investigation of surface oxides after exposure to ambient conditions compared to the surface properties of clean semiconductor surfaces prepared under well-defined conditions is a prerequisite of any surface engineering approach, especially for III-V semiconductors.

In short, an ideal protection layer for a photoelectrode would combine chemical stabilization with good charge transfer properties and surface recombination passivation. Fig. 7 shows the band diagrams of two different photocathodes with a metal oxide

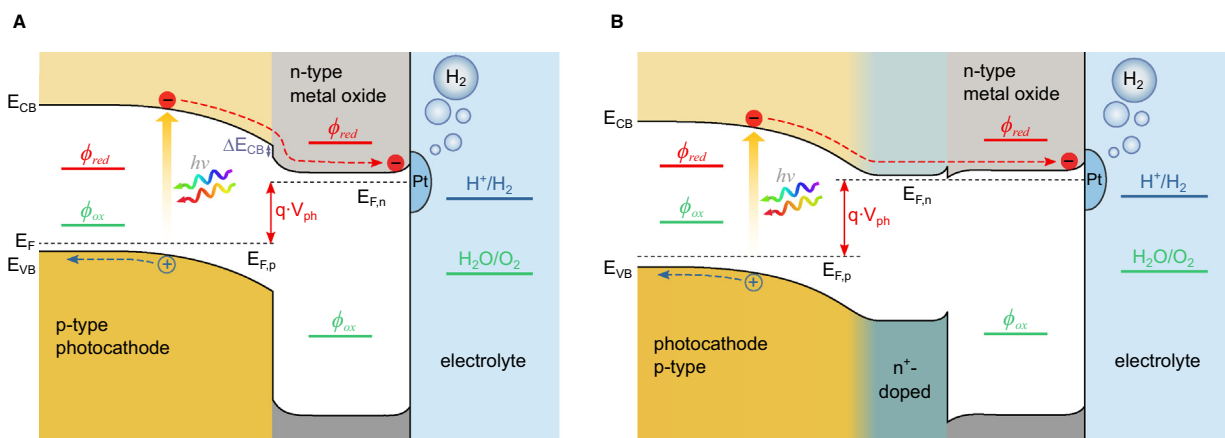


**Fig. 7** Schematic illustration of the band diagrams of p-type photocathodes equipped with an n-metal oxide protection layer and platinum catalyst particles.<sup>17</sup> Upon illumination, electrons are excited from the valence into the conduction band and the change of the electron population in both bands leads to a splitting of the Fermi level  $E_F$  into the quasi-Fermi levels  $E_{F,n}$  for the electrons and  $E_{F,p}$  for the holes. The difference between the two energy levels defines the photovoltage  $V_{ph}$  of the system. Figure a) shows the case of a p-semiconductor/n-metal oxide heterojunction and Fig. b) shows the protection of a buried pn<sup>+</sup>-junction. Although  $\phi_{ox}$  of the photocathode is higher in energy than the H<sub>2</sub>O/O<sub>2</sub> level, the photocathode is protected against hole oxidation because the oxide layer with its low VBM acts as a hole-blocking layer. The band alignment of the materials only allows the electrons to migrate toward the electrolyte and confines the holes in the photocathode.

protection layer that would result in a good photoelectrochemical performance. One way for achieving this is a photocathode that exhibits a high built-in potential. The built-in potential of a pn-junction depends on the work function difference between the p-type and the n-type semiconductor. This implies for a p-type photocathode/n-type metal oxide heterojunction that the oxide material should be selected with regard to the cathode material. GaInP<sub>2</sub> e.g., has an electron affinity of  $\chi = 3.9\text{--}4.1\text{ eV}$ <sup>88,89</sup> and thus the work function of a p-GaInP<sub>2</sub> photocathode should be around 5.7 eV. The oxide protection layer should therefore have a work function that is considerably lower than this value. The built-in potential of the heterojunction leads under short-circuit conditions to a band bending inside the two semiconductors, which separates the photo-generated electrons and holes from each other. Since the electron–hole pairs are generated inside the photocathode, it can be beneficial if the band bending extends from the interface far into the photocathode material. This can be achieved if the donor density in the overlayer is significantly higher than the acceptor density in the photoabsorber ( $N_D \gg N_A$ ), and therefore a high doping density inside the metal oxide protection layer is of advantage.<sup>46</sup> The different doping densities in the absorber and in the protection layer are indicated in Fig. 7 by the different band bending in the two materials. It has to be noted, however, that a more general description of efficient design principles considers the gradient of the electrochemical potential as the main driving force, opening up additional design routes for charge-selective contacts without the bending of energy bands.<sup>25</sup>

Another important aspect are the band offsets which form at the interface of a heterostructure. The conduction band offset  $\Delta E_{CB}$  between photocathode and protection layer in Fig. 7A should be as small as possible because it leads to an energy loss for the photoelectrons flowing toward the electrolyte. Since the conduction band offset is determined by the electron affinity difference of the two semiconductors, the electron affinity of the metal oxide should be similar to the one of the photocathode. On the other hand, a large offset of the valence band edges is beneficial because it produces a large barrier for photoholes flowing toward the electrolyte and therefore prevents current flow in the wrong direction that would reduce the photovoltage of the device.<sup>18</sup> Additionally, the gradient of the electrochemical potential on both sides of the semiconductor/metal oxide interface, as depicted by the bending of the band edges in Fig. 7A, should drive electrons and holes away from the interface and thereby reduce possible charge recombination over interfacial defect states.<sup>90</sup> If defect states are present at the heterojunction, the interface between the two materials may be charged. A possible interface sheet charge influences the position of the bands in the space charge region and can result in an additional potential loss for the photoelectrons, which reduces the open-circuit voltage of the photoelectrode.<sup>46</sup>

Thus, the protection of a semiconductor photocathode in the form of a semiconductor/metal oxide heterojunction has the advantage of the formation of a built-in potential. However, the interface between the two different materials is prone to defect formation that can diminish the open-circuit potential of the device by Fermi level pinning, charging or enhanced recombination. An alternative approach that circumvents some of these issues is the use of a photoelectrode with an internal pn-junction, a so-called buried junction. The schematic band diagram of a buried junction with a metal oxide protection layer is shown in Fig. 7B. The advantage of a buried junction device is that the junction that provides the built-in potential can be produced as a defect-free pn-junction, which maximizes the built-in potential of the photoelectrode. The photoabsorber/protection layer interface is still important for the efficiency of a photoelectrochemical cell based on a buried junction, but not as crucial as for the heterojunction device. In a buried junction, no pinning of the Fermi level limits the built-in potential, and electrons and holes are separated from each other further away from possible recombination sites. The requirements for efficient charge transport across the semiconductor/metal oxide interface are the same as discussed above for the heterojunction. In the schemes of Fig. 7 also a platinum particle at the surface of the protection layer is shown. It should represent the presence of catalyst nanoparticles on the metal oxide surface. Since protective metal oxides are in general poor HER catalysts, cocatalysts are generally required to improve the kinetics of the charge transfer from the electrode to the electrolyte solution.<sup>19</sup> In addition to the catalytic activity, the contact properties of the metal oxide/catalyst interface are important. The Fermi level in a metallic catalyst should be well aligned with the CBM of the metal oxide to allow for a small Schottky barrier height and similarly, for a nonmetallic catalyst, the electron affinities of the two semiconductors should match to reduce the band offset. Ideally, the metal oxide/catalyst contact should show ohmic behavior with a very low interface resistance. With a cocatalyst in the form of particles, the photoelectrode/electrolyte interface is inhomogeneous and the energetic alignment at the interface is determined by a combination of the metal oxide/catalyst alignment and the metal oxide/electrolyte alignment. However, if the catalyst particles are sufficiently small and well separated, the alignment is mainly dominated by the metal oxide/electrolyte junction.<sup>91</sup>

Finally, since it is the dominant solid–liquid junction, the conduction band edge of the protection layer should be well-aligned with the water reduction potential  $H^+/H_2$  in the electrolyte under operation conditions. Ideally, the photo-generated electrons have exactly the amount of energy to overcome the kinetic overpotential  $\eta_c$  of the HER. Any misalignment of the conduction band edge with respect to the potential  $\phi = \phi(H^+/H_2) + \eta_c$  will result in an additional voltage loss equal to the amount by which the band edge is misaligned.<sup>11</sup> The alignment of the band edges with respect to the water redox potentials depends on the electron affinity of the protection layer and on the voltage drop at the Helmholtz double layer, which develops due to the interaction of the material with the electrolyte.<sup>92,93</sup> It is possible to alter the electron affinity of the semiconductor or to change the voltage drop at the Helmholtz layer by modifying the semiconductor surface with polar molecules to improve the energetic alignment.<sup>91,94</sup> Thus, the protection layer material should be selected depending on its energetic alignment with the photoabsorber material as well as with the electrolyte solution. Additionally, trapping of charge carriers on the surfaces of the electrode due to surface states or slow charge transfer may lead to additional potential shifts across the electrochemical double layer under operational conditions depending on the relative rates of charge separation compared to the charge transfer reactions.

As shown by the preceding discussion, a multitude of factors has to be considered for choosing a material for the protection of a photoelectrode in surface engineering approaches. Since some of the needed material properties affect each other, the selection of a suitable material and the optimization of the different interfaces is a complex and challenging task. With regard to possible interface engineering approaches, section 4 presents surface science experiments which were employed to determine the band energy diagrams in dependence on different surface conditionings.

Unprotected photoelectrodes based on semiconductors which are chemically or electrochemically unstable in aqueous electrolytes used for water splitting will show a fast photocurrent decay during operation either due to dissolution, or the corrosion can lead to an increased surface defect density and with that to a higher surface recombination rate. The formation of a surface oxide that prevents the semiconductor from further corrosion, on the other hand, can inhibit the efficient charge transfer if a rather thick insulating oxide layer is formed. The purpose of a passivation layer is to prevent these detrimental effects.

In general, a passivation layer for a photoelectrode should perform the following functions<sup>95,96</sup>

1. prevent reactions between the photoabsorber material and the electrolyte (chemical passivation),
2. eliminate already existing defects and prevent the formation of new interface states in the band gap (electrical passivation) and
3. allow an efficient charge transfer from the photoabsorber to the electrolyte solution.

Fig. 8 illustrates how a passivation layer works. The unprotected photocathode (Fig. 8A) exhibits a high density of surface states within the band gap, which leads to pinning of the Fermi level at the semiconductor/liquid junction.<sup>97,98</sup> This reduces the possible band bending in the cathode and with that the maximum open-circuit voltage of the PEC cell. Furthermore, the surface states act as a trap for the photo-generated electrons and lead to increased recombination with the majority carriers of the cathode. The charge transfer to the  $\text{H}^+/\text{H}_2$  level competes with the trap-site-induced surface recombination. Without an HER catalyst, the kinetics  $k_{\text{HER}}$  of the water reduction reaction are low, which leads to an accumulation of electrons at the solid/liquid interface and an even higher recombination rate  $k_{\text{re}}$ . The function of the passivation layer in conjunction with the HER catalyst in Fig. 8B is to reduce the corrosion at the semiconductor surface by a suitable band alignment and to improve the interfacial charge transfer rate to the electrolyte. If possible, the density of defect states at the semiconductor surface should also be reduced by a favorable bonding structure at the interface, which saturates dangling bonds at the semiconductor surface.

### Water/III-V interactions from density-functional theory for modeling semiconductor/electrolyte interfaces

As mentioned in the previous section, the rapid corrosion of the III-V-based photoelectrodes under operating conditions is one of the major problems still to be solved. This requires a detailed understanding of the water/III-V interaction also from a computational point of view, as many experimental results can only be understood in context with electronic structure calculations. Furthermore, a close interplay between experiment and theory can accelerate discoveries. Here, electronic structure calculations are typically performed on a DFT level.

While clean III-V surfaces are well understood, relatively little is known about their microscopic structure and electronic properties in contact with water. The adsorption of water—ranging from single molecules to complete overlayers—on III-V(001) surfaces has been the subject of various density-functional theory studies, frequently also combined with molecular dynamics (DFT-MD) to account for the kinetics of the dynamic solid–liquid interface. While the solid–electrolyte interface can be in principle modeled by explicit water molecules or an implicit solvation model,<sup>99</sup> we will focus on explicit approaches due to their potentially higher accuracy, albeit at increased computational costs. The existing studies indicate that the water/III-V interface depends on the

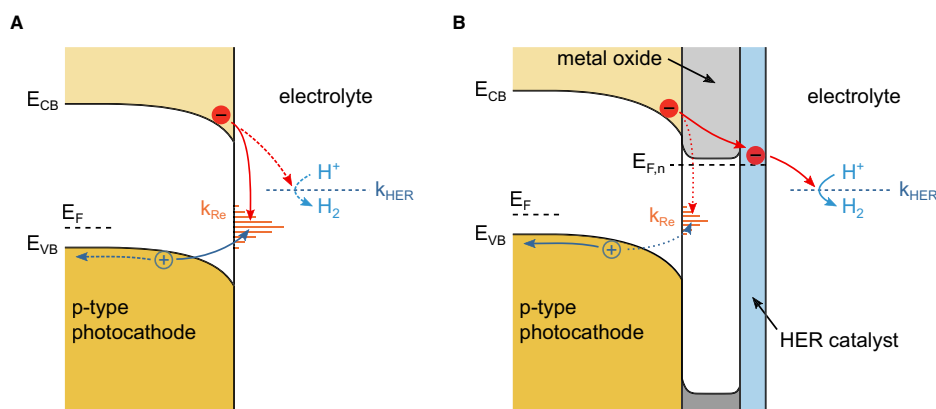


**Fig. 8** Schematic illustration of the surface passivation for a photocathode.<sup>17</sup> The band structures with the possible charge transfer pathways are shown for an unprotected photocathode (A) and for a photocathode passivated with a metal oxide in conjunction with an HER catalyst (B). Defects states on the semiconductor surface act as trap sites for recombination. The surface recombination rate  $k_{\text{re}}$  should be much smaller than the reaction rate  $k_{\text{HER}}$  for the HER. This can be achieved by reducing the density of trap sites at the semiconductor surface and by increasing  $k_{\text{HER}}$  with the help of the HER catalyst. Adapted from Ref. 95.

semiconductor material as well as on its surface reconstruction: A density-functional study by Wood et al.<sup>100</sup> finds the dissociative adsorption of water favorable for GaP(001) surfaces, but not for InP(001). In case of In-rich InP(001) surfaces, single molecules attach preferably to three-fold coordinated surface In atoms. Water dissociation is energetically favorable, but hindered by an energy barrier that decreases with increasing water coverage. There is an attractive interaction between InP adsorbed water molecules that leads to the formation of molecular clusters and complete water films for water-rich preparation conditions. Water films on InP are stabilized by anchoring to surface bonded hydroxyl groups. With increasing thickness, the water films resemble the structural properties of (common) ice Ih. In case of GaP it was noted that the Ga-rich surfaces show a higher reactivity than P-rich surfaces.<sup>51,101</sup>

Much work has been dedicated to clarify the water adsorption on the In-rich InP(001)( $2 \times 4$ ) surface, which is stable for a wide range of preparation conditions and hence experimentally readily accessible. This surface reconstruction features a single In–P hetero-dimer in the uppermost atomic layer.<sup>55,102</sup> A systematic approach to the water adsorption mechanism is provided by potential-energy surface (PES) calculations. In Fig. 9A the PES experienced by single water molecules on InP(001)( $2 \times 4$ ) as calculated in Ref. 102 is shown. It indicates that three-fold coordinated surface In atoms provide the most favorable bonding sites for water, corresponding to the sites A, B, and C identified already in Ref. 100. Adsorption at surface P, i.e. the sites D suggested in an experimental study,<sup>30</sup> is less favored. In combination with the PES calculated for the adsorption of OH and H (Fig. 9B and C respectively), the most relevant configurations for the low-coverage stage of the water-InP interface can be identified.

The adsorption geometry along with the adsorption-induced charge density redistribution for water at the most favorable site B is shown in Fig. 10A. The water donates electrons of its  $1b_1$  HOMO orbital into the empty In dangling bond of  $p_z$  character.<sup>103</sup> This results in a weak 2.5 Å O–In bond formed at the surface. The substrate geometry is modified only slightly upon adsorption.

The total-energy calculations<sup>103</sup> support dissociative adsorption: The hydroxyl group is attached to an In–In bond (site E in Fig. 9) and the hydrogen adsorbs at the mixed-dimer P atom, as shown in Fig. 10B. This configuration is 0.1 eV lower in energy than the most favorable molecular adsorption at site B. The dissociative adsorption leads to a marked distortion of the InP(001) surface geometry, induced in particular by the oxygen insertion from the hydroxyl group into the second-layer In–In bond. As seen by the charge-density redistribution in Fig. 10B, strong In–O–In and P–H bonds form.

The energy barrier for water dissociation has been calculated in Ref. 102 using the nudged elastic band method, see Fig. 11A. The transition state corresponds to the hydroxyl group transfer from position A to position E. An energy barrier of 0.87 eV is obtained. This is of the same order of magnitude as determined earlier for a different dissociation path.<sup>100</sup>

For a slightly increased water coverage, the adsorption of two molecules per surface unit cell was considered in Ref. 102. The minimum energy configuration for molecular adsorption corresponds to the molecules bonded at sites B and B', cf. Fig. 9A. Compared to single molecules adsorbed at these sites, an energy reduction of 0.09 eV per molecule was obtained. This demonstrates an attractive interaction and suggests the study of higher water coverages. In Ref. 102, water coverages up to 56 molecules per ( $2 \times 4$ ) surface unit cell were considered. It was found that the one-monolayer configuration (Fig. 12A) is more favored than small

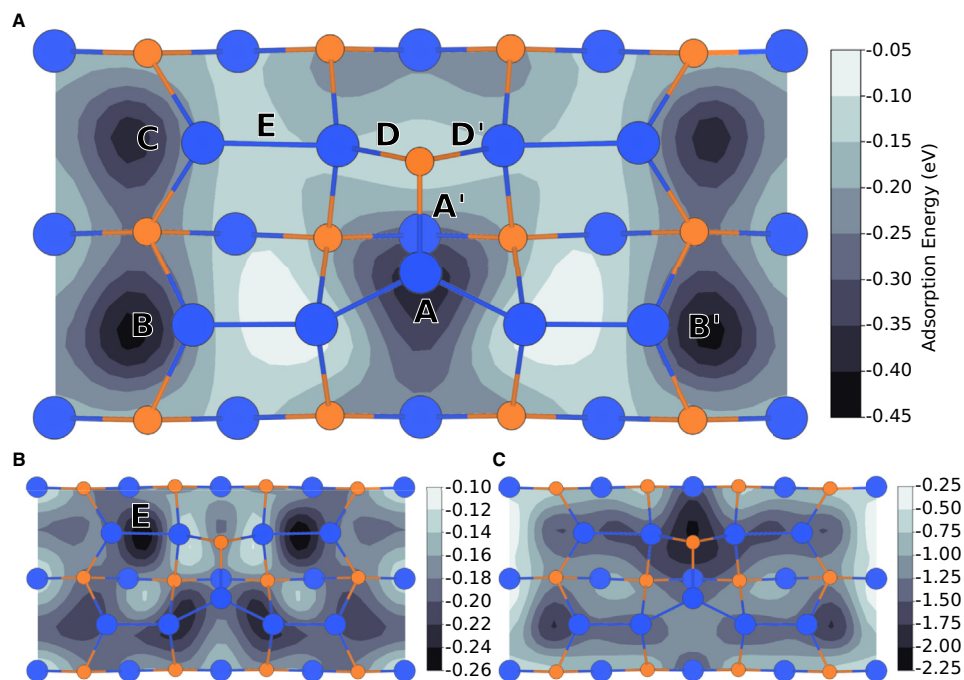


**Fig. 9** Calculated potential energy surfaces for (A) single water molecules, (B) an OH group, and (C) an H atom on the InP(001)( $2 \times 4$ ) mixed-dimer surface. Blue and orange spheres indicate In and P, respectively. From Ref. 103.

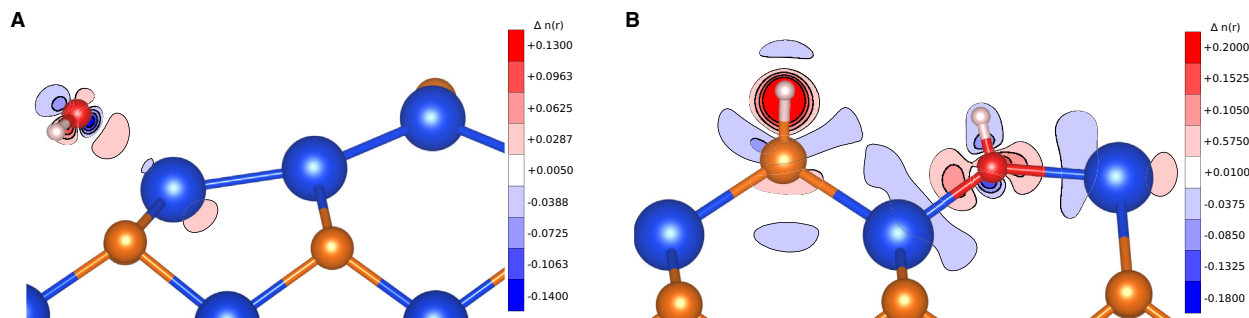


**Fig. 10** Structural configuration and water-induced charge redistribution for water adsorbed on InP(001) on site B (A) and dissociatively adsorbed water with OH on site E and H on the top P (B). Red and blue isosurfaces indicate regions of charge accumulation and depletion, respectively. Blue spheres represent In atoms, orange spheres P atoms. From Ref. 102.

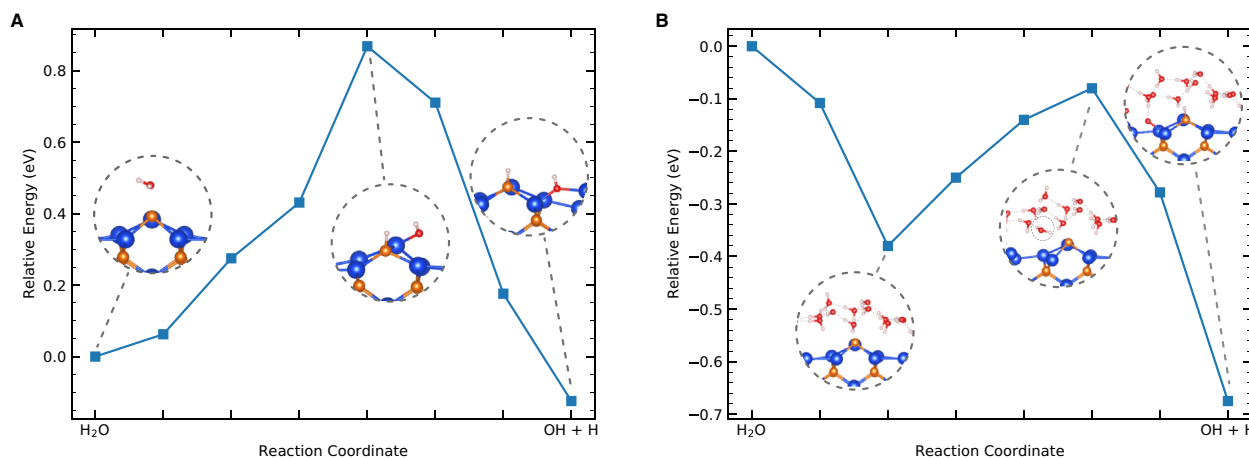


**Fig. 11** Minimum energy path for dissociative adsorption of water molecules (A) on the InP(001) surface and (B) embedded at the water-InP interface. The starting point in (A) is the water molecule adsorbed at site A, for the final point see Fig. 10B. From Ref. 103.

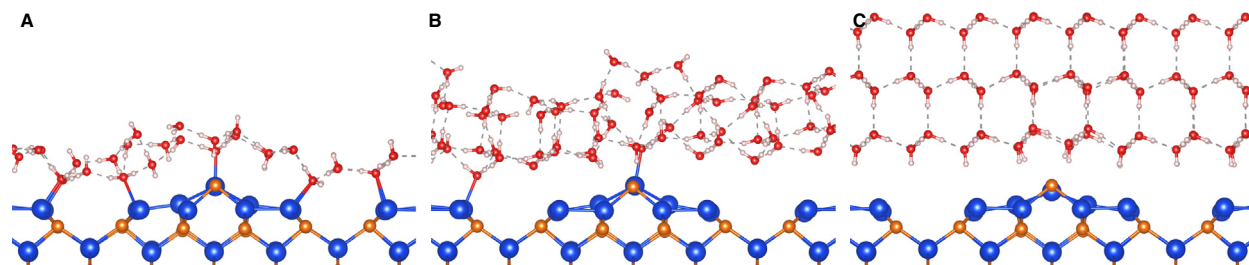


**Fig. 12** Energetically favorable In-P(001)(2 × 4) structures with (A) one, (B) two, and (C) three adsorbed water layers. From Ref. 103.

molecular clusters comprising up to five molecules. Even more favorable, however, is the water bilayer (Fig. 12B). According to Ref. 103, for intermediate values of the water chemical potential, corresponding roughly to standard pressure at room temperature, there will be a direct transition from the clean InP surface to the water-bilayer-covered surface. For more water-rich conditions, even thicker water layers will form.

Structurally, the water layer configurations in Fig. 12 bear some similarity to the ice phase Ih, in particular for the largest coverage in Fig. 12C. Due to the incommensurability of the ice Ih basal plane with the InP(2 × 4) surface unit cell as well as due to the InP surface morphology, however, some disorder arises. In particular, irregular pentagons and hexagons form. The mono- and bilayer structures are characterized by water O bonded to three-fold coordinated In atoms, resembling the single molecule bonding to sites A, B, and C in Fig. 9. The number of these bonds reduces upon formation of the water bilayer. They are completely quenched for the three-layer structure. The InP surface phase diagram in dependence on temperature and water partial pressure is shown in Fig. 13A. At the transition between the clean InP surface and the water covered substrate, some variety of adsorption configurations can be



Ref. 103 with the water oxidation and hydrogen reduction potentials, 1.23 and 0.00 eV, respectively. This corresponds to  $-5.67$  and  $-4.44$  eV on the standard vacuum scale. The calculations for InP bulk result in  $\Delta\Phi = 5.79$  eV. This leads to OER and HER potentials that are both inside the band gap, albeit close to the edges. The mixed-dimer terminated InP(001) surface has a lower ionization energy  $\Delta\Phi = 4.49$  eV due the surface dipole.<sup>102</sup> Thus, the oxidation potential is no longer above the valence band. Water adsorption further enhances the surface dipole and decreases the ionization energy, see dashed lines in Fig. 14. The calculations for clean and water-covered InP surfaces<sup>103</sup> thus suggest the surface primarily for hydrogen rather than oxygen evolution. The need to obtain an accurate energetic alignment, especially between two different phases such as liquid water and a solid semiconductor, does, however, have implications on the level of theory to be used and hence the associated computational costs. While standard-relativistically inexpensive-DFT on a generalized gradient level is reasonably accurate for III-V semiconductors and their solid interfaces if one neglects the band gap error, this is not necessarily the case for the interface to water. Here, hybrid functionals might be needed, changing levels by up to more than one eV,<sup>105</sup> but at the same time typically increasing computational costs by about one order of magnitude.

In summary, single adsorbed water molecules on the In-rich InP(001) surface bond preferentially to three-fold coordinated In surface atoms. Dissociative adsorption is more favorable than molecular adsorption, but hindered by a sizable energy barrier. Upon dissociation, the hydroxyl group preferentially bonds to In-In dimers, while hydrogen adsorbs at the mixed-dimer P atom. Upon increasing the water coverage, an attractive interaction between the water molecules governs the interface morphology. There is a small range of preparation conditions corresponding to intermediate values of the water chemical potential where a variety of structures are nearly degenerate and single molecules, molecular clusters and completely water-covered surface patches coexist. For water-rich conditions, water layers form. This leads to a distinct reduction of reaction barriers, e.g., for water dissociation. While the morphology of the monolayer water film is strongly influenced by the InP surface structure and characterized by numerous surface In - water oxygen bonds, the bilayer and multi-layer structure resemble strongly the molecular arrangement in ice Ih. Surface bonded hydroxyl groups formed upon dissociation of water act as anchor points for the water overlayer.

It must be stated, however, that the conclusions drawn from the theoretical modeling are based on well-defined surfaces. Which effects are related to defects in the surface structure due to non-ideal surface conditions, needs to be checked with experimental surface studies.

### InP(001), GaP(001) and GaInP<sub>2</sub>(001)surfaces after surface processing

In contrast to the elemental semiconductor silicon, which can form a nearly ideal interface with its native oxide SiO<sub>2</sub>, most of the III-V semiconductor compounds do not form defect-free interfaces with their native oxides.<sup>96,106,107</sup> This can be explained by the different bonding schemes of oxygen to the group-III and group-V elements forming different native oxide layers.<sup>107,108</sup> In the oxide layer on InP, for example, binary compounds like In<sub>2</sub>O<sub>3</sub> or In(OH)<sub>3</sub> as well as ternary oxides like InPO<sub>4</sub> can coexist.<sup>107</sup> Similarly, the native oxides of GaP<sup>44,109</sup> and also of the ternary compound GaInP<sub>2</sub><sup>94,110,111</sup> provide poor passivation layers. Additionally, these oxide layers induce a high density of defect states at the semiconductor/native oxide interface.<sup>112</sup> These states lead to pinning of the Fermi level around the middle of the band gap, limiting the built-in potential of III-V semiconductor devices. In addition, the defect states can act as efficient electron-hole recombination centers that result, e.g., in a reduced current density of the photoelectrochemical cell.<sup>96</sup> For these reasons, methods to passivate the surface of group-III-phosphide semiconductors are necessary if these materials should be used as photoabsorbers in efficient water-splitting devices. The easiest way to avoid the formation of a surface oxide is to produce the complete device in one vacuum system, so that the as-grown semiconductor surface is never exposed to the ambient atmosphere during the production process. With this in situ deposition approach, high-quality III-V semiconductor/insulator interfaces can be formed.<sup>106</sup> The alternative is to remove the native oxide layer from the semiconductor surface before the passivation layer is deposited.

This section focuses on the composition and electronic structure of the native oxides of GaInP<sub>2</sub> in comparison to the native oxides of InP and GaP as well as on possible additional surface processing steps to prepare clean surfaces. As mentioned above, the native oxides that are formed on group-III-phosphide semiconductors can be detrimental to the performance of a photoelectrochemical cell. In particular, Fermi level pinning at the semiconductor/oxide interface strongly reduces the photoelectrochemical performance since it prevents the exploitation of the entire band gap for the built-in potential of the device. Therefore, the possible causes for the Fermi level pinning at these interfaces as well as possible processing steps to reduce the pinning are of great interest. They are discussed in great detail in Ref. 17. In the following, an overview of the results from Ref. 17 should be given.

The wet-chemical processing steps to remove the native oxide layers from III-phosphide surfaces were performed in an integrated (electro-)chemical cell as shown in Fig. 15. It allows to perform experiments in a controlled atmosphere and the transfer of samples into UHV without exposure to ambient conditions. The etching solution is stored in a pipette and can be released in droplets onto the sample surface. The etching solution can be drained off by tilting the sample holder with the help of the UHV manipulator. After the etching is done, the residual etching solution can be removed by rinsing it in a water or alcohol jet from a syringe. The pipette connected to the argon gas supply is used to blow the sample and the sample holder dry at the end of the treatment. The consumed etching and rinsing solutions are collected in the gas-wash bottles, which separate the setup from the ambient atmosphere.

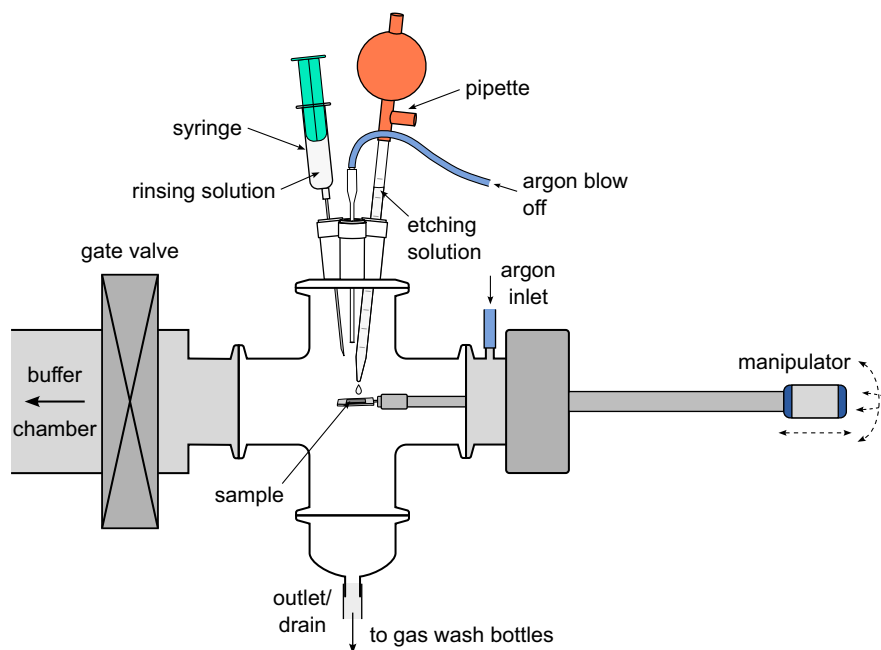


**Fig. 15** Sketch of the electrochemical cell connected to the integrated UHV system. It shows the setup used for wet-chemical etching of the sample surfaces.<sup>17</sup>

### Native oxides of III-phosphide semiconductors

#### *InP(001) and GaP(001)*

First, results of XPS measurements of the native oxide on GaP(001) and InP(001) surfaces are presented, cf. Fig. 16. The samples were cleaned in an ultrasonic bath with acetone and 2-propanol for 3 min respectively prior to the XPS measurements. As can be seen in the indium and gallium core level spectra, the amount of native oxide on the surface is higher for the GaP sample. This can be explained by the different oxidation times of the corresponding samples. Significant differences can also be found in the chemical composition of the oxides on the two materials. For the deconvolution of the spectra into components from specific oxide and phosphate compounds, it was assumed that these compounds are present as stoichiometric phases. This is most likely a simplification because the native oxides are probably amorphous, as it is the case for surface oxides on oxidized InP surfaces.<sup>113</sup>

Based on a thorough analysis of measured binding energies compared to published literature data and a detailed analysis of the relative intensities of the measured components in relation to their compositions considering the sensitivity of our XP spectrometer, it is evident that the native oxide on InP mainly consists of  $\text{In}(\text{OH})_3$  and  $\text{InPO}_x$  (possibly with  $x \approx 3$ ). Hofmann et al. identified the in air grown oxides on etched and annealed *p*-InP as a mixture of  $\text{In}(\text{OH})_3$  and  $\text{InPO}_4$  based on the atomic ratios in the oxide layer.<sup>114</sup> Hollinger et al. found that the XP spectra of In-rich oxides on *n*-InP are similar to spectra from  $\text{In}(\text{OH})_3$  powder.<sup>113</sup>  $\text{In}_2\text{O}_3$  was not identified as one of the main components of these oxides, in contrast to thermal oxides grown on InP in oxygen atmosphere.<sup>115</sup> The depth distribution of the InP oxide compounds is inconsistent throughout the literature. While thermally grown oxides and some anodic oxides show a phosphorus excess at the oxide/InP interface,<sup>115–117</sup> thermal oxides grown at low temperature or oxides grown in air at room temperature exhibit an In-rich interface layer and a P-rich surface layer.<sup>114,118</sup> Taking into account the results from the wet-chemical etching of the InP surface in the subsequent sections, it is probable that the In atoms at the InP/oxide interface are in a bonding configuration similar to  $\text{In}_2\text{O}_3$  because these atoms remain after the etching (see Fig. 16A), while the phosphates are completely removed.

The chemical composition of the native oxide on GaP is quite different from the composition on InP. The oxide layer from Fig. 16B does not show an excess of group-III atoms. The total Ga P ratio from the peak areas is 1.02, which is in accordance with the ratio which is expected from the GaP substrate. If only the oxide components from the fitting are considered, the Ga P ratio is approximately 0.9. This indicates that the native oxide layer on GaP is slightly enriched in phosphorus. The phosphate peak in the P 2p spectrum of the GaP surface has a chemical shift of approximately 5.1 eV. This is 0.8 eV higher than for the phosphates on the InP surface and very close to the binding energy shift of 5.1 eV which is expected for  $\text{GaPO}_4$ .<sup>119–121</sup> The amount of oxide in the Ga 3d spectrum, however, is too small to be compatible with the assumption that the phosphate is solely  $\text{GaPO}_4$ . Therefore, the P-rich gallium metaphosphate  $\text{Ga}(\text{PO}_3)_3$  component, which is one of the possible stable phases of the Ga–P–O system,<sup>122</sup> was added to the fitting model. The binding energy of the other phosphate component is given by the fit to be around 4.8 eV and is therefore smaller than the literature value for  $\text{GaPO}_4$ . Dong et al. assign the native oxide on GaP to  $\text{GaPO}_4 \cdot x\text{H}_2\text{O}$  with a P 2p binding energy shift of 4.5 eV compared to GaP.<sup>120</sup> Similarly, Hollinger et al. reported a reduced indium phosphate binding energy if it contains

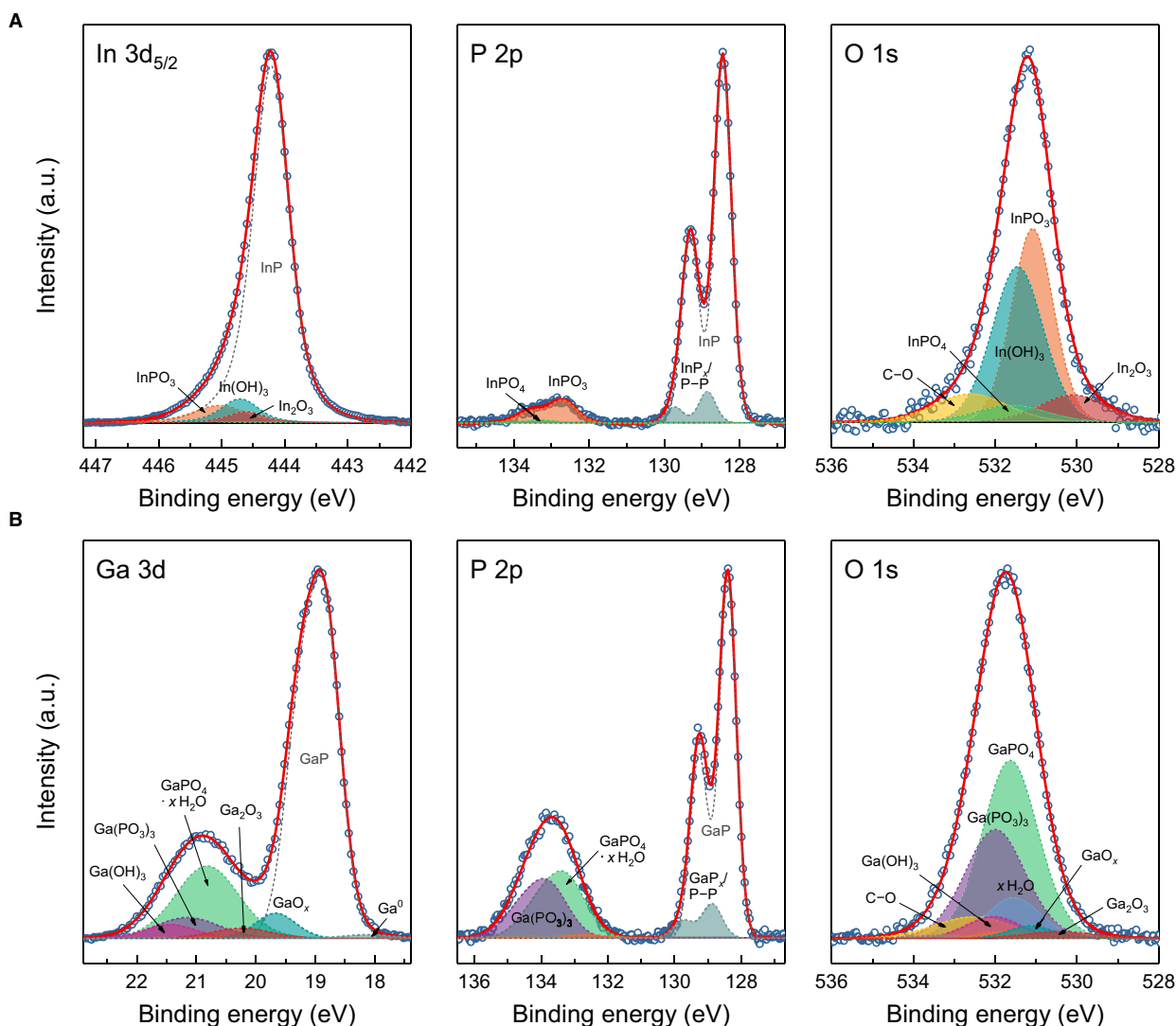


**Fig. 16** XP detail spectra of the native oxide layers on  $p\text{-InP}(001)$  (A) and  $p\text{-GaP}(001)$  (B) after background subtraction. The chemical composition of the oxides was determined by fitting components for possible oxide compounds to the measured data (blue circles). The sum of the fitted components is shown by the red solid line. From Ref. 17.

water.<sup>113</sup> Hence, it seems likely that the gallium phosphate component with smaller binding energy can be assigned to  $\text{GaPO}_4 \cdot x\text{H}_2\text{O}$ .

The nature of the Ga–O species can be studied more precisely in the Ga 3d spectrum. Based on the phosphate intensity in the P 2p spectrum, the main constituent of the native oxide should be gallium phosphate. The fitting result of the Ga 3d spectrum agrees with that conclusion. The maximum of the oxide peak is at a binding energy of 20.9 eV. Although this is slightly below the values reported for  $\text{GaPO}_4$ , the chemical shift of 1.8 eV fits well to the shift of 1.7 eV found by Iwasaki et al. during the thermal oxidation of GaP, which they attribute to the formation of  $\text{GaPO}_x$  or  $\text{GaPO}_4$ .<sup>119</sup> An additional important Ga–O species is gallium suboxide  $\text{GaO}_x$ , which is the most stable bound native oxide on GaAs and InGaAs surfaces.<sup>123</sup> Similarly, the gallium suboxide on GaP remains after wet-chemical etching (cf. Fig. 20B below) and at least one oxide component is needed to fit the resulting Ga 3d spectrum accurately. The fitting of the spectrum from the native-oxide-covered surface shows that this component is not formed during etching, but is already present in the native oxide layer. It is shifted by 0.7 eV to higher binding energies from the GaP substrate peak. The binding energy of 19.7 eV fits with values that are reported for  $\text{Ga}_2\text{O}_3$ ,<sup>124,125</sup> but also with components where the assignment is unclear like  $\text{Ga}_2\text{O}/\text{GaOH}$ <sup>126</sup> and  $\text{Ga}_2\text{O}/\text{GaO}$ .<sup>127</sup>

In summary, the native oxide layer on well-oxidized GaP(001) is a P-rich oxide that contains Ga atoms in various binding states. The phosphate peak is found at a binding energy fitting for  $\text{GaPO}_4$ , but the atomic ratios suggest that the phosphate species is not single-phase  $\text{GaPO}_4$ . The P/Ga ratio greater than unity can be explained by the presence of phosphor atoms in a similar bonding configuration as in gallium metaphosphate ( $\text{Ga}(\text{PO}_3)_3$ ). Furthermore, the high O/P ratio suggests that additional oxygen is embedded in the oxide layer, probably as water. At the GaP/oxide interface the oxide layer consists of Ga–O species. The gallium

oxide is predominantly composed of the suboxide  $\text{GaO}_x$ , but also a small component from  $\text{Ga}_2\text{O}_3$  can be fitted into the spectra. As compared with InP, this result shows that the air-grown native oxide on GaP is closer to the thermodynamically favored oxide compound  $\text{GaPO}_4$  ( $\text{InPO}_4$  for InP).<sup>128</sup> This could possibly be explained by the fact that the thermal budget for simultaneous diffusion of all elements is much lower for GaP than it is for InP, which leads to near-equilibrium oxidation of GaP for most temperatures.<sup>129</sup> Another explanation could be that the oxide on GaP was closer to the thermodynamically favored phase because of the longer oxidation time of the GaP wafer. Nevertheless, both phosphides have in common that the native oxide layer consists of several phases rather than a well-defined single phase.

### *GaInP<sub>2</sub>(001)*

The composition of the native oxide layer on the ternary alloy  $\text{GaInP}_2$  was determined on the basis of the fitting results for the binary group-III phosphides in the previous section. As explained there, components for stoichiometric oxide compounds were used to fit the spectra. The result of this fitting procedure for a *p*- $\text{GaInP}_2$  (001) sample after ultrasonic cleaning with acetone, 2-propanol and ultra-pure water is shown in Fig. 17. The fitting result for the overlapping Ga 3d and In 4d core level spectra in Fig. 17 shows that the native oxide on *p*- $\text{GaInP}_2$ (001) is In-rich. This was the case for all analyzed  $\text{GaInP}_2$  (001) surfaces, which showed on average an In/Ga ratio of around two. In addition to the  $\text{InPO}_4$  component (chemical shift of +1.5 eV compared to InP), also  $\text{InPO}_3$  (chemical shift of +1.0 eV),  $\text{In}_2\text{O}_3$  (+0.4 eV) and  $\text{In}(\text{OH})_3$  (+0.6 eV) are identified in the In 3d<sub>5/2</sub> spectrum. The binding energy shifts are comparable to those observed for the InP surface. Furthermore, a metaphosphate  $\text{In}(\text{PO}_3)_3$  component was added to the fitting model for  $\text{GaInP}_2$ . Faur et al.<sup>117</sup> and Mikushkin et al.<sup>130</sup> use the same binding energy for  $\text{In}(\text{PO}_3)_3$  as for  $\text{InPO}_4$ . However, Hollinger et al. report a large binding energy for the P 2p peak of crystalline  $\text{In}(\text{PO}_3)_3$ , which is 0.9 eV higher than the value they report for  $\text{InPO}_4$ .<sup>113</sup> Therefore, it was assumed that the In 3d<sub>5/2</sub> binding energy of the metaphosphate is slightly larger than that of the orthophosphate  $\text{InPO}_4$ . The fitting of the In 3d<sub>5/2</sub> core level results in a small component of  $\text{In}(\text{PO}_3)_3$  with a binding energy of 445.6 eV (+1.6 eV).

The gallium atoms on the *p*- $\text{GaInP}_2$  (001) surface are oxidized to a minor degree compared to the *p*-GaP(001) surface in Fig. 16B. In particular, the amount of gallium phosphate is much smaller, as can be seen in the Ga 3d spectrum. The spectrum was fitted with the model from Fig. 16B, which contains  $\text{GaPO}_4$ ,  $\text{GaPO}_3$  and  $\text{Ga}(\text{PO}_3)_3$  components. Because the resulting phosphate components had very small areas, they were summed up and are shown as  $\text{GaPO}_x$  component with a binding energy of approximately 20.8 eV (+1.7 eV). The  $\text{GaO}_x$  and the  $\text{Ga}_2\text{O}_3$  component have similar chemical shifts as found for the GaP surface. To simplify the fitting of the spectra,  $x = 1$  was assumed for the  $\text{GaO}_x$  contribution.

The chemical shifts of the indium phosphate components  $\text{InPO}_3$  and  $\text{InPO}_4$  in the P 2p spectrum are the same as those used for InP. According to the fitting result, these two compounds are the main phosphate species in the native oxide on *p*- $\text{GaInP}_2$ . The chemical shift of the much smaller  $\text{In}(\text{PO}_3)_3$  component is +5.4 eV, which is slightly less than the average of the literature values of about +5.8 eV.<sup>113,117,130</sup> For  $\text{Ga}(\text{PO}_3)_3$ , the fit gives a shift of +5.6 eV, similar to the result for the GaP surface. The fitting model allows to assess the proportion of indium to gallium atoms in the phosphate layer on  $\text{GaInP}_2$ . The calculated ratio from the phosphate component areas is approximately In : Ga = 7. The average chemical shift of the phosphate peak in Fig. 17 is approximately +4.6 eV, which is in between the values of +4.3 eV for InP and +5.1 eV for GaP. Similarly to the P 2p peak of the binary phosphide semiconductors, the peak of the *p*- $\text{GaInP}_2$  substrate could only be fitted with an additional  $\text{GaInP}_x$  or P–P component (+0.40 eV). The peak of the native oxide on *p*- $\text{GaInP}_2$  (001) in the O 1s spectrum is around 531.3 eV. This corresponds well with the binding energy for the  $\text{PO}_x$  components as well as of In or Ga-oxides and hydroxides; the relative contributions in this fit are deduced from the fitting results of the other elements and are found to be consistent with each other.

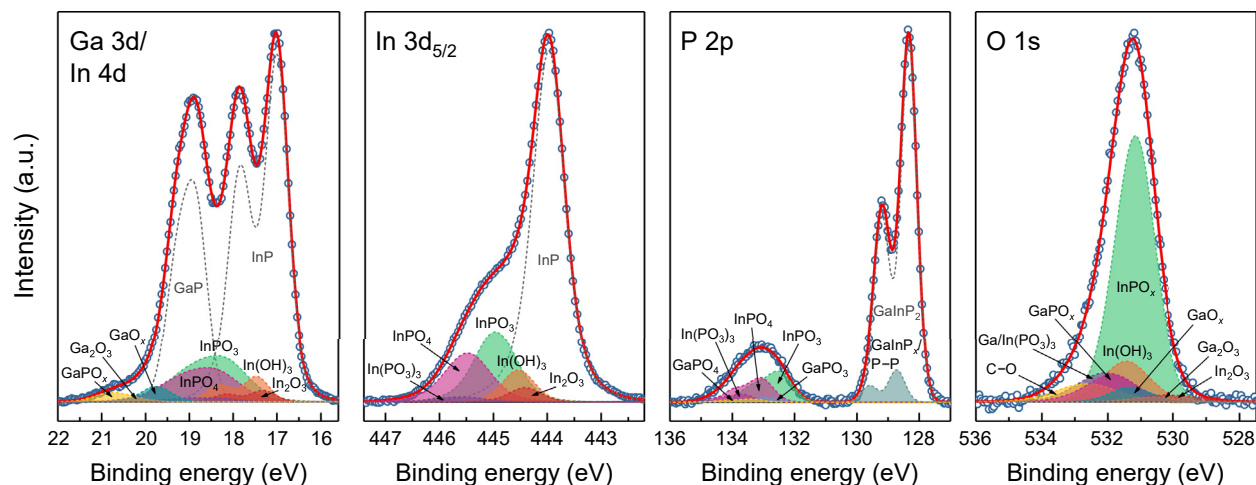


**Fig. 17** XPS detail spectra of the native oxide layer on *p*- $\text{GaInP}_2$ (001) after background subtraction. The chemical composition of the oxide was determined by fitting components for possible InP and GaP oxide compounds into the measured data. From Ref. 17.

In summary, the results, including also detailed measurements<sup>17</sup> at a synchrotron source to change the surface sensitivity (not discussed here), show that the native oxide on GaInP<sub>2</sub> (001) is rather complex and consists of a wide range of different oxygen species. The gallium and indium oxides Ga<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> are, similar to the native oxides on GaP(001) and InP(001), not the dominant phases. The majority of the native oxide layer consists of phosphates. The chemical shift of the phosphate species in the P 2p spectrum grows with oxidation time and reaches values of around 4.6 eV, which is slightly less than the 5-eV-shift that is reported for the stoichiometric orthophosphates GaPO<sub>4</sub> and InPO<sub>4</sub>. The decomposition of XP spectra measured with synchrotron radiation into oxide and phosphate species suggests that the oxygen concentration increases toward the oxide surface, which is consistent with an increase in the chemical shifts relative to the bulk core levels and of the relative phosphate concentration toward the surface. The data suggest that the oxide species with lower oxidation states, as In<sub>2</sub>O<sub>3</sub> and GaO<sub>x</sub>, are primarily located at the GaInP<sub>2</sub>/oxide interface and that the oxide surface mainly consists of InPO<sub>x</sub>. Our results are in good agreement with the few previous XPS studies on the composition of the oxide layers on GaInP<sub>2</sub> surfaces.<sup>131,132</sup>

### Valence band spectra and band energy diagrams

The electronic structure of the thin native oxide layers on the group-III-phosphide semiconductors can be studied via ultraviolet photoelectron spectroscopy (UPS) in addition to using XP valence band spectra. Because of their high surface sensitivity, UPS measurements probe mainly the oxide layer on the samples, whereas the valence band of the III-phosphide substrates below can be measured by applying XPS. Thus, it is possible to deduce the valence band edge of the substrate (III-phosphide semiconductors, cf. Fig. 18B) in relation to the oxide surface layers (cf. Fig. 18A). The VBM of the native oxide on *p*-GaInP<sub>2</sub> is around 3.7 eV, which lies between the values for *p*-InP with 3.5 eV and *p*-GaP with 4.0 eV. The VBMs of the substrates are 0.4 eV for GaInP<sub>2</sub>, 0.6 eV for InP and 0.5 eV for GaP. This gives an offset in the valence band at the semiconductor/oxide interface of 3.3 eV for GaInP<sub>2</sub>, 2.9 eV for InP and 3.5 eV for GaP.

Based on the above-given results, the band diagrams of the studied III-phosphide/native oxide interfaces can be constructed. The band offsets and interface dipoles were calculated from the VBMs from Fig. 18, the calculated bulk Fermi level position as given by the doping and the work functions measured by XPS. The resulting band diagrams of the semiconductor/native oxide interfaces for *p*-GaP(001), *p*-InP(001) and *p*-GaInP<sub>2</sub> (001) are shown in Fig. 19. Since the band gap energies of the oxide layers could not be measured, they were estimated based on the known literature values of the formed oxides/phosphates. The position of the CBMs, which were calculated from these estimated band gaps and the measured VBMs, are drawn with dash-dotted lines. In order to compare these CBMs with the ones which would be expected for single-phase oxide layers, these are also given in the diagrams. They represent the upper and lower limits for the estimation of the CBM positions. The thicknesses of the native oxide layers were calculated for the different core level lines from the XP spectra. For the bands in the native oxide films in Fig. 19, flat-band conditions were assumed because the VBM of the oxides could be determined solely from the UPS measurements. On the other hand, the absence of band bending seems to be a reasonable assumption because the oxide layers are very thin and presumably possess only few free charge carriers. The interface dipole  $\delta$  can be calculated from the electron affinity  $\chi$  of the semiconductor substrates and the other quantities given in the band diagrams. The values for  $\chi$  were taken from Ref. 89. As a general conclusion it should be noted that the Fermi level of *p*-doped III-phosphide semiconductors after air oxidation tend to pin at a level around 0.5 eV above the valence band edge.

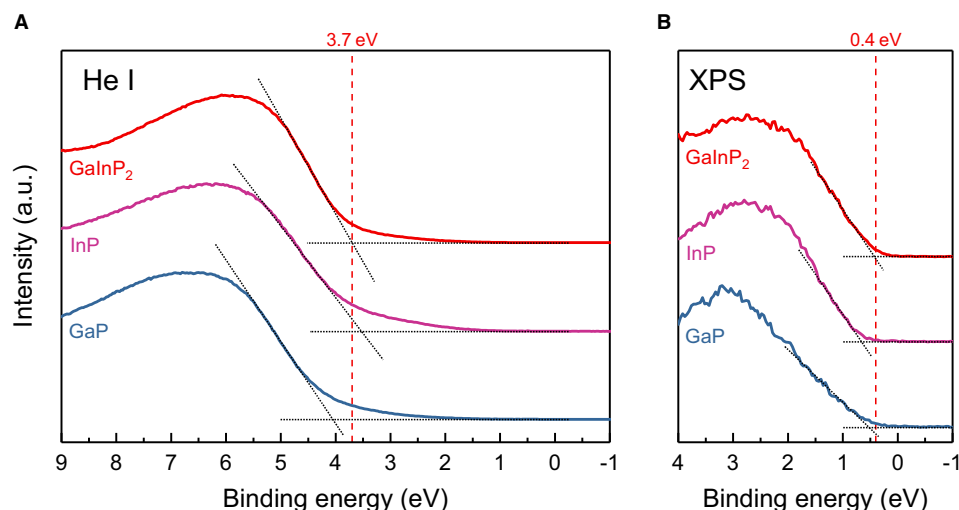


**Fig. 18** Normalized photoemission spectra of the valence band edges of the three studied III-phosphide semiconductor substrates. Graph (A) was measured surface-sensitively using He I radiation and shows the valence band edge of the thin native oxide layer, while graph (B) was measured using the Al X-ray source and shows the valence band edge of the underlying substrate. From Ref. 17.

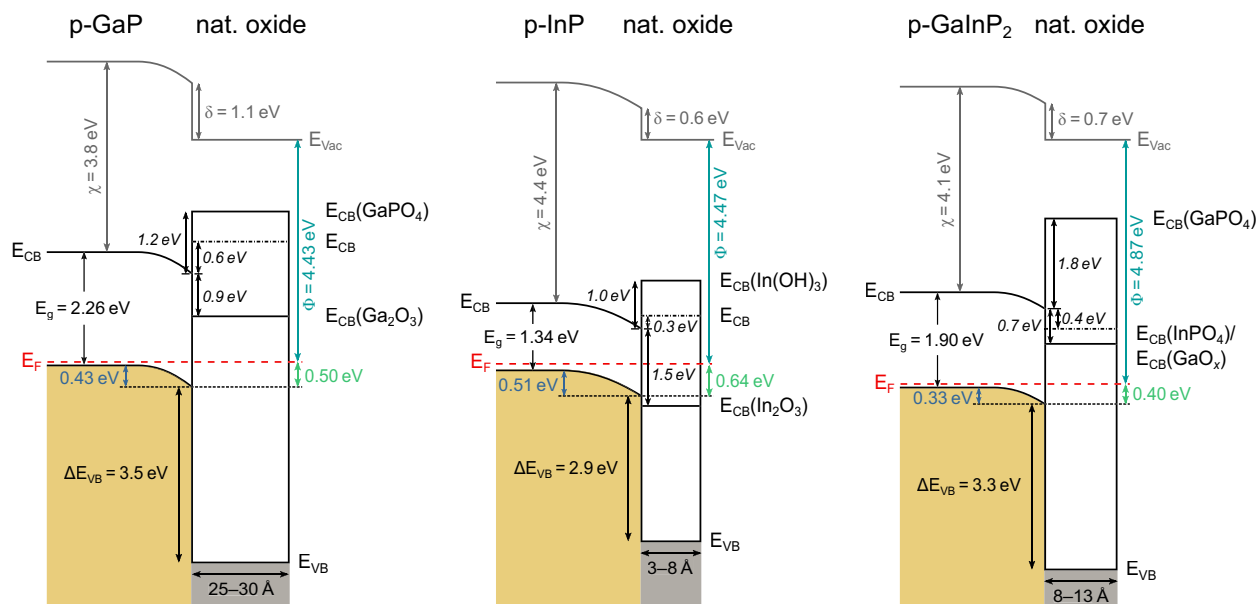


**Fig. 19** Band diagrams of the native-oxide-covered III-phosphide semiconductors. The band alignment is derived from the valence band edge positions in Fig. 18, the literature values for the bulk semiconductors and the work function  $\Phi$  measured with XPS. The conduction band edges cannot be derived from the XPS and UPS measurements. Therefore, lower and upper limits for the CBMs are depicted based on the band gaps of the different species in the oxide layers. The conduction band offsets printed in italics were calculated from an estimation of the band gap energies according to the relative species concentrations given by the fitting results. With the electron affinity  $\chi$  of the bulk material, also the interface dipole  $\delta$  at the semiconductor/oxide interface can be calculated. It leads to a step in the vacuum level at the interface. For the sake of clarity, the oxide layers are depicted much larger compared to the space charge regions in the semiconductors than it is the case in the real structures. From Ref. 17.

It should be mentioned at this point that we have also studied n-doped III-V semiconductors: They also show Fermi level pinning, but the band bending is found into an upward direction from the bulk to the surface with surface states which are situated in closer proximity to the conduction band edge (typically 0.5 eV below the conduction band edge).<sup>17</sup> Because we are concentrating our review on the properties of photocathodes for water splitting we will not discuss these results in detail here. Nevertheless, one should keep in mind that the properties and energetic effects of surface states will not only depend on the material used, but also on the bulk doping, its surface orientation and possible contact materials.

### Wet-etching of III-phosphide surfaces

The exposure of group-III-phosphide surfaces to ambient air leads to the formation of a native oxide layer. As it was discussed above, this oxide layer is expected to be detrimental to the performance of III-phosphide photoelectrodes as it pins the Fermi level at the interface to the oxide and impairs the proposed favorable energetic alignment of the semiconductor bands with the redox levels of the electrolyte solution. For group-III-phosphide semiconductors, a variety of surface cleaning techniques can be found in the literature. For InP(001) surfaces, ion sputtering and subsequent annealing, atomic hydrogen cleaning, chemical etching and sulfur passivation were employed.<sup>133</sup> Sputtering, etching and sulfur treatments have also been used for GaP.<sup>44,109,112,134</sup> For GaInP<sub>2</sub>, mainly chemical treatments were applied in the literature so far.<sup>110,135–138</sup> Within this review, we report on wet-chemical etching and annealing for native oxide removal from the InP(001) and GaP(001), and GaInP<sub>2</sub>(001) surface. Also sputtering was applied, but will not be reported here as additional surface states were introduced enhancing pinning effects.

Wet-chemical etching procedures are widely applied in semiconductor device fabrication. The advantage of wet-chemical surface treatments is that they are much less damaging to the surface than, e.g., ion sputtering and therefore do not produce as many surface defects. The etch rate can be controlled by the concentration of the etching solution, the solvent, the etch time, and the temperature. This allows a precise control over the surface termination and morphology. Different etch solutions were tested in our experiments following surface preparation approaches in the literature. Etching in a HCl in 2-propanol solution was also applied to InP(001) surfaces.<sup>139</sup> It resulted in oxide-free well-ordered surfaces with an overlayer of InCl<sub>x</sub> and elemental phosphorus, which could be removed by low-temperature annealing. Because of the good etching results for InP surfaces, HCl in 2-propanol solution was selected as one of the etching solutions for GaInP<sub>2</sub>. For comparison, also aqueous HCl and HClO<sub>4</sub> solutions were investigated. These solutions removed the native oxide layer from GaP(001) surfaces relatively well.<sup>44</sup> In papers which report on the oxide removal from GaP and InP surfaces with different etching solutions, HCl solution is among the most effective etchants.<sup>44,109,133,140</sup> Similar results were obtained by some research groups with hydrofluoric acid (HF) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).<sup>109,140</sup> For concentrated H<sub>2</sub>SO<sub>4</sub> solution, Kocha et al. reported previously that it can remove non-radiative recombination

sites from GaInP<sub>2</sub> surfaces.<sup>110</sup> Later, Young et al. showed that this surface passivation is likely caused by water adsorption on the H<sub>2</sub>SO<sub>4</sub>-etched surface.<sup>141</sup> Nevertheless, several research groups used etching in concentrated H<sub>2</sub>SO<sub>4</sub> solution as pretreatment step in their fabrication of efficient photoelectrodes from GaP and GaInP<sub>2</sub>.<sup>94,142,143</sup> Therefore, concentrated H<sub>2</sub>SO<sub>4</sub> solution was also tested as an etching solution.

To minimize re-oxidation after the surface treatments with the etching solutions, the etching was conducted in the glass cell described above (see Fig. 15). It is continuously purged with argon and allows wet-chemical treatments without exposure to ambient air. In summary, all of the acidic etching solutions remove the surface oxide/phosphate layers quite efficiently, as has been proven by the XPS measurements. However, the amount of remaining O and C contamination have been found to be still different and for this reason we concentrate in our report here on the application of HCl in 2-propanol which lead to the surfaces with the lowest contamination layer. The samples were etched for 5 min with 1.25 M HCl in 2-propanol solution in the electrochemical cell of our integrated system of the DAISY-FUN laboratory. After the etching treatment, the samples were rinsed with pure 2-propanol, dried in an argon jet and transferred back to the UHV within 30 minutes. Fig. 20 shows the corresponding XP detail spectra for InP(001) (Fig. 20A) and for GaP(001) (Fig. 20B). To allow a comparison with the spectra of the native-oxide-covered surfaces, the corresponding curves are also shown in the graphs as gray dashed lines.

The spectra in Fig. 20 were fitted with the same model as the spectra in Fig. 16, which takes intensity ratios following from the stoichiometry of the different species into account. As can be seen in the O 1s spectra, the etching with HCl in 2-propanol solution removes most of the native oxide from both surfaces. For InP(001), however, the oxide removal is more effective and only a very small amount of In(OH)<sub>3</sub> and an insignificant amount of In<sub>2</sub>O<sub>3</sub> can be found on the surface after etching. Additionally in contrast to the GaP(001) surface, visual etch pits were observed on the InP(001) surface. This indicates that the etch rate of the solution is higher for InP than for GaP and that a shorter etch time should be used for InP. The indium phosphates are

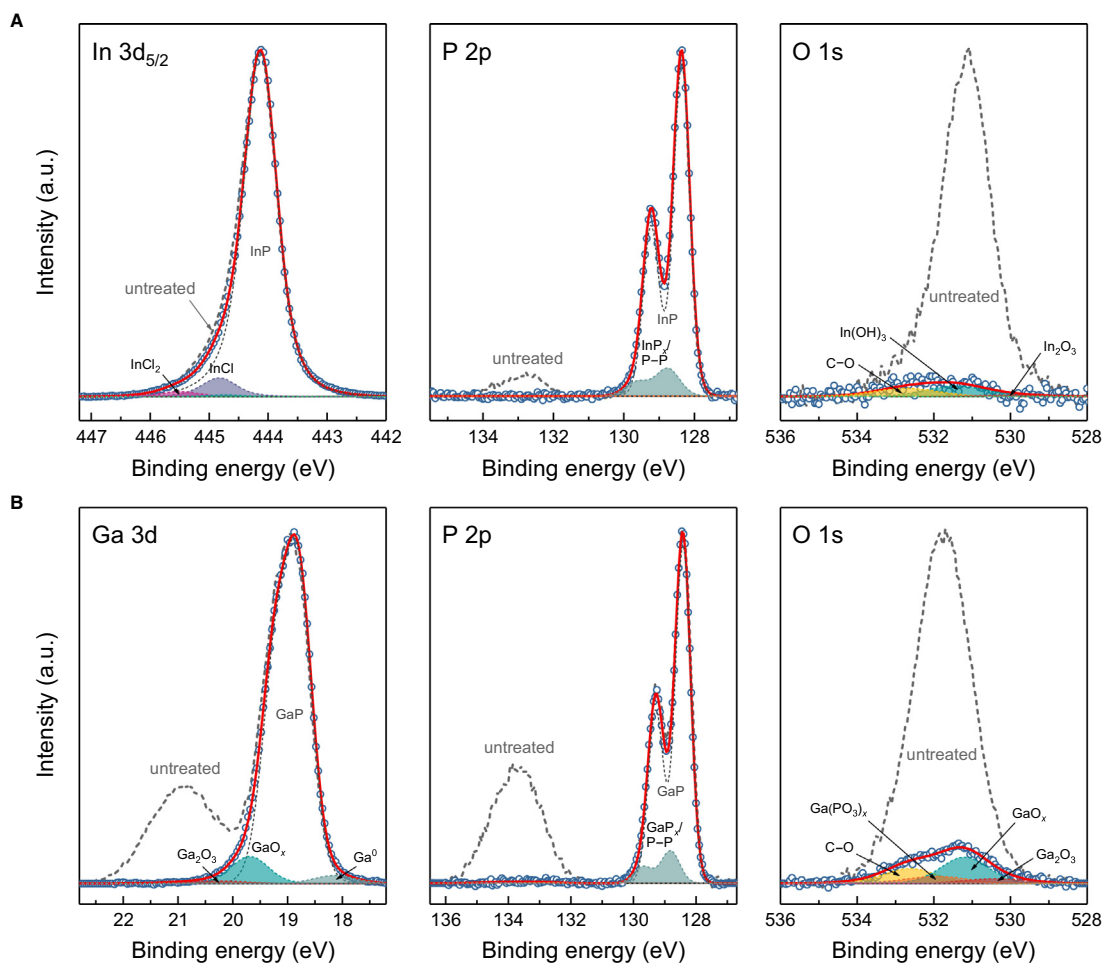


**Fig. 20** XPS detail spectra of wet-chemically etched p-InP(001) (A) and p-GaP(001) (B) after background subtraction. Both samples were etched simultaneously on the same sample holder to ensure similar experimental conditions. The chemical composition of the resulting surface layer was determined by fitting the data with the fitting model from Fig. 16. The gray dashed line is the spectrum of the untreated sample (from Fig. 16) after intensity normalization (with the exception of the O 1s spectrum) and a binding energy shift which takes the change of the surface band bending into account. From Ref. 17.

completely removed by the etching treatment, as shown in the P 2p spectrum. On the other hand, a P component, which is shifted by approximately +0.4 eV from the InP bulk peak, is increased compared to the native-oxide-covered surface. We assign this to the formation of an  $\text{InP}_x/\text{P-P}$  component. The results for  $\text{GaP}(001)$  show that slightly more oxide species remain on the surface after the etching treatment than in the case of  $\text{InP}(001)$ . The peak position in the O 1s spectrum is slightly shifted to lower binding energies by 0.3–0.4 eV. This indicates a change in the chemical composition of the oxide layer, albeit the main components of the O 1s spectrum should still originate from gallium oxide species. As the P 2p spectrum shows, the gallium phosphates are nearly completely removed by the etching treatment. However, a small feature around 133 eV indicates some residual phosphate in contrast to the InP surface. The main residual oxide species is gallium (sub-)oxide. Because of the large chemical shift of  $\text{Ga}_2\text{O}_3$ , most of the gallium oxide species has to be present as  $\text{Ga}_2\text{O}$  or  $\text{GaOH}$ . Contrary to the InP surface, the etching with HCl in 2-propanol does not significantly increase the amount of P–P species on the GaP surface. Therefore, the gallium phosphate species from the native oxide layer are probably dissolved as a whole without breaking of the P–O bonds.

The results of the wet-chemical etching of the  $\text{GaInP}_2(001)$  surface are shown in Fig. 21. The XP detail spectra show the  $p\text{-GaInP}_2$  before (cf. Fig. 21A) and after 5 min of etching with 1.25 M HCl in 2-propanol solution in a clean argon atmosphere (cf. Fig. 21B). Similar to the results for the binary III-phosphides presented above, the indium and gallium phosphates can be nearly completely removed by the etching solution. The residual oxides are mainly  $\text{GaO}_x$ ,  $\text{In}(\text{OH})_3$  and  $\text{In}_2\text{O}_3$  in accordance with the results of the etching of GaP and InP. The O 1s signal is reduced by a factor of nine, which is more than for GaP (factor of 7), but less than for InP (factor of 14). Interestingly, the analysis of several etched and annealed  $\text{GaInP}_2$  samples showed that this is not always the case. For some samples, the spectra indicate both  $\text{GaCl}_x$  and  $\text{InCl}_x$  formation, for others, only one of the two species seems to be formed. In contrast, all P 2p spectra show a loss of intensity around 130 eV after the vacuum annealing treatment. The features around 130 eV might be due to P–Cl, but also P–P and P–H species have to be considered. The different results for different samples indicate that the surface termination after etching with HCl in 2-propanol depends on the exact experimental conditions. These

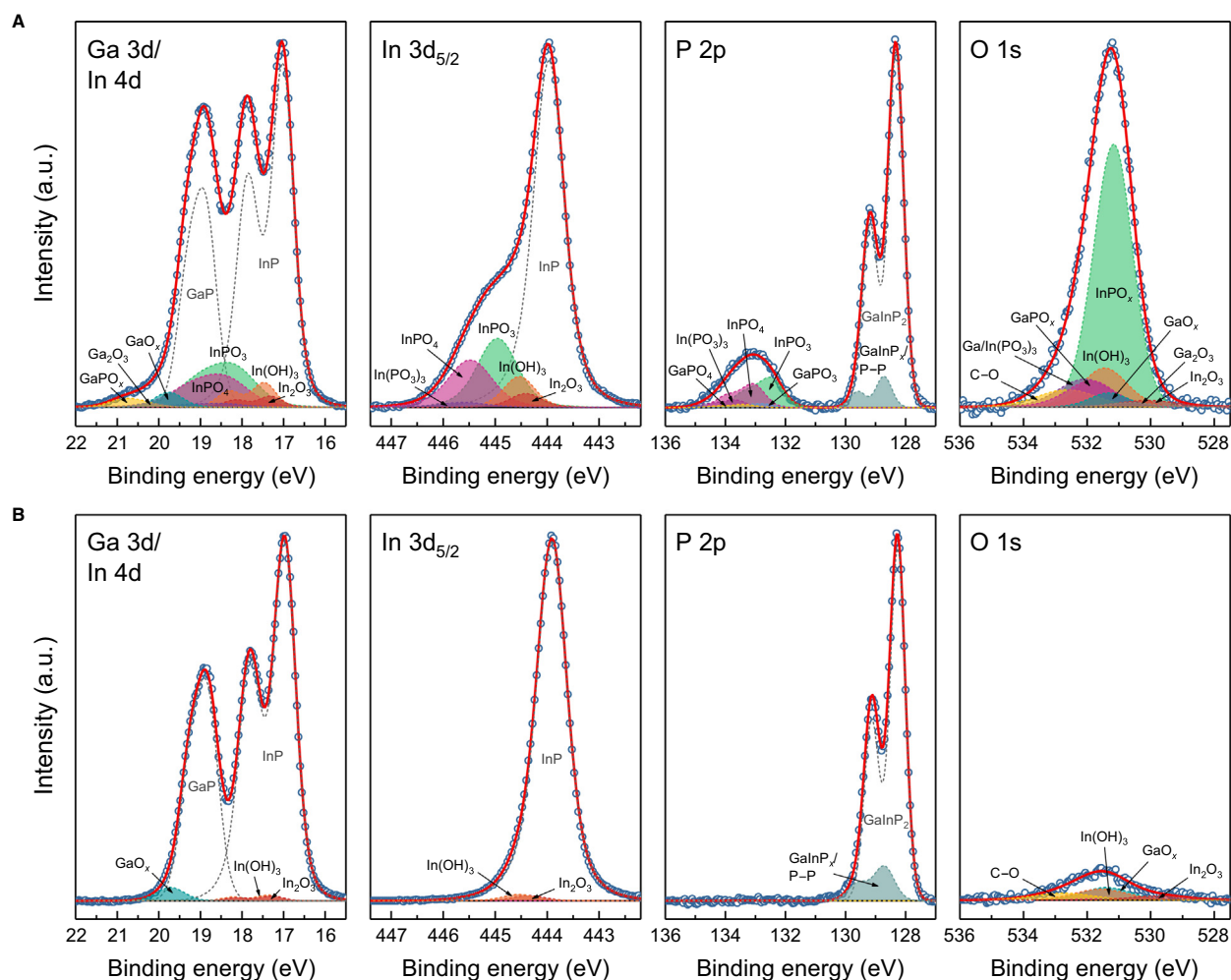


**Fig. 21** XP detail spectra of  $p\text{-GaInP}_2(001)$  before (A) and after (B) wet-chemical etching with HCl in 2-propanol solution. All spectra are shown after subtraction of a background curve. The chemical composition was determined by fitting the spectra with the model from Fig. 17. From Ref. 17.

might result in topmost surface layers with different amounts of Ga, In and P atoms. Following a model of Haber and Lewis to calculate the surface termination,<sup>144</sup> the calculated chlorine coverage of the sample from Fig. 21 is only 0.13 ML. We therefore suggest that the GaInP<sub>2</sub> (001) surface is mostly terminated with P–P or P–H bonds after the applied etching procedure. The results presented here are supported by synchrotron measurements obtained with different surface sensitivities.<sup>17</sup>

### Band energy diagrams of etched III-phosphide surfaces

The band diagrams of the wet-chemically etched III-phosphide semiconductors can be constructed based on the results from the preceding subsections. The properties of the thin layers of residual oxide can be estimated as for the native oxide layers. For GaP, the residual oxide mainly consists of GaO<sub>x</sub> with an estimated band gap energy of 4.7 eV. For InP, In(OH)<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> were identified as the main constituents of the oxide layer after etching. Since this only results in small deviations from the values for the native oxide, the same values as for the native oxide layer were used (band gap energy of 4.5 eV). The residual oxide on GaInP<sub>2</sub> consists of GaO<sub>x</sub>, In(OH)<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> and, hence, exhibits slightly different values relative to those of the native oxide, leading to an estimated band gap energy of 4.4 eV. The resulting band diagrams for p-GaP(001) (cf. Fig. 22A), p-InP(001) (cf. Fig. 22B), p-GaInP<sub>2</sub>(001) (cf. Fig. 23A) and n-GaInP<sub>2</sub>(001) (cf. Fig. 23B) before and after the etching treatment with 1.25 M HCl in 2-propanol solution are depicted in Figs. 22 and 23. The band diagrams of the binary III-phosphides show that the surface band bending for both materials is slightly reduced by approximately 0.05 eV due to the etching treatment. Although the residual oxide layer on InP is much thinner than on GaP and is estimated to be below 1 Å, the Fermi level shift is very similar to that of the GaP surface. Both etched surfaces are far away from flat-band conditions. Therefore, it can be concluded that the etching treatment did not remove the Fermi level pinning. The band diagram of the etched p-GaInP<sub>2</sub>(001) surface is very similar to those of the etched binary surfaces representing the average of several samples etched with HCl in 2-propanol. The band bending is only reduced from 0.40 to 0.33 eV by the treatment, indicating that the surface Fermi level pinning remains mostly unchanged for the p-doped samples also after chemical etching. For n-GaInP<sub>2</sub>(001), on the other hand, the average upward band bending is increased from 0.37 to 0.51 eV. The band diagrams from Figs. 22 and 23 show furthermore that the etching treatment with HCl in 2-propanol increases the work function of the III-phosphide surfaces as measured by the electron cut-off of the XP spectra.

### Vacuum annealing of chemically etched surfaces

As a final step of the attempts to prepare clean III-phosphide semiconductor surfaces, a sputter-cleaning step with subsequent vacuum annealing was applied to the chemically etched surfaces. It was indeed possible to reduce the remaining small amounts of O and C contamination on GaInP<sub>2</sub> after mild sputtering with Ar at 0.5 keV, but the chemical composition of the remaining surface species measured for the Ga 2p, In 3d, and P 2p signals after the chemical etching step were nearly not affected. But due to the introduction of sputter induced defects, a strong change in band bending is observed, which shifts all spectral features by about 1.2 eV to lower binding energies. Since n-doped samples were investigated, this indicates a shift of the Fermi level from a position close to the CBM to a position close to the VBM upon sputtering. Attempts to reduce the sputtering defects by an annealing step

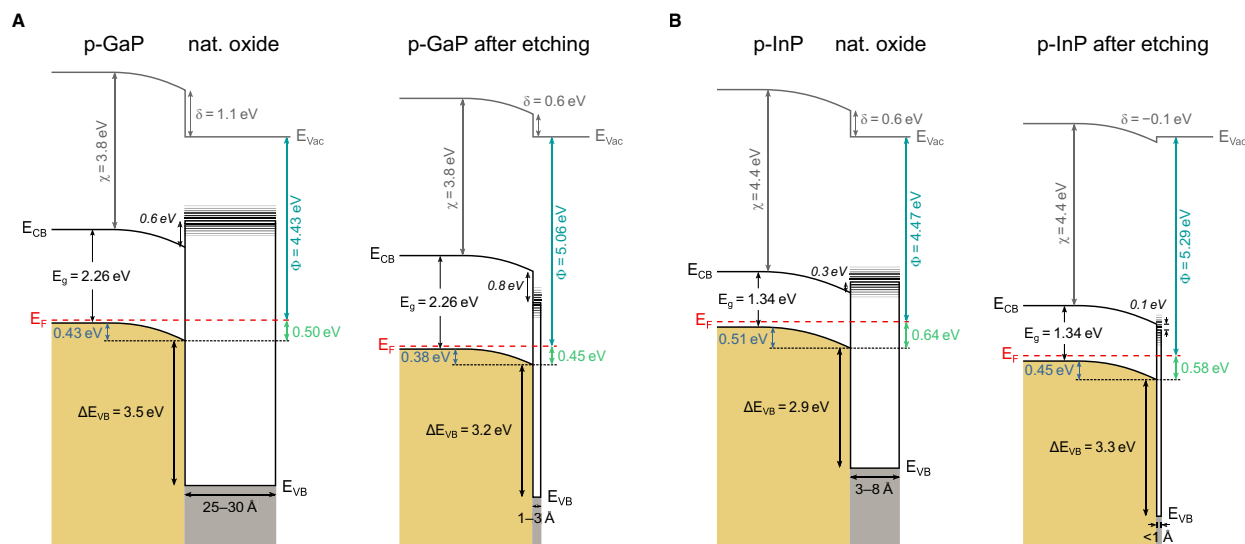


**Fig. 22** Band diagrams of the p-GaP(001) (A) and the p-InP(001) (B) before and after etching with HCl in 2-propanol. The surface band bending was calculated from the binding energy of the P 2p<sub>3/2</sub> substrate peaks. The VBM of the remaining oxide layer after etching was determined from the valence band spectra in Fig. 25. Because of the uncertainty of the estimated band gap energies, a possible range for the oxide CBMs is indicated in the diagrams. As in Fig. 19, the oxide layers are not depicted in proportion to the widths of the depletion regions in the semiconductors. From Ref. 17.

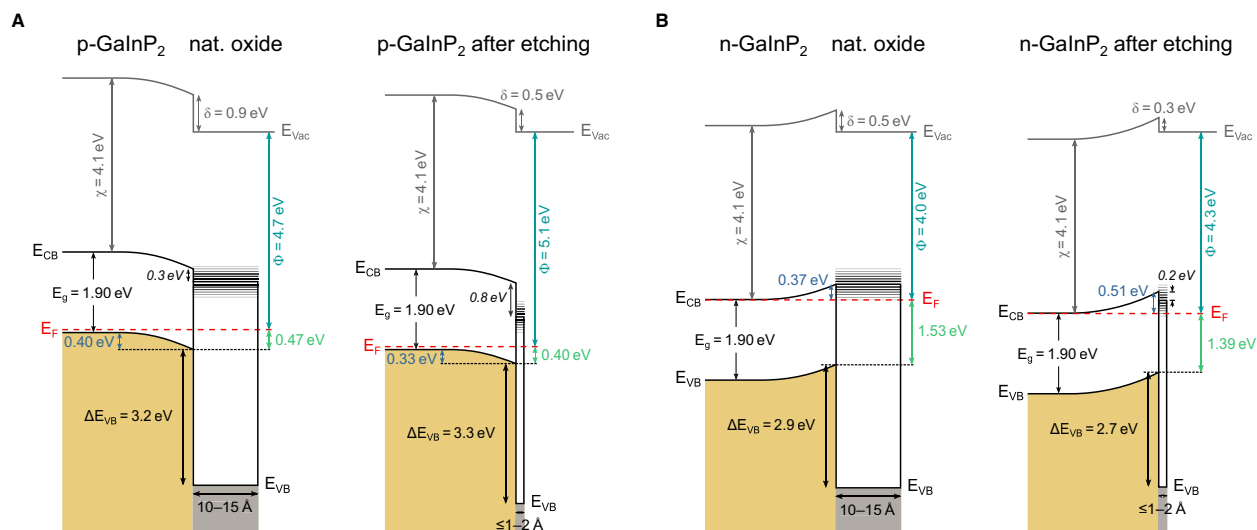


**Fig. 23** Band diagrams of the *p*-GaInP<sub>2</sub>(001) (A) and *n*-GaInP<sub>2</sub>(001) (B) before and after etching with HCl in 2-propanol. The given values for the valence band edge position, the valence band offset and the work function are average values over several samples. From Ref. 17.

at elevated temperatures only lead to a partial reduction of the sputter-induced band bending but also to a change in surface stoichiometry. For this reason, only a vacuum annealing step at 230 °C was employed as additional surface-cleaning treatment. It was found not to affect the surface composition.<sup>17</sup> The XP spectra of InP and GaP as well of GaInP<sub>2</sub> show only minor changes with surface annealing after the chemical etching step. We therefore only show the XPS results for GaInP<sub>2</sub> before (see Fig. 24A) and after vacuum annealing (see Fig. 24B). Overall, all spectral features of Ga, In, P, as well of the small contribution of O can be fitted in a similar manner as for the spectra obtained after the chemical etching step. There is, however, a significant reduction of the Cl and C contamination, with the latter being a result of the transfer from the etching solution into the UHV.

Because of the strong reduction of the surface contamination, the valence band spectra of the remaining GaO<sub>x</sub>/P<sub>x</sub> surface passivation layer on top of the GaInP<sub>2</sub> bulk can be measured (see Fig. 25). In contrast to Fig. 18 of the air-exposed and oxidized samples, where the He I spectrum only shows the valence band edge of the surface passivation layer and only the XP spectrum provides information about the position of the valence band edge of the semiconductor substrates, the He spectra shown in Fig. 25A provide the information on both valence band edges due to the very thin overlayer thickness. From the He I spectra, it is obvious that even the small remaining contamination layer after etching greatly influences the position of the valence band edge. From Fig. 25A and B, it is moreover apparent that the valence band edge of the etched and annealed samples consists of two edges: one for the residual oxide and Ga(In)P<sub>x</sub> layer, which is only visible in the spectra in a) and one for the III-phosphide substrates, which is visible in both graphs. Since the XP valence band spectrum from the substrates is quite flat from 2 to 4 eV, the substrate contribution to the oxide valence band edge was assumed to be constant. The horizontal baselines in graph a) take this constant offset from the substrates into account. The VBM for the residual surface reaction layer on GaInP<sub>2</sub> at 3.7 eV is at the same position as for the native-oxide-covered sample from Fig. 18. Similar to the native oxides, it lies between the one for InP and GaP, but this time the VBM for the oxide residues on InP is with 3.9 eV higher than the one for GaP with 3.6 eV. This is mainly due to the steeper edge of the oxide on the InP sample. GaInP<sub>2</sub> and GaP show a large tail, which extends beyond 2.5 eV. Despite some evident variations in the determined values, which may be due to some undetected surface photovoltage effect, the valence band edge in both experiments is very close to each other, and can be used for the construction of the final band energy diagrams of GaP(001) (cf. Fig. 26A), InP(001) (cf. Fig. 26B), and GaInP<sub>2</sub>(001) surfaces (cf. Fig. 27A for *p*-type and Fig. 27B for *n*-type) as obtained after chemical surface cleaning of these samples.

It is interesting to note that the band energy diagrams remain mostly unchanged compared to the surface conditioning obtained directly after the chemical etching step. The Fermi level of *p*-doped samples of InP, GaP, and GaInP<sub>2</sub> are found about 0.4 eV above the valence band edge. For *n*-GaInP<sub>2</sub> the Fermi level is situated about 0.5 eV below the conduction band edge. They remain in all cases to be determined by severe Fermi level pinning, leading to very similar Fermi level positions due to band bending. It is also worth mentioning that the observed values are also very similar to the results obtained for samples exposed to ambient conditions. It is interesting to compare these values and the related surface compositions to samples which have been prepared by MOCVD synthesis and were presented in section 2.2. The pinning position of the Fermi level in Fig. 26B is very similar to that of the well-defined *P*-rich InP(001) surface from Fig. 6A. As discussed in Ref. 17, the Fermi level pinning at the (001) surfaces of GaP, InP and GaInP<sub>2</sub> is probably related to *P* bonds, which is in agreement with the proposed *P* dangling bonds of the MOVPE-prepared InP(001)(2 × 2)-2D-1H surface. However, the exact causes of the Fermi level pinning on III-phosphide (001) surfaces still remain under debate and deserve further investigations in the future.

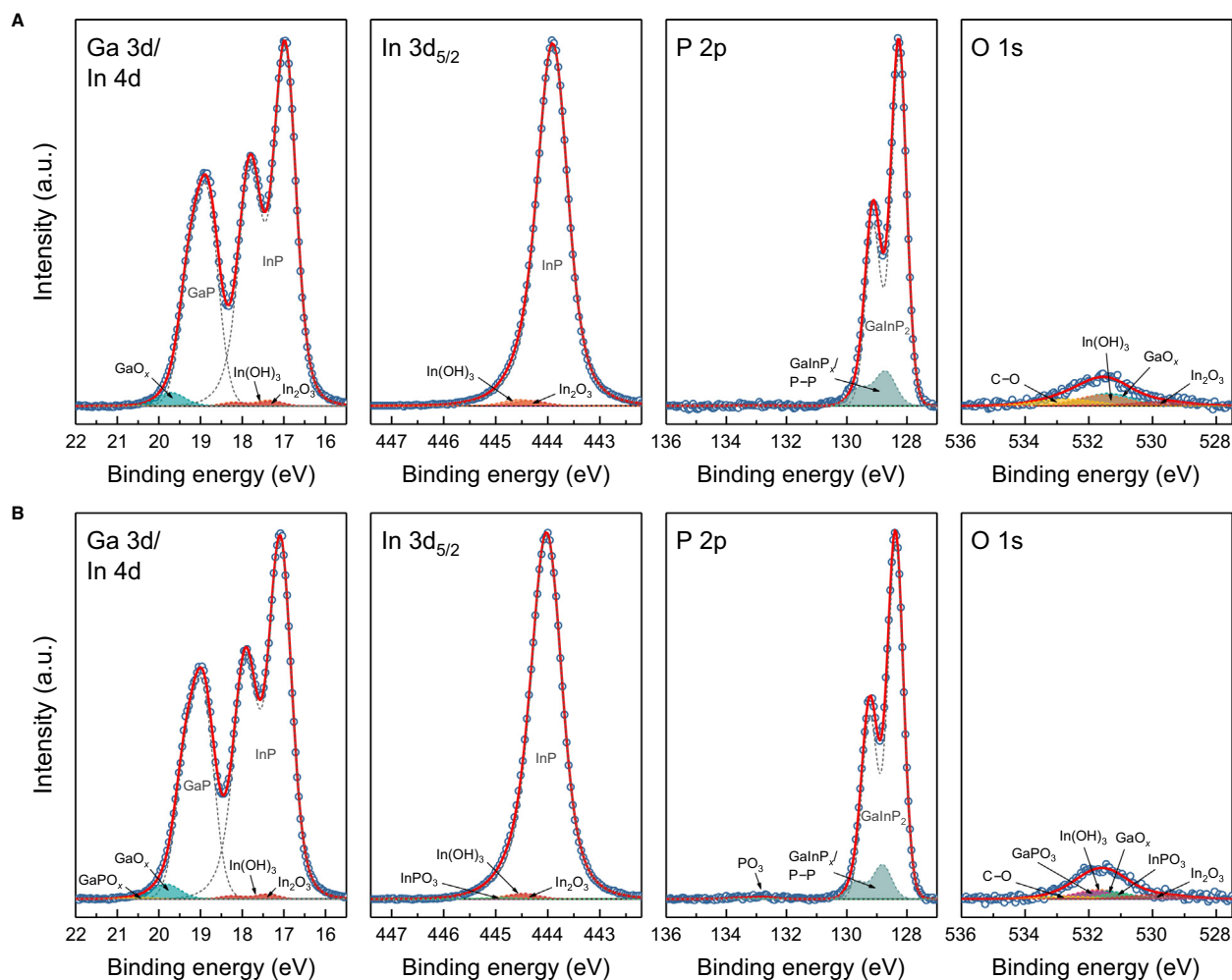


**Fig. 24** XP detail spectra of *p*-GaInP<sub>2</sub>(001) before (A) and after (B) vacuum annealing at 230 °C. All spectra are shown after background subtraction. The intensity scales are normalized except for the scale of the O 1s spectra, which is the same as in Fig. 21. From Ref. 17.

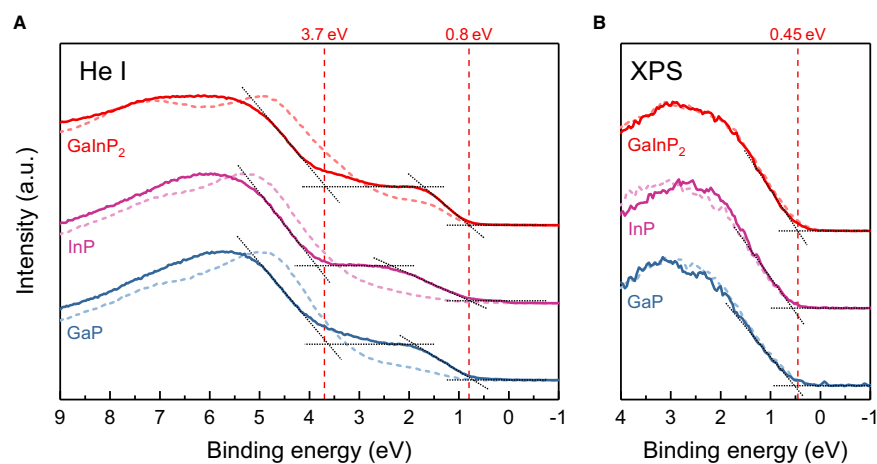


**Fig. 25** Normalized photoemission spectra of the valence band edges of the three studied III-phosphide semiconductors after etching (dashed lines) and after vacuum annealing (solid lines). Spectrum (A) was measured using He I radiation and spectrum (B) using the Al X-ray source. From Ref. 17.

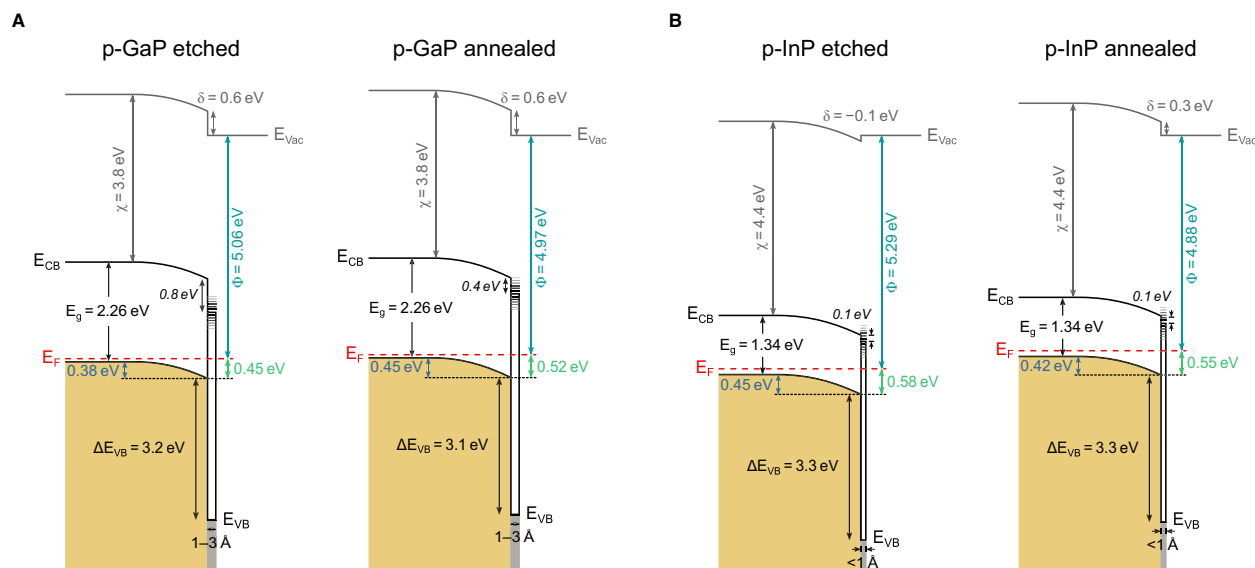


**Fig. 26** Band diagrams of the  $p$ -GaP(001) (A) and the  $p$ -InP(001) (B) before and after vacuum annealing at 230 °C. The surface band bending was calculated from the binding energy of the P  $2p_{3/2}$  substrate peaks. The position of the oxide's valence band edge in relation to the Fermi level was assumed to be the same for the etched and the annealed surfaces and was taken from Fig. 25. From Ref. 17.

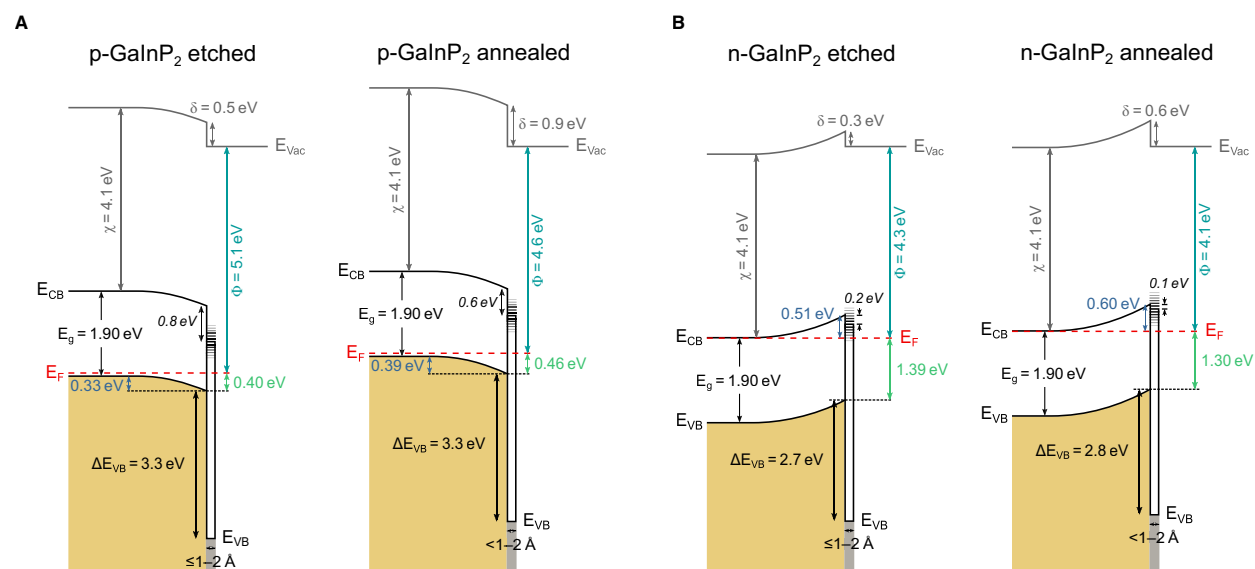


**Fig. 27** Band diagrams of the  $p$ -GaInP<sub>2</sub>(001) (A) and  $n$ -GaInP<sub>2</sub>(001) (B) before and after vacuum annealing at 230 °C. The surface band bending was calculated from the binding energy of the P  $2p_{3/2}$  substrate peaks. The position of the oxide's valence band edge in relation to the Fermi level was assumed to be the same for the etched and the annealed surfaces and was taken from Fig. 25. From Ref. 17.

## Surfaces exposed to H<sub>2</sub>O as models for liquid/electrolyte contacts

### III-phosphide surfaces exposed to H<sub>2</sub>O

The design principles for efficient photoelectrodes discussed in the sections above emphasize the requirement to passivate the photoelectrode surface both electronically and (electro)chemically. In the following, we discuss a series of model experiments in UHV, at, unlike many low-temperature studies, room temperature, that prepared the ground for the development of an interface functionalization approach outlined in the next section. In Ref. 30, the behavior of P-rich,  $p(2 \times 2)/c(4 \times 2)$  and In-rich,  $(2 \times 4)$  InP(001) surface reconstructions upon the adsorption of either water or oxygen under ultra-high vacuum conditions was investigated by means of photoelectron spectroscopy and reflection anisotropy spectroscopy. Room temperature conditions were chosen to approach the operating conditions of a device in terms of temperature, while the idealized conditions of low pressure (UHV)

were maintained. These ambient temperature conditions result in significantly reduced sticking coefficients and higher exposures in the order of several 10 kL when compared to low-temperature experiments, where exposures typically stay in the range of 10 L.

Changes of the interfacial structure were monitored in a time-resolved manner during exposure to  $\text{H}_2\text{O}$  or  $\text{O}_2$  by RAS (Fig. 28A and C). For the case of water, the intensity of the RA signal decreases, but does not vanish even after 28 kL, meaning that some surface ordering persists. The same experiment with molecular oxygen does, on the other hand, reveal a decay to an optically isotropic surface already at 18 kL, with the exemption of a small anisotropy around 3.2 eV. This indicates that an oxygen-rich surface layer of low ordering was formed. To investigate the stability of the formed surface species, surfaces were transferred back to MOVPE environment via UHV and annealed at temperatures up to 570 K, again under RAS control. While the RA spectrum of the water-exposed surface goes back toward the original spectrum after annealing, the oxygen-exposed surface does not recover completely, indicating a lower degree of reversibility for the oxidation by oxygen when compared to water. The P-rich surface of InP(001), on the other hand, showed a higher reactivity toward water, combined with a reduced reversibility of the surface modification.

As a complementary method, photoelectron spectroscopy was used to study the impact of the two adsorbates on the electronic structure and to identify the chemical species formed. Ultraviolet photoelectron spectroscopy (UPS) shows a flattening of the valence band maximum onset for both water and oxygen exposure, most likely related to the quenching of a surface state. A pronounced difference, however, is the change in the work function after exposure, most likely from a dipole as evidenced by the absence of a significant binding energy shift. This surface dipole is much more pronounced (310 meV) for oxygen exposure than for water exposure (70 meV). Also UPS indicates a reduced reversibility of the oxygen-induced surface chemistry. X-ray photoelectron spectroscopy after exposure in Fig. 28B and D shows two peaks at  $531.6 (\pm 0.2)$  (referred to as  $\text{O}_\text{I}$ ) and  $529.8 (\pm 0.2)$  eV ( $\text{O}_\text{II}$ ), respectively. While hydroxyl groups would be in principle expected from a dissociative adsorption of water, the absence of an additional peak at higher binding energies of 533 eV and beyond (see Ref. 145) in XPS indicates either that hydroxyl groups are not present after water exposure or the peak was not experimentally resolved. From literature references, the peak  $\text{O}_\text{I}$  was assigned to In–O–P bonds, and ( $\text{O}_\text{II}$ ) to In–O–In bonds. For oxygen exposure, both signals were much more pronounced, and a relatively higher fraction of In–O–In signal was found when compared to water.

The results of this investigation can be interpreted in a way that there are distinct surface reaction mechanisms for water and oxygen. Oxygen from water appears to be symmetrically inserted at the In–O–P site, which leads to the formation of In–O–P–O–In and the release of hydrogen. The complete reversibility of the reaction indicates that the In backbonds are not involved in the reaction. For the reaction with oxygen, there is a high tendency for the In–In backbonds and the P–In bonds to be involved in the reaction, which leads to the formation of In–O–In and P–O–In. In addition, there is a higher tendency for oxygen to diffuse into the bulk, which makes the reaction of oxygen with InP non-reversible. For a water-splitting device, this suggests that water exposure is not (as) detrimental for the device performance as oxygen exposure, reducing the density of In–O–In motifs, which were proposed to act as charge-carrier recombination centers.<sup>100</sup> And indeed, this interpretation was corroborated later by in situ photoluminescence on the ternary compound GaInP.<sup>141</sup>

Yet these results are, to some extent, in contradiction to the computational studies presented in the sections above (see Fig. 11A). There could be several reasons for this: Either, the peak assignment for the experimental XPS was erroneous, which could also include the failure to detect a given peak due to a lack of instrument resolution. A second reason could be the more complex experimental setup when compared to the computational approach: Surface defects, changed energetics from doping, or the impact of illumination from the optical spectrometer during exposure could, in principle, also alter reaction pathways qualitatively. A third option could be collective effects, i.e. that the interaction of two water molecules (or their remainders after dissociation) change the reaction path qualitatively. Evidence for the latter could be the very slow adsorption reaction kinetics observed for UHV-based water exposure: The lifetime as a measure for the suppression rate of a given RA signal with exposure increases with increasing water pressure.<sup>30</sup>

Room-temperature water exposure on GaP(001) in UHV, on the other hand, shows a pronounced difference in terms of surface chemistry when compared to the analog experiment with InP(001).<sup>51</sup> Here, the P-rich surface reconstruction is surprisingly stable against oxidation by water, even exposures in the order of 100 kL do not result in an oxygen signal by lab-based XPS, even after integration times of several hours under a tilt of  $60^\circ$  against the surface normal to increase surface-sensitivity (see Fig. 29B).

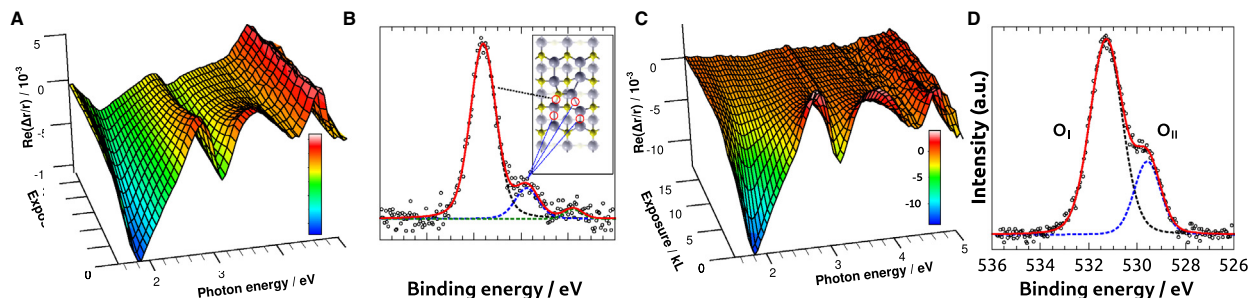


**Fig. 28** Water (A,B) and oxygen (C,D) exposure of In-rich InP(001) at room temperature. (A) Time-resolved reflection anisotropy during water exposure in UHV. (B) X-ray photoelectron spectroscopy (sample tilted  $60^\circ$  against normal emission) of the sample after exposure (C,D) Equivalent representations for oxygen exposure. Adapted from Ref. 30.

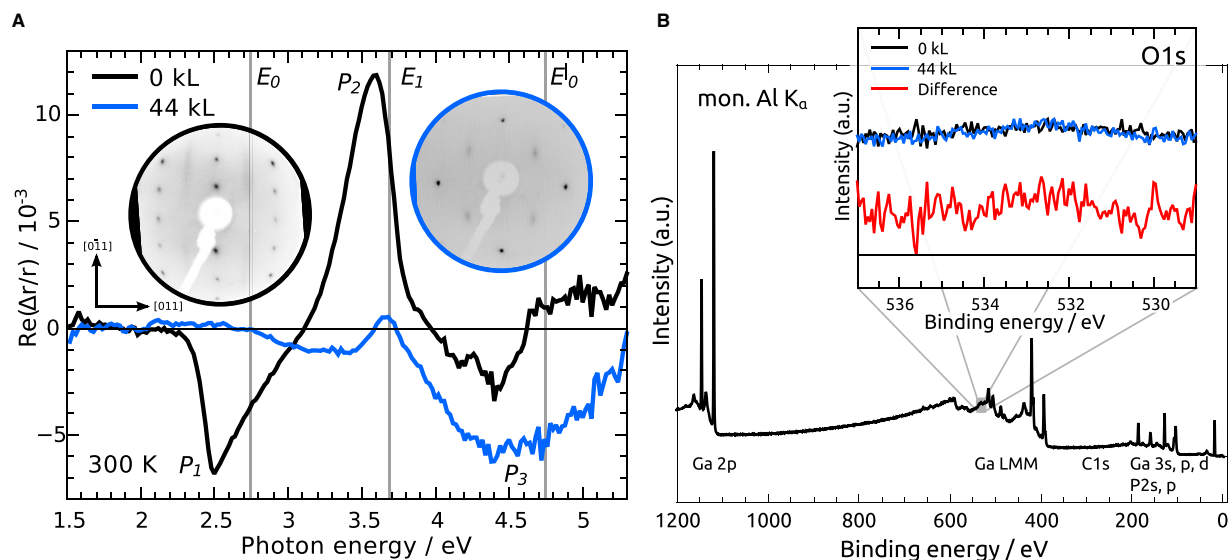


**Fig. 29** Water exposure on P-rich GaP(001). (A) RA spectra and low-energy electron diffraction (insets) before and after exposure to 44 kL water at room temperature in UHV. (B) XPS overview spectrum and scan of the O 1s region, tilted 60° against the surface normal for enhance sensitivity. Adapted from Ref. 51.

Structurally, however, the significantly altered RA spectrum shows a transformation to a different surface reconstruction, as also evidenced by LEED, as shown in Fig. 29A). The new  $c(2 \times 2)$  surface is free of oxygen and hence water/hydroxyl, leaving potentially hydrogen as a remaining ingredient of the surface reconstruction, which would not be visible by XPS. Gentle annealing, similar to the InP experiments mentioned above, can only (almost) fully recover the surface reconstruction if also molecular hydrogen is offered during the annealing process in the MOVPE environment. A subsequent computational study<sup>145</sup> comparing theoretically derived RA spectra with experimental data could then evidence that this is most likely a water-induced transformation to a hydrogen-rich,  $c(2 \times 2)$ -2P-3H surface phase, where the P dimers stabilized by one hydrogen are broken up and the two P atoms share three hydrogen atoms. A similar structure was found experimentally after exposure of a P-rich InP(001) surface to atomic hydrogen.<sup>146</sup> Whether this extraordinary stability of the P-rich GaP(001) surface still persists in contact with liquid water is still an open question, but if that would be the case, it could be instrumental for the design of photoelectrodes, allowing (photo)electrochemical functionalization in aqueous electrolytes without undesired interfacial oxidation.

An ubiquitous challenge for combined computational-experimental studies is that significant deviations between simulated and real solid-liquid interface properties can originate from surface contamination and structural defects. The influence of both was studied in a work on GaP(001) focusing on the dynamical evolution of RA spectra during water exposure in UHV.<sup>147</sup> Under the assumption of a Langmuir-type adsorption process, the fractional coverage of the surface is proportional to the attenuation of the RA signal (transient). Hence, exponential decays can be fitted to the time-resolved transients at specific photon energies (Fig. 30A), allowing to determine the lifetime (in Langmuir) of the different adsorption processes (Fig. 30B) and, under certain

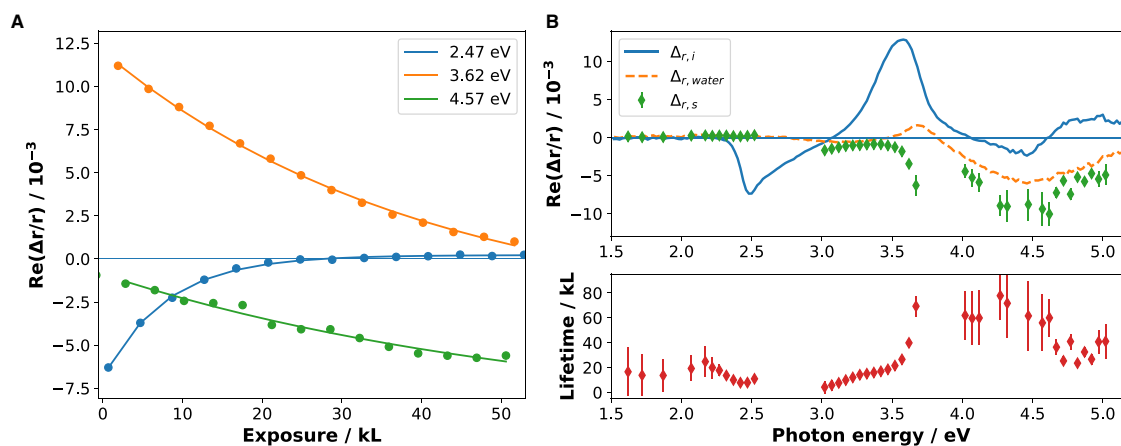


**Fig. 30** RAS of P-rich GaP(001) without outcut during water exposure. (A) Transients with mono-exponential decay fits for selected energies. (B) Initial RA spectrum (blue) together with the spectrum after 58 kL of water (orange, dashed) and the saturation values from exponential decay fits (green). The lower part of the plot shows the corresponding lifetimes  $\tau$ . Values with large errors as well as negative  $\tau$  were omitted. Adapted from Ref. 148.

assumptions, estimate their adsorption energies. Defect densities on the surface were systematically varied by changing the crystal off-cut from  $0^\circ$  to  $2^\circ$  and hence the density of step edges for a given area. An increasing step edge density was found to reduce the overall lifetime, i.e. increase the surface reactivity. In addition to this quantitative effect, the interaction was also changed qualitatively, as the P-rich GaP(001) surface suddenly also incorporated oxygen upon water exposure, in contrast to surfaces without offcut.<sup>51</sup> Interestingly, also the slightest carbon contamination measurable by XPS had the same effect. A similar phenomenon was found on GaInP<sub>2</sub>, where residual native oxide, that was not fully removed after sample preparation by etching, was found to introduce a similar effect, promoting water dissociation as well.<sup>148</sup>

The examples outlined above emphasize that for a comparison between a (DFT-)modeled surface and experiment, slightest deviations from the ideal crystal structure in experiment can qualitatively change the picture and therefore have to be carefully evaluated.<sup>147</sup> However, in many experimental studies, highly relevant parameters such as the crystal offcut and hence the step edge density remain unreported.

### III-nitride surfaces exposed to H<sub>2</sub>O

The possibility of in vacuo studies of as-grown III-nitrides is an ideal precondition to study the interaction of molecules with the bare (reconstructed) surface in particular in the lower coverage regime. Thereby the theoretical predictions are still to some extent contradictory as will be summarized for GaN first. In an early work, Hu et al.<sup>149</sup> concluded that the dissociation of water at the surface is done stepwise. First, the water molecule is still intact. By “climbing” over an energy barrier at  $-21.45 \text{ kcal mol}^{-1}$  it will split into an OH group and an H atom. At room temperature the molecules stay in this state, because further dissociation is hindered by a barrier of  $17.69 \text{ kcal mol}^{-1}$ . Similarly, Wu et al.<sup>150</sup> predicted by DFT spontaneous dissociation of water at 300 K. Thereby the H atoms are bound to the nitrogen, whereas OH groups are bound to gallium to form Ga–OH.

More recent calculations by Sato et al.<sup>151,152</sup> present a more complex picture: For an “effective coverage” (sum of “number of adsorbates  $i$  per surface Ga atom”  $\times$  “number of covalent bonds adsorbate  $i$  can form”) up to  $\frac{3}{4}$ , dissociation is predicted and at this coverage there is no Fermi level pinning. At  $\frac{3}{4}$ , dissociative adsorption becomes unfavorable and physisorption of H<sub>2</sub>O can increase the adsorption energy. Moreover, at low coverage, the complete dissociation (2 H atoms, one O atom) is the most stable one configuration, followed by the partially dissociated form (1 H atom, one OH group) at intermediate stage. When the “effective coverage” reaches  $\frac{3}{4}$ , physisorption of H<sub>2</sub>O becomes the dominant adsorption process. As a result three-quarters of the first wetting layer is dissociated, and the rest formed by intact water molecules. When the coverage further increases, a second fully water based wetting layer is formed. Similarly Li et al.<sup>153</sup> performed first-principles DFT calculations of water adsorbed on GaN(0001) surface. As Sato et al., they used six double atomic layers. At the bottom, the dangling bonds are saturated by H and the upper surface is gallium terminated where the water molecules can be adsorbed. Simulations of different layer thicknesses from 0.1 to 5.0 ML with different adsorption sites and orientations of the water molecules were made. At low coverages (0.1–1.0 ML), the O atoms of the water molecules prefer the top site of Ga surface atoms. From single molecules (0.1 ML) over zigzag chains (0.2–0.7 ML), a network of H<sub>2</sub>O molecules is formed (0.8 ML). The second wetting layer prefer hydrogen bonds to the first layer and do not follow the structure of GaN leading to the assumption that there is a weaker interaction with the substrate as the first wetting layer. The higher the coverage, the lower the interaction with the GaN surface: The calculated binding energy between H<sub>2</sub>O molecules of the second layer and the substrate is only 60% of the binding energy of first water layer and substrate and a further decrease by 40% is observed for the third layer, before it remains constant. In their calculations, a coverage of 1 ML presents a particular high stability. Using the Bader charge analysis, Li et al.<sup>153</sup> estimated that the quantity of electron transfers from GaN(0001) to the adsorbed water molecules increases by the water coverage. Additionally, the work function of the GaN(0001) surface is tuneable by the water coverage. The calculated work function of a pristine surface is 4.38 eV and decreases to 2.71 eV with a coverage of 1 ML. As it is confirmed by Zhang et al.<sup>154</sup> the Fermi level is pinned to the surface states originating from the dangling bonds of Ga at low coverage as Sato et al.<sup>151</sup> described. By dissociative adsorption of water, this surface states are removed from the gap, and the Fermi<sup>154</sup> level becomes free from pinning. The pristine upward band bending is 0.55 eV and the decrease of this value by exposure of water on a ideally terminated GaN(0001) surface is calculated by first-principles calculations.<sup>152</sup> The calculations predict a flat band condition with an effective coverage of  $\frac{3}{4}$  ML. During the exposure to water, band bending is decreased with increased coverage of the surface. Band bending saturates at 1.5 ML what is considerably higher than the predicted value of  $\frac{3}{4}$  ML.

With respect to water adsorption on GaN, experimental studies also point toward a complex scenario. In an early study, Bermudez and Long<sup>155</sup> investigated the chemisorption of water on GaN(0001). They found initial dissociative adsorption and a small reduction of the upward band bending at room temperature. Furthermore, they found evidence that initially formed OH groups form O (and H) only after heating to 200 °C. Zhang and Ptasińska<sup>154</sup> investigated the temperature dependency of the water dissociation. They found that with increasing temperature more hydroxyl and oxide species are formed accompanied by an increased upwards band bending up to 1.2 eV. The above described theoretical predictions by Sato et al.<sup>151,152</sup> are supported by photoelectron spectroscopy studies<sup>151,152,156</sup> over a wide pressure/coverage range. In Ref. 156 also the results with respect to band bending obtained by other groups are summarized. Based on the early work of Bermudez and the possibility of in vacuo analysis of as-grown III-nitrides (avoiding additional preparation steps and allowing to study samples with different surface reconstructions), Krischok and coworkers studied the water adsorption on GaN and InN as well. For GaN (0001)  $2 \times 2$ , they found<sup>157</sup> that the initial sticking coefficient for water is rather high and adsorption leads to a fast disappearance of the original surface states (by UPS) as expected. Moreover, they found evidence that already at RT the adsorption processes are rather complex and that the formed species are strongly dependent on coverage. In particular, they found three different O1s peaks in the XPS spectra—similar to later studies.<sup>152</sup>

In the UPS valence band spectra, two strong adsorbate-induced peaks at about 6 and 11 eV binding energy are observed, which are not in line with molecular adsorption. From that, dissociative adsorption was concluded. However, the observed adsorbate induced peaks do not reflect the typical fingerprints of OH groups. Since the adsorption of O<sub>2</sub> molecules leads to similar valence band structures,<sup>158</sup> it appears more likely that the adsorbed species are pure O species. However, the analysis of the nitride-related peak shifts reveals that the change in band bending differs for oxygen and water adsorption. This could be explained by a complete desorption of water molecules leading to the presence of O and H adsorbates, generally in line with Sato et al.<sup>151,152</sup> Comparing the data for InN with the corresponding ones of GaN (see, e.g., Refs. 158,159), a very similar behavior is found. Summarizing the available results for water adsorption on wurzite GaN and InN, first of all a strong interaction is found. There is strong indication that the resulting species are strongly dependent on temperature and coverage and complete dissociation, OH-formation (plus H adsorption) and molecular adsorption can be obtained depending on the particular conditions. However, the details are still matter of debate and deserve further investigations.

### III-V based liquid electrolyte contacts for H<sub>2</sub>O splitting

#### Initial *operando* studies

While the previous sections showed how reflection anisotropy spectroscopy has proven instrumental for the preparation of well-defined surfaces in growth ambient and the study of water adsorption in model UHV experiments, it can also be employed to scrutinize electrochemical processes in real environments. The studies on in situ surface-functionalization of InP and derived compounds for water-splitting photoelectrodes showed that the interfaces formed to electronically and (electro)chemically passivate the interface are typically of amorphous nature with thicknesses of one to about 10 nm.<sup>1</sup> Yet these processes were developed with only very limited real-time control, mostly restricted to feedback from the measured photocurrent during photoelectrochemical functionalization. Monitoring the actual structure in the electrochemical environment would enable a higher precision for these interface transformations and hence be expected to ultimately improve the performance of the photoelectrodes. A recent case study therefore explores the capabilities of RAS as *operando* probe for the interface between InP(001) and different electrolytes.<sup>34</sup>

It could be shown that the potential-dependent changes of the structure of the InP–HCl and InP–H<sub>2</sub>SO<sub>4</sub> interfaces are indeed precisely observable by RAS. For low electrolyte concentrations, transient measurements under cyclic voltammetry conditions (Fig. 31A and B) reveal the reversible build-up of specific RAS fingerprints at anodic and cathodic potentials, indicating the formation of well-ordered interfaces. In HCl, the processes are attributed to the dissolution of the InP native oxide layer at cathodic potentials followed by chlorine and hydrogen adsorption. The latter is indicated by the strong anisotropy arising at 2.25 eV (see Fig. 31B) at cathodic potentials (Fig. 31C). Computational RAS qualitatively corroborates the hypothesis of an InCl<sub>x</sub> surface film with the presence of adsorbed hydrogen. Yet the large, multi-dimensional space formed by the constituents In, P, O, H, and Cl could only be covered by the computational spectroscopy to a small extent, which is most likely the reason for the limited agreement between theory and experiment. XPS in a similar fashion as described above would be an option to study the exact chemical nature of this interface. Alas, time-resolved potential step measurements showed that the surface prepared at cathodic potentials is not stable when the potential is set back to OCP, the time window for which specific states are expected to be observable can be as short as a few seconds.<sup>34</sup> This hampers the study of the exact chemical nature of this interface state by in-system XPS approaches and indicates that probably ambient-pressure XPS would be required.

Going from cathodic toward anodic potentials, the oxide layer is reformed, potentially with a higher degree of ordering, as indicated by the stronger negative anisotropy in Fig. 31 at 3.25 and 4.00 eV starting from the second cycle. Interestingly, the higher HCl concentrations typically used for the functionalization processes showed a very different picture: The processes are no longer reversible at cathodic potentials (see Fig. 31D, E and F), probably due to the formation of a thicker, more stabilized, but also less ordered InCl<sub>x</sub> layer.<sup>34</sup> This was evidenced by transient measurements during cyclic voltammetry, which show a progressive decay in the optical anisotropy, indicating a loss in the interface ordering. From a methodological point of view, this already shows that, even without a fully developed microscopic understanding of the optical signatures in the *operando* environment, lessons can be learned on structural reversibility of the interfacial processes. On the application side, an important point from this study is the finding that also for InP, a highly reactive III-V semiconductor in electrochemical environments, highly ordered interfaces can be prepared and conserved in electrolytes.

#### Highly efficient photocathodes

Their flexible opto-electronic properties and high performance in photovoltaics render III-V semiconductors promising candidates to realize direct or highly integrated solar water splitting where the absorber is fully immersed into the electrolyte. The requirement for a minimum voltage to drive the water splitting reaction renders dual-junction photoabsorbers the optimum to achieve highest efficiencies. In a study from 2015, a combined route of in situ surface functionalization of such a III-V based tandem absorber together with photoelectrodeposition of a co-catalyst lead to the then highest reported solar-to-hydrogen (STH) efficiency of 14%.<sup>1</sup> The starting point was a GaInP/GaInAs dual junction grown epitaxially at Fraunhofer ISE on a Ge substrate, and the GaInP top cell was covered by a charge-selective AlInP window layer. The band diagram under illumination is displayed in Fig. 32A. While the overall device was based on a metamorphic tandem typically used in photovoltaics,<sup>159</sup> the band gaps were slightly adapted to account for the spectral shaping by the catalyst-water stack on top of the absorber. After chemical etching of a GaAs cap layer in an

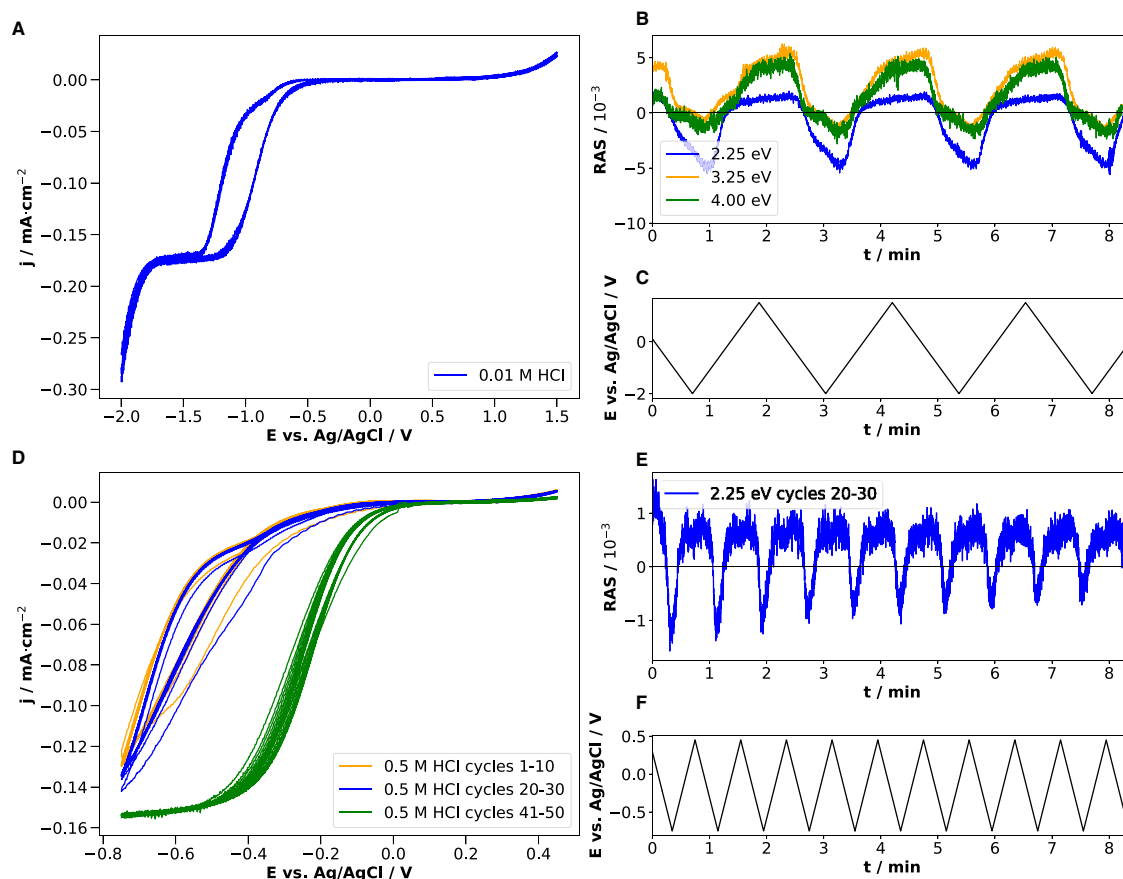


**Fig. 31** Operando RAS of InP(001). Cyclic voltammogram of InP(001) in 0.01 M HCl (A) with corresponding RAS transients at 2.25 eV, 3.25 eV, and 4.00 eV (B) and the applied potential (C). Potential plotted against Ag/AgCl, scan from open-circuit potential (OCP) toward  $-2$  V and then to  $+1.5$  V for three cycles, with a scan rate of  $0.05$  Vs $^{-1}$ . (D) CV in 0.5 M HCl (D) with associated transients at 2.25 eV for cycles 20–30 (E) and the applied potentials (F). CV scan from OCP toward  $-0.75$  V and then to  $+0.45$  V with a scan rate of  $0.05$  Vs $^{-1}$ . Adapted from Ref. 34.

$\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  solution, the resulting highly n-doped AlInP surface needs to be chemically transformed before the catalyst deposition to prevent undesired surface oxidation. From the water and oxygen adsorption studies discussed in the previous section, the general guideline was derived to process the interface ideally in an aqueous environment, minimizing exposure to ambient air in order to avoid the formation of unfavorable surface states promoting charge-carrier recombination. Hence, after etching, the device was immersed in an  $\text{RhCl}_3$  solution from which the Rh co-catalyst nanoparticles were to be deposited. Immersion into the aqueous solution revealed an oscillating behavior of the OCP illumination. Catalyst photoelectrodeposition was started when a maximum of the OCP had been reached. While the exact nature of this process is still not fully understood, XPS measurements at maximum and minimum voltage during the oscillation suggest that the maximum OCP is associated with a minimum oxide layer thickness and vice versa. This could lead to a variation of the charge neutrality level and hence a variation in the band-bending when in contact with the electrolyte.<sup>43</sup> In this view, the OCP minimum would then be associated with an unfavorable upward band-bending at the solid–liquid interfaces, hindering charge-transfer toward the electrolyte.

Furthermore, photoelectron spectroscopy (see Fig. 32C and D) indicates that the formation of  $\text{PO}_x$  phases at the interface is beneficial for the overall efficiency and stability, also reducing the band offset between the photovoltaic window layer (AlInP) and the electrochemical window layer that additionally involves oxygen species. The subsequent Rh co-catalyst photoelectrodeposition resulted in weakly interconnected, polycrystalline nanoparticles with diameters in the order of 10 nm (see Fig. 32B). Here, an important aspect for high efficiencies is the design of layer stack in a way that it both reduces reflection losses as well as absorption from the metallic nanoparticles. As the two subcells of the multi-junction are monolithically connected in series, the device is highly sensitive to changes in the incident spectrum, which can induce a current mismatch between junctions. A significant drawback of the results was the limited stability of the device, dropping to about half of the initial photocurrent after 40 h of operation. One reason for this rather rapid degradation were point defects in the passivation layer, serving as points of attack for (photo)corrosion.

In a subsequent study, it was attempted to further improve the performance by the introduction of a  $\text{TiO}_2$  protection layer, combined with an improved absorber core that featured a tunnel junction with higher transparency.<sup>16</sup> The preparation of the front interface started again with the same etching procedure and surface functionalization, leading to the formation of an  $\text{AlInPO}_x$  layer (see Fig. 32C and D). In the subsequent step, a crystalline anatase  $\text{TiO}_2$  was deposited by atomic layer deposition, improving

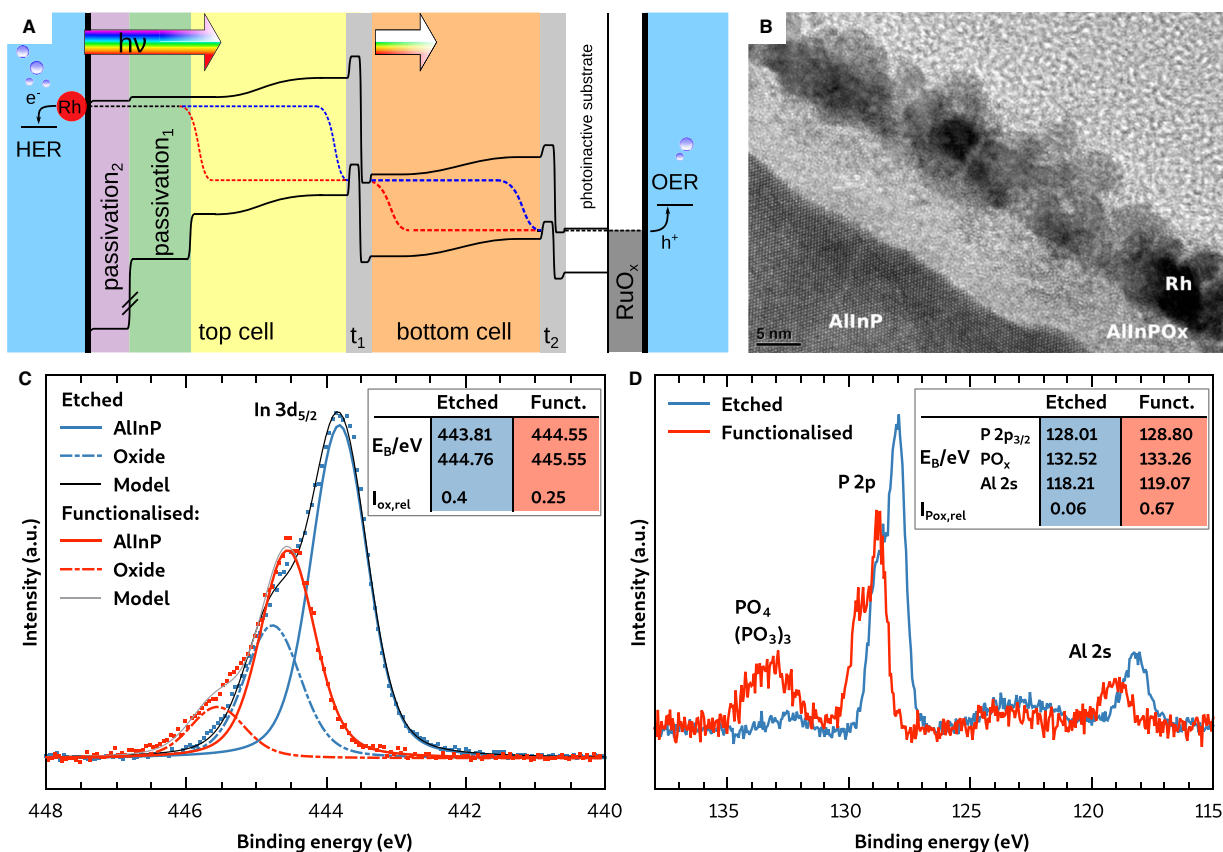


**Fig. 32** Dual-junction photoelectrode for efficient solar water splitting. (A) Band diagram of the photoelectrode under illumination with quasi-Fermi level of the electrons (blue) and holes (red), and the tunnel junctions between sub-cells,  $t_{1,2}$ . (B) Transmission electron microscopy cross-section of the topmost layer stack showing the epitaxial AlInP passivation layer 1, and the photoelectrochemically formed, amorphous AlInPO<sub>x</sub> passivation layer 2 (C,D) XPS of the interface after etching and after functionalization. Binding energy shifts are partially from the photovoltage developed between back contact and front surface due to residual white-light emission from the monochromated Al K <sub>$\alpha$</sub>  source. Adapted from Refs. 1,43.

protection against corrosion and at the same time serving as antireflection coating. In the last step, Rh nanoparticles were photoelectrodeposited from a RhCl<sub>3</sub> solution.

The cell was tested in a 1 M HClO<sub>4</sub> acid solution (pH=0), showing an STH efficiency of 19.3% at 0 V versus the RuO<sub>2</sub> counter electrode with 15.7 mAc<sup>-2</sup> under AM 1.5 G conditions. The STH efficiency was also measured under two other conditions: neutral and anion exchange membrane (AEM). In a 0.5 M phosphate buffer neutral solution (pH=7), an STH efficiency of 18.5% was reached, while the use of an AEM only showed 14.8%. However, the higher efficiency obtained in an acidic solution comes with a downside; the photocurrent decreases to a fraction of its initial value in the acidic solution already after 7 h. In contrast, in the neutral solution, the photocurrent density remains 83% of its initial value after 20 h. This is attributed to the limited stability of the TiO<sub>2</sub> protection layer at pH=0.

While both studies show that high STH efficiencies can be reached by careful interface design, the major challenge of the limited photocathode remains. As some of the interface functionalization approaches are not yet fully understood on a microscopic level, we expect that more in-depth studies, ideally with *operando* methods as outlined above, could lead to a better understanding and finally to the design of more robust passivation layers by (photo)electrochemical functionalization.

## Summary and conclusions

### Current state of knowledge of fundamental aspects of well-defined III-V compounds and their interfaces for photoelectrochemical water splitting

For their application in photoelectrochemistry, we have reviewed well-defined interfaces of multinary III-V compounds, which are well-known semiconductors allowing for band gap engineering, i. e. tuning their electronic structure, lattice constants and optoelectronic properties as desired for the device of choice. Efficient solar energy conversion, high optoelectronic device performance, and controlled photo-induced interfacial reactions are requiring precise observation and understanding of the corresponding interfacial scenarios on all length scales down to the, preferably, atomic scale. With that, record conversion efficiencies in solar cells<sup>3</sup> and

photoelectrochemical cells for water splitting<sup>1</sup> have been achieved utilizing multi-junction cells based on epitaxial III-V compound semiconductor structures and appropriate interfacial preparation. For a dual absorber structure, the combination of III-V semiconductors with Si promises efficiencies close to optimum, both for PV and water-splitting applications.<sup>160</sup> Such a tandem absorber device requires ideal preparation of all the manifold involved interfaces. It is therefore important to understand the interface formation and reactions of relevant epitaxial III-V semiconductor compounds step-by-step.<sup>161</sup>

Liquid and complex chemical environments are particularly challenging to gain thorough insights into microscopic and chemical reaction mechanisms at the interface. Thus, we applied a suitable spectrum of analytic methods for the observation, control, and understanding of all the interfacial reactions relevant for device preparation and operation to specify (photo-)electrochemical surface properties. Here, we focused on well-defined III-P and III-N semiconductors, such that appropriate spectroscopy routes are capable to monitor critical physico-chemical reactions in situ.<sup>162</sup> In this way, interfacial reactions in chemical vapor ambient, during adsorption of water, and in the liquid have been scrutinized down to the atomic scale in real-time, also accounting for energetically versus kinetically driven processes, equilibrium versus non-equilibrium reaction paths.<sup>163</sup> Altogether, these steps of understanding may accelerate essential progress in the realization of efficient energy materials and photo-induced processes with epitaxial semiconductor materials. In particular, chemical bonds and the electronic structure including interfacial defect levels, and stability are properties, which need to be screened, as the interfaces do not only determine electronic properties of the device; their atomic order also highly affects reaction kinetics as well as concomitant unwanted (photo-)chemical reactions such as corrosion. Moreover, the design of liquid/solid- and hybrid interfaces determines their selective chemical reactivity. In situ monitoring of interfacial preparation and reactions together with surface sensitive benchmarking of the in situ signals have been proven to be particularly beneficial for process control paired with a detailed understanding of interface formation mechanisms, in order to specifically modify and tune the interface formation just as desired for the application of choice. However, there is still a mismatch between our understanding of surface properties and reactions, characterizing surfaces with idealized composition and structure, and real surfaces, where certain concentrations of defect levels and structural non-ideal surface terminations do exist. For this reason, also the defect chemistry or non-idealized surface properties of real III-V surfaces must be taken into further account.

### Experimental and theoretical concepts and research strategies needed to improve our knowledge on III-V semiconductor liquid interfaces

Efficient photoelectrochemical devices require precise control of both, solid-liquid and solid-solid interfaces. While the latter can be prepared by MOVPE using optical in situ control during growth, it is still a matter of active research to what extent specific, MOVPE-prepared surfaces impact the formation of the solid-liquid interface under operating conditions. Here, well-defined epitaxially prepared interfaces, such as (001) surfaces and layers of InP, GaP, AlInP, and GaInP are specifically relevant for high-efficiency solar-driven photoelectrochemical cells. The current record devices relied on shaping such interfaces (photo-)electrochemically after wet-chemical etching processes. The atomic order of this composition of surfaces and interfaces and their specific gas-phase or (electro)chemical preparation routes have been and must be further studied and understood in depth. III-V semiconductors are ideally suited to demonstrate the interplay of in situ spectroscopy, density functional theory and benchmarking to a broad range of surface science techniques due to the possibility to prepare highly ordered interfaces both by MOVPE growth, but also (photo-)electrochemically in the electrolyte. These well-defined III-V structures were the starting point for in-depth studies of surface chemistry and electronic structure relevant for photoelectrochemical applications. Yet the study of catalytic and (photo-)electrochemical processes at these interfaces is far from exhausted and for further atomistic understanding requires spatial as well as temporal resolution in a broad range. Here, a great challenge for in situ/*operando* techniques is the necessity to transfer information through the liquid environment. For real photoelectrodes, electronic and chemical passivation may be required, which introduces additional solid/solid and solid/liquid interface combinations that need to be studied on the microscopic level, as well.

In general, idealized model interface studies can help to provide initial information for a given system, yet also real defective interfaces must be studied in detail. A comprehensive research ansatz to this end combines synthesis, processing, surface characterization, theoretical modeling, and finally (photo-)electrochemical measurements as well as performance evaluation. With respect to electronic structure modeling, the III-V semiconductors show a relatively benign behavior with respect to the level of theory, affording to probe, e.g., many structures or long DFT-MD trajectories with reasonable computational effort. Yet also the crystalline nature of typical III-V-based photoelectrodes in experiment improves comparability with the idealized computational models of high ordering. Hence this material class is also suitable for the development of electronic structure methods relevant for the field of (photo-)electrochemistry.

A necessary next step for improving our knowledge is to further improve the sensitivity and the applicability of surface science techniques to *operando* conditions. Additionally, the effect of defects, non-idealities and inhomogeneities must be further evaluated, which leads to further challenges for the surface science of electrochemical interfaces.

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