InP and AlInP(001)(2 × 4) Surface Oxidation from Density Functional Theory

Isaac Azahel Ruiz Alvarado,* Marsel Karmo, Erich Runge, and Wolf Gero Schmidt

ABSTRACT: The atomic structure and electronic properties of the InP and AlInP(001)(2 × 4) surfaces at the initial stages of oxidation are investigated via density functional theory. Thereby, we focus on the mixed-dimer (2 × 4) surfaces stable for cation-rich preparation conditions. For InP, the top In–P dimer is the most favored adsorption site, while it is the second-layer Al–Al dimer for AlInP. The energetically favored adsorption sites yield group III–O bond-related states in the energy region of the bulk band gap, which may act as recombination centers. Consistently, the In p state density around the conduction edge is found to be reduced upon oxidation.

INTRODUCTION

III–V compound semiconductors, such as indium phosphide, and their ternary and quaternary alloys, find extensive applications in high-speed integrated circuits, photonic devices, and high-efficiency solar cells or artificial leaves for solar-to-hydrogen conversion, and high-technology applications such as nanowires and quantum dots. Most of these devices are based on, often alloy-based, heterojunctions or quantum wells. The oxides that form on III–V compounds have been determined about their data that water adsorption mainly leads to the formation of In–O–In bonds. The oxidation of AlInP(100) surface, Jeon and co-workers found a Ga–O–Ga bond formation after adsorption of a water molecule and subsequent decomposition. The oxidation of AlInP, on the other hand, was found to occur faster with a higher Al content and to result in oxide layers with excellent insulating properties.

RESULTS AND DISCUSSION

The stability of InP(001) has been investigated previously. The mixed-dimer (2 × 4) surface (cf. Figure 2) is stable for a
wide range of In-rich preparation conditions and will be exclusively studied here.

The equilibrium atomic structures of AlInP(001) surfaces are essentially unknown. Therefore, we perform total-energy calculations for various CuPt-B-type Al$_{0.5}$In$_{0.5}$P(001) surface structures derived from the plethora of stable III–V(001) surfaces.$^{9,10}$ Four of these structures are found to be stable, as can be seen in the phase diagram in Figure 1 and 2.

**Figure 1.** Dependence of energetically favored AlInP(001) surface structures, see Figure 2, on the Al and P chemical potentials. The thermodynamically allowed range of the chemical potentials according to eqs 2 and 5 is indicated by the dashed lines.

Interestingly, the In–P and Al–P mixed-dimer (2 × 4) surface structures stable for cation-rich preparation conditions differ from the InP mixed-dimer (2 × 4) surface in terms of the second-layer cation arrangement: The difference in the In and Al covalent radii leads to a staggered arrangement of the second-layer cation dimers in the case of the ternary compound; cf. Figures 2 and 3.

Next, we explore the oxidation of the cation-rich mixed-dimer (2 × 4) surfaces. First, we calculate the potential energy surface (PES) for a single adsorbed oxygen atom. A lateral mesh of 5 × 10 equidistant points is used to map the adsorption energy. In the calculations, the oxygen adatom is positioned on these points, and allowed only to relax along the surface normal. The substrate structural degrees of freedom are freely relaxed. The adsorption energies thus calculated refer to the spin-triplet ground state of molecular oxygen. The PES obtained in this way gives indications for the most favorable adsorption sites. The results are shown in Figure 3. As obvious from the calculated data, there are qualitative differences between the O adsorption characteristics on InP and AlInP: (i) For the ternary surface, the maximum adsorption energy is more than twice the value obtained for the binary compound. In particular, adsorption on Al–Al bonds is energetically favorable. This is in accordance with the higher heat of formation of aluminum oxide (−17.37 eV$^{24}$) compared to indium oxide (−9.57 eV$^{25}$). (ii) Furthermore, the calculated PES suggest a different O diffusion behavior (see Figure 3, bottom). Oxygen atoms on the InP(001)(2 × 4) surface can be expected to diffuse along the [110] direction, parallel to the InP dimer, hindered by rather shallow barriers of ~0.3 eV. On the ternary surfaces, in contrast, diffusion is hindered by considerably larger barriers of ~2 to 4 eV. This is related to the...
very favorable O adsorption on surface Al cations. (iii) The III–V bond of the topmost dimer is a favorable O adsorption site for InP, in contrast to AlInP, where it is outfavored by adsorption close to second-layer Al–Al dimer.

Starting from the most favorable O adsorption sites, derived from the PES, we explore adsorption on InP and AlInP(001) surfaces, as well as insertion into deeper layers. To do so, we explored the following bonding sites: top In–P dimer, In–P bonds between the first and second layers, second-layer In–In dimers, and In–P bonds formed by the second and third layers. In the case of the ternary surfaces, the following sites were probed: second-layer Al–Al dimers, trench between the Al–Al dimers, top cation-P dimer, and Al–In bonds between the first and second layers. In the case of substitutive insertion, all atoms within the uppermost three layers were tentatively replaced by oxygen. Altogether, considering all possible combinations, more than 600 starting geometries were structurally relaxed and analyzed with respect to their energetics. The complete set of energetically relevant structures considered here for O adsorption and substitution on the mixed-dimer InP(001)(2×4) surface can be seen in Figures S1 and S2 in the Supporting Information (SI). Figure 4 summarizes the most favorable geometries.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Energetically favorable O adsorption and substitution structures calculated for the mixed-dimer InP(001)(2×4) surface. The number in the notation indicates the number of O atoms adsorbed (a) or substituted (s). The complete set of relevant structures considered in the present work is shown in Figures S1 and S2 in the Supporting Information.

To compare these structures energetically, the complete thermodynamically allowed range of the In chemical potential, $-0.41 \leq \Delta \mu_{\text{In}} \leq 0$, was probed. It turns out, however, that the specific choice does not affect the general trend. Therefore, we assume in the following discussion an intermediate value of the In chemical potential, $\Delta \mu_{\text{In}} = -0.2$ eV, and vary the oxygen chemical potential. As can be seen in Figure 5, the surface thermodynamic stability increases with increasing oxygen content, even for a low oxygen partial pressure. This clearly indicates, even without explicit calculation of barriers, that as long as oxygen is available, the oxidation process is only kinetically hindered.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Surface grand-canonical potential vs oxygen chemical potential of the energetically most favored O adsorption and substitution geometries for InP. For the P chemical potential, an intermediate value, $\Delta \mu_{\text{P}} = -0.2$ eV, is assumed. The O chemical potential on the bottom axis is given relative to molecular oxygen. The temperature and pressures are given by eq 6.

In particular, substitutional oxidation can be expected to lead to a rapid loss of surface order (see Figure 4). Most commonly, In–O–P bonds are formed during oxidation. This occurs in all stable O adsorption geometries. In–O–In bonds appear slightly less favored. This corresponds well to the experimental findings of May et al. Oxygen substitution reactions under oxygen-rich conditions ($\Delta \mu_{\text{O}} = 0$) replace In and P atoms with roughly equal probability. The tendency to substitute surface In or P atoms for low values of the O chemical potential ($\Delta \mu_{\text{O}} \ll 0$) depends on the phosphorous chemical potential (see Figure 6). The P replacement results in oxygen atoms that are two-, three-, and fourfold coordinated to In atoms (see Figure S2 in the SI), as previously found in refs 17, 28. P–O–P bonds

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Phase diagram of the most energetically favored O substitution geometries of InP(001) in the stability range of the In chemical potential given by eqs 2 and 3 (dashed lines) and in dependence on the O chemical potential.
are less frequent. The threefold O coordinated on the top dimer is the most stable substitution, as observed during initial substitution (see Figure S1, InP1s). In the case of oxidized GaAs(001) surfaces, O bonding to anion–anion dimers was observed by Yi et al.,14 while the preferential formation of Ga–O–Ga bonds was observed in ref 15. In the case of the GaP(001)(2 × 4) mixed-dimer surface, water adsorption was found to lead to Ga–O–Ga bonds, and, energetically less favored, Ga–O–P bonds.20

The energetically stable oxygen-adsorbed and oxygen-substituted AlInP(001)(2 × 4) surface structures explored here are shown in Figures S3–S6 in the SI. Figure 7 summarizes the most relevant geometries. Energetically, we observe similarities to the binary case. The stability of the surface increases with the amount of oxygen; see Figure 8. The adsorption of eight O atoms, i.e., the highest number investigated here, leads to the most stable geometries for a very large range of the oxygen chemical potential for both the Al–P and In–P mixed-dimer derived structures. As in the binary case, this indicates that as long as oxygen is available, the oxidation process is only kinetically hindered. In the case of substitutional O, the P atom replacements are the most common, as can be seen in Figure 9. Besides these similarities, there are also differences to the binary case: In contrast to the In–O–P and In–O–In bonds, which are most common for binary surfaces, Al-containing bonds Al–O–P, Al–O–Al, and In–O–Al are most frequently formed at O-adsorbed ternary surfaces. The second-layer Al–Al dimer is the preferred adsorption site, leading to Al–O–Al bonds. In addition, we find O coordinated to two In and one P as well as coordinated to two Al and one P. Substitutional oxidation of ternary surfaces leads most frequently to Al–O–Al bonds, compared to the In–O–In-type bonds found in the binary case. Oxygen adsorption on Al–P and In–P mixed-dimer AlInP surfaces follows a similar pattern and results in similar geometries that differ, however, from the adsorption on InP. This behavior is due to second-layer Al–Al dimers being the most favorable adsorption site for oxygen on ternary surfaces; see Figure 3. A trench along the [110] direction forms as a result of the bonds breaking and bond rearrangement in the second layer. As already observed for InP, substitutional oxidation can be expected to lead to a rapid loss of surface order; see Figure 7.

To explore the influence of the oxidation on the III–V surface electronic properties, we calculate the density of states (DOS) for the most relevant geometries. The clean InP surface is characterized by a high density of In and P p states at the valence band edge, while the conduction band edge is dominated by In p and s states; see Figure 10a. Adsorption of oxygen induces in some instances a midgap state, composed primarily of In, P, and O p states; see Figures 10b and S7 in the SI. The appearance of this state is closely correlated to the oxygen coordination of surface P atoms and corresponds to an O-modified P dangling bond. Oxygen adsorption also reduces
The sensitivity of this state to InP surface oxidation was noted earlier by time-resolved two-photon photoemission spectroscopy. The sensitivity of this state to InP surface oxidation was noted earlier by time-resolved two-photon photoemission spectroscopy. This feature disappears upon oxidation. At the same time, the In p state contribution near the conduction band edge is reduced, and an In s state emerges below the CBM; see Figures 10d and S8. These changes are related to the rearrangement of the second-layer In atoms upon trench formation; see Figure 7. Phosphorous-related p states emerge below the CBM, as more oxygen is adsorbed to the third-layer P and O–P bonds form.

The In–P mixed-dimer model differs from the Al–P case, as it does not form an additional state above the bulk VBM. Rather, it is characterized by an additional In p state below the bulk CBM; see Figure 10c. Upon oxidation, this state is pushed up in energy; see Figures 10f and S9. Similar to the case of the Al–P model, this is related to the formation of a trench by a rearrangement of the second-layer In atoms. As oxidation increases, and an In–O–P bond is formed in the top dimer, the In p contribution on the CBM is reduced (cf. s9 and 14a). Therefore, the top In–P surface is responsible for the In p midgap state. Furthermore, for higher O coverages, the P p states in the valence band are pushed up upon In–O–P bond formation between the second- and third-layer atoms.

Altogether, it is clear from the calculations here that the initial stages of oxygen adsorption do not lead to passivation of III–V(001) surface states. Rather, the existing states are modified, and new states appear, in many instances in the region of the bulk band gap. These states may behave as charge traps that affect the carrier generation and recombination process at the interface and thus worsen the electric and optical efficiency. Thus, strategies to avoid the formation of Al/In oxides at the surface are needed. May et al. used Rh deposition to transform AlInP surfaces, leading to the formation of a POx layer and thereby achievement of the passivation of the surface, increasing the efficiency.

CONCLUSIONS

In conclusion, the present DFT calculations show that the AlInP(001) surface geometries are different from that of InP: While cation–anion heterodimers form in the topmost layer for both surfaces in cation-rich preparation conditions, the second-layer dimer arrangement is different. Even larger differences are observed concerning the oxidation. The Al–Al dimers provide more favorable O adsorption sites than found on InP surfaces. This is related to the considerably larger heat of formation of aluminum oxide compared to indium oxide and explains experimental findings that suggest the oxidation of AlInP to occur faster with higher Al content.

Oxidation of AlInP leads more frequently to AlOxides at the surface are needed. May et al. used Rh deposition to transform AlInP surfaces, leading to the formation of a POx layer and thereby achievement of the passivation of the surface, increasing the efficiency.
electronic and optical surface and interface properties may result.

**METHODOLOGY**

In detail, the DFT calculations are performed using the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional is used to model the electron exchange–correlation interaction. The electron–ion interaction is described by the projector-augmented wave (PAW) scheme. The electronic wave functions are expanded into plane waves up to a kinetic energy cutoff of 500 eV. The Brillouin zone integration is performed using $\Gamma$-centered $6 \times 6 \times 1$ meshes. The (001) surfaces are modeled by supercells containing 8 and 13 atomic layers (each containing 8 atoms in the ideal case) for InP and AlInP, respectively, and a vacuum region of $\sim 12$ Å. The AlInP supercells were modeled according to the CuPt-B-type crystal ordering. The slab bottom dangling bonds are saturated with fractionally charged H atoms ($Z = 1.25$ and $0.75$ for group III and V atoms, respectively). The electronic field resulting from the inequivalence of the two surfaces is taken into account by a dipole correction to the electrostatic potential. The atoms are considered to be in their relaxed ground-state positions when the forces acting on the ions are lower than $0.02$ eV/Å.

To compare the various clean and oxidized surfaces energetically, one must take into account the chemical potentials $\mu_{A_i}$ of the respective surface constituents. The surface ground state is determined by the thermodynamic potential minimum

$$\Omega = U - TS - \sum \mu_{A_i} n_{A_i}$$

where $U$ is the total energy of the system. In solids, the entropy term, $TS$, contributes very little to the difference in $\Omega$ under usual experimental conditions and is neglected in the following. The chemical potentials $\mu_{A_i}$ for $A_i = \text{In, Al, and P}$ are restricted by their bulk values $\mu_{A_i}^{bulk}$ (2)

Furthermore, in the case of InP surfaces, they are related to each other by

$$\mu_{\text{In}} + \mu_{\text{P}} = \mu_{\text{InP}}^{bulk}$$

where $\Delta H_{\text{InP}}$ being the heat of formation of InP. Consequently, the formation energy may be written as a function of a single variable, which we will take to be $\Delta \mu_{\text{In}}$

$$-\Delta H_{\text{InP}} \leq \Delta \mu_{\text{In}} = \mu_{\text{In}} - \mu_{\text{InP}}^{bulk} \leq 0$$

This limit can be related to preparation conditions: $\Delta \mu_{\text{In}} = 0$ corresponds to In-rich conditions, where the surface In atoms are in equilibrium with bulk In. $\Delta \mu_{\text{In}} = -\Delta H_{\text{InP}}$ corresponds to In-poor conditions, where the surface P atoms are in equilibrium with bulk P.

A single chemical potential is not sufficient to characterize the stability of AlIn$_{\text{0.5}}$In$_{\text{0.5}}$P(001) surfaces. In this case, the relation...
\[ \mu_{Al} + \mu_{In} + 2\mu_{P} = 2\mu_{Al_{2}In_{2}P_{3}^{bulk}} = \mu_{Al_{2}In_{2}P_{3}^{bulk}} + \mu_{In_{2}P_{3}^{bulk}} + 2\mu_{P_{3}^{bulk}} - 2\Delta H_{Al_{2}In_{2}P_{3}^{bulk}} \]

allows us to formulate the formation energy depending on \( \Delta \mu_{P} \) and \( \Delta \mu_{Al} \). For the heats of formation \( \Delta H_{Al_{2}P_{3}^{bulk}} \) and \( \Delta H_{AlInP_{3}^{bulk}} \) we calculate values of \(-0.41\) and \(-1.52\) eV, respectively.

In the case of oxidized surfaces, the oxygen chemical potential provides an additional and independent degree of freedom. In the approximation of a two-atomic ideal gas, it is written depending on partial pressure \( p \) and temperature \( T \) as

\[
\Delta \mu_{O}(p, T) = \frac{k_{B}T}{2} \left[ \ln \left( \frac{p \lambda}{k_{B}T} \right) - \ln Z_{rot} - \ln Z_{vib} \right] - \frac{1}{2} \mu_{O_{2}}
\]

where \( k_{B} \) is the Boltzmann constant, \( \lambda \) is the de Broglie thermal wavelength of the \( O_{2} \) molecule

\[
\lambda = \sqrt{\frac{2\pi \hbar^{2}}{mk_{B}T}}
\]

and \( Z_{rot} \) and \( Z_{vib} \) are its rotational and vibrational partition functions, respectively.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06019.

Relevant InP(001) and AlInP(001)(2 × 4) surface geometries and calculated density of states for relevant surface structures (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Isaac Azahel Ruiz Alvarado – Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany; orcid.org/0000-0002-4710-1170; Email: azahel@mail.upb.de

**Authors**

Marcel Karmo – Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany

Erich Runge – Institut für Physik, Technische Universität Ilmenau, 98693 Ilmenau, Germany

Wolf Gero Schmidt – Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany; orcid.org/0000-0002-2717-5076

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c06019

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

Financial support by DFG (SCHM1361/26, RU1383/6) is gratefully acknowledged. The authors thank the Paderborn Center for Parallel Computing (PC²) and the Höchstleistungs-Rechenzentrum Stuttgart (HLRS) for grants of high-performance computer time.

**REFERENCES**


InP and AlInP (001)(2×4) surface oxidation from density-functional theory

Isaac Azahel Ruiz Alvarado,*† Marsel Karmo,† Erich Runge,‡ and Wolf Gero Schmidt†

†Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, 33095 Paderborn, Germany
‡Institut für Physik, Technische Universität Ilmenau, Gustav-Kirchhoff-Straße 5, 98693 Ilmenau, Germany

E-mail: azahel@mail.upb.de
Data files underlying all figures are available to the authors and will be accessible upon request.

1  I. Relevant InP(001) and AlInP(001) (2×4) surface geometries

Figure S1: Top view of the models explored here for O adsorption at the mixed-dimer InP(001)(2×4) surface. The number in the notation indicates the number of O atoms adsorbed (a).
Figure S2: Top view of the most relevant models explored here for O substitution at the mixed-dimer InP(001)(2×4) surface. The number in the notation indicates the number of substitute O atoms (s).
Figure S3: Top view of the models explored here for O adsorption at the Al-P mixed dimer AlInP(001)(2×4) surface. The number in the notation indicates the number of O atoms adsorbed (a).
Figure S4: Top view of the most relevant models explored here for oxygen substitution at the Al-P mixed dimer AlInP(001)\((2\times4)\) surface. The number in the notation indicates the number of substitute O atoms \(s\).
Figure S5: Top view of the models explored here for O adsorption at the In-P mixed dimer AlInP(001)(2×4) surface. The number in the notation indicates the number of O atoms adsorbed (a).
Figure S6: Top view of the most relevant models explored here for O substitution at the In-P mixed dimer AIIInP(001)(2×4) surface. The number in the notation indicates the number of substitute O atoms (s).
2 II. Calculated density of states for relevant surface structures

Figure S7: Calculated electron densities of states for oxidized mixed-dimer InP(001)(2×4) surfaces in comparison to the clean surface. In addition to the total density, species-resolved $s$ and $p$ contributions are shown.
Figure S8: Calculated electron densities of states for oxidized Al-P mixed-dimer AlInP\(001\)(2\(\times\)4) surfaces in comparison to the clean surface. In addition to the total density, species-resolved \(s\) and \(p\) contributions are shown.
Figure S9: Calculated electron densities of states for oxidized In-P mixed-dimer AlInP(001)(2×4) surfaces in comparison to the clean surface. In addition to the total density, species-resolved $s$ and $p$ contributions are shown.