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STRUCTURE AND REACTIVITY OF III-V SEMICONDUCTORS FOR PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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Introduction

Semiconductor-based photoelectrochemical (PEC) hydrogen production from water represents an attractive approach for sustainable fuel production. In a PEC device, the semiconductor acts both as a photon harvester and as a catalytic surface for interfacial hydrogen evolution from water.¹ For optimal efficiency, the semiconductor band gap must be matched to the solar spectrum to maximize collection, and the valence and conduction band edges should closely match the redox potentials of water. Recognizing this, past efforts have concentrated on engineering the band gap and level alignment to the redox potential of water. Nevertheless, although results have demonstrated that one can achieve sufficiently high solar-to-fuel conversion efficiency², this efficiency has come at the expense of short device lifetime due to fast degradation of the electrode.^{6–8} Further progress has been limited by a poor fundamental understanding of the hydrogen evolution and corrosion processes at the electrode-water interface.

It has been suggested that oxygen contaminants on (001) surfaces of III-V semiconductors may play a significant role in motivating both the surface photocorrosion and the catalytic water splitting reaction.^{7,9} Given the apparent connection between high catalytic activity and high potential for surface degradation in III-V systems, evaluating this potential role of oxygen represents a high priority for developing a complete understanding of PEC device shortcomings under real-world operating conditions. Nevertheless, the role of surface oxygen has not been explored in detail theoretically. Here we use *ab-initio* molecular dynamics simulations and total-energy calculations based on density functional theory (DFT) to understand the microscopic hydrogen evolution reaction mechanism at a model electrode/electrolyte interface between oxidized InP(001) and water. Our results are used to explore the impact of oxide and hydroxide surface morphologies on surface stability and reactivity.

Methods

Results are based on density functional theory using the plane-wave pseudopotential formalism as implemented in the Quantum-ESPRESSO code.¹⁰ The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used.¹¹ Ultrasoft pseudopotentials¹² were used for all elements, and semi-core *d* states were included in the electronic valence description for indium.

For the static calculations, slabs were five layers thick with two In-rich surfaces and a 12 Å vacuum separation inserted between periodic slab images. Car-Parrinello molecular dynamics results were obtained using seven-layer (4×4) surface slabs (16 atoms per layer) and an interlayer spacing accommodating 142 D₂O molecules at ambient density. The fictitious electronic mass was chosen as 700 a.u., using a time step of 12 a.u. All simulations were run within the canonical *NVT* ensemble at 400 K in order to properly reproduce the structural properties of liquid water¹⁵ (boiling temperature is elevated in molecular dynamics simulations). Simulations were run for 15 ps each.

Results and Discussion

We extracted low-energy oxide configurations by adsorbing atomic oxygen on high-symmetry sites of an initially unreconstructed In-rich InP(001) surface slab. The atoms were then allowed to relax to their local-minimum configuration. Atop, hollow, bridge x, and bridge y sites were tested in the high-coverage (1.0 ML) limit (here we distinguish the bridge x site from the bridge y site as one sitting directly above a subsurface phosphorus). Site symmetry was broken by slightly displacing oxygen atoms in patterned symmetric and antisymmetric configurations. This procedure allowed us to extract seven metastable structures.

The formation energies of the relaxed oxide structures are given in Table 1. Energies are given with respect to two reference configurations. Both use InP(001) $\delta(2\times 4)$ as the reference surface configuration, but the first uses molecular O₂, whereas the second uses H₂O, and H₂. The results show that incorporation of oxygen is strongly thermodynamically favored with respect to the clean surface in the presence of gaseous O₂, in agreement with experimental observations of high surface oxygen contamination under exposure to air.^{7,9,18} However, incorporation is endothermic in water.

Comparing the geometries of the relaxed surface oxide structures (not shown) allows us to extract key oxygen bond topologies that act as building blocks for all cases. These include the In–O–In bond topology and the In–O–P bond topology. In the former, the oxygen remains as a surface moiety. In the latter, the oxygen is usually carried into the subsurface, since our III-rich model has no exposed phosphorus atoms. Table 1 lists the bond topologies that comprise each relaxed surface, along with the location (surface or subsurface) of the oxygen. The results show that oxygen is generally more stable in the subsurface, reflecting the strength of the In–O–P bond with respect to the In–O–In bond. Consistent with this interpretation, the least energetically favorable configuration (bridge y) features all In–O–In bonds, whereas the most favorable (bridge x) features all In–O–P bonds.

We also find that the oxygen bond topology is a key determiner of reactivity for water dissociation. When single water molecules were adsorbed near the oxygen on each of the morphologies in Table 1, we found that oxygen sites in In–O–P bonds bind water weakly and do not encourage dissociation, whereas sites in In–O–In bonds promote spontaneous dissociative adsorption. For morphologies containing both types of oxide bonds, reactivity depends on the specific adsorption site.

To understand the reaction mechanics near the In–O–In bonds, we ran a dynamics simulation of the bridge y oxide surface at the interface with liquid water. In agreement with the zero-temperature calculations, we see spontaneous dissociative adsorption of water at the interface. The mechanism is depicted in Fig. 1. The reaction begins with the adsorption of a water molecule on a surface indium site to form a bond between the water oxygen (O1) and the indium. The water molecule is initially oriented such that one of the O1–H bonds lies generally parallel to the surface, with the other pointing upwards into the solution. The parallel-lying O1–H bond is thereby free to engage in hydrogen bonding with one of the surface oxygens (O2). The subsequent cleavage occurs via proton transfer across the O1–H ··· O2 complex, such that the covalent and hydrogen bonds are exchanged. The result is the hydroxylation of two neighboring indium atoms. For many water cleavage events, the reaction culminates in two surface hydroxyl groups (O1–H and O2–H). However, there are also instances in which O2 further binds to a second-layer phosphorous and is pulled into the subsurface. This phenomenon can be seen in Fig. 1e & f.

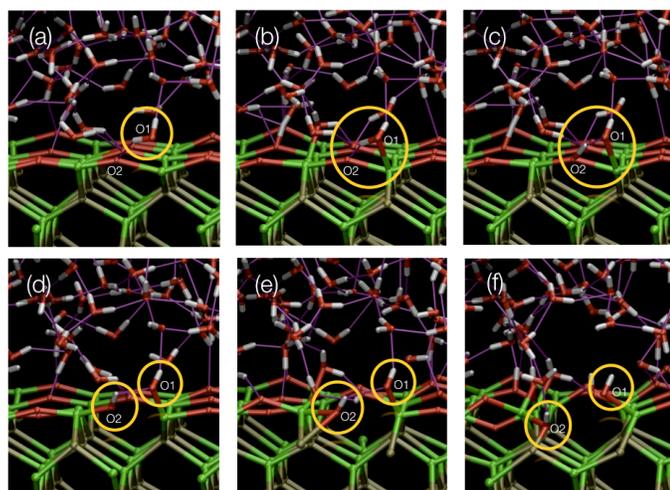


Figure 1. Mechanism of water dissociation on a bridge y oxide of InP(001). O1 and O2 refer to the oxygen atoms originally associated with the water molecule and the oxide surface, respectively. (a) & (b) O1 binds to indium, and a hydrogen bond is formed with O2. (c) The water molecule transfers a hydrogen across the O1-H...O2 complex. (d) The In-O2 bond breaks. (e) & (f) Optionally, O2 is pulled below the surface to form a bond with P. Color scheme: In=green, P=gold, O=red, H=white.

Table 1. Formation energies (E_f), initial oxygen adsorption sites, final oxygen locations, and oxygen bond topologies for InP(001) surface oxides.

Initial ads. site	E_f (eV per O) ¹	E_f (eV per O) ²	Oxygen location	% In-O-In	% In-O-P
Atop	-2.465	+0.894	both	50	50
Atop	-2.512	+0.848	surf.	75	25
Atop	-2.558	+0.801	surf.	75	25
Bridge x	-3.018	+0.341	subsurf.	0	100
Bridge y	-1.969	+1.390	surf.	100	0
Hollow	-2.554	+0.806	subsurf.	0	100
Hollow	-2.704	+0.655	subsurf.	0	100

¹Reference state: H₂/O₂

²Reference state: H₂/H₂O

Table 2. Formation energies (E_f) and initial hydroxyl adsorption for InP(001) surface hydroxides.

Initial ads. site	E_f (eV per O) ¹	E_f (eV per O) ²
Atop	-3.630	-0.271
Bridge y	-3.692	-0.333
Hollow	-3.629	-0.270

¹Reference state: H₂/O₂

²Reference state: H₂/H₂O

Given that the result of water reaction with certain bridge oxide structures is local surface hydroxylation, we explored hydroxyl adsorption by placing OH in high-symmetry sites and relaxing the system. In contrast to the rich array of oxides in Table 1, only three unique relaxed configurations were found for OH coverage. These are listed in Table 2. We find only two dominant oxygen bond topologies: one bridging two indiums and one attached to only one indium. Unlike the oxide case, hydroxide formation is thermodynamically favored both with respect to the molecular H₂/O₂ reference and respect to the H₂O/H₂ reference. This means hydroxylation should be common in solution as well as vacuum. In addition, the hydroxide surfaces are universally more stable than the

oxides, suggesting the outer surface of actual water-exposed InP(001) is likely covered with hydroxyl groups rather than oxygen.

Interestingly, the most stable hydroxylated configuration is the bridge y, which is the least stable oxide configuration that we tested. This indicates that the surface In-O-In bridge oxide behaves as a transition state for In-OH-In formation. However, this pathway is not unique. Instead, there is a competition between three possibilities for the product hydroxide groups: formation of a bridge y hydroxide; formation of an atop hydroxide which strongly hydrogen-bonds with the solution; and subsurface incorporation of the oxygen to form a In-O-P bridge. Qualitatively, the choice between these three seems to be related to the nature of the surrounding hydrogen-bond network. To be pulled into the subsurface, the product oxygen must not be engaged in significant hydrogen bonding. On the other hand, to be converted into the atop hydroxyl configuration, a product oxygen must be engaged in very strong hydrogen bonding. For intermediate cases, the in-plane bridge y configuration is preferred (although the preexistence of a bridge y structure precludes formation of a second, pushing the system towards one of the other two possibilities). Since we have already established that subsurface oxygen that bridges In and P is not generally reactive, the choice the system eventually makes can have significant consequences on further surface catalytic activity.

Conclusions

In summary, we have performed extensive total-energy calculations and *ab-initio* molecular dynamics simulations of water interactions with oxide- and hydroxide-decorated surfaces of the model semiconductor InP(001). Whereas several unique surface oxide structures are identified, only three hydroxide configurations are found. Oxygen prefers to burrow into the subsurface layer and bridge indium to phosphorous, but it can also remain on the surface a bridge between two indium atoms. The first configuration is found to be inactive towards dissociation of water molecules, whereas the second catalyzes spontaneous dissociation of water at the interface. On the surface, hydroxyl binding is preferred over oxygen binding, suggesting real III-V (001) surfaces have an outer hydroxide layer that forms on the surface oxide. Taken together, our results suggest that oxygen contaminants play an active role in stabilizing transition states and driving dissociative adsorption of water in contact with III-V semiconductor surfaces.

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References

- (1) Lewis, N.S. and Nocera, D. G. *PNAS* **2006**, *103*, 15729.
- (2) Khaselev, O. and Turner, J. A. *Science* **1998**, *280*, 425.
- (3) Menezes, S.; Miller, B.; and Bachmann, K. J. *J. Vac. Sci. Technol. B* **1983**, *1*, 48.
- (4) Vigneron, J.; Herlem, M.; Khoumri, E. M.; and Etcheberry, A. *Appl. Surf. Sci.* **2002**, *201*, 51.
- (5) Lewerenz, H. J. and Schulte, K. H. *Electrochem. Acta* **2002**, *47*, 2639.
- (6) Heller, A. *Science* **1984**, *223*, 1141.
- (7) Giannozzi, P. *et al. J. Phys. Condens. Matt.* **2009**, *21*, 395502.
- (8) Perdew, J. P.; Burke, K.; and Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (9) Grossman, J. C.; Schwegler, E.; Draeger, E. W.; Gygi, F.; and Galli, G. *J. Chem. Phys.* **2004**, *120*, 300.
- (10) Deutsch, T. G.; Koval, C. A.; and Turner, J. A. *J. Phys. Chem. B* **2006**, *110*, 25297.