

ADSORPTION OF CYCLOPENTENE ON GaAs(001) AND InP(001), A COMPARATIVE STUDY BY SYNCHROTRON-BASED CORE LEVEL SPECTROSCOPY

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1. Abstract

The interface formation between cyclopentene and the (2×4) reconstructed GaAs(001) and InP(001) surfaces has been studied by soft X-ray photoemission spectroscopy (SXPS). After preparation of an uncontaminated (2×4) reconstruction under ultra-high vacuum (UHV) conditions the surfaces were exposed to cyclopentene. The changes in the In 4d and P 2p, as well as the Ga 3d, As 3d and C 1s, core level emission lines indicate a covalent bonding of cyclopentene to the topmost atoms of these surfaces. Based on these results and due to the comparison between the results for the different III-V semiconductors, two different adsorption structures of cyclopentene are found. Our results suggest that cyclopentene adsorbs onto the InP(001) (2×4) surface by the formation of two bonds, in a cycloaddition-like reaction. For the adsorption of cyclopentene on the GaAs(001) (2×4) surface, only a single bond formation is found. The difference in the adsorption structures are explained by the different dimer configurations of the substrate surfaces.

2. Introduction

Synchrotron based photoemission spectroscopy (SXPS) is suitable for the investigation of clean reconstructed semiconductor surfaces as well as for the characterization of the interface formation between organic molecules and such surface reconstructions. This method can help to elucidate bonding configurations based on the analysis of core level emission line shapes, the identification of surface core level components and the chemical composition of the surface. Therefore, adsorption structures of organic molecules on semiconductor surfaces are presented based on SXPS data. By the understanding of the interface formation of such heterostructures, new applications can be developed or improved. Since organic molecules can be synthesized chemically, we can choose from a large variety of organic molecules in terms of structure and functionality.¹⁻³

Until now, most results concern the interface formation between organic molecules and the Si(001)(2 × 1) reconstructed surface.^{1,2,4-12} In that context, it was shown that the surface dimer structure is a basic prerequisite for the bonding mechanism. For example, a bonding via a [2 + 2]-cycloaddition reaction is only allowed for a bonding on an asymmetric surface dimer, which is the case for the Si(001)(2 × 1) surface.^{2,13,14} In order to clarify the role of the surface dimer structure on the bonding mechanism, investigations of molecule adsorption on different dimer configurations are necessary. Such different dimer configurations are provided in our investigations by GaAs(001) and InP(001) surfaces,^{15,17} as can be seen in Fig. 1.

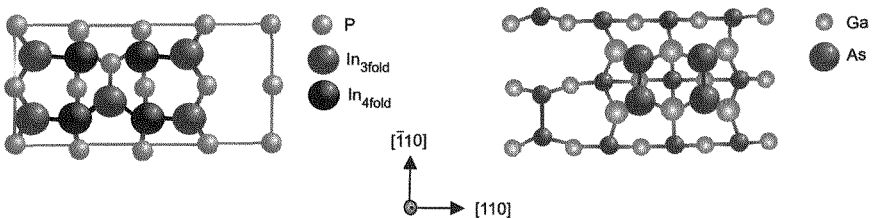


Fig. 1. On the left: topview of the InP(001)(2 × 4) surface reconstruction. On the right: topview of the GaAs(001)(2 × 4) surface reconstruction.

The atomic structures of the clean reconstructed InP(001)(2 × 4) and the GaAs(001)(2 × 4) surfaces have been investigated in recent years. The InP(001)(2 × 4) surface is well described by the so-called asymmetric ‘mixed-dimer’ model, a structure that consists of an In-P hetero-dimer with a filled dangling bond at the P atom and an empty dangling bond at

the In atom.^{16,17} These dimer atoms are bonded to fourfold coordinated second layer In atoms. The outer In atoms of the second layer are threefold coordinated.

For the GaAs(001)(2 × 4) the topmost layer consists of As atoms forming dimers with double occupied dangling bonds which are bonded to second layer Ga atoms.¹⁸

Core level spectroscopy was performed to investigate the interface formation between the III-V (001) surfaces and cyclopentene. Numerical analysis of the In 4d, P 2p, Ga 3d, As 3d and C 1s core level emission lines by best fit reveals information on the interface formation. Additionally, reflectance anisotropy spectroscopy (RAS) measurements were performed to monitor the deposition process. Based on the experimental results, structure models for the cyclopentene–surface linkage on the two (2 × 4) reconstructed surfaces, the InP(001)(2 × 4) and the GaAs(001)(2 × 4) surfaces, were developed.

3. Experimental

The Sb-doped InP(001) samples, investigated here, were grown by metal-organic vapour phase epitaxy (MOVPE) using phosphine (PH₃) and trimethylindium (TMIn) as precursors. Directly after growth, the samples were capped with an amorphous phosphorous/arsenic double layer by photo-decomposition of PH₃ and AsH₃ in the MOVPE reactor.¹⁹ The GaAs(001) samples used in this work were Si-doped (nominal $n = 5 \times 10^{17} \text{ cm}^{-3}$), grown by molecular beam epitaxy (MBE) and capped with amorphous arsenic directly after growth using an As₂ flux.²⁰

After transfer of the samples to UHV, contamination free and well ordered (001) surfaces were prepared by heating to approximately 400°C(±20°C) for 15 min for InP and to 420°C(±20°C) for 15 min for the GaAs(001)(2 × 4). After this procedure the surface reconstructions were determined by low energy electron diffraction (LEED) showing a clear (2 × 4) pattern in both cases. The base pressure throughout all experiments was below 2×10^{-10} mbar.

Cyclopentene with a purity higher than 97% was introduced from gas phase into the chamber using a variable gas-inlet valve. During the deposition, the samples were held at room temperature (RT). In order to avoid decomposition of the molecules, all filaments inside the chamber, e.g. ion gauges, were switched off during the exposure. The effective cyclopentene layer thickness was estimated from SXPS measurements to be approximately one monolayer. The whole deposition process was monitored by

RAS.

Synchrotron based photoemission measurements were performed at the Russian-German beamline (RGLB) at the synchrotron facility BESSY II. The spectra were taken in normal emission with a total instrumental resolution (beamline plus analyser) of 120 meV at an excitation energy of 75 eV. Kinetic energies (binding energies) of the In 4d, P 2p, As 3d, Ga 3d and C 1s core level emission lines refer to the Fermi edge determined by photoemission from a molybdenum sample holder in electrical contact with the samples. The core level spectra were analyzed by numerical deconvolution into pairs of spin orbit-split doublets each of which consists of convoluted Lorentzian and Gaussian line shapes corresponding to lifetime and experimental broadening, respectively. The measured data points (spheres in Fig. 2-4) are shown together with best-fit from numerical analysis (full lines). For all measurements at the InP samples, a lifetime broadening for the In 4d (P 2p) core levels of 0.1 eV (0.06 eV), a branching ratio of 1.5 (2.0), an experimental broadening of 0.46 eV (0.41 eV), and a spin-orbit splitting of 0.86 eV (0.87 eV) were found. For the measurements at the GaAs samples, a lifetime broadening for the As 3d (Ga 3d) core levels of 0.1 eV (0.1 eV), a branching ratio of 1.5 (1.7), an experimental broadening of 0.50 eV (0.39 eV), and a spin orbit-splitting of 0.69 eV (0.43 eV) were found. The resulting residuum is shown below each fit.

4. Results and Discussion

4.1. *Results for the adsorption of cyclopentene on the InP(001)(2 × 4)*

For the adsorption of cyclopentene on the InP(001)(2 × 4) reconstructed surface, it is well known that the two different surface bonding sites lead to a change for the surface core level components in In 4d and P 2p core levels, as seen in Fig 2. These changes are explained by an adsorption of cyclopentene on the ‘mixed-dimer’ as the main surface adsorption site. Additionally, subsequently bonding to the second layer *In-In* bonds is observed as we could show in our previous work.²¹

Beside the two surface components in the In 4d core level emission line^{22,23} (shaded) which are revealed by numerical analysis, an additional component after cyclopentene saturation is found. This component shifted towards lower kinetic (higher binding) energies, *In-C*, is assigned to a bond formation of cyclopentene to the topmost In atoms.²¹ For the P 2p core level a second surface related component shifted towards lower kinetic (higher

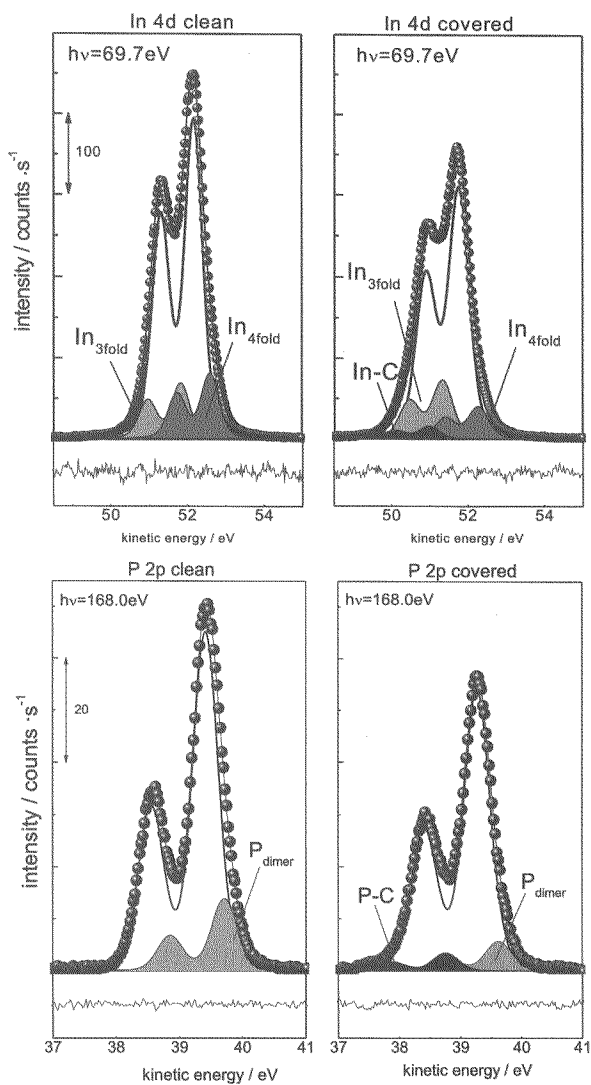


Fig. 2. The In 4d (first row) and P 2p (second row) core level emission lines for the clean (left) and cyclopentene saturated (right) InP(001)(2 × 4) reconstructed surface from.²¹

binding) energies, $P-C$, is found too. This component is assigned to a bond formation of cyclopentene to the topmost P atoms.²¹

These components are explained to stem from In and P atoms which bond to carbon atoms of the cyclopentene molecules. The shift towards higher binding energies results from a charge transfer from In and P (1.8 and 2.2) to C (2.5) due to the higher electronegativity of the latter.

These observations are supported by the C 1s core level, as shown on the left graph of Fig. 3. Three main components have been revealed by the numerical analysis, $C-C$, $C-In$ and $C-P$, and the energy shifts of the latter components are given with respect to the $C-C$ component. These components are assigned to carbon atoms with $C-C$ single bonds, to carbon atoms involved in a $C-In$ (shift of +1.54 eV) bond and to C atoms involved in a bond formation to P atoms (shifted by +0.50 eV). The shifts in the energy level are in agreement with the different electronegativity values of phosphorus, indium and carbon. The fourth small component is shifted by -1.17 eV towards lower kinetic (higher binding) energies with respect to the $C-C$ component. This component is believed to result from carbon atoms participating in $C=C$ double bonds of cyclopentene as observed by Liu and Hamers.²⁴

These observations are explained by the adsorption of cyclopentene on the ‘mixed-dimer’ as the main surface adsorption site and subsequently bonding to the second layer $In-In$ bonds as discussed before and are supported by theoretical DFT calculations.²¹

The resulting adsorption structures are based mainly on the analysis of the C 1s core level emission lines. The interpretation and comparison of these results to the ones found for the adsorption of cyclopentene on the GaAs(001)(2×4) surface will help discussing the resulting adsorption structures for the latter.

4.2. Results for the adsorption of cyclopentene on the GaAs(001)(2×4)

The clean (2×4) reconstructed GaAs (001) surface (see Fig. 4 left), two surface related components are found in the emission line shape analysis. One component As_1 is shifted towards lower kinetic (higher binding) energies with respect to the bulk component which is not yet clearly assigned, and another component shifted towards higher kinetic (lower binding) energies are related to the As dimer atoms of the topmost layer of the surface.

In Fig. 4 (middle) the As 3d core level emission line taken after the adsorption of cyclopentene is shown. An additional component ($As-C$) is revealed

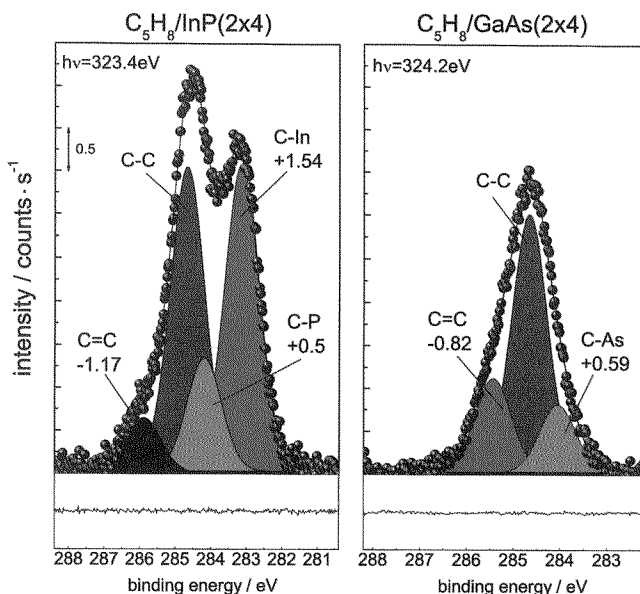


Fig. 3. The C1s core level for the cyclopentene covered InP(001)(2 × 4) (left) and the cyclopentene covered GaAs(001)(2 × 4) (right) reconstructed surfaces. The shifts are given in eV with respect to the C – C components.

in the fit shifted towards lower kinetic (higher binding) energies. Due to the different electronegativities of C and As (2.5 and 2.2, respectively), this component is assigned to a bond formation between C and As atoms of the topmost layer.

In the Ga3d core level emission line shape no change could be found after the adsorption of cyclopentene. In Fig. 4 (right) the Ga3d core level emission line of the cyclopentene covered surface is depicted. Three components are evaluated two of which can not yet clearly be assigned, namely the Ga_1 shifted towards lower kinetic (higher binding) and Ga_2 shifted towards higher kinetic (lower binding) energies. The $Ga_{2ndlayer}$ component, is related to Ga atoms of the second layer.

In Fig. 3 (right side) the C 1s core level emission line taken after the saturation with cyclopentene is shown. Before deposition, no traces of carbon could be detected by SXPS. In the core level line shape analysis three components are found. The first pronounced component is assigned to C atoms

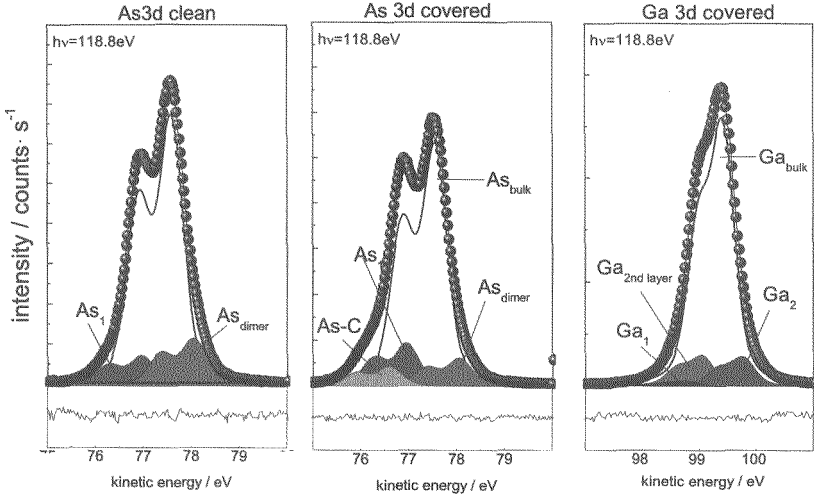


Fig. 4. On the left: the As 3d core level of the clean (2×4) reconstructed surface. In the middle: the As 3d core level taken after saturation with cyclopentene. On the right: the Ga 3d core level taken after the saturation with cyclopentene. The core level line shape did not change and no new component was revealed in the best fit.

involved in a $C-C$ single bond. The energy shifts of the other two components are given with respect to the $C-C$ component. The second component, shifted towards lower kinetic (higher binding) energies by -0.82 eV stems from C atoms involved in a double bond ($C=C$), and the third component, shifted towards higher kinetic (lower binding) energies by $+0.59$ eV, is assigned to C atoms involved in a bond formation to As atoms of the topmost layers, $C-As$. The latter one corresponds to the $As-C$ component in the As 3d core level emission line. The shifts in energy levels agree well with the results of cyclopentene adsorbed on the $InP(001)(2 \times 4)$ reconstructed surface. Comparing the two different substrates, As and P have nearly the same electronegativity of 2.2 which explains the comparable energy shifts of 0.59 eV and 0.50 eV, respectively. Indium has an electronegativity of 1.8, which leads to a larger shift towards higher kinetic (lower binding) energies, as shown in Fig. 3. In both core level spectra the $C-C$ components have the same binding energy of approximately 284.7 eV.

The $C=C$ components, however reveal different energy shifts relative to the $C-C$ component for GaAs and InP (0.82 eV and 1.17 eV, respectively).

At the cyclopentene\GaAs(001)(2 × 4) surface, the $C=C$ component stems from cyclopentene molecules that are covalently attached to the surface. In contrast, on the cyclopentene\InP(001)(2 × 4) surface the $C=C$ component stems from cyclopentene molecules that are only physisorbed and not covalently attached to the surface. The different energy shifts of the respective component could possibly be explained by the different bonding mechanisms of those molecules containing the $C=C$ bonds.

The difference in the intensities of the $C-C$, the $C=C$ and the $C-As$ contribution for the adsorption of cyclopentene on the GaAs(001) surface shows that cyclopentene adsorbs by a dissociation of one hydrogen atom as well as by a splitting of the double bond. This is in contrast to the adsorption of cyclopentene on the InP(001)(2 × 4) surface where the $C=C$ component is less pronounced with respect to the $C-C$ component. Therefrom, it can be concluded that during the adsorption of cyclopentene on the GaAs(001)(2 × 4) surface, the double bond remains intact while a splitting of the double bond occurs for the adsorption of cyclopentene on the InP(001)(2 × 4) surface. These observations result in two different adsorption structures, as shown in Fig. 5, which reveal the influence of the different surface dimer configurations. In case of the InP(001)(2 × 4) surface, the asymmetric dimer configuration leads to a [2 + 2]-cycloaddition-like reaction with a formation of two bonds between cyclopentene and the surface. Contrary to this, on the GaAs(001)(2 × 4) surface cyclopentene forms only one bond to As dimer atoms of the surface which have a symmetric dimer arrangement.

This single bond formation could involve a charge transfer to the second Ga dimer atoms, or it could also be the case that dissociated hydrogen atoms of the cyclopentene molecules bond to the second As dimer atoms, which are not directly involved in the covalent bonding to the adsorbed molecules, as indicated in Fig. 5.

5. Summary

In this paper, we have shown a comparison between the adsorption configuration of cyclopentene on two different III-V surfaces, the InP(001)(2 × 4) and GaAs(001)(2 × 4) reconstructions. The dimer configurations on these surfaces are different and result in two different adsorption configurations for cyclopentene. In the case of the InP(001)(2 × 4) surface, two bonds to the surface are formed. This is possible due to the asymmetric arrangement of the ‘mixed-dimer’ atoms in the topmost layer of the surface. The underlying bonding mechanism could therefore be described by a [2 + 2]-cycloaddition reaction as observed for cyclopentene adsorbed on the Si(001)(2 × 1) sur-

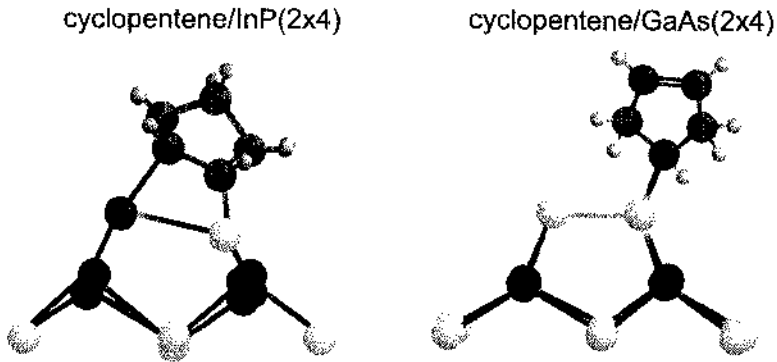


Fig. 5. On the left: schematic representation of the adsorption of cyclopentene at the 'mixed-dimer' of the InP(001) (2 x 4) surface. On the right: scheme for the adsorption configuration of cyclopentene on the GaAs(001)(2 x 4) surface. The light balls represent the group-V (P As) and the dark one the **group-III** (In, Ga) elements.

face.² In the case of the GaAs(001)(2 x 4) surface, the topmost layer consists of symmetric As dimers where a 'cycloaddition' reaction is not allowed. Consistently, only a single bond formation to one of the topmost As dimer atoms could be observed. Hence, we can conclude that the asymmetry of the 'mixed-dimer' of the **InP(001)(2 x 4)** surface supports the formation of two bonds, as found for the adsorption of cyclopentene on the Si(001) (2 x 1) surface. This is not the case for the symmetric dimer of the GaAs(001)(2x4) surface.

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