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Water-induced modifications of GaP(100) and InP(100) surfaces studied by photoelectron spectroscopy and reflection anisotropy spectroscopy

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ABSTRACT

In this work, we investigate the initial interaction of water and oxygen with different surface reconstructions of GaP(100) applying photoelectron spectroscopy, low-energy electron diffraction, and reflection anisotropy spectroscopy. Surfaces were prepared by metal-organic vapour phase epitaxy, transferred to ultra-high vacuum, and exposed to oxygen or water vapour at room temperature. The (2×4) reconstructed, Ga-rich surface is more sensitive and reactive to adsorption, bearing a less ordered surface reconstruction upon exposure and indicating a mixture of dissociative and molecular water adsorption. The $p(2 \times 2)/c(4 \times 2)$ P-rich surface, on the other hand, is less reactive, but shows a new surface symmetry after water adsorption. Correlating findings of photoelectron spectroscopy with reflection anisotropy spectroscopy could pave the way towards optical in-situ monitoring of electrochemical surface modifications with reflection anisotropy spectroscopy.

Keywords: GaP, InP, water adsorption, water-splitting, photoelectron spectroscopy, in-situ reflection anisotropy spectroscopy

1. INTRODUCTION

The direct, photoelectrochemical splitting of water requires semiconductor devices that are both efficient and stable in an aqueous electrolyte. For photovoltaic devices, III-V semiconductors are currently the material class of choice for the design of multi-junction cells with efficiencies beyond 40% due to their tunable electro-optical properties.^{1,2} Also for water-splitting, the hitherto highest efficiencies were achieved using III-V semiconductors in half-cell approaches³ or bias-free cells.⁴ The III-V semiconductor GaP is of interest for potential water-splitting tandem applications, as it is the basis for the dilute nitride $\text{GaP}_{1-x}\text{N}_x$, which can be grown lattice-matched to silicon.^{5,6} InP, on the other hand, enables already an efficient half-cell for water-splitting.³

Current record water-splitting devices, however, are often prone to corrosion.⁷ A passivation of the semiconductor surface against (photo-)decomposition can be achieved via the formation of appropriate oxide species,^{1,3} but these can also hinder charge transfer to the electrolyte in the wake of an unfavourable band alignment.⁸

A detailed understanding of the processes involved at the initial contact between semiconductor surface and electrolyte is therefore desirable to control the formation of this crucial interface. Several theoretical studies investigated this question for GaP(100) and InP(100) identifying surface motifs which can act as charge carrier traps.^{9–11} Water adsorption studies in ultra-high vacuum (UHV) on cleaved InP(110) samples revealed the

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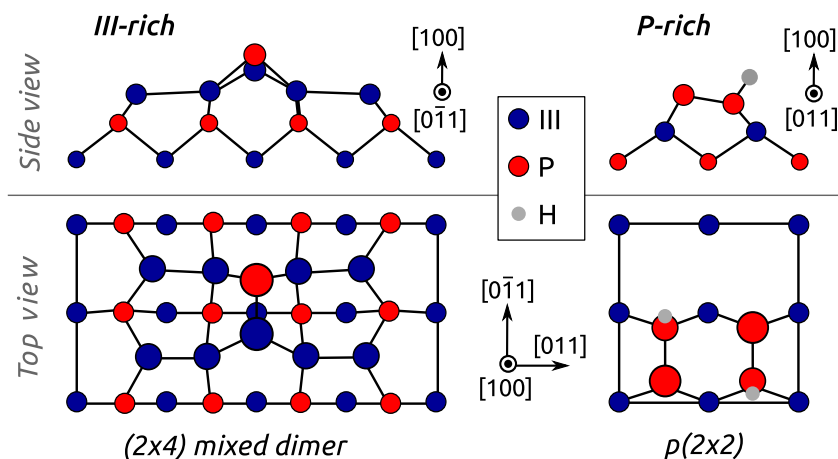


Figure 1. Ball-and-stick model of the III-rich, mixed dimer and the P-rich, hydrogen stabilized surface reconstructions, which are typical for MOVPE-prepared InP(100) and GaP(100). In the top view, size increases with proximity to the surface.

electronic (surface) structure upon exposure to H_2O finding a dissociative adsorption resulting in the formation of P-H and In-OH groups.¹² We perform water and oxygen adsorption in UHV on GaP and InP grown by metal-organic vapour phase epitaxy (MOVPE) at near-ambient pressure.^{1,13} MOVPE allows for the preparation of atomically well-defined interfaces and surfaces in an industrially scalable manner. Typical surfaces, that lie within the scope of this method, are the III-rich, (2×4) surface reconstruction and the P-rich, $p(2 \times 2)/c(4 \times 2)$ reconstruction (see Fig.1), which differ significantly from UHV-prepared surfaces due to the process gas hydrogen.^{14–17}

Optical in-situ control with reflection anisotropy spectroscopy (RAS) enables the distinction of different surface reconstruction in gas atmosphere already during growth, featuring a highly surface-sensitive growth control.¹⁸ This optical technique is also applicable to the solid–electrolyte interface and was previously also used for adsorption experiments in UHV.^{13,19,20} Therefore, it could in principle also serve as an in-situ probe for surface modifications induced by electrochemical treatment.

In this paper, we present experiments investigating the initial interaction of adsorbed water with MOVPE-prepared GaP and InP(100) surfaces and compare it with oxygen adsorption. Changes in electronic structure and morphology are monitored by photoelectron spectroscopy (PES), reflection anisotropy spectroscopy, and low-energy electron diffraction (LEED). We find that the III-rich and the P-rich surfaces differ significantly in their behaviour upon adsorption.

2. EXPERIMENTAL DETAILS

2.1 Sample Preparation with RAS in-situ Control

Samples were prepared by homoepitaxial MOVPE-growth with the process gas hydrogen and the precursors tertiarybutylphosphine, triethylgallium for GaP, and trimethylindium for InP.²¹ During growth, buffer layers were not intentionally doped, resulting in slightly n-doped buffer layers on n-type wafers. Growth was monitored in-situ by RAS enabling the selective preparation of III- or P-rich surfaces, see the literature for details.^{21,22} The samples were then transferred contamination-free to UHV via a dedicated transfer system enabling further analysis with LEED and PES.²³

Reflection anisotropy spectroscopy is a highly surface-sensitive and destruction-free optical method probing dielectric anisotropies.²⁴ Linearly polarized light in the energy range of ca. 1.5 to 5.3 eV is irradiated on a sample and the anisotropy of the reflection of two perpendicular axes is detected. Therefore, RAS can e.g. serve as a tool to monitor surface reconstructions of cubic semiconductors and control their preparation in-situ.²⁴

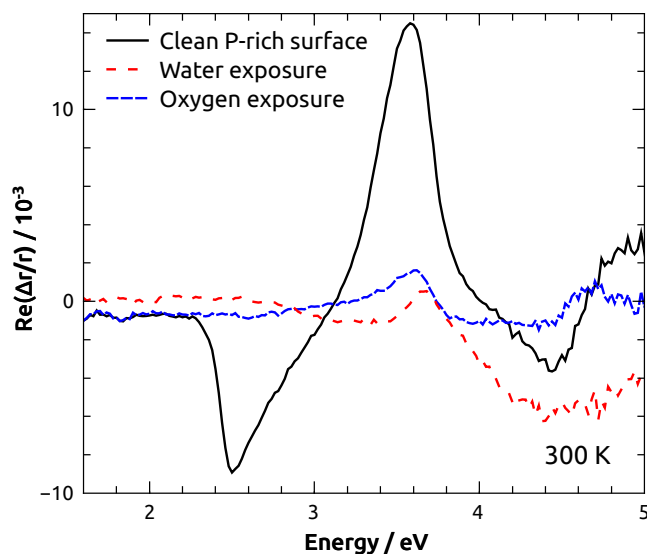


Figure 2. RA spectra at room temperature of the P-rich GaP(100) surface before and after saturation exposure to O₂ (blue curve, broken line) and H₂O (red curve, dashed line).

2.2 Adsorption Studies

After growth and the specific preparation of the III- or P-rich surface reconstruction, samples were transferred to UHV and probed with PES as well as LEED, confirming clean surfaces free of contaminations such as carbon or oxygen. For each of the different adsorbates and surface types, a new sample was prepared in a very reproducible fashion as confirmed by RAS. A dedicated UHV adsorption chamber was equipped with an optical window enabling in-situ RAS during exposure to ultra-pure water vapour or oxygen. Adsorption was conducted at room temperature and pressures in the range of 10^{-6} to 10^{-5} mbar. Subsequent in-system PES and LEED enabled the identification of water-induced surface modifications.¹³

3. RESULTS

3.1 GaP(100) Surfaces

3.1.1 P-rich surface

P-rich samples were prepared by homoepitaxial buffer growth on a GaP(100) wafer and subsequent annealing at 680 K for 10 min in hydrogen, but without precursor flow applying RAS in-situ control. After growth, RA spectra of the pristine surface were measured both in the MOVPE reactor and the adsorption chamber. During adsorption, RA spectra were continuously recorded and the maximum dosage was defined by a saturation behaviour of the spectra.¹³ Relatively high water dosages in the order of several 10 kL (and in the order of 100 kL for oxygen) had to be applied to impact the RA spectrum, as the sticking coefficient is relatively small at room temperature. This is in contrast to low-temperature adsorption experiments on UHV-cleaved InP(110) surfaces¹² where exposures did not exceed several Langmuirs. It does, however, conform well to oxygen adsorption experiments on MOVPE-prepared InP(100) at more elevated temperatures.²⁰

Figure 2 shows RA spectra of the P-rich GaP(100) surface acquired in the adsorption chamber before and after exposure. The pronounced minimum around 2.5 eV as well as the maximum around 3.6 eV are typical features of the clean, P-rich, $p(2 \times 2)/c(4 \times 2)$ reconstruction.¹⁷ After oxygen exposure up to saturation of the RA spectrum, we basically observe almost a zero-line with weak features in the higher-energetic region. The initial surface reconstruction is not observable in LEED any more. Water exposure, however, leads to a different RA spectrum, especially in the region above 4 eV. In LEED, a new, $c(2 \times 2)$ superstructure is observed.¹³

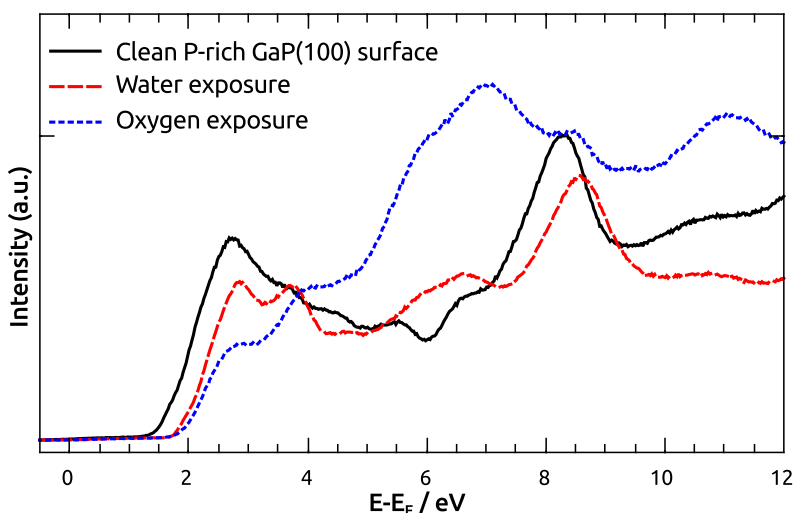


Figure 3. He I photoelectron spectra of the P-rich GaP(100) surface before (black curve) and after exposure to O₂ (blue, dashed line) and H₂O (red, broken line).

Annealing the sample under RAS in-situ control shows that this negative anisotropy disappears at temperatures around 500 K.

He I photoelectron spectra of the P-rich surface are presented in Fig. 3. Comparing the spectrum of the clean sample with the water-exposed surface, a shift of the spectral features towards higher binding energies can be observed. An analysis in context of the secondary electron cut-off (not shown here) indicates a mixture of downward change of band bending as well as a negative surface dipole (negative end towards the surface, reduced work function) as source of this shift.¹³ Additionally, a reduction of the peak near the valence band maximum can be observed. Apart from that, the spectrum remains largely unchanged with the exception of some new features in the binding energy range of 6 eV. The oxygen-exposed surface, in contrast, does exhibit a significant increase of the signal in the region around 6-8 eV binding energy and a further decrease of the peak around 2.5 eV. X-ray photoelectron spectroscopy (XPS) with monochromated Al K_α does not reveal any detectable oxygen after exposure.

3.1.2 Ga-rich surface

The Ga-rich surfaces were prepared similar to the P-rich samples, but with a final annealing at 970 K without TBP supply for 5 min. The required saturation dosage for water was in the order of 10 kL, about a quarter of the dosage needed for the P-rich surface. The dosage for oxygen was in the order of several 10 kL. Again, the RA spectra (Fig. 4) of the exposed surfaces lose most of their features. Though there are minor deviations in the region above 3.5 eV, there is no clear difference between water and oxygen exposure, which is in contrast to the P-rich surface. This is in line with LEED, which does not show any superstructure upon exposure for neither of the surfaces.

With UPS (Fig. 5), we observe a removal of electronic states near the valence band maximum for both adsorbates. For water exposure, again we find a mixture of downward band bending and surface dipole, but this time, the dipole is positive. The additional signal for the water-exposed surface suggests a mixture of Ga-OH groups and molecular water,¹³ similar to UHV-cleaved InP(110),¹² which is also confirmed by XPS (inset of Fig. 5). The coverage is, however, with less than a monolayer very low.

3.2 InP(100) surfaces

Preliminary results for P-rich InP(100) surfaces show similar behaviour to the P-rich GaP(100) surface, albeit without the formation of a new superstructure. In-rich InP(100) surfaces exhibit – again similar to the closely related Ga-rich GaP(100) surface – an increased reactivity.

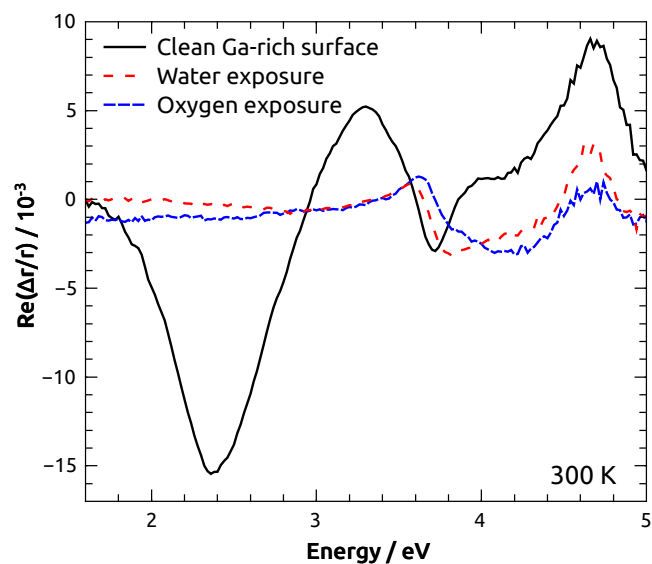


Figure 4. RA spectra of the Ga-rich GaP(100) surface before (black) and after exposure to O₂ (blue, broken line) and H₂O (red, dashed line).

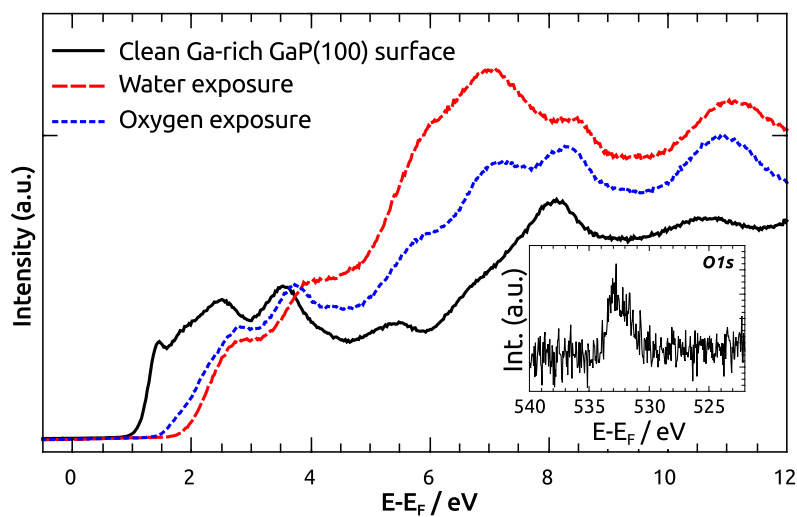


Figure 5. He I photoelectron spectra of the Ga-rich GaP(100) surface before (black) and after exposure to O₂ (blue, dashed line) and H₂O (red, broken line). The inset shows an XP difference spectrum (monochromated Al K α) of the O1s region after water exposure.

4. DISCUSSION

Reflection anisotropy spectroscopy reveals a distinctly different behaviour of the P-rich surface upon water or oxygen exposure. Though the low-energetic part of the spectral features, which are most sensitive to the actual surface reconstruction, disappear in a very similar fashion, there is a strong feature in the high-energetic region upon water exposure, which does not exist for oxygen exposure. With LEED showing a $c(2 \times 2)$ superstructure, that is not present for oxygen-exposed surfaces, we tentatively correlate this feature in RAS with the superstructure induced by water-adsorption. UPS, however, only reveals very weak additional features, which could be interpreted as the signature of a very low coverage with molecular water.^{13,25} Oxygen exposure leads to a strong feature between 6 and 8 eV below E_F . Compared to calculations of Wood et al.,¹⁰ this would point towards Ga-O-P as a structural motif, which is expected to exhibit the highest density of states in the energy range of the considered structures. The peak around 2.5 eV in Fig. 3, attributed to a surface state specific for the P-rich surface,⁶ is reduced in intensity for water exposure, but almost disappears after oxygen adsorption indicating a stronger disturbance of the original surface for oxygen. The lack of an oxygen signal in XPS could be explained by the somewhat low surface-sensitivity for the available excitation energy (mon. Al K_α) along with a very low effective coverage. This is indeed similar to P-rich InP(100) surfaces, that were exposed to molecular oxygen at room temperature.²⁰

For the Ga-rich surface, the water-exposed surface shows a more significant change of the valence band structure when compared to oxygen exposure. This indicates a higher reactivity of the Ga-rich surface for water than for oxygen, but also an increase in comparison to the P-rich surface. The oxygen signature, which consists of two contributions, suggests a mixture of molecular water and OH-groups, pointing towards a hydroxylation of the surface followed by co-adsorbed, molecular water, similar to for example GaAs surfaces exposed to water.²⁶ This would also be in line with calculations on the Ga-rich GaP(100) surface finding a multi-step process of water adsorption, comprising molecular water that finally dissociates.¹¹

5. CONCLUSION

P-rich and Ga-rich surfaces exhibit very different behaviour upon the initial contact with water or oxygen. While the P-rich GaP(100) surface is more stable and even shows a new surface ordering after water exposure, the higher reactivity of the Ga-rich GaP(100) surface dissociating adsorbed water could actually benefit water-splitting. If the two surface reconstructions do actually exhibit a similarly different behaviour in a more realistic, liquid electrolyte ambient, still has to be evaluated.

Reflection anisotropy spectroscopy has demonstrated to be a tool very sensitive to adsorbate-induced surface modifications. Applicable also in-situ during annealing procedures subsequent to adsorption, it is possible to draw conclusions about the stability of the adsorbed species.¹³ Our findings are the basis to study the interface of III-V semiconductors with “real” electrolytes by monitoring electrochemically induced transformations of their surfaces in-situ with RAS.

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