

Exploring Electronic States and Ultrafast Electron Dynamics in AlInP Window Layers: The Role of Surface Reconstruction

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AlInP (001) is widely utilized as a window layer in optoelectronic devices, including world-record III-V multi-junction solar cells and photoelectrochemical (PEC) cells. The chemical and electronic properties of AlInP (001) depend on its surface reconstruction, which impacts its interaction with electrolytes in PEC applications and passivation layers. This study investigates AlInP (001) surface reconstructions using density functional theory and experimental methods. Phosphorus-rich (P-rich) and indium-rich (In-rich) AlInP surfaces are prepared with in situ monitoring of the process by reflection anisotropy (RA) spectroscopy and confirmed by low-energy electron diffraction and photoemission spectroscopy. The experimental RA spectra closely match the theoretical predictions obtained by solving the Bethe–Salpeter equation. It is shown that missing hydrogen on P-rich surfaces and formation of In–In 1D atomic chains on In-rich surfaces introduce mid-gap surface states that pin the Fermi level and induce band bending. Time-resolved two-photon photoemission measurements reveal ultrafast near-surface electron dynamics for both P-rich and In-rich surfaces, demonstrating photoexcited electrons reaching the surface conduction band minimum and relaxing to mid-gap surface states on about hundreds of fs. This work provides the most extensive AlInP surface analysis to date, allowing for more targeted surface and interface engineering, which is crucial for the optimization and design of III-V heterostructures.

1. Introduction

III-V semiconductors are extensively utilized in various optoelectronic devices, including light-emitting diodes, detectors, high-electron-mobility transistors, electro-optic modulators, and photovoltaic (PV) devices. In particular, III-V-based multijunction solar cells have held the record for efficiency in PV energy conversion since the early 1990s.^[1–5] Ternary III-V semiconductors, especially III-P compounds, are of significant interest because their adjustable bandgaps enable effective absorption across a broad range of wavelengths within the solar spectrum. In addition, type III-P compounds possess excellent thermal stabilities and high electron mobilities, making them ideally suited to applications in high-performance optoelectronic devices and multijunction solar cells.^[6]

One of the critical aspects of III-V-based multijunction and optoelectronic devices is the electronic structure at essential heterointerfaces, as this dictates the complex

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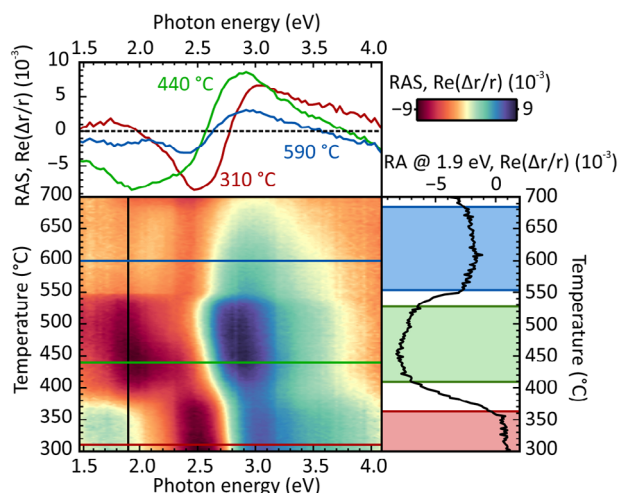


Figure 1. Color plot of in situ RAS recording surface changes during the heat-up run.

charge carrier dynamics at the interface, namely the selective transport of charge carriers and the interfacial recombination of photogenerated electron–hole pairs.^[7,8] A particularly technologically important III–V semiconductor is aluminum indium phosphide (AlInP), which has received considerable interest for its application as a window layer in a variety of state-of-the-art optoelectronic and photoelectrochemical (PEC) systems.^[1,9–13] The driving force for charge carrier transport is given by the gradient of the electrochemical potential, thus employing a window layer as a highly charge carrier-selective contact is essential for the efficient extraction of the chemical (free) energy given by the difference of the (quasi-) Fermi energies of electrons and holes. In addition, losses due to interfacial charge carrier recombination at contacts must be avoided.^[7] refs. [7, 8, 13] describe that selective transport at contacts is a fundamental principle in the design of efficient devices, and outline various advanced methodologies and device structures in the development of highly selective contacts. Therefore, in any III–V-based optoelectronic device, it is necessary to find a suitable heterocontact with favorable bandgaps and band offsets.

To achieve favorable band alignments in heterostructure devices, the bandgap of the window layer is tuned; in the example of AlInP, this occurs by adjusting the composition of $\text{Al}_x\text{In}_{1-x}\text{P}$.^[14–16] This allows for tuning of E_g in the range of 1.35 and 2.45 eV, corresponding to the bandgaps of indium phosphide (InP) and aluminum phosphide (AlP), respectively;^[15,17–21] the most commonly used compositions in practical applications are around $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$. The direct–indirect bandgap crossover point of AlInP lies at 2.33 eV, corresponding to $x = 0.43$, as presented in Figure 1 of reference.^[15,22] In addition to its bandgap tunability, the ubiquitous use of AlInP as a window layer is also related to its ability to be lattice-matched to many other III–V materials, such as GaAs, allowing for its efficient integration in many state-of-the-art III–V devices. AlInP possesses the highest direct bandgap among materials in the conventional (non-nitride) III–V semiconductor alloy system, making it ideal for amber and yellow-green light-emitting diodes.^[14] Moreover, previous studies have demonstrated that incorporating AlInP in high electron mobil-

ity transistor devices improves electron transfer and transport properties.^[23]

Cheng et al. used an AlInP window layer in their record-setting multijunction III–V PEC cell in 2018, achieving a 19% solar-to-hydrogen efficiency, over 85% of the theoretical maximum.^[10] Their design combined a GaInP/GaInAs/GaAs (001) tandem photoabsorber with an n^+ -doped AlInP window layer to achieve selectivity for electron transport. One of the main benefits of AlInP in PEC applications is its ability to adjust both the bandgap and the band edge positions with respect to the water reduction potential while maintaining lattice matching with the underlying sublayers. The window layer is especially relevant to the efficiency of concentrator solar cells, as shown by Ochoa et al. using 2D physically based numerical modeling^[24] of n -AlInP window layers lattice-matched to GaInP/GaAs/Ge absorbers. At 3000 suns concentration, the overall device efficiency of a III–V cell with a 25 nm AlInP window layer was found to vary by more than 1% depending on the doping of the AlInP window layer and other parameters related to the window layer, including its bandgap, the energy level of the Fermi level, rates of interfacial recombination via near-surface states, the doping level of the layer, and its thickness. Allowing for efficient charge carrier separation while reducing absorption and recombination in the window layer then requires a detailed experimental understanding of the surface reconstructions of AlInP, as well as the resulting surface states and near-surface electron dynamics.

Lepkowski et al. demonstrated the influence of the window layer parameters, such as thickness and doping, on photocurrent loss.^[11] The extension of the depletion layer, induced by surface states pinning the Fermi level at the window/air interface into regions of active photoabsorption, has been attributed to the mechanism for increasing the interface recombination velocity (IRV). However, since the internal electric field does not drive the charge carriers, a more plausible explanation for the increased IRV is that the hole concentration at the interface becomes higher due to charge carrier displacement at the contact, causing band bending (BB) (in the dark) and increased interfacial recombination;^[7] an increased density of bandgap states may be another reason. Their experiments showed that improper choices of AlInP thickness and doping concentration in a metamorphic $\text{GaAs}_y\text{P}_{1-y}$ structure result in an up to 50 % increase in photocurrent loss, as indicated by the integrated internal quantum efficiency. Nevertheless, no experiments have been conducted to ascertain the energetic position of surface states that pin the Fermi level on AlInP surfaces, or to determine the nature of the surface defects that may induce these states.

While AlInP is commonly used in state-of-the-art PV, PEC, and optoelectronic devices, little is known about its electronic structure and near-surface electron dynamics, especially how this is affected by the choice of surface termination. This is particularly relevant in view of the thin layer thicknesses often used for window layers, in the tens of nm and below.^[1,10,11] In previous publications by some of the present authors, total energy and electronic structure calculations based on density functional theory (DFT) were performed to determine the atomic structure and electronic properties of clean and hydrogen-adsorbed $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$ (001) surfaces.^[12] In addition, the surface optical anisotropy of AlInP (001) surfaces was studied both theoretically and experimentally, focusing on the phosphorus-rich

(P-rich) surface reconstruction.^[25] Apart from these previous publications, there is currently no literature on the band alignment and BB on AlInP surfaces. Similarly, experimental and theoretical data on surface defect states and the near-surface conduction band energetic positions are lacking. This information is highly relevant for the further design and improvement of AlInP-based devices. Understanding near-surface defect states and electron dynamics is key to performance in different applications, as they will affect charge carrier separation and recombination. Therefore, a better understanding of the most common AlInP surfaces is needed to enable optimized surface passivation and defect reduction, which is crucial for the engineering of AlInP window layers. The lack of literature on the AlInP surface is to some extent related to the high experimental difficulty of working with these surfaces, as oxidation occurs even with minimal exposure to oxygen or water. This is confirmed by DFT calculations^[26] showing that cation-rich AlInP surfaces in particular are highly reactive to oxygen. When oxygen adsorbs on the surface, it tends to form III–O bonds, favoring Al–O bonds. The formation of these bonds leads to bandgap states that impact the electronic and optical properties of the surface. In order to understand AlInP surfaces, it is therefore essential to focus first on well-defined model structures. Indeed, we have found that meticulous treatment and ultra-high vacuum (UHV) handling of the AlInP (001) surfaces is critical when studying their properties.

In the present work, we employ a combination of experimental methods and DFT calculations to understand the properties of P- and In-rich AlInP surfaces. Reflection anisotropy (RA) spectroscopy is used to observe and control the formation of the AlInP surface reconstructions in a metalorganic vapor phase epitaxy (MOVPE) process. DFT calculations elucidate the interband transitions present in RA spectra, acting as a distinctive identifier for each surface. We utilized photoemission spectroscopy (PES) to examine the chemical and electronic characteristics of AlInP along with its band diagram. Furthermore, the behavior of charge carriers in the near-surface area of AlInP surfaces was analyzed using time-resolved two-photon photoemission (tr-2PPE).

2. Results and Discussion

2.1. Reflection Anisotropy Spectra of AlInP (001) Surfaces

Additional post-growth steps are necessary to prepare a specific atomically well-ordered surface reconstruction of AlInP. The compensation for P-desorption during epilayer growth and cooling results in a surface containing a high phosphorus concentration, but lacking an atomically well-ordered surface reconstruction.^[27,28] Such a surface contains carbon contamination due to the presence of metalorganic compounds of TBP on the surface. To determine the annealing temperature necessary to achieve an atomically well-ordered surface reconstruction, the heat-up process was conducted on a test sample, with surface changes monitored in situ by RAS. **Figure 1** shows the color-coded RA spectra recorded during the heat-up run. As temperature increases, so does P-desorption from the surface, leading to a transition from a P-rich to an In-rich surface;^[28,29] this transition is evident in the distinct RA spectra associated with both surface reconstructions. By increasing the temperature to approximately 400 °C, a sudden red shift of the spectrum is ob-

served. The line shapes of the RA spectra are altered, resulting in the emergence of peaks at 1.9 and 2.9 eV. When a surface reconstruction remains stable across a broad temperature range, an increase in temperature generally causes peak intensities to diminish;^[25,30] however, for AlInP, increasing the temperature from 340 to 440 °C leads to intensified peaks, indicating an alteration in the surface reconstruction as the source of RAS signal. The color-coded RA spectra show three distinct temperature regions, illustrated by color-coding as seen in **Figure 1** (red, green, and blue). The red and green lines show extracted RA spectra of the P-rich $p(2 \times 2)/c(4 \times 2)$ at 310 °C and In-rich (2×4) surfaces at 440 °C, respectively. The black line represents the extracted transient at 1.9 eV, enabling real-time monitoring of the surface formation; a dashed line denotes the 0 line for each spectrum.

Compounds with a more negative enthalpy of formation release more energy during their formation, indicating a greater level of stability in the resulting product. Given that AlP has an enthalpy of formation of $-166.6 \text{ kJ.mol}^{-1}$, which is lower than the $-92.1 \text{ kJ.mol}^{-1}$ of InP, Al–P bonds are thus thermodynamically more stable than In–P bonds.^[31] Hence, increasing sample temperature breaks the In–P bonds first, causing the creation of an In-rich surface termination at lower temperatures than for an Al-rich surface termination. For InP, annealing the P-rich surface over 370 °C without phosphorus stabilization leads to increased surface phosphorus desorption and depletion, as shown in reference.^[27] Notably, substituting the group III element in binary III–P compounds with an element of lower atomic number increases the required temperature for P-desorption from the (001) surface, with other conditions remaining the same. For instance, in GaP (001), it was observed that a transition from a P-rich surface reconstruction to a Ga-rich surface reconstruction via an intermediate surface occurs at temperatures exceeding approximately 490 °C.^[28]

As depicted in **Figure 1**, temperatures between ca. 410 and 540 °C, highlighted in green, are expected to be associated with an In-rich surface reconstruction. This expectation is subsequently validated through X-ray photoelectron spectroscopy (XPS), ultra-violet photoemission spectroscopy (UPS), and low-energy electron diffraction (LEED) in the following section of this paper. Subjecting the AlInP surface to temperatures higher than 540 °C during the annealing process can result in the formation of either a different In-rich termination, with no atomic ordering and In clusters on the surface, or an Al-rich surface (blue region in **Figure 1**). However, AlInP surfaces with a high concentration of indium and especially aluminum lead to a decrease in surface stability, and an increase in the likelihood of contamination within the MOVPE reactor as well as during UHV transfer, posing significant challenges to the use of any surface-sensitive characterization. The P-rich and In-rich samples were individually produced by subjecting the AlInP surfaces to annealing processes at temperatures of 310 and 440 °C, respectively. **Figure 2** presents the RA spectra of P- (red) and In-rich (green) AlInP surfaces at room temperature in UHV. The experimental RA spectra are compared with the models calculated using DFT, revealing a reasonable correspondence between the theoretical predictions and the experimental data.

The top views of stable, relaxed P- and In-rich AlInP surface reconstructions are depicted in **Figure 2** using a ball-stick model. The (2×2) -2D-2H surface, which corresponds to the P-rich

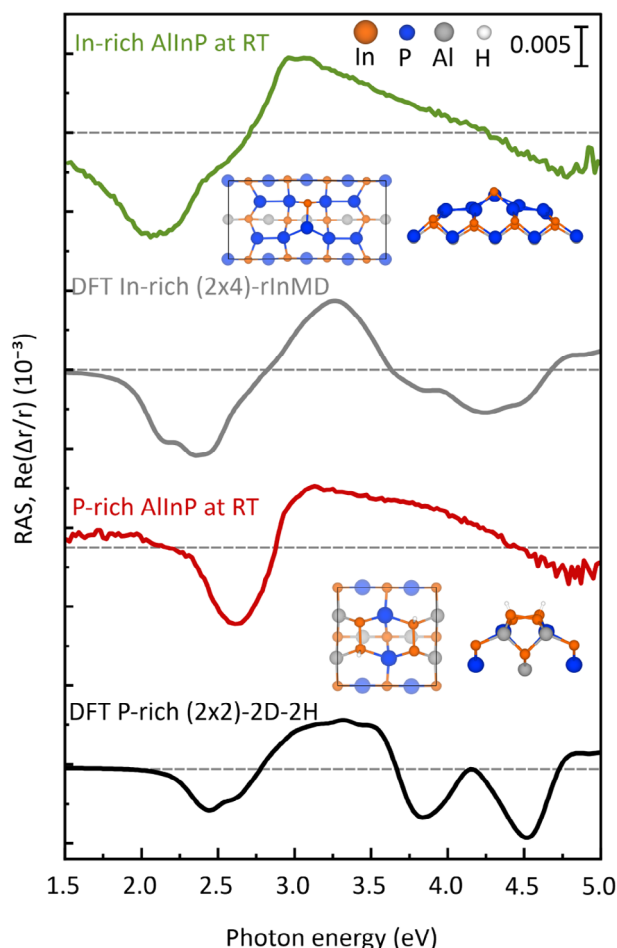


Figure 2. RA spectra of as-prepared P-rich (red) and In-rich (green) AlInP (001) surfaces, compared with theoretical calculations. The DFT-calculated RA spectrum of (2 × 2)-2D-2H is adopted with permission.^[25] Copyright 2023, American Physical Society. The graph includes both top and side views of (2 × 2)-2D-2H and (2 × 4)-rInMD AlInP surface reconstructions.

$p(2 \times 2)/c(4 \times 2)$ surface, displays two P–P dimers and two hydrogen atoms per unit cell on the surface (see Figure S1a (Supporting Information), which illustrates the $p(2 \times 2)/c(4 \times 2)$ configuration). The (2 × 2)-2D-2H surface is stable across a wide range of hydrogen chemical potentials ($-0.8 \text{ eV} \geq \Delta\mu \geq -0.2 \text{ eV}$).^[12] This surface reconstruction is analogous to the P-rich InP model, with the distinction that in InP, all P atoms are bonded to In, whereas in AlInP, P atoms can form bonds with In, Al, or both simultaneously.^[12,26,32]

The (2 × 4)-rInMD model displays a surface with a greater indium concentration than the bulk material. The initial monolayer reveals the presence of In–P mixed dimers, while the second monolayer illustrates the existence of In–In dimers. The (2 × 4)-rInMD of AlInP and (2 × 4)-InMD of InP exhibit similarities in the presence of In–P and In–In bonds in the first and second atomic layer, respectively. However, they differ in the presence of Al in the third monolayer.^[26,33,34] While it is anticipated that Al–Al dimers will be present in certain In-rich surfaces (see refs. [12, 26] for more information), none were detected in our ex-

perimental analyses. This is a result of the experimental preparation conditions and annealing at a modest temperature of 440 °C. Coupled with the fact that calculated RA spectra for the (2 × 4)-InMD do not match any of the experimental RA spectra for the In-rich surfaces, we looked for possible new candidates that could explain our observations. The new In-rich (2 × 4)-rInMD surface reconstruction, lacking Al at the surface, is proposed here; see Figure 2. Furthermore, the RA spectra match with experimental results, reproducing both the negative feature around 2 eV and the peak at 3 eV, although the calculated spectra are shifted to slightly higher energies.

2.2. X-Ray and UV Photoemission Spectroscopy of P- and In-Rich AlInP (001)

Figure 3a displays the XP survey spectra of P-rich AlInP after being transferred in UHV at a 15° emission angle, providing more surface sensitivity than a 90° emission angle. Figure S2a (Supporting Information) depicts a schematic of the sample, beam, and orientation of ejected electrons at 90° and 15° emission angles. The high-resolution scans of the C 1s and O 1s core levels did not reveal any clear signature of carbon or oxygen contamination, confirming that the transfer process was contamination-free (see Figure S3, Supporting Information).

Figure 3b–d shows the high-resolution XP spectra of P 2p, In 3d_{5/2} and Al 2p lines, respectively; a Shirley background subtraction was used before fitting all core levels. To fit the P 2p XP spectrum, a ΔE of 0.85 eV was considered for spin-orbit splitting of the 2p_{3/2} (solid lines) and 2p_{1/2} levels (dashed lines) Refs. [35, 36]. The 2p core level is fitted by two pairs of spin-orbit splitting peaks, where one represents a bulk contribution at lower binding energies (BE) (yellow), and one is a surface component (red) as shown in Figure 3c. The main contribution originates from III–P compounds, specifically In–P and Al–P. The surface contribution, on the other hand, is caused by phosphorus in P–P dimers. It is known that P–H can appear at this energy; however, in this particular scenario, hydrogen is also bonded to one of the phosphorus atoms in the surface P–P dimers.^[32,37] As it is shown in Figure S4a (Supporting Information), the contribution of the P–P component is enhanced by reducing the take-off angle, providing evidence that this contribution originates from a surface component. This observation is corroborated by the presence of a positive signal in the difference spectrum at higher binding energies. It is consistent with the findings of Vogt et al. in their investigation of an MOVPE-prepared P-rich InP surface, which was analyzed using soft XPS (SXPS).^[35] They showed that the P–P component in the P 2p line is shifted toward higher BE by approximately 0.98 eV relative to the In–P component, which aligns with our observations in P-rich AlInP. The results of highly surface-sensitive SXPS measurements of In, P, and Al core levels at different incident X-ray energies (ranging from 120 to 620 eV) are illustrated in Figure S5 (Supporting Information). Changes in the spectral line shape indicate the existence of a surface component solely in P 2p, supporting our results obtained from XPS measurements utilizing a monochromatic Al K α X-ray source at various emission angles.

Upon analysis of the Al 2p and In 3d_{5/2} core levels of P-rich AlInP, we have not detected any distinct surface components as

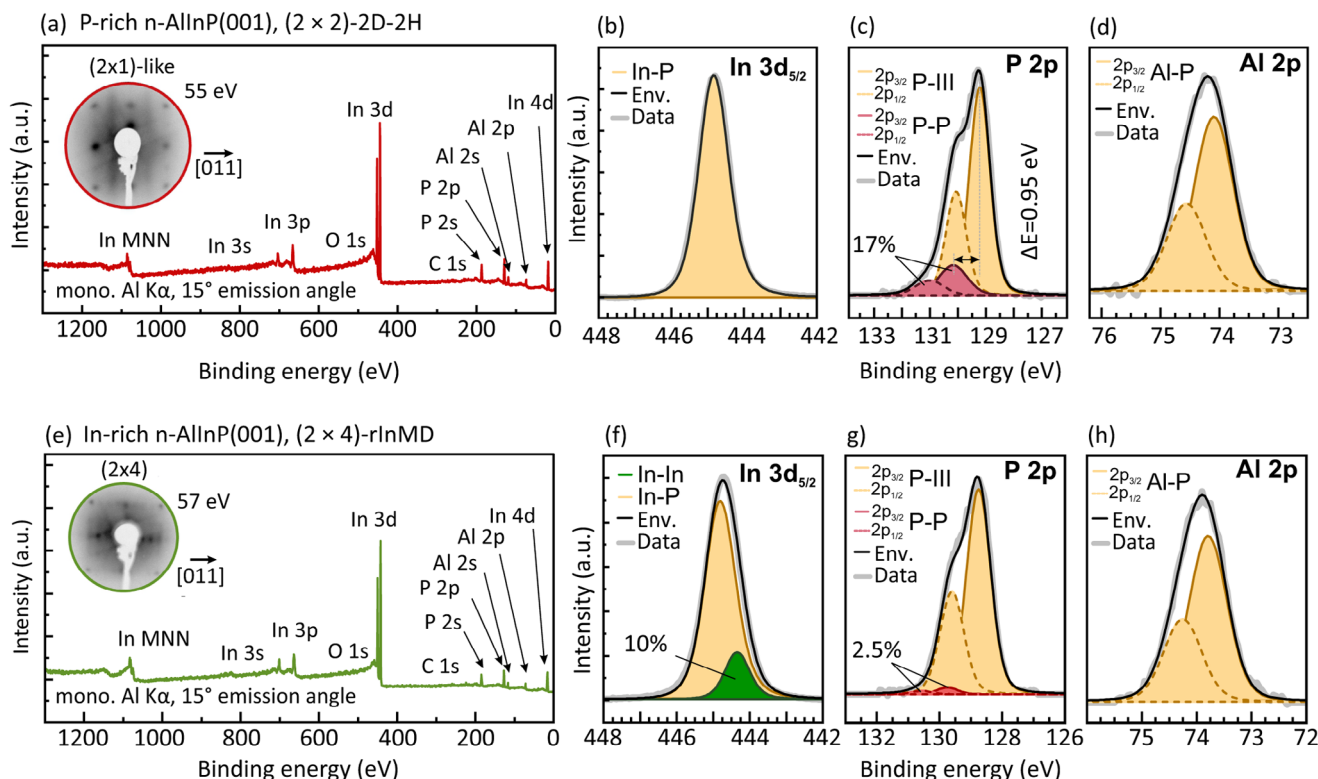


Figure 3. XPS spectra of P-rich and In-rich AlInP (001) in the first and second row, respectively. XPS measurements are performed at a 15° emission angle. XP a) survey spectrum, fitted with b) In 3d_{5/2}, c) P 2p, and d) Al 2p core levels of P-rich AlInP. All yellow curves are bulk-like components, representing III-P bonds; the red curves are correlated to P–P/P–H bonds on the surface. XP e) survey spectrum, fitted with f) In 3d_{5/2}, g) P 2p, and h) Al 2p core levels of In-rich AlInP; the green curve in (f) is correlated to In–In bonds on In-rich AlInP. The (2 × 1)-like LEED pattern at 55 eV of P-rich AlInP is shown (a) top left, the (2 × 4) LEED pattern at 57 eV of In-rich AlInP is shown (e) top left.

seen in Figure 3b,d. The spin-orbit splitting for the Al 2p core level was determined to be 0.45 eV. The solid lines represent the 2p_{3/2} state, while the dashed lines represent the 2p_{1/2} state. Consequently, any bonds involving Al and In atoms are considered bulk-like bonds, specifically Al–P and In–P bonds. Additionally, the LEED pattern at 55 eV exhibits a (2 × 1)-like surface reconstruction, with half order spots and diffuse half order streaks along the [110] direction as seen in Figure 3a top left. For P-rich InP, it is shown that the stabilization of buckled P dimers with atomic hydrogen, which adsorbs during the MOVPE process due to the use of H₂ as a carrier gas, can be arranged in-phase, resulting in a p(2 × 2) unit cell, or out-of-phase, corresponding to a c(4 × 2) unit cell.^[38,39] The characteristic (2 × 1)-like LEED pattern with half-order streaks in the x2 direction is produced by the superposition of both unit cells. In accordance with its XPS and RAS results, the (2 × 1)-like LEED of P-rich AlInP also represents the p(2 × 2)/c(4 × 2) reconstruction.^[12]

Figure 3e shows the XP survey spectrum of the as-prepared In-rich AlInP at a 15° emission angle, with no evidence of oxygen and carbon contamination observed at 530 ± 5 eV and 285 ± 5 eV, respectively (see Figure S3, Supporting Information). A diffuse (2 × 4) LEED pattern at 57 eV was observed as seen in Figure 3e top left. Diffused spots may indicate a low level of ordering in specific directions, or a low concentration of contamination that was difficult to resolve with XPS that uses monochromatic Al K α , due to its high X-ray excitation energy.

When comparing the P-rich and In-rich surfaces, the In 3d_{5/2} core level for the P-rich surface, shown in Figure 3b, displays a dominant bulk-like contribution (yellow) corresponding to In–P bonds. In contrast, the In-rich surface, illustrated in Figure 3f, reveals a new surface component at a lower binding energy of 444.15 eV (green). Figure S6a (Supporting Information) presents the difference spectrum for P- and In-rich samples, highlighting the additional component within the In core level with improved clarity. As the emission angle decreases, the increase in the contribution of this component is verified to be associated with a surface component, as demonstrated in Figure S4b (Supporting Information). This surface component is found within the BE range of the anticipated indium metallic bonds, and represents In–In in the second layer of In-rich AlInP;^[33] about 10% of the total In 3d_{5/2} core level contributes to the In–In pairs.

In Figure 3g, the presence of a minor trace of P–P dimers in the P 2p core level (2.5%, red) may suggest that P–P dimers were preserved in some domains during the post-annealing step. The majority of the contributions in P 2p come from P–III bonds, which are bulk-like components. As depicted in Figure 3h, no surface component is detected in the Al 2p core level for In-rich AlInP, suggesting that the aluminum atoms in this sample are exclusively bonded to phosphorus atoms. Although the high X-ray energy of XPS with an Al K α source affects the resolution and makes it challenging to detect very low traces of surface components, varying the emission angle and comparing the results with

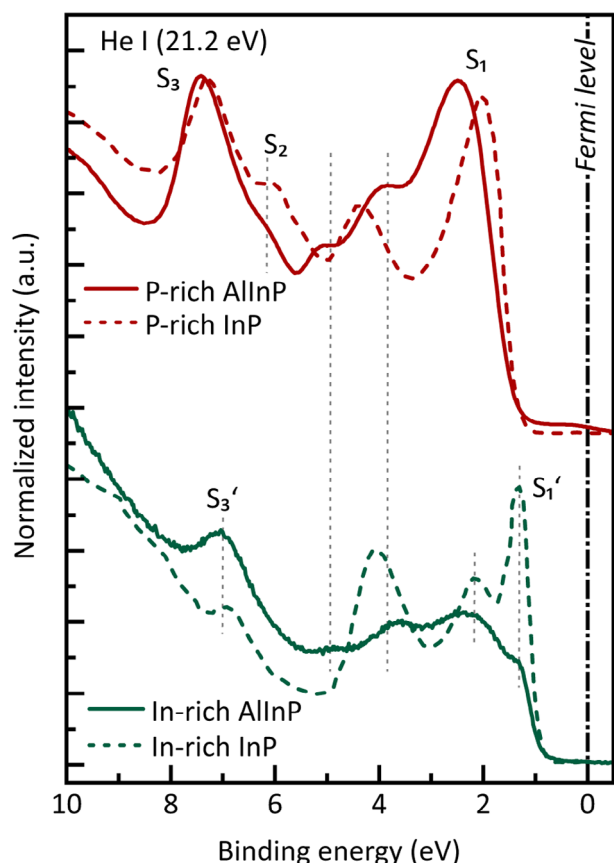


Figure 4. Comparison of UPS spectra of P- and In-rich AlInP (red and green solid lines, respectively) with P- and In-rich InP (red and green dashed lines, respectively). InP spectra are adopted with permission.^[40] Copyright 2000, Elsevier. The gray dashed lines serve as visual aids to assist in comparing the positions of the peaks.

SXPS improves the analysis and helps to resolve these components. Furthermore, RA spectroscopy, which is sensitive to the first few monolayers, would be affected if other Al components were present, as their presence would alter the RAS signal. Taken together, the comparison of XPS results at different emission angles, along with SXPS data and the specific RA signal supported by DFT, suggests the absence of other Al components. Nevertheless, a negligible concentration of additional Al components cannot be entirely ruled out.

Possible changes in III-V surfaces at elevated temperatures are crucial, particularly for post-processing like the deposition of passivation layers using techniques such as atomic layer deposition, which may include annealing steps. For AlInP, we have shown that at high temperatures up to 550 °C, the P-desorption mostly impacts In–P bonds, resulting in the formation of a surface enriched in indium. The presence of P–P dimers on the surface can be attributed to strong bonds formed between phosphorus atoms in the surface P-dimers and aluminum atoms in the second layer, which are far stronger than In–P bonds.^[31]

Figure 4 compares the UPS spectra of P-rich (red solid line) and In-rich (green solid line) AlInP with P-rich (red dashed line) and In-rich (green dashed line) InP. The InP spectra are taken from a prior investigation.^[40] The VB spectrum of P-rich InP shows

a peak at 2.0 eV (S_1), which is attributed to a combination of bulk and surface states, particularly those associated with surface P dangling bonds.^[40] Additionally, a peak at 6.0 eV (S_2) is identified as a surface resonance, while the peak at 7.5 eV (S_3) is enhanced on the P-rich surface, indicating a correlation to phosphorus.^[40] The density of states (DOS) of P-rich AlInP is primarily influenced by the indium and phosphorus orbitals in the valence band, with no significant contribution from aluminum, as the bulk AlP-related electronic states are expected to occur at higher BEs. This suggests that AlInP and InP have similar bonding characteristics. However, despite the overall similarity in the UPS spectra of InP and AlInP, some differences are observed due to the P–Al bonds in AlInP, which cause splitting states that are not present in InP. These splitting features are related to bulk-like properties, while the spectral similarities between InP and AlInP are linked to their surface states. This implies that the peak found at 4.4 eV in P-rich InP is instead split into two peaks at 4.0 and 5 eV in P-rich AlInP, as a consequence of the electron state division in a ternary material. When examining the UPS spectra of In-rich samples, there is a noticeable, consistent splitting at approximately the same binding energies of 4 and 5 eV. The S'_1 peak in In-rich InP is recognized to correlate with surface states, and the intensity of S'_1 indicates the degree of atomic ordering of the In-rich InP (2x4) surface reconstruction. However in AlInP, S'_1 manifests as a shoulder beneath the valence band minimum (VBM). Despite variations in intensities, analogous VB characteristics at 2 eV and 7 eV were discerned in both In-rich InP and AlInP. Nonetheless, the variations in intensities may arise from varying measurement setups, influencing the UPS background, as well as discrepancies in the production of the binary and ternary samples.

Looking closer at the valence band edges, a shift to higher binding energies is obvious when comparing In-rich to P-rich InP. This behavior is similarly observed between the In-rich and P-rich AlInP surfaces, suggesting a change in BB between surface reconstructions due to the change in mid-gap surface states available for pinning of the Fermi level.

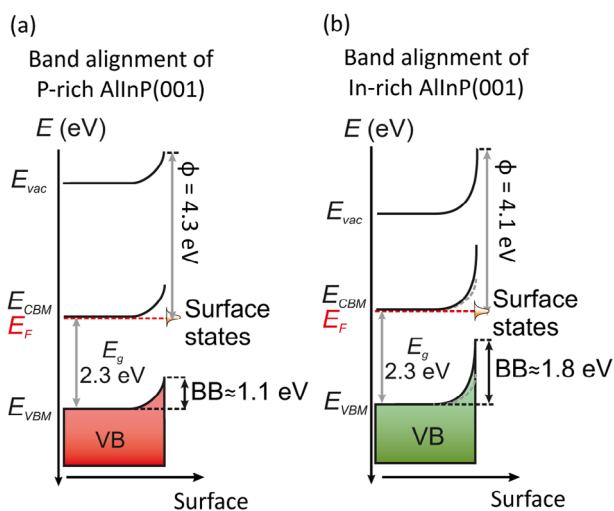


Figure 5. Band energy diagrams of a) P- and b) In-rich AlInP based on experimental results.

Table 1. Surface charge density of P- and In-rich AlInP.

Sample	V_{BB} [eV]	$-\sigma_s$ [C.cm ⁻²]	$N_{sur, def.}$ [cm ⁻²]
P-rich AlInP	1.1	1.67×10^{-6}	1.05×10^{13}
In-rich AlInP	1.8	2.14×10^{-6}	1.34×10^{13}

Figure 5a,b shows the energetic band alignment of P- and In-rich AlInP, respectively, based on doping concentration and XPS and UPS results. The Fermi level position in the bulk material is calculated by using the Equation (1),

$$E_{CBM} - E_F = k_B T \ln \frac{N_C}{n_D} = 6 \text{ meV} \quad (1)$$

where n_D is the doping concentration of the AlInP layer ($8 \times 10^{18} \text{ cm}^{-3}$, Si as a donor dopant), $k_B T$ is the Boltzmann term, and N_C is the AlInP's effective conduction band DOS, which is taken as the average of the AlP and InP DOS.^[41] According to this calculation, the bulk Fermi level is approximately 6 meV below the conduction band minimum (CBM) in both samples. Through XPS and UPS measurements, the VBM of the P-rich AlInP surface is determined to be 1.2 eV below the Fermi level, as shown in Figure S2b (Supporting Information). This indicates the presence of surface states near the mid-gap position, given an AlInP bandgap of 2.3 eV.^[15] The difference between the measured and calculated positions of the Fermi level relative to the valence band suggests a significant BB toward the surface, with

a value of $BB = 1.1 \text{ eV}$. This phenomenon is due to the presence of surface states with electron displacement to the surface, hence pinning the Fermi level. This is illustrated in Figure 5a.

For In-rich AlInP, the VBM at the surface was determined to be 0.5 eV lower than the Fermi level as seen in Figure S2c (Supporting Information), which suggests a significant BB of 1.8 eV toward the surface. When comparing 90° and 15° XPS measurements, a BE shift to lower values in all core levels and of the VBM was observed for both surface reconstructions, confirming upward BB near the surfaces as reported in Table S1 (Supporting Information). Furthermore, the shift of the core levels (Al 2p, In 3d, and P 2p) in In-rich AlInP compared to the core levels in P-rich AlInP by ca. 0.3 eV at 15° measurement angle toward lower binding energies indicates a difference in surface BB between the two samples. Therefore, both samples have electron acceptor mid-gap surface states, which are about half-filled; however, the surface features causing these states are different. The origin of surface states is crucial for use in heterostructure devices, where there is contact between the semiconductor surface and other layers, such as metallic catalysts, a passivation layer, or exposure to an electrolyte.^[42,43] In the case of a semiconductor/metal contact, the space charge below the semiconductor surface remains constant, if the concentration of surface states is sufficiently high to accept additional charges without significantly changing the energy to which the surface states are filled. Consequently, the position of the Fermi level stays relatively stable. Hence, if a small number of electrons are displaced from the surface to the metal, the height of the barrier at the interface remains unchanged. The contact potential at the interface is thus solely determined by the properties of the semiconductor surface, and is confined to a narrow range.^[42,43] However, certain contact materials, such as metals or n⁺-doped semiconductors, can displace larger numbers of electrons into the acceptor states. If the displaced electrons completely fill the acceptor states, the latter are effectively passivated, and the BB will be reduced.

Additionally, it is interesting to compare the band energy diagrams of well-defined surfaces with those of oxidized and chemically treated surfaces, which represent more accessible and practical cases. Hajduk et al. observed that the band energy diagrams of III-Ps, such as p-doped InP, GaP, and GaInP, remain largely unchanged after chemical etching.^[44,45] For p-doped samples, the Fermi levels are positioned approximately 0.4 eV above the valence band edge, while for n-GaInP, they are about 0.5 eV below the conduction band edge. These Fermi levels are consistently influenced by strong Fermi level pinning, resulting in similar positions under various conditions, including ambient exposure. The observed values are consistent with those of MOVPE-prepared samples. The similarity in pinning positions aligns with previously studied P-rich InP (001)^[46,47] and GaInP surfaces.^[48]

The surface charge density (σ_s , C.cm⁻²) can be determined using Equation (2), taking into account the potential drop within the AlInP space charge region (SCR),

$$-\sigma_s = \sqrt{2\epsilon_r \epsilon_0 q V_{BB} n_D} \quad (2)$$

where ϵ_r is the relative permittivity of AlInP (11.25),^[49] ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ F m}^{-1}$), q is the electron charge ($1.6 \times 10^{-19} \text{ C}$), and V_{BB} is the surface BB.^[46] The number of surface atoms involved in charged defects ($N_{sur, def.}$),

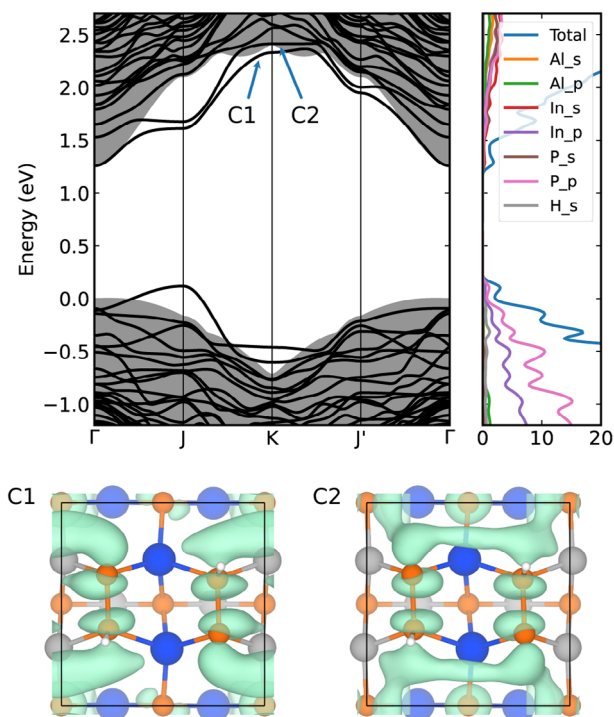


Figure 6. Band structure for the P-rich (2 × 2)-2D-2H surface. The shaded gray area is the projected bulk band structure. The right panel shows the orbital resolved density of states. At the bottom, the orbital character of surface states C1 and C2 is shown.

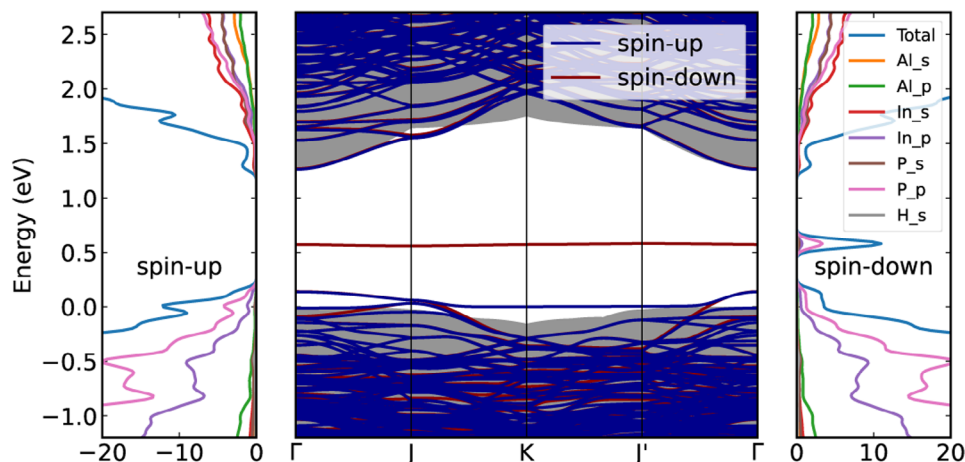


Figure 7. Spin resolved band structure of the (2×2) -2D-1H surface of P-rich AlInP (001). The gray-shaded area is the projected bulk band structure. On the left (right) panel, the spin up (down) density of states is shown; calculations are performed in a 4×4 cell.

determined based on the surface charge densities for P- and In-rich AlInP, is presented in Table 1. Comparing the $N_{\text{sur,def}}$ of P- and In-rich AlInP samples reveals a higher amount of them on the In-rich sample. This suggests that in P-rich AlInP, approximately 1.6% of the surface atoms are involved in charged defects, whereas for In-rich AlInP the proportion is 2.1%.

The In-rich AlInP surface is significantly less stable compared to P-rich AlInP due to the existence of In–In bonds on the surface.^[26,46,47] The work function (WF) and BB of the samples exhibited rapid changes with time after initial preparation, even in UHV and during PES and 2PPE studies. The gray dashed line in Figure 5b represents the band diagram obtained after a few days of sample storage in UHV for PES and 2PPE studies.

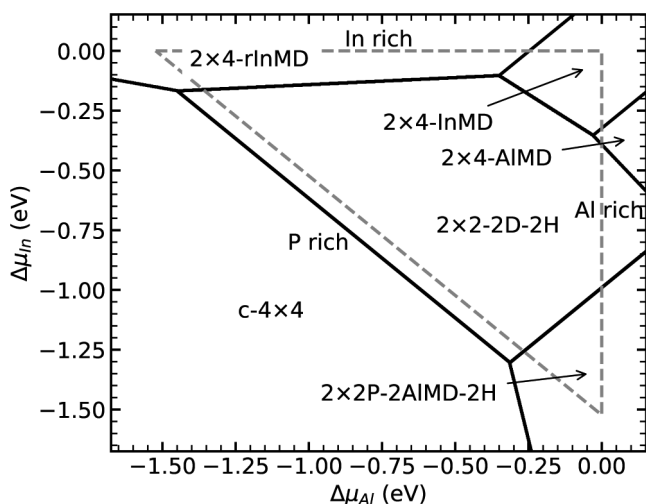


Figure 8. Phase diagram for AlInP (001) surfaces depending on the Al and In chemical potential, with a H chemical potential of -0.6 eV (usual growth conditions). The different surfaces are taken from reference,^[12] while also including the new In-rich (2×4) -rInMD surface discussed in the text. The dashed lines indicate the thermodynamically allowed region. In the dashed lines, the structures are in equilibrium with an elemental bulk material and are related to that particular element-rich growing conditions.

After conducting a series of experiments, we detected a minimal amount of carbon and oxygen adsorption, resulting in a reduction of surface BB to 0.7 eV. In interpreting the tr-2PPE data, we considered the changes in the band alignment of In-rich AlInP.

The presence of strong BB toward both surfaces of AlInP, with varying magnitudes, raises the question: Which particular surface defects cause the BB for both surfaces?

2.3. Electronic Properties of P- and In-Rich AlInP (001) Surfaces

In a previous study by some of the present authors it was demonstrated that in P-rich InP (001) the desorption of hydrogen atoms from P–P dimers on P-rich InP (001) surface and the subsequent formation of the (2×2) -2D-1H surface results in mid-gap states pinning the Fermi level.^[46,50] The concentration of hydrogen vacancies as a function of temperature and pressure,^[46] as well as doping levels,^[50] have been studied, and it was shown that the concentration of H vacancies at typical growing conditions is sufficient to cause Fermi level pinning for InP surfaces. Our present investigation revealed that hydrogen desorption from P-rich AlInP alters the surface's electronic characteristics comparable to our observations in InP.^[46,50] In Figure 6 the band structure of 2D-2H is shown, and in Figure 7 for a surface with one H vacancy, the (2×2) -2D-1H reconstruction. The shape of the band structure for the AlInP 2D-2H surface resembles that of the InP surface.^[32]

However, some bands that were degenerate for InP (001) around the K-point are split in the case of AlInP. The states C1 and C2 are examples of this effect, their orbital character is shown in Figure 6. The charge distribution for the C1 state is concentrated around the Al–P bonds between the top and second atomic layers, while the C2 state shows a charge distribution around the In–P bonds. This effect is also observed for other bands, which are degenerated in InP but split in AlInP. This could be the origin of the peak splitting observed in the UPS results (Figure 4).

The calculations for the 2D-1H surface were performed in a 4×4 cell to reduce the interaction between defect sites. Indeed, in Figure 7 we observe an only weakly dispersing defect state,

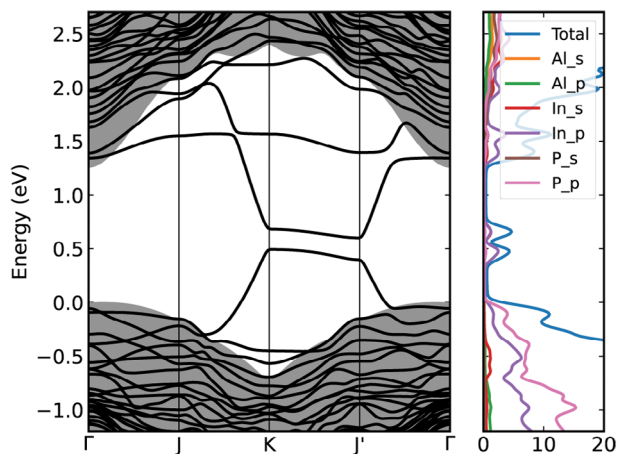


Figure 9. Band structure for the (2×2) -2InMD-2H AlInP surface reconstruction. The shaded gray area is the projected bulk band structure; the right panel shows the orbital resolved density of states.

elucidating the generation of a surface state within the bandgap feature by the H vacancy. The mid-gap state here results from the P dangling bond p-state with the H vacancy, similar to the observations for the analogous InP surface. This defect explains the Fermi level pinning for the P-rich surface of AlInP in analogy to InP (001).

Due to the preparation of the In-rich AlInP surface reconstruction at elevated temperatures ($T > 440^\circ\text{C}$), the H-passivated P–P dimers are essentially eliminated. Additionally, the energy of surface states on In-rich AlInP is different compared to P-rich AlInP, indicating the presence of different types of defects on the respective surfaces. As suggested in reference,^[12] the formation of a (2×2) -2InMD-2H structure can be anticipated under appropriate preparation conditions, where the cation-rich surface is exposed to hydrogen (higher H chemical potential). The (2×2) -2InMD-2H structure features an In–In 1D atomic chain extending in the $[110]$ direction, causing two highly dispersive electronic bands. The two bands, one occupied and one empty, are divided by a narrow energy gap and pin the Fermi level energy at the midpoint of the bandgap. However, the present total-energy calculations indicate the formation of an In-rich (2×4) -rInMD surface for In-rich preparation conditions, see **Figure 8**. A top view of the rInMD surface model proposed here is shown as an inset in **Figure 2**. This model agrees with the calculation of $N_{\text{sur,def}}$ for In-rich AlInP, which indicates that 2.1% of the surface atoms are involved in a charged defect. These results show that the majority of the surface consists of a (2×4) -rInMD structure, with around 2.1% of the surface in a (2×2) -2InMD-2H structure.

Two highly dispersive bands are present in the band structure for the (2×2) -2InMD-2H surface, shown in **Figure 9**. The two bands, one occupied and one empty, are separated by roughly 0.1 eV along the J' -K direction and pin the Fermi level within the bandgap, leading to a noticeable increase in upward BB.

Figure 10 shows the In-rich surface band structure, which exhibits a surface band slightly above the bulk VBM, reminiscent of the $\beta 2$ surface.^[12] This low dispersive band originates from the In–In σ -bonds of the second layer, similar to the InP (2×4) -MD

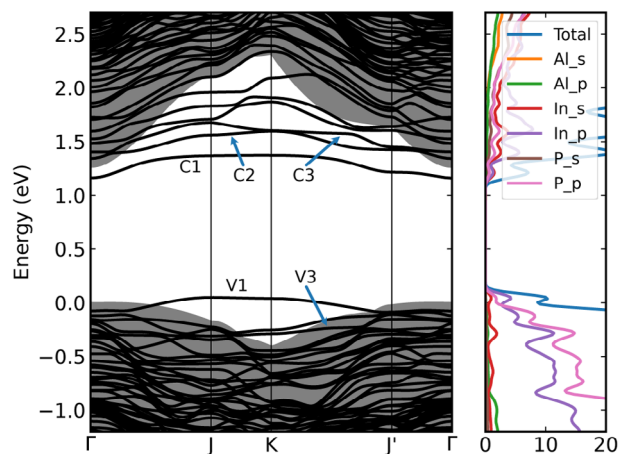


Figure 10. Band structure of In-rich (2×4) -rInMD AlInP. The shaded gray area is the projected bulk band structure. The right panel shows the orbital resolved density of states.

surface.^[34] All surface unoccupied states lie above the bulk CBM, except for one. The occupied and unoccupied surface states are primarily In p-states due to the In–In dimers of the second layer as well as the In at the In–P dimer.

In **Figure 11**, DFT IPA optical calculations reveal that the main negative peak of the RA spectra below 2.5 eV (see **Figure 2**) originates from V1–C2 with smaller contributions from the V1–C3 transition, with V1–C1 and V3–C1 also present. The unoccupied state C2 is mainly related to the In dangling bonds of the three-fold In atoms in the second atomic layer. In other words, the In–In bonds of the second layer from the surface are responsible for the negative peak, similarly for the rest of the transitions contributing to **Figure 11**, i.e., due to the In–In dimers. Unsurprisingly, this feature shares a similar origin to its counterpart for the InP (2×4) -MD surface,^[51] as both systems present the same surface reconstruction and composition, coupled with RA spectra being a surface probe technique.

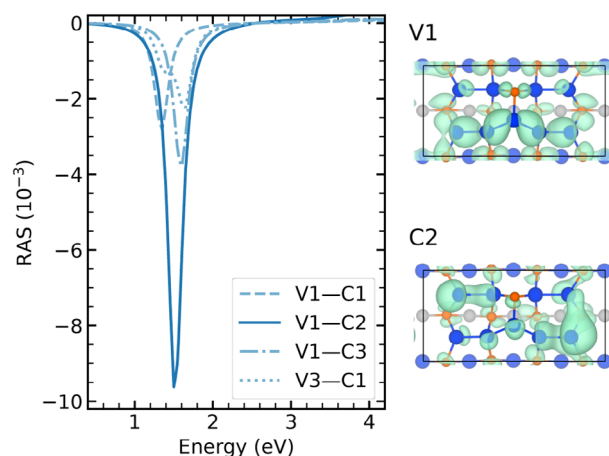


Figure 11. Calculated RA spectra of In-rich (2×4) -rInMD AlInP due to the most prominent electronic transitions. On the right, the orbital character of the V1 and C2 bands is shown (see **Figure 10**).

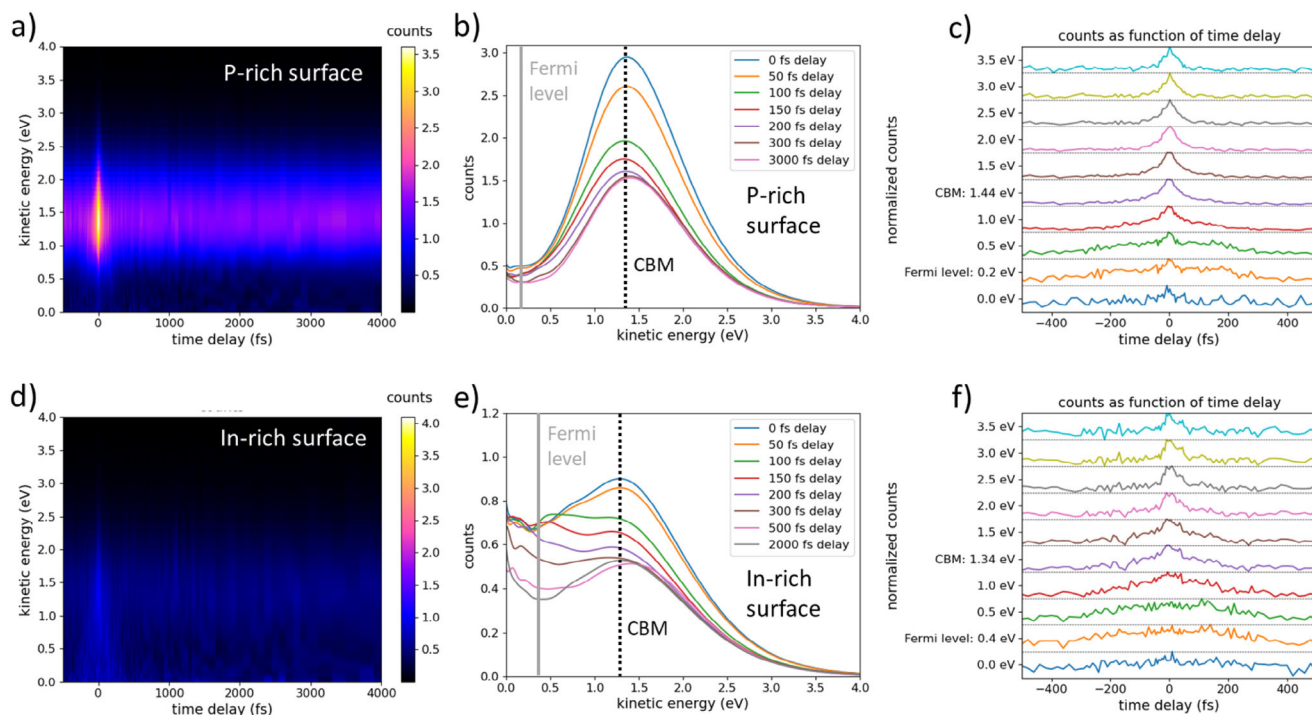


Figure 12. Tr-2PPE data for the P-rich (top row) and In-rich surfaces (bottom row) for UV pump and probe (UV–UV) excitation at 276 nm/4.49 eV. 3D transients are shown in (a) and (d), the corresponding spectra in (b) and (e), and the temporal development of emission is given in (c) and (f). For both surfaces, roughly Gaussian peaks with both time-dependent and time-independent features around 1.3–1.5 eV are observed, associated with the CBM from UPS results.

The DFT calculations and experimental findings concur in delineating the electronic structure of P- and In-rich AlInP surface reconstructions. Hydrogen vacancies in P-rich AlInP surface create surface states that pin the Fermi level and cause BB. In contrast, in In-rich AlInP surface, the formation of In–In 1D atomic chains within a minority of surface domains results in Fermi level pinning and subsequent BB.

2.4. Charge Carrier Dynamics in the Near-Surface Region of P- and In-rich AlInP

2.4.1. Time-Resolved Two-Photon Photoemission of P- and In-rich AlInP surfaces

To get an overview of the ultrafast electron dynamics at the bare P- and In-rich AlInP surfaces, tr-2PPE measurements were performed. The excitation and relaxation paths of electrons affect how AlInP window layers may interact with deposited layers or catalysts, with no detailed data reported for the AlInP surface to date. Plotting tr-2PPE data while subtracting the applied bias results in the 3D transients and spectra shown in Figure 12. The UV–UV pump-probe 3D transients in Figure 12a,d reveal an emission signal that is largely time-independent across the majority of the shown delay range, except for a few hundred fs around the point of temporal overlap. The corresponding spectra are plotted in Figure 12b,e for a range of time delays, focusing primarily on the delay range below 300 fs. There is a large, roughly Gaussian peak visible at photoelectron kinetic energies around

1.44 eV and 1.34 eV for the P-rich and In-rich surfaces, respectively. Subtracting the UV photon energy of 4.49 eV used here, this corresponds to emission from states at –3.05 and –3.15 eV vs vacuum, so 1.15 and 1.05 eV above the Fermi level, likely corresponding to the CBM position as deduced from UPS. The work functions of the P- and In-rich surfaces are 4.3 and 4.1 eV, respectively; the corresponding emission energies are denoted in the spectra in Figure 12b,e. A slowdown in electron relaxation is observed around the CBM as well as around the Fermi level; this is resolved in more detail in Figure 12c,f. Electrons are initially photoexcited to virtual intermediate states, from where they relax to the CBM within about 200 fs for both surface reconstructions. From the CBM they reach the surface states that pinned the Fermi level around the mid-gap position, at ca. 400 fs, and further carrier relaxation is observed at larger pump-probe delays. Emission is roughly symmetric about $t = 0$ fs as both pump and probe beams share the same photon energies, though the 2:1 intensity ratio as well as limited fine-tuning of the set-up can introduce some asymmetry as observed. At all energies above the CBM a central emission peak at $t = 0$ fs is observed, this is related to two-photon photoemission from the VBM and from occupied states below the Fermi level. The CBM position is less clearly resolved for the In-rich surface in (e) compared to the P-rich surface in (b), which is attributed to the higher concentration of acceptor surface states of the In-rich surface, as demonstrated in the DFT results. Electrons emitted from the CBM near-surface state originate both from absorption in the AlInP layer, but especially from the underlying GaAs substrate, tunneling through the 30 nm window layer. As AlInP has an indirect bulk bandgap, and

the layer is only 30 nm thick, likely a significant fraction of recombination occurs at the surface, rather than in the bulk of the window layer.

In a previous paper by some of the present authors we studied the P-rich InP surface, similar in reconstruction to the P-rich AlInP surface measured here.^[52] In follow-up research, we had found InP surface states to be preserved under TiO₂ deposition; we would expect this to be the case for Al-InP as well.^[53] This would indicate that the near-surface CBM state identified here would likely still influence behavior after deposition of further layers when using AlInP as a window layer, such as in the 2018 record-efficiency PEC cell by Cheng et al.^[10]

To confirm the interpretation of emission around 1.3–1.5 eV as being related to emission from the CBM, photon energies in UV–UV are varied, and the resulting shift in the energetic position of features are observed.^[52] The working principle is described in Figure S7 and Note S1 (Supporting Information). Emission peaks are identified as correlating to 1PPE or 2PPE via the gradient of their kinetic energies with photon energies; 1× scaling indicates 1PPE, 2× scaling indicates 2PPE. The data for these measurements is given in Figure S8 (Supporting Information), UV pump and probe photon energies are varied from 3.99 eV/311 nm to 4.54 eV/273 nm in four steps. The variation in final state energy vs photon energy is given in Figure S9 (Supporting Information), providing a gradient within uncertainty of 1. This confirms the feature as being related to an initially unoccupied state, consistent with a conduction band state such as at the CBM.

To reveal further details of the relaxation process, we plot the time-dependent emission features by subtracting time-independent emission from the data in Figure 12. The time-independent signal consists of background and secondary (scattered) electron emission, as well as emission via 1PPE or 2PPE from just the pump or probe beams separately. The time-dependent signal can then be calculated as the emission counts for any delay slice from Figure 12b,e, minus the steady-state emission signal, which is taken by averaging over a wide delay range to reduce noise. For this, a 4000 fs-wide slice centered at 3000 fs is used as the steady state background, and is subtracted from each emission spectrum. This analysis uses data starting at 1000 fs to average over; this is appropriate since the relaxation of hot electrons appears to occur within around 400 fs, meaning at 1000 fs, the signal has already reached its steady state value. The resulting data is given in Figure 13, showing hot electron relaxation from the CBM to states situated between the CBM and the mid-gap surface states. Overall, the relaxation of hot electrons to the CBM occurs about an order of magnitude faster (200 fs vs 2 ps) for the AlInP (001) surface studied here as compared to P-rich InP (001) previously studied by some of the present authors.^[52] This is likely related to the fact that only a single near-surface state around the CBM is observed for AlInP, as compared, e.g., to at least six conduction band near-surface states in InP (001), leading to a more complex, slower relaxation process. To date only non time-resolved 2PPE is available for GaP (001),^[54] and no such data for AlP (001) are available, due to the experimental difficulties in time-resolved studies of these bare III V surfaces.

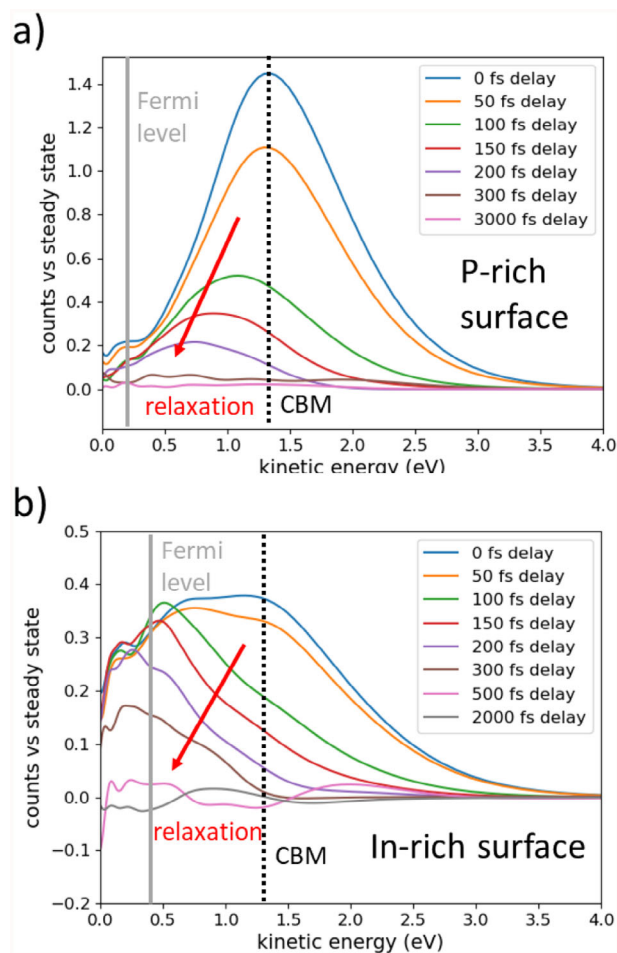


Figure 13. Time-dependent component of emission in UV - UV from Figure 12b,e is given in (a) and (b), for the P-rich and In-rich surface reconstructions, respectively. The pinned Fermi level position by surface states is given, as well as the CBM position from Figure 12. Relaxation from the CBM to the mid-gap surface states can be tracked visually, indicated in red.

2.4.2. VIS–UV tr-2PPE of the Bare AlInP Surface

To complement the UV–UV measurements discussed before, VIS–UV measurements were performed using a 2.33 eV VIS pump, and the same 4.49 eV UV probe as previously. The obtained tr-2PPE spectra are shown in Figure 14. Only a single time-independent feature corresponding to the CBM is observed for both surface reconstructions. This requires pumping of electrons to this feature via the VIS pump. The VIS photon energy is 2.33 eV, larger than the indirect bandgap of AlInP, but less than its direct bandgap, which ranges from 2.5 to 2.7 eV.^[12] Therefore, emission from the CBM is significantly reduced in VIS–UV as compared to UV–UV excitation in Figure 12. Figure 14 shows time-dependent emission below the CBM, indicating hot electrons are photoexcited and relax back toward the surface states pinning the Fermi level. The bandgap surface state is a potentially important factor in the behavior of AlInP in optoelectronics and other applications.^[11,12] To demonstrate the effect of

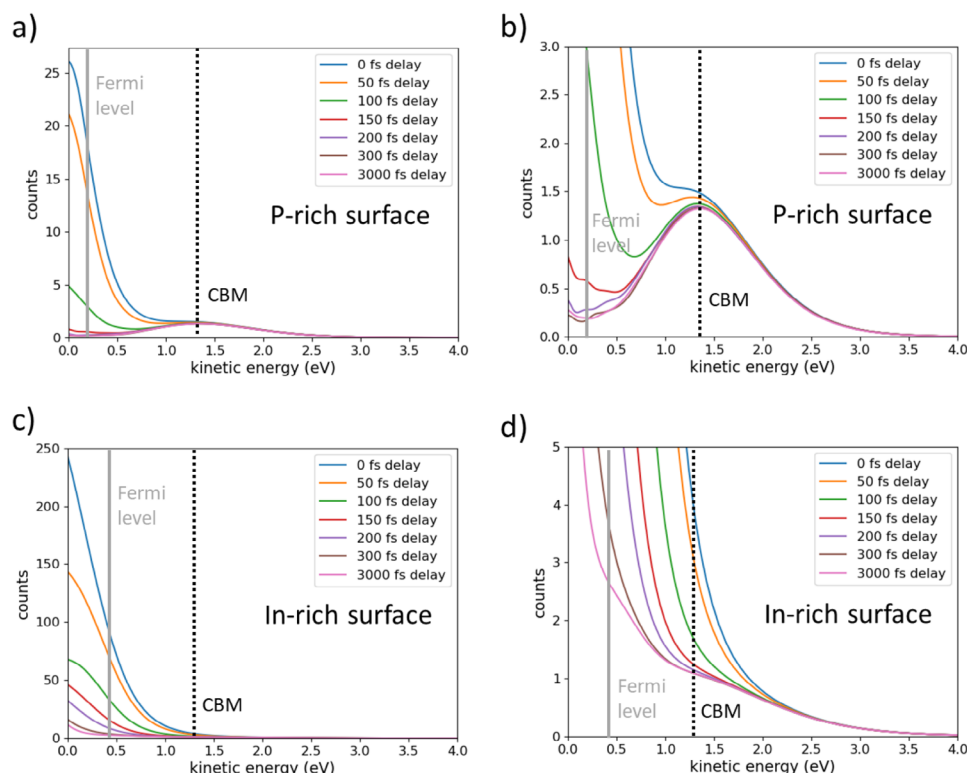


Figure 14. VIS–UV spectra of the bare AlInP surface are shown for the P-rich AlInP surface in (a,b) and the In-rich surface in (c,d) all using a 2.33 eV VIS pump. The right column provides zoomed-in versions of the spectra in the left column, showing the CBM signal, which is much less pronounced as compared to UV–UV in Figure 12b,e.

not efficiently pumping across the indirect bandgaps, increased VIS photon energies of 2.60/2.57 eV are utilized; this is given in Figure S10 (Supporting Information). CBM emission is still largely time-independent on the P-rich surface and is not observed on the In-rich surface. There does seem to be some pumping of the CBM for the P-rich surface in Figure S10a,b (Supporting Information), consistent with the direct bandgap at 2.5–2.7 eV. The absence of near-surface electronic states, except at the CBM, may explain why AlInP functions so effectively as a window layer. Minimizing interfacial states near device surfaces mitigates undesirable electronic interactions that may result in parasitic losses, thereby improving overall device performance. Understanding how CBM state dynamics evolve under TiO_2 or catalyst deposition would then be a useful next step in interface engineering AlInP window layers, e.g., to enhance carrier separation and transport to the surface.

Figure 15 illustrates a schematic of tr-2PPE excitation pathways. Excitation using VIS light with photon energies around the indirect bandgap energy is inefficient, as compared to excitation at energies well above the bandgap energy, such as when using UV. For both P- and In-rich surfaces, filling the near-CBM state occurs within ca. 200 fs. The relaxation to the surface state pinning the Fermi level takes about another 200 fs.

In summary, the tr-2PPE results of near-surface charge carrier dynamics of the P- and In-rich reconstructed AlInP (001) surfaces support, in good correspondence with the steady state measurements, that the surface bandgap of AlInP is indirect, as it is in the bulk. We found a state at the surface CBM persisting after

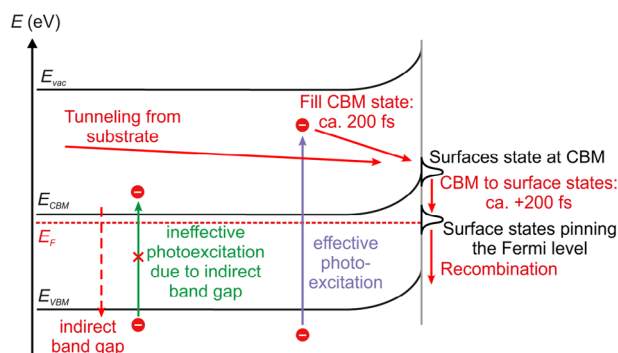


Figure 15. Schematic of tr-2PPE excitation pathways.

small amounts of oxidation, with relaxation from this state to the mid-gap surface states where the Fermi level is pinned, occurring on the order of hundreds of fs. The absence of other surface conduction band states, which would slow the relaxation and recombination of electrons as well as potentially introduce parasitic losses at device interfaces, helps to explain the excellent performance of AlInP as a window layer. It also underlines the importance of the CBM state in interface engineering of the AlInP surface, be it via passivation to reduce its impact, or by actively using it for tunneling or modification of electron transport in III–V heterostructures.

3. Conclusion

In this study, we comprehensively analyzed the P- and In-rich surface reconstructions of AlInP (001) using a combination of experimental techniques and DFT calculations. P- and In-rich surface reconstructions were achieved by annealing the AlInP surface at 310 and 440 °C, respectively. RA spectroscopy was used to monitor and control sample growth; DFT calculations support experimental results and provide further insight into the band structures and interband transitions of these surfaces. Optical response calculations on the Bethe–Salpeter equation explain the experimental RA spectra for In-rich samples in terms of a newly proposed and energetically stable In-rich (2×4) -rInMD surface. Additional DFT calculations reveal the origin of the spectral fingerprint, with the minimum at around 2 eV, involving transitions between In–In bonds. The UP spectra of the AlInP surface reveal the splitting of electronic states in AlInP, which is not present in InP surfaces. DFT links this phenomenon to the splitting of surface states in AlInP that were degenerate in InP. Splitting occurs for In-P states, now separated into Al-P and In-P contributions, AlInP being a ternary material.

Using PES, we found 1.1 and 1.8 eV of upward BB toward the surface of AlInP. Hydrogen-related defects were identified as the source of Fermi level pinning on P-rich AlInP. On the other hand, for In-rich surfaces, the (2×2) -2InMD-2H structure forming In–In 1D atomic chains is suggested as being responsible for the surface Fermi level pinning by producing two highly dispersive electronic bands within the bandgap. Around 1.6% and 2.1% of surface atoms contribute to the charged defects on the P- and In-rich AlInP surfaces, respectively. The P- and In-rich, n-doped AlInP surface reconstructions were characterized using tr-2PPE, revealing a clear CBM signature in the near-surface region, as well as evidence for surface states pinning the Fermi level. No further surface resonances within the conduction band were observed. Relaxation of photoexcited electrons from ca. 2 eV above the CBM occurs within about 200 fs to the CBM, and within about 400 fs total to the Fermi level. This provides a detailed view of the ultrafast near-surface dynamics in AlInP.

The observed BB and the Fermi level pinning on both surface types underlines the significant impact of surface defects on the electronic properties of AlInP (001). Identifying these surface states and their role in pinning the Fermi level is crucial for optimizing AlInP for use in optoelectronic and PEC devices. Our findings suggest that precise control over surface preparation can be used to tailor the electronic properties of AlInP, which could lead to enhanced performance in devices where surface interactions play a critical role. Additional experiments on the modifications of these surface states, considering the presence of an additional contact layer and operational conditions, are essential for comprehending their impact. A thorough investigation of the surface oxidation reaction mechanisms after exposure H_2O , O_2 , or air, using high-resolution spectral and surface-sensitive techniques, including synchrotron radiation, is also essential. Future work should explore ways to mitigate surface defects and further refine surface passivation techniques, potentially unlocking new applications and improving the efficiency of AlInP-based devices.

4. Experimental Section

Sample Preparation: All epilayers were prepared in a horizontal MOVPE reactor (Aixtron, AIX-200) at 100 mbar using H_2 as a carrier gas. n-GaAs (001) wafers (Si-doped, $2 \times 10^{18} \text{ cm}^{-3}$) with a 0.1° miscut toward the [111] direction served as the substrate. Tertiarybutylarsine (TBAs), trimethylgallium (TMGa), tertiarybutylphosphine (TBP), trimethylindium (TMIn), and trimethylaluminum (TMAI) were used as precursors for As, Ga, P, In, and Al, respectively. Ditertiarybutyl silane (DTBSi) was utilized as a precursor for Si for n-type doping of samples. The AlInP layer is doped to a relatively high level of $8 \times 10^{18} \text{ cm}^{-3}$, chosen to match the doping levels found in window layer of device structures.^[1,11]

All MOVPE processes were monitored in situ using reflection anisotropy spectroscopy (RAS, LayTec), which is a highly surface-sensitive method.^[55] As-prepared samples were transported to UHV-based characterization stations using a mobile UHV shuttle operating at a base pressure of $<5 \times 10^{-10}$ mbar.^[56] The Supporting Information, Section S4, elaborates on MOVPE processes, the “heat-up” procedure, and sample transfer using UHV.

Experimental Surface Characterization Techniques: At TU Ilmenau, UHV-transferred samples were measured by LEED (Specs ErLEED 100-A) and calibrated XPS (Specs Focus 500/Phoibos 150/1D-DLD-43-100, monochromatic Al-K α line). UPS was measured using the same spectrometer, with excitation provided by a helium gas discharge lamp. The He I emission line with an energy of 21.22 eV was used for UPS. XPS measurements were performed on the SoLiAs endstation at the undulator beamline UE56-2 PGM-2 at the BESSY II synchrotron using a SPECS PHOIBOS 150 spectrometer calibrated by the Fermi level edge of a sputtered Ag sample.

In tr-2PPE, electrons from occupied electronic states in the near-surface region, usually either from the valence band or surface states within the bandgap, are photoexcited by a pump pulse. These so-called “hot” electrons then relax toward the CBM, and from there to mid-gap surface states and valence band (Figure S7 and Figure S11, Supporting Information). After a time delay Δt , set by a computer-controlled delay stage, a probe pulse is incident. This probe pulse photoemits the electrons, which are measured using a time-of-flight (TOF) spectrometer (Figure S7, Supporting Information). The time delay Δt is varied in steps over a range of picoseconds or more, both in the direction of the pump pulse leading the probe pulse, as well as vice versa, this is denoted by positive and negative time delays respectively. The inelastic mean free path (IMFP) of the photoelectrons in tr-2PPE is around 2–7 nm^[52,57] allowing for emission from both the surface- and near-surface region to be observed, but discriminating against bulk signals. Within the near-surface region, this then allows observing the electron dynamics in unoccupied conduction band or bandgap states; these dynamics are not accessible using single-photon spectroscopic methods such as XPS and UPS.^[13,58,59] Further descriptions of the experimental parameters as well as a detailed introduction to tr-2PPE may be found in reference.^[52]

Further information on characterization techniques is available in the Supporting Information, Section 2.

DFT Methodology: The calculations in the present work are based on DFT and performed using the Vienna ab initio Simulation Package (VASP).^[60] The electron exchange and correlation functionals are treated in the general gradient approximation (GGA) using the PBE functionals.^[61] The electron-ion interactions are described in the projected augmented wave (PAW)^[62,63] formalism. The plane-waves are expanded up to a cut-off energy of 350 eV. A slab models the semi-infinite structures; a vacuum region of $\approx 15\text{Å}$ along the surface normal is used to decouple the periodic images. The bottom layer of the modeled slab is passivated with partially-charged hydrogen, with $Z = 1.25$ and $Z = 0.75$ for group-III and group-V terminated slabs, respectively. The dipole correction along the surface normal is used to quench the electric field resulting from the two non-equivalent slab surfaces. The group-III and group-V terminated slabs contain 11 and 12 atomic layers, respectively. The bulk material underneath the surface is modeled as $\text{Al}_{0.5}\text{In}_{0.5}\text{P}$, where the cations are arranged in the cubic D4 ordering to ensure optical isotropy. The calculations

are performed for undoped and charge-neutral supercells. Therefore, unless the Fermi level is pinned by surface states, it will be positioned close to the middle of the bandgap.

The optical spectra calculations, local field effects, and electron-hole attractions are taken into account by solving the Bethe–Salpeter Equation.^[64–66] For numerical reasons, a model dielectric function is used to calculate the screened potential,^[67,68] and the quasiparticle shifts are approximated with a scissors operator. This methodology leads to an Al-InP bulk dielectric function that is in agreement with the experiment. Individual contributions of specific transitions to the RA spectra are calculated on the DFT level of theory.

Following refs. [69–72], the reflection anisotropy is obtained as

$$\frac{\Delta r}{r}(\omega) = \frac{4\omega}{c} \Im \left[\frac{2\pi\Delta\alpha^{hs}(\omega)}{\epsilon_b(\omega) - 1} \right] \quad (3)$$

where $\epsilon_b(\omega)$ is the AlInP bulk dielectric function, and $\Delta\alpha^{hs}(\omega)$ is the difference of the diagonal tensor elements of the half-slab polarizability corresponding to the respective polarization directions. The $\Delta\alpha^{hs}$ contains necessarily not only the surface optical anisotropy, but also contributions from the hydrogen-passivated bottom layer. Fortunately, these contributions are small, and occur only for photon energies above 3.5 eV. In a previous publication,^[25] it has been shown that this issue can be resolved by averaging the half-slab polarizabilities for slabs terminated with hydrogen bonds oriented along the [110] and $\bar{[110]}$ directions. This approach has been used here as well.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aluminium indium phosphide, charge carrier dynamics, DFT calculations, electronic structure, solar energy conversion

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ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Exploring Electronic States and Ultrafast Electron Dynamics in AlInP Window Layers: The Role of Surface Reconstruction

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Supporting Information: Exploring Electronic States and Ultrafast Electron Dynamics in AlInP Window Layers: The Role of Surface Reconstruction

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1 Relevant ball-stick models

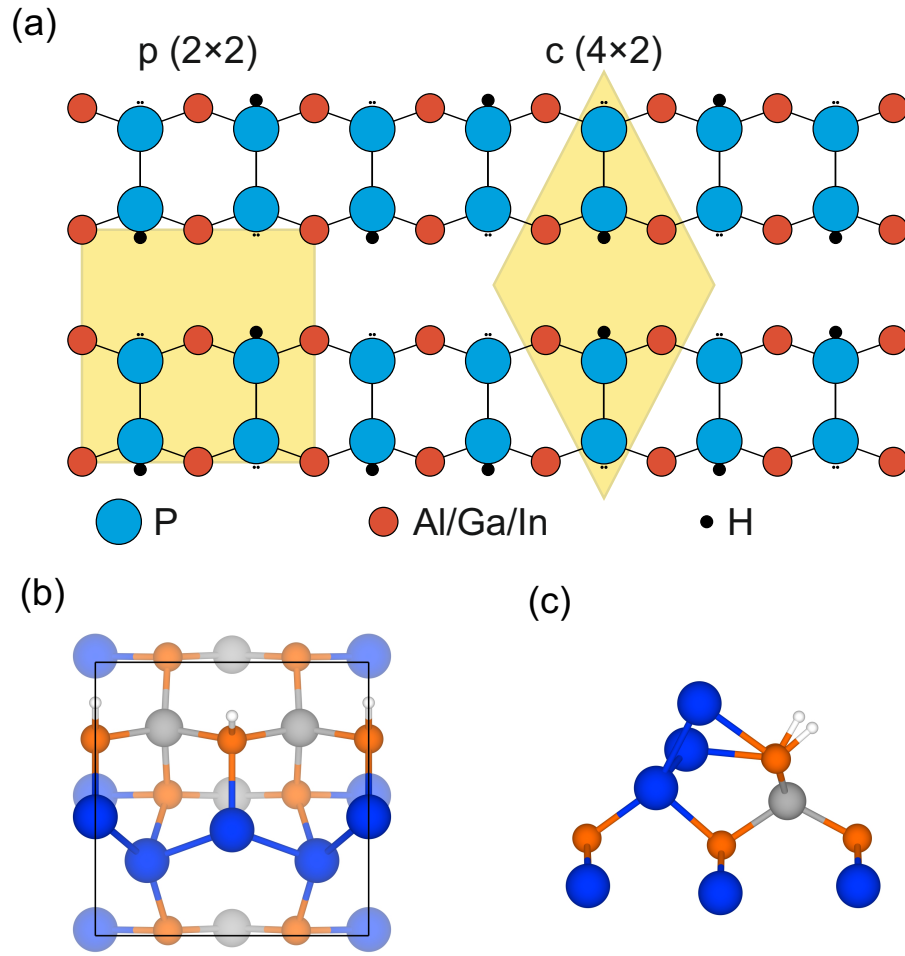


Figure S1: (a) Superposition of two unit cells with different periodicities $(2 \times 2)/c(2 \times 4)$. (b) Top and (c) side views of $\text{AlInP } (2 \times 2)\text{-}2\text{InMD}$ surface.

2 Photoemission spectroscopy results

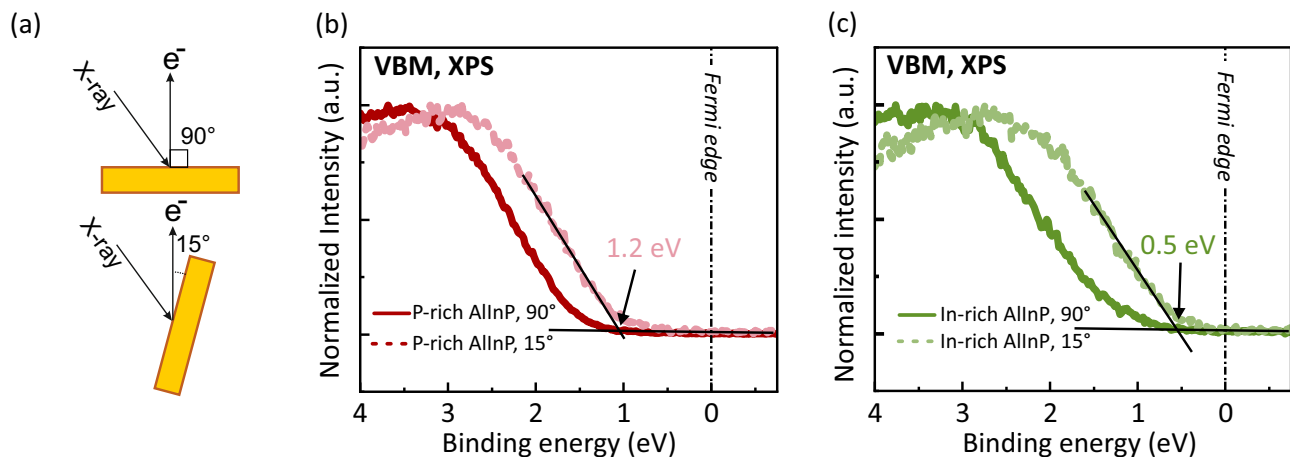


Figure S2: (a) Schematic of sample, beam, and ejected electrons orientation in 90° and 15° emission angles are shown. (b,c) XPS valence band cutoffs of P- (red) and In-rich (green) AlInP at 90° (solid lines) and 15° (dashed lines) emission angle. Shift of VBM to lower binding energy by decreasing the emission angle confirms the upward band bending toward the surface in the both type of samples. VBM of In-rich AlInP is closer to the fermi level compared to P-rich AlInP which indicates higher magnitude of band bending in this sample.

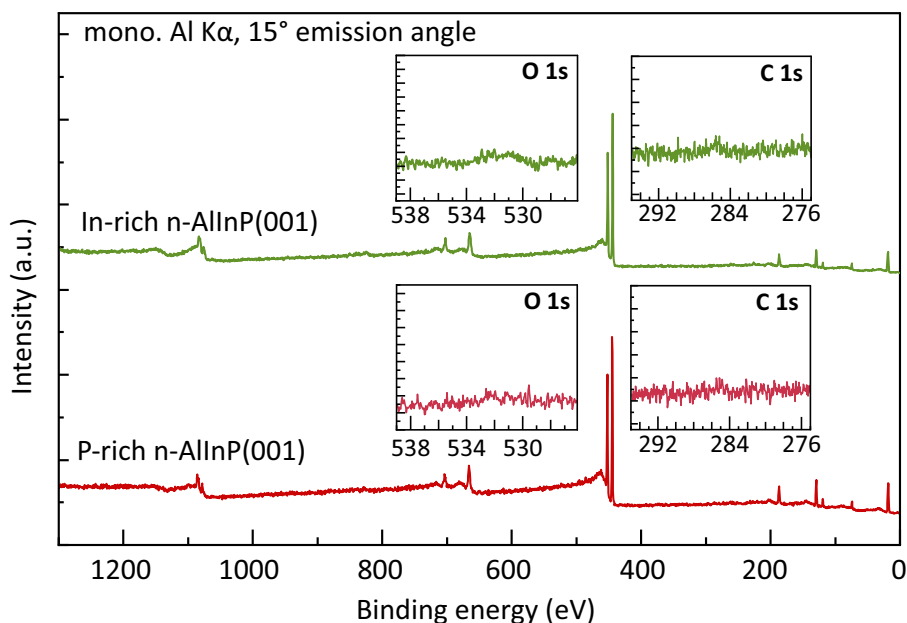


Figure S3: XP survey spectrum of as prepared P- (red) and In-rich (green) AlInP. High resolution scans of O 1s and C 1s region confirms the contamination free UHV transfer from the MOVPE reactor to analysis chamber.

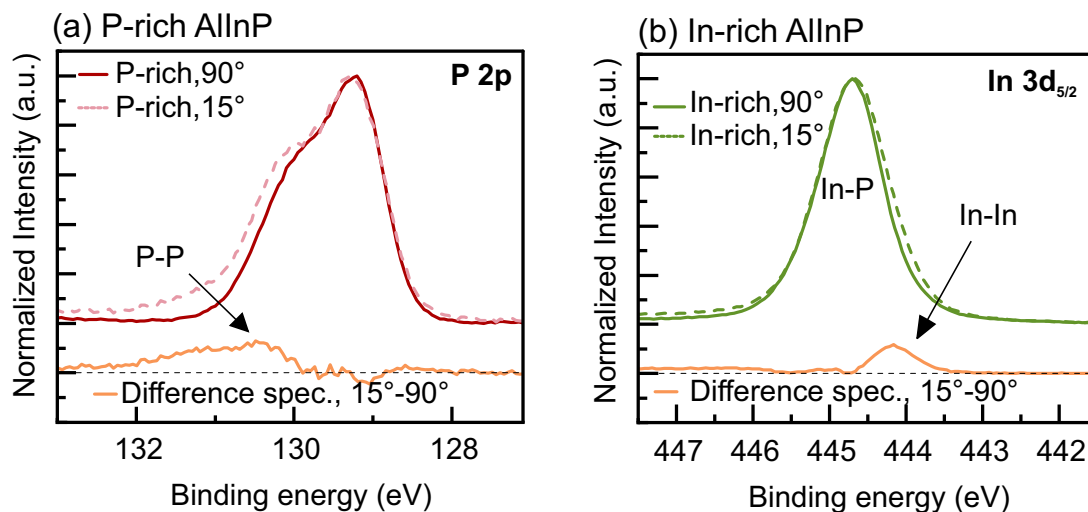


Figure S4: (a) XPS spectra of the P 2p core level for phosphorus-rich samples at 90° and 15° angles. The enhancement of surface sensitivity through a reduction in emission angle indicates that the positive signal in the difference spectra at higher binding energies reveals the existence of a surface component in P 2p associated with P–P dimers on the surface. (b) XPS spectra of the In 3d_{5/2} core level in In-rich AlInP at 90° and 15° angles. The positive signal in the difference spectra at lower binding energy signifies the existence of a surface component in the In 3d_{5/2} core level, which is associated with the energy connected to In–In bonds.

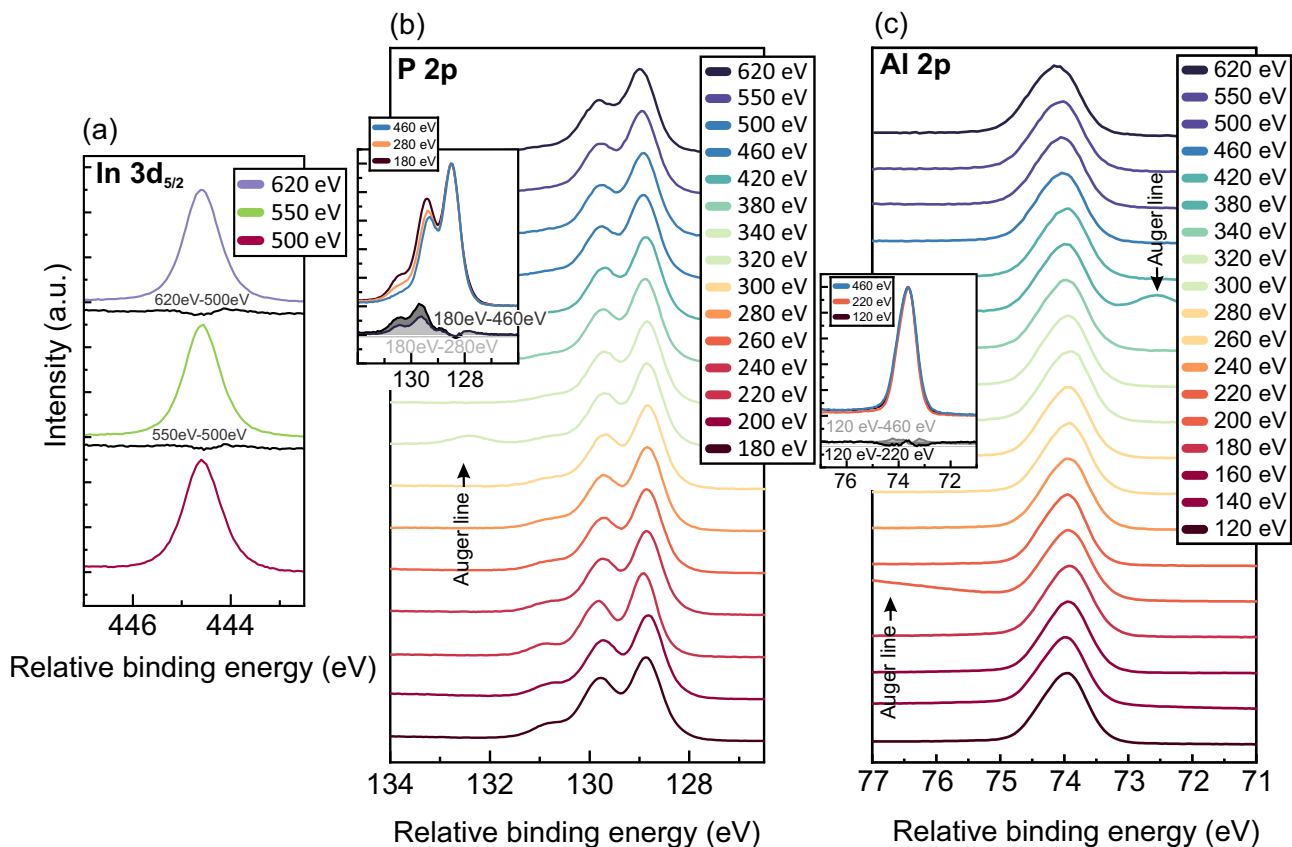


Figure S5: Soft X-ray photoemission spectroscopy of P-rich AlInP. XP spectra of In $3d_{5/2}$ (a), P 2p (b), and Al 2p (c) at varying incident X-ray energies are presented. To demonstrate the differences in the line shape resulting from varying X-ray energies, difference spectra are depicted. The difference spectra of P 2p at 180 eV, 280 eV, and 460 eV distinctly demonstrate that decreasing the X-ray energy results in an increase in contributions at higher binding energies, which correlates with P–P dimers on the surface. Nonetheless, no substantial changes in the line shape of Al 2p and In $3d_{5/2}$ were detected. The spectra are shifted in order to resolve only changes in the line shape; therefore, the X-axis is “relative binding energy.” Minor alterations visible in the difference spectra pertain to the variations in resolution at various incident X-ray energies.

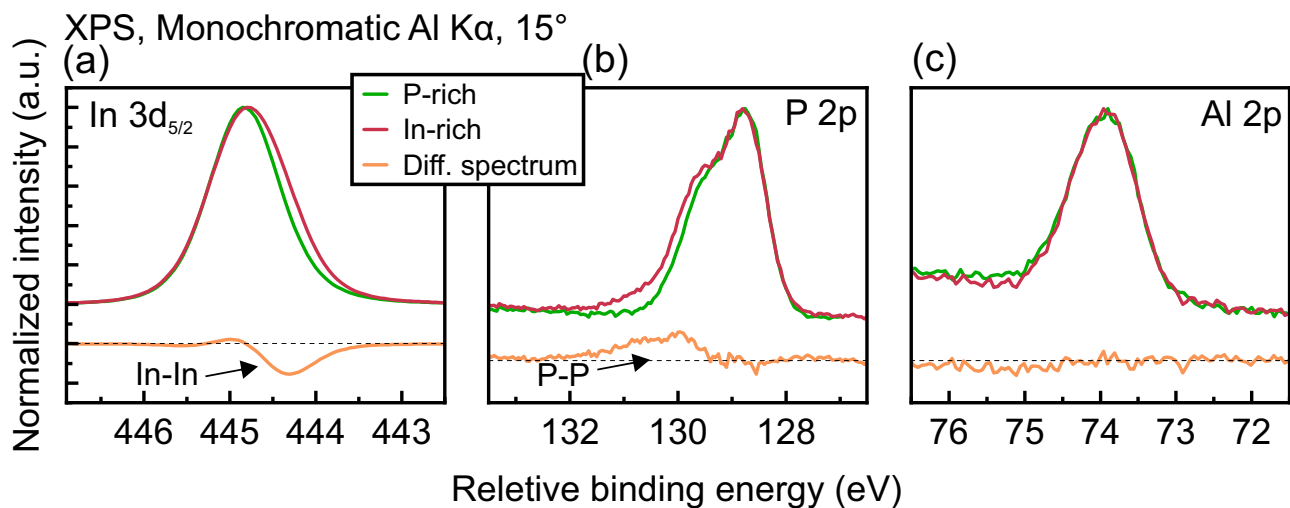


Figure S6: XP spectra of P- (red) and In-rich (green) AlInP core levels at a 15° emission angle. The difference spectra were obtained by subtracting In-rich from P-rich and are depicted in orange. The negative signal at lower binding energies in the difference spectrum of In 3d_{5/2} signifies an extra component in In-rich AlInP associated with In–In bonds. The positive signal at higher binding energies in the difference spectra of P 2p implies an extra component in P-rich AlInP corresponding to P–P dimers. Nevertheless, the Al 2p spectra of P- and In-rich samples exhibit identical line shapes, indicating the absence of additional Al components in both samples. The spectra are shifted in order to only resolve any changes in the line shape; therefore, the X-axis is “relative binding energy.”

Table S1: Peak maxima positions for P- and In-rich AlInP core levels, as well as VBM, measured at 90° and 15° setup configurations.

Samples	VBM 90°	VBM 15°	Al 2p 90°	Al 2p 15°	P 2p 90°	P 2p 15°	In 3d _{5/2} 90°	In 3d _{5/2} 15°
P-rich AlInP	1.4 eV	1.2 eV	74.4 eV	74.2 eV	129.2 eV	129.1 eV	444.9 eV	444.8 eV
In-rich AlInP	1.3 eV	0.5 eV	74.2 eV	73.9 eV	129.0 eV	128.7 eV	444.7 eV	444.5 eV

Table S2: atomic concentration of P- and In-rich AlInP based on XPS measurements at 15°.

Sample	Atomic concentrations (%)		
	Al	In	P
P-rich	23.1	25.0	51.9
In-rich	26.2	32.5	41.3

3 Time-resolved two-photon photoemission (tr-2PPE) spectroscopy

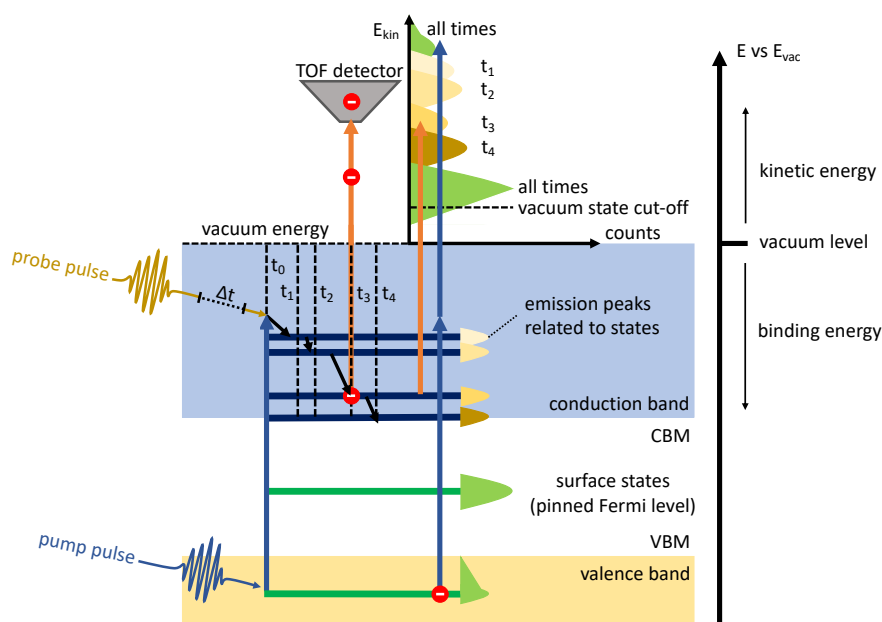


Figure S7: Schematic showing the excitation and emission pathways for tr-2PPE. Electrons are photoexcited from occupied states in the valence band, or surface states in the band gap by a pump pulse at $t = 0$. Photoexcited electrons thermalize through conduction band states, from where they are photoemitted by a probe pulse after a variable time delay. By scanning over time delay and recording the kinetic energies of electrons in a TOF detector, electron relaxation paths and electronic band structure in the near-surface region are obtained. Reproduction under terms of the CC-BY 4.0 license. [1], 2024, published by American Chemical Society.

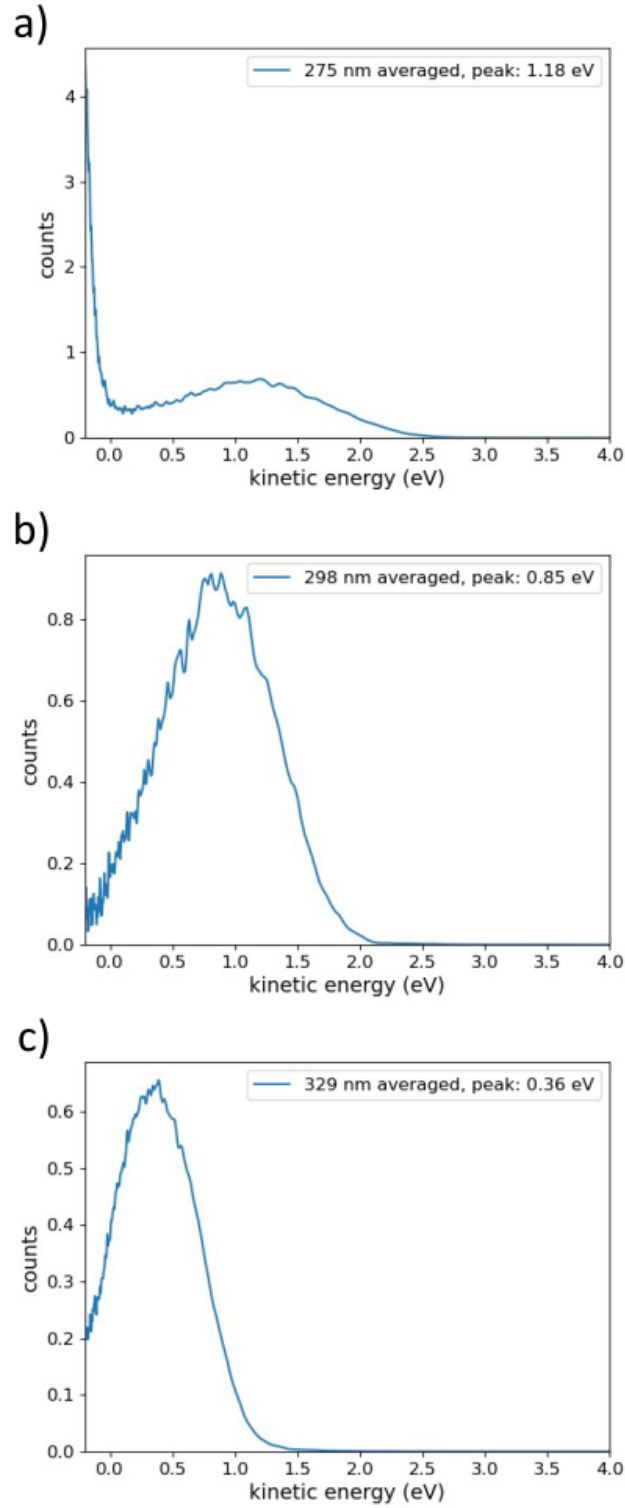


Figure S8: UV – UV excitation of the P-rich AlInP surface, averaged over time delays. UV wavelengths used are 275 nm / 4.51 eV (a), 298 nm / 4.16 eV (b) and 329 nm / 3.77 eV. As photon energy decreases from (a) to (c), the signal related to surface states at low kinetic energies is no longer observed, and the suspected conduction band states shift to lower emission energies. Peak positions can then be tracked and plotted as given in Figure S9

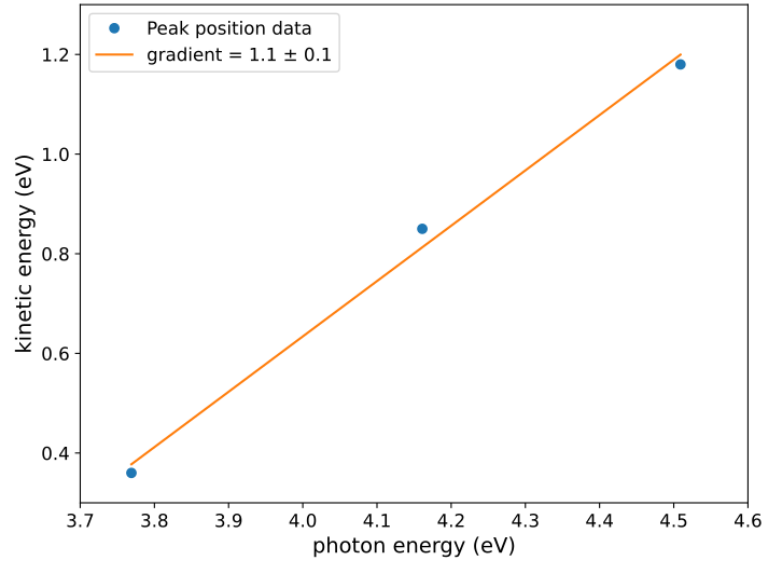


Figure S9: Peak positions for the conduction band features in Figure S8 are plotted vs photon energy. This results in a scaling within uncertainty of 1, confirming this peak as being related to initially unoccupied states, combined with energetic positions of the feature this clearly indicates this feature as belonging to the conduction band / CBM.

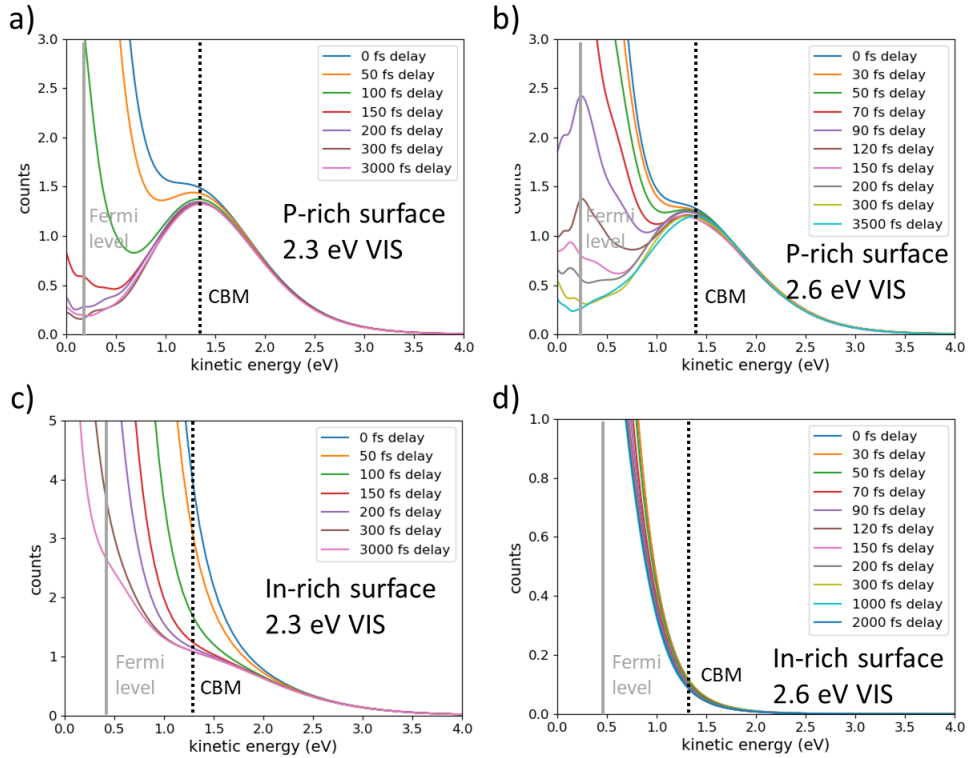


Figure S10: VIS – UV spectra for the P-rich and In-rich surfaces, analogous to those shown in Figure 14. Increased VIS pump energies of 476 nm / 2.60 eV and 482 nm / 2.57 eV are used. However, no time-dependent emission from the CBM is observed in either case, showing that these increased VIS wavelengths still do not effectively pump the conduction band. Zoomed-in versions of the spectra in the left column are provided in the right column for each surface.

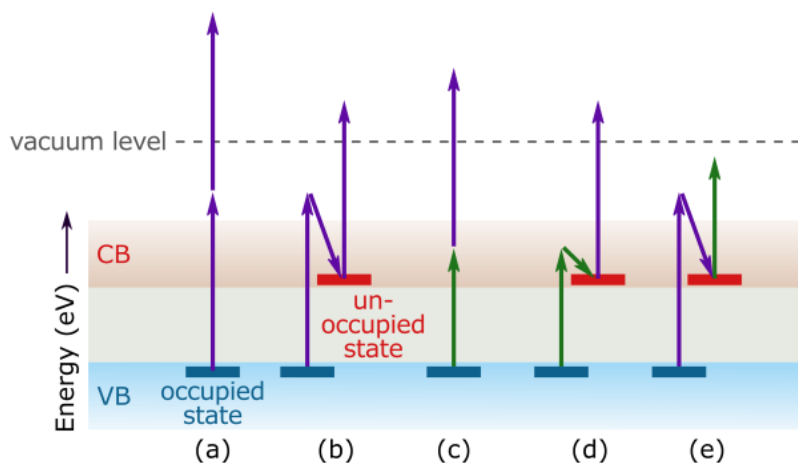


Figure S11: Schematic of two-photon photoemission using two different frequencies as pump or probe (to scale for 276 nm UV and 533 nm VIS) Reproduced under terms of the CC-BY 4.0 license. [1], 2024, published by American Chemical Society. In (a), two UV photons are incident simultaneously, in (b) a UV photon photoexcites an electron, which decays down to the next-lowest state and is emitted from there by a second UV photon. (c) and (d) show a combination of two different photon energies. In (c), a VIS photon pumps an electron which is emitted by a UV photon. In (e) an electron is pumped by the UV photon, but then thermalizes too much energy before incidence of the VIS photon, and no emission of electrons is observed.

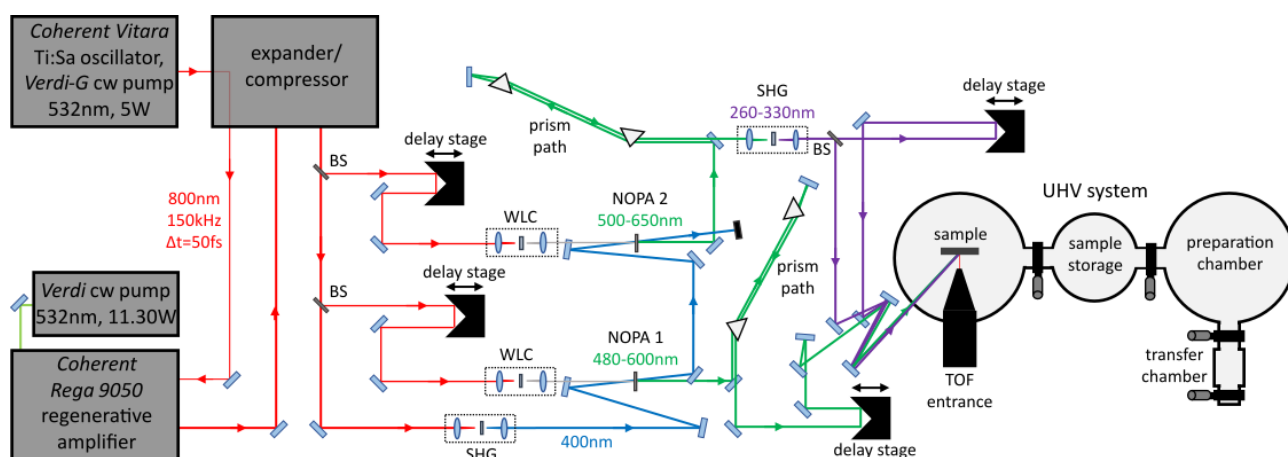


Figure S12: Schematic of the overall tr-2PPE set-up, simplified to enhance presentation, Reproduced under terms of the CC-BY 4.0 license. [1], 2024, published by American Chemical Society. The pulse-generating and -amplifying elements are on the left, NOPA 1 and 2 including 800 nm to 400 nm SHG in the middle. A prism path after each NOPA is shown, the output of NOPA 1 serves as the VIS pump, the output of NOPA 2 is frequency doubled in SHG and split to generate the UV pump and probe beams. All three beams are co-incident on the sample, which is placed in the UHV system, with the TOF detector placed 3-5 mm from the sample.

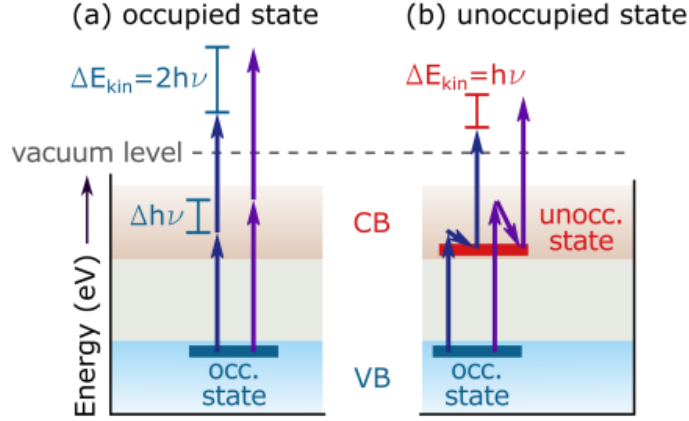


Figure S13: Tr-2PPE pathways are shown for an occupied valence band (VB) state (a), and for an unoccupied conduction band (CB) state (b). Reproduced under terms of the CC-BY 4.0 license. [1], 2024, published by American Chemical Society.

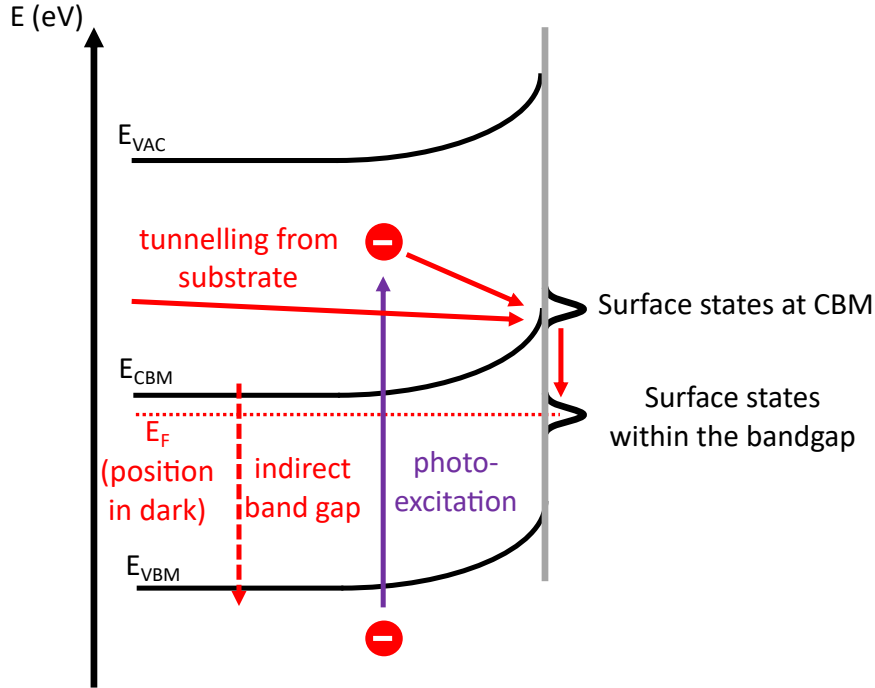


Figure S14: Schematic of photoexcitation and relaxation step by 2PPE measurements.

4 Methodology

4.1 Details of MOVPE process and sample transfer steps

The first step in sample preparation was deoxidation of the GaAs(100) substrates at 620 °C (surface temperature) under TBAs flow [2]. Following deoxidation, the surface temperature was reduced to 600 °C for the growth of all epilayers. At first, 100 nm n-GaAs buffer layers were grown using TBAs and TMGa, with the V/III ratio set to 20. Then, 30 nm AlInP layers were grown with a V/III ratio of 63, while adjusting the TMAI/TMIn ratio to ensure that $x = 0.51$ in $\text{Al}_x\text{In}_{1-x}\text{P}$, achieving lattice matching with GaAs [3]. The DTBSi/III ratio was adjusted during growth of all epilayers to set the doping level of the GaAs layers to $2 \times 10^{18} \text{ cm}^{-3}$, and that of the AlInP layers to $8 \times 10^{18} \text{ cm}^{-3}$. The AlInP epilayer growth step was ended by closing all precursor sources except TBP, and starting the cooling process towards 300 °C. To compensate for surface and bulk P desorption

during cooling, the TBP precursor was provided until temperatures dropped below 320 °C. In an experiment known as a "heat-up run", the surface temperature was raised from 300 to 700 °C under H₂ flow at a rate of 2 °C/min to obtain detailed information on the dependence of the AlInP surface reconstruction on temperature. Figure S15 schematically depicts these preparation steps in the heat-up run as a function of time.

Well-defined P- and In-rich AlInP surfaces were prepared on different samples by annealing the surfaces at 310 °C and 440 °C, respectively. The annealing time was determined by monitoring the RA spectra during heating, stopping when a steady-state RA spectrum was reached. As soon as sample temperatures dropped below 300 °C, samples were immediately moved to a UHV chamber at a pressure of $2 - 4 \times 10^{-10}$ mbar. As-prepared samples were transported to UHV-based characterization stations using a mobile UHV shuttle operating at a base pressure of $< 5 \times 10^{-10}$ mbar.

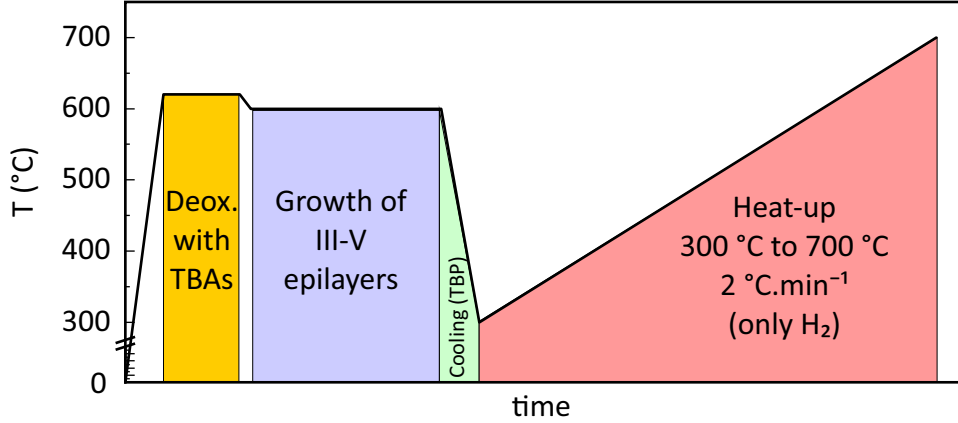


Figure S15: Schematic of the MOVPE preparation process, including the heat-up run step.

4.2 Characterization Techniques

RAS measures the difference in reflection between two perpendicular axes along the surface plane under exposure to linearly polarized light. The amplitude of all RA spectra was calibrated using a baseline obtained from an isotropic Si(110) reference sample.

The epilayer lattice matching of AlInP layers to the GaAs substrate was tested *ex situ* by high-resolution X-ray diffractometry (HR-XRD) $\omega/2\theta$ scans on a reference sample (Bruker AXS D8 Discover using a Ge(022) $\times 4$ asymmetric monochromated and Goebel mirror, using Cu- $K\alpha$ radiation with $\lambda = 1.5405$ Å). We verified that the overlayer's lattice constants matched the lattice constant of the GaAs(100) substrate. The doping profile of reference samples was measured using an electrochemical capacitance-voltage profiling technique (ECVP, WEP-CVP 21) [4].

4.2.1 Photoemission spectroscopy

UHV-transferred samples were measured by XPS (Specs Focus 500/Phoibos 150/1D-DLD-43-100, monochromatic Al- $K\alpha$ line). The spectrometer was calibrated by setting the Fermi level edge of Au, Ag, and Cu to 0 eV BE and adjusting the binding energies to BE(Au 4f_{7/2}) = 83.98 eV, BE(Ag 3d_{5/2}) = 368.26 eV, and BE(Cu 2p_{3/2}) = 932.67 eV, with deviations of ≤ 50 meV. The survey and high-resolution spectra were measured in the fixed analyzer transmission mode, with a pass energy of 30 eV (step size 0.50 eV, dwell time 0.1 s) and 10 eV (step size 0.05 eV, dwell time 0.1 s), respectively.

For UPS measurements, the pass energy, step size, and dwell time were set to 1 eV, 0.02 eV, and 0.2 s, respectively.

Before conducting tr-2PPE measurements at HZB, XPS and UPS analyses were carried out to confirm the absence of contamination with O and C and the preservation of the surface reconstructions during UHV transfer.

4.2.2 tr-2PPE

The tr-2PPE experimental set-up (Figure S12) allows for the use of ultraviolet (UV) pump and probe beams, as well as for the option to use a visible (VIS) pump beam. In the present work, VIS pump pulses of 533 nm (2.33 eV), at an energy per pulse of 3-12 nJ, and with a FWHM of ca. 40 fs were used. UV pump and probe beams were set to 276 nm (4.49 eV), with a FWHM around 30 fs. UV pulse energies were around 0.27 nJ for the pump and 0.13 nJ for the probe. Pump and probe intensities were chosen to avoid surface charging, which

would, e.g., reduce surface band bending and minimize the effects of increased excitation rates on electron dynamics. Electrons were measured in a time-of-flight (TOF) detector with a 7.3° acceptance angle, positioned 3-5 mm from the sample surface. Both pump and probe beams are incident on the sample at an angle of 45° to the surface normal. Emitted electrons are detected using a TOF spectrometer as described above, outputting flight times through the detectors drift tube. These flight times are converted to kinetic energies, and further processed in custom-made python scripts, including binning of data, and Gaussian smoothing to reduce noise, whilst preserving relevant features. Spectra and time-development plots are obtained via slicing of the processed data.

Data processing of tr-2PPE

As a nonlinear optical process of the second order, the intensity of 2PPE signals increases with the square of the laser pulse intensity. This is due to the likelihood of an electron encountering two photons within the same pulse scaling with the square of intensity, which itself is proportional to the number of photons incident per unit area at a given photon energy. This means that at $t = 0$ fs delay, when pump and probe beams are temporally co-incident, there is an increase in emission counts. For UV - UV measurements especially, which are roughly symmetric around $t = 0$ fs, the peak in emission can then be used to ensure that the temporal overlap sits accurately at 0 fs, and is not shifted. This should roughly be the case in the raw data already, due to adjustment of the setup before measurement; however, this can be off by up to 30 fs in practice. As pump and probe beams are incident at an angle to each other, if the sample being measured is positioned slightly differently than the reference Cu sample used to determine temporal overlap, this can introduce small shifts in temporal overlap. For materials with thermalization behavior on the order of picoseconds and above, this is not an issue; however, for materials where a significant part of thermalization occurs in the tens of fs these shifts will introduce inaccuracies when analyzing electron dynamics. To avoid this, the position of tr-2PPE 3D transients and spectra is corrected in the time domain by re-positioning the emission peak at $t = 0$ fs to ensure plots are centered correctly.

Note S1: The scaling of the kinetic energy of emitted electrons relative to the pump and probe energies depends on the initial occupancy of a state. In direct two-photon photoemission from an occupied state, illustrated in Figure S13 (a), the variation in kinetic energy is equal to twice the alteration in photon energy. Conversely, for an unoccupied state, as depicted in Figure S13 (b), the variation in pump photon energy is dissipated thermally; hence, the kinetic energy corresponds to a single instance of the photon energy.

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