Etching of the InP(001) Surface by Halogens: Reaction Mechanisms Obtained by Density-Functional Calculations

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Reaction energies and related barrier heights of halogenated InP(001) surface structures are calculated using the density functional theory and molecular models for typical local surface structures. The obtained data show how the elementary mechanisms of the chemical etching depend on the applied halogen (X = F, Cl, Br, I). Two reaction regimes are determined, which are consistent with the α and β state discussed for the Cl_2+InP(001) system: Under low halogenation (β-state) the In atoms leave the surface as InX (19−35 kcal/mol). The P atoms are removed as P_2 (32−37 kcal/mol) or after combination as P_4 independently of the used halogen. Formed PF, PCl, PBr, and InX_2 surface groups require a higher energy expense (> 50 kcal/mol) or a higher halogenation for the desorption. A smaller energy is necessary for the PI removal (37 kcal/mol). Under high halogenation (α-state), In atoms could leave the surface as InX_3 (F: 21 kcal/mol; Cl, Br, I: 7−10 kcal/mol). However, a relatively stable corrosion phase composed of bound InX_3 molecules is formed on the surface. P atoms can be removed as PX_3 (20−24 kcal/mol) or PX_2 (26−31 kcal/mol). The rate-limiting steps are the P_2 and the PX_3 (InF_3) desorption for low and high halogenation, respectively. Practically, a higher temperature has to be used for obtaining a high etch rate by reason of the transport of the etch gas to and the products from the surface.

1. Introduction

Reactive etching is an important technological process for the manufacturing of microelectronic devices. For the development and optimization of etching processes, knowledge of the chemical mechanisms can be helpful. InP is a frequently used material but the elementary etching mechanisms are largely unknown.[1] A different reaction behavior of the halogens is expected by reason of the large difference between the atomic radii and the electronegativities. Only one theoretical[2] and a few experimental studies[3−6] exist on chemisorption structures and product distributions of the Cl_2 + InP etching. No such studies have been found for the other halogens contrary to the GaAs etching (see references in ref 7). Quantum chemical calculations with surface models on the elementary etching mechanisms are not known for InP.

By thermodynamic calculations for steady-state etching with chlorine, McNevin[2] shows that below 430 K the surface consists entirely of solid $InCl_3$ and there is negligible chemical etching. Above 430 K, the surface consists roughly of 65% $InCl_2$ and 35% P and significant chemical etching occurs. The predicted gaseous etch products are P_4 and a mixture of $InCl_2$ and InCl. At larger Cl_2 pressure the etch products are $InCl_3$ (In_2Cl_6) and PCl_3. Auger and mass spectrometric observations by McNevin[3] are largely consistent with the thermodynamic predictions.

Murrell et al.[4,5] investigate the reaction of chlorine on the InP(001) surface and find a strongly bound chemisorbed monolayer (β-phase) during low gas exposure. From the chlorinated layer, P_4 and InCl are sputtered by ion beam irradiation or desorb at higher temperatures (570 K). High gas exposure leads to bulk corrosion (α-phase). An In-rich chloride film is formed, which desorbs $InCl_3$ (410 K). No phosphorus is in the α-state. The activation energy of the α-phase desorption is estimated at 26 kcal/mol.

Hung et al.[6] obtain a clean In-rich InP(001) surface with 4 × 2 pattern by ion sputtering or chlorine etching followed by annealing to 650 K. The exposure of the surface to various amounts of chlorine at 110 K provides InCl, $InCl_2$, small amounts of $InCl_3$, and PCl species on the InP surface. When the surface is heated to 400 K, $InCl_3$ is completely depleted and a small amount of InCl and $InCl_2$ desorbs from the surface. When the surface is annealed to 600 K, all indium chlorides and phosphorus chlorides desorb from the surface. Argon-ion sputtering enhances the surface reactivity so that the sputtered surface can be chlorinated to a higher extent than the unsputtered one. $InCl_3$, PCl_2, and PCl_3 species desorb from this surface after heating the substrate to 250 K. However, $InCl_2$, InCl, and PCl can still remain on the surface.

In this study the reaction behavior of differently halogenated surface structures is obtained from calculated reaction energies and related barrier heights. The obtained surface structures and desorption products are assigned to the frequently discussed α and β surface state. The determined rate-limiting steps provide barrier heights, which agree well with activation energies

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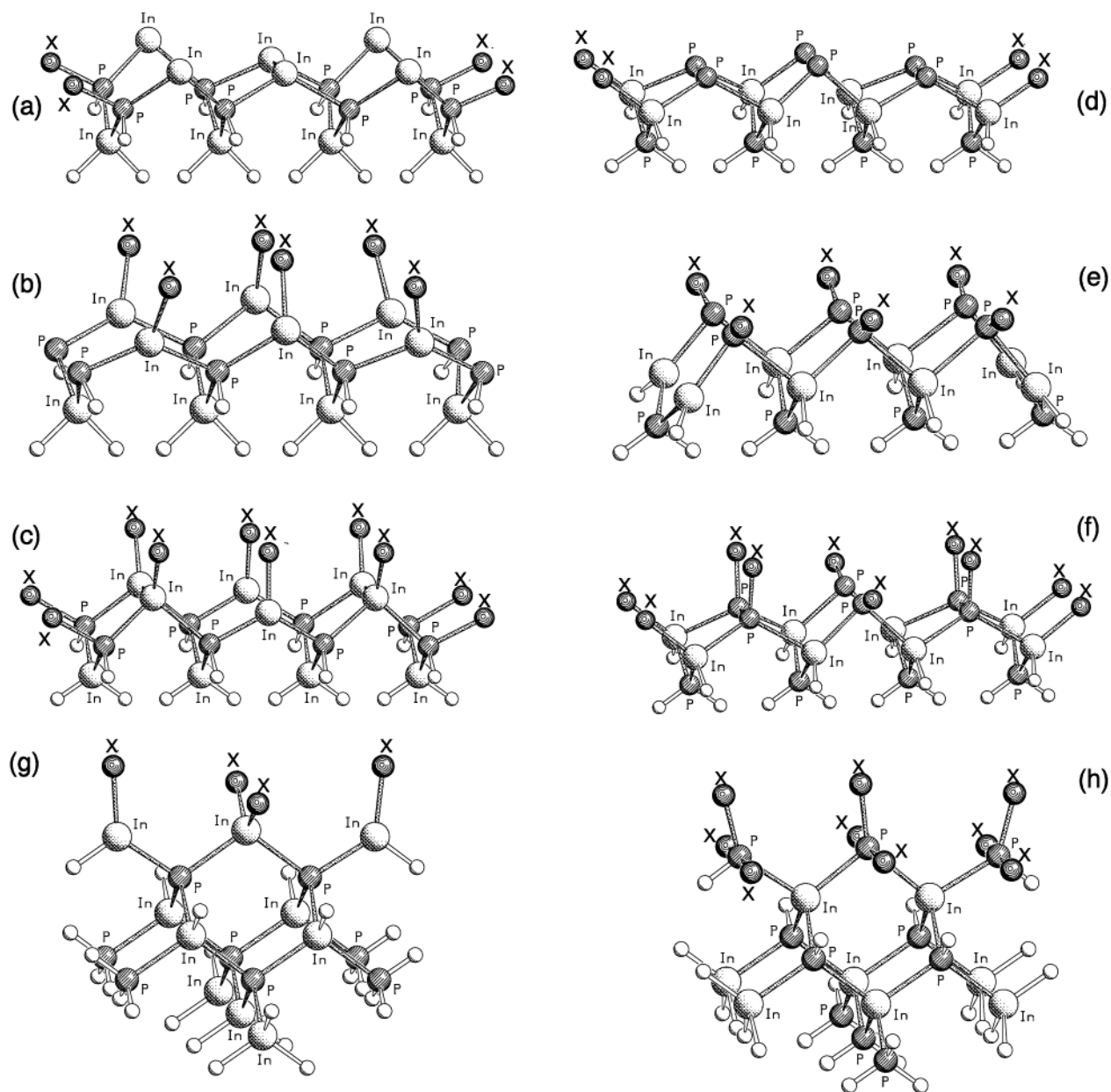
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Figure 1. Models used for the In-rich (left side) and the P-rich (right side) surfaces with various halogenation (X = F, Cl, Br, I). The structures (g) and (h) are examples used for the investigation of the InX_2 and PX_3 desorption, respectively.

obtained from experiments. Differences in the reaction mechanisms of the four halogens are discussed.

2. Models

The investigation of etch reactions requires not only the modeling of the formation and decomposition of chemisorption structures with various surroundings as plane surfaces or steps but also different halogenation. In general the reaction zones are not represented by the stable reconstructions of the clean surfaces. Therefore, the reactions are investigated by relatively small molecular models (clusters) with typical local structures as, for example, dimers or edges. Two principal model types, which well reproduce experimental results for the systems Cl_2 + GaAs(001),[8] HCl + GaAs(001),[9] and halogens + GaAs-(001),[7] are transferred to the InP(001) surfaces.

The dimer models for In-rich (Figure 1a–c) and the P-rich (Figure 1d–f) surface are well suited for investigation of non- and lowly halogenated surface structures. They allow the

modeling of the chemisorption/desorption of X_2, In_2, P_2, InX, and PX at/from a plane surface (middle) and at/from an edge (X = F, Cl, Br, I).

The monomer model for the In-rich (Figure 1g) and the P-rich (Figure 1h) surface can be used to study various highly halogenated surface structures with InX_m and PX_m desorption (m = 1–3).

Both model types allow to investigate the influence of the chemisorption at neighbor positions on the desorption of surface species. The artificial dangling bonds at the cluster boundaries directed into the bulk are saturated by hydrogen atoms. The structure of the molecules and the reaction zones of the clusters (In and P atoms in the surface and the subsurface layer as well as the halogen atoms) are relaxed. The regions of the clusters simulating the bulk, including the H atoms, are fixed at the experimental atomic distances (InP bulk, InH_3, and PH_3) and the ideal bond angles. Detailed explanations on the models are presented in refs 7–9.

3. Method

The energy calculations and the structure relaxation are done by the density functional theory (DFT) with the exchange functional of Becke[10] and the correlation functional of Lee et al.[11] (BLYP). The electronic core potentials (ECP) and valence double-ζ basis set of Wadt and Hay[12] (LanL2DZ) are augmented by a set of Cartesian d functions for non-hydrogen atoms. The d exponents are optimized on bond energies of homonuclear diatomic molecules (In: 0.09, P: 0.5, F: 1.08, Cl: 0.52 Br: 0.32, and I: 0.22). The comparison of dissociation energies of relevant diatomic molecules calculated with frequently used DFT functionals show that the BLYP values provide the best agreement with experimental and good theoretical data (Tables 1S−3S in Supporting Information). The influence of the basis set superposition error (BSSE) has been tested at dissociation energies of relevant diatomic molecules and some important desorption reactions (Table 4S). The found small BSSE have no influence on the conclusions about the pathways of the considered reactions. The barrier heights are estimated by a procedure proposed by Ohno.[13] The calculations have been done by the Gaussian 98 program system.[14]

4. Results and Discussion

The reaction mechanisms at the surface are determined from probable halogen-free and variously halogen-terminated local surface structures. At first, the reaction energies are calculated for all the possible reactions of a considered surface structure (desorption of species from the surface and transfer of atoms at the surface). The most favorable reaction is obtained by the selection of the reaction with the lowest barrier. The barrier is calculated for the reaction with the lowest reaction energy only. If this barrier is lower than the next higher reaction energy then the most probable reaction is found. In the other case, the barrier calculation has to be done for the reaction with the next higher reaction energy and so on.

The desorption of species from a starting structure creates a new surface structure, which can desorb species from special surroundings, as monolayer steps with or without second layer atomic pairs (consecutive reactions).

In Figures 2−10, the reaction energies are connected by dashed lines and the related barrier heights by straight lines. The starting reactions are presented by filled symbols and the consecutive reactions by empty symbols.

4.1. Low Halogenation: X_2, In_2, P_2, InX, and PX Desorption ($X = F$, Cl, Br, I). *4.1.1. In-Rich Surface.* 4.1.1.1. Monohalogenation of the Second Layer P Atoms at the Edge Only (Figure 1a and 2). The desorption of In dimers from this structure requires significantly high energies (> 82 kcal/mol). Recombinative desorption of the heavy halogen molecules from the second layer P atoms of the edge (outside) is possible. However, the transfer of halogen atoms to the surface In atoms (edge) is exothermic and has a lower barrier (14−20 kcal/mol). Furthermore, the reaction path calculations show that during the X_2 attack, the system attempts to form In-X bonds: either the halogen atoms go to the In atoms (free reaction path) (see Figure 1b) or the In atoms go to the halogen atoms (during the P attack), so that the structure of Figure 1a does not play a role for etching.

4.1.1.2. Monohalogenation of the Surface In Atoms Only (Figure 1b and 3). All the halogen atoms are strongly bound to the In atoms so that a recombinative X_2 desorption is not possible. The preferred reaction is the InX desorption from the middle position (E_A: about 22 kcal/mol). The InX at the edge is much more strongly bound (E_A: about 40 kcal/mol).
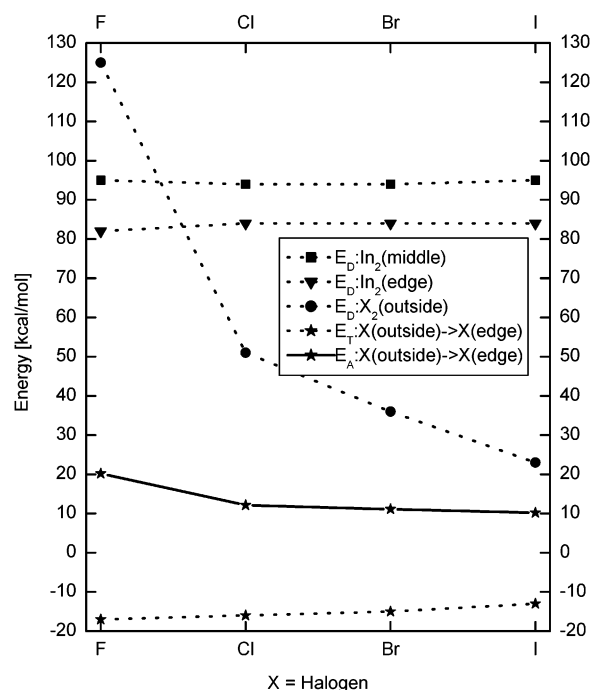

Figure 2. Desorption E_D and transfer energies E_T and related barrier heights E_A (kcal/mol) for the In-rich surface with monohalogenation of the second layer P atoms at the edge (outside) (see Figure 1a).
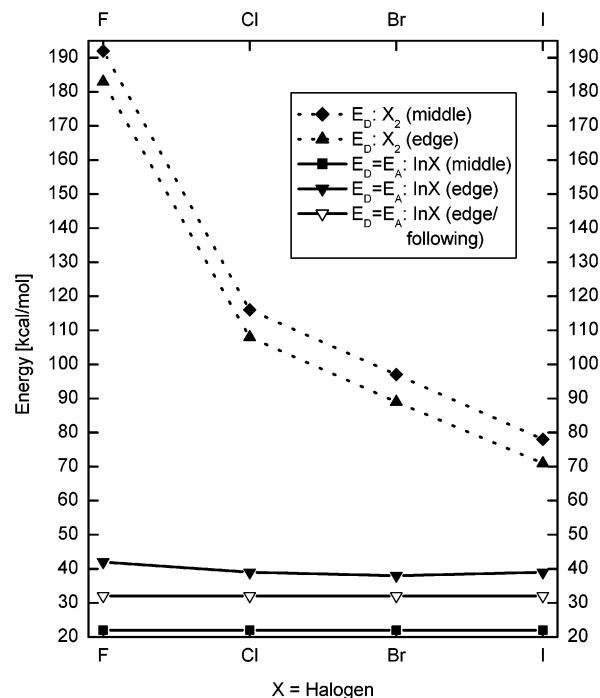

Figure 3. Desorption energies E_D and related barrier heights E_A (kcal/mol) for the In-rich surface with monohalogenation of the surface In atoms (middle and edge) (see Figure 1b).

However, the barrier height of this desorption is reduced after the InX removal from the middle position (E_A: about 32 kcal/mol). The variation of the halogen atoms does not influence the InX desorption.

4.1.1.3. Full Monohalogenation (Figure 1c and 4). The bond strength of the halogen atoms to the surface strongly decreases from F to I so that the recombinative I_2 desorption from the outside P atoms (E_D: 20 and E_A: 37 kcal/mol) is a possible reaction (for the consecutive reactions see 4.1.1.2.). However,
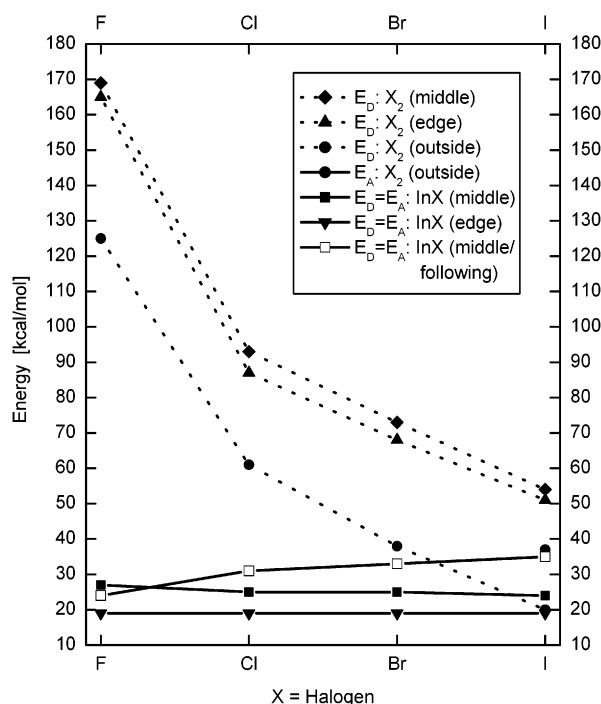
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Figure 4. Desorption energies E_D and related barrier heights E_A (kcal/mol) for the In-rich surface with monohalogenation of the surface In atoms (middle and edge) and the second layer P atoms at the edge (outside) (see Figure 1c).
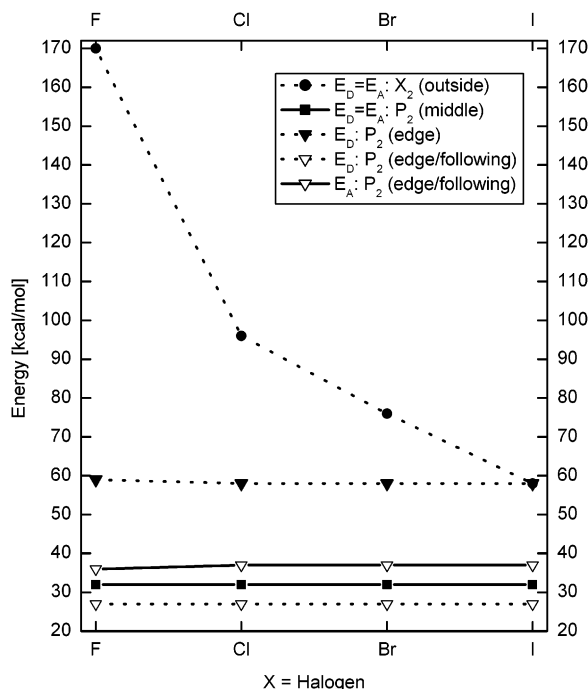

Figure 5. Desorption energies E_D and related barrier heights E_A (kcal/mol) for the P-rich surface with monohalogenation of the second layer In atoms at the edge (outside) (see Figure 1d).

the InX desorption, especially from the edges, is more probable independently of the halogen (E_A: about 19 kcal/mol). The following InX desorption from the middle position has a higher barrier (E_A: 24−35 kcal/mol). The InF removal requires the smallest energy expense (24 kcal/mol).

4.1.2. P-Rich Surface. 4.1.2.1. Monohalogenation of the Second Layer In Atoms at the Edge Only (Figure 1d and 5). The halogen atoms are strongly bound at the second layer In atoms of an edge (outside), so that a recombinative X_2
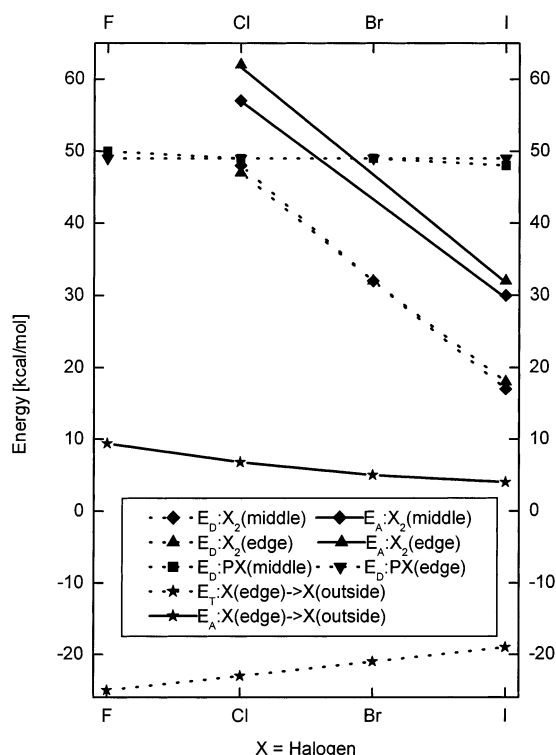

Figure 6. Desorption E_D and transfer energies E_T and related barrier heights E_A (kcal/mol) for the P-rich surface with monohalogenation of the surface P atoms (middle and outside) (see Figure 1e).

desorption is not probable. Large differences are found for the P_2 desorption. The P_2 removal from the middle position requires about 32 kcal/mol, but about 58 kcal/mol are necessary for the P_2 desorption from the edge independently of the bound halogen. The latter one is reduced after the desorption of the middle P dimer (E_D: about 27 and E_A: about 37 kcal/mol). This P atom removal is the most probable reaction path and the rate-limiting step for the etching under low halogenation. The related barrier height for Cl_2 etching (P_2 desorption: 37 kcal/mol) agrees well with the activation energy (34.5 kcal/mol) experimentally found by chlorine plasma etching.[15] P_2 can combine to P_4 (−36 kcal/mol). The variation of the halogen atoms does not influence the mechanism.

4.1.2.2. Monohalogenation of the Surface P Atoms Only (Figure 1e and 6). The PX species are relatively strongly bound at the surface (E_D: 48−50 kcal/mol). The bond strength of the halogen atoms to the surface decreases with increasing halogen mass. A barrier of 30 kcal/mol has to be overcome for the recombinative I_2 desorption from the middle. The halogen transfer from the surface P atoms to the outside In atoms of the edge is much more probable (E_D: −25 to −19, E_A: 9 to 4 kcal/mol). This transfer leads to structures discussed in 4.1.2.1. and 4.1.2.3.

4.1.2.3. Full Monohalogenation (Figure 1f and 7). Here, two different mechanisms are obtained in dependence on the halogen. Fluorine and chlorine are strongly bound at the surface, so that the recombinative X_2 desorption is not probable. The PF and PCl desorption, especially from the middle position (48 and 50 kcal/mol), is the most probable reaction. The following PX desorption from the edge (Figure 8) requires a similar energy (52 and 49 kcal/mol). The P removal of this structure is only possible by higher temperatures or higher halogenation (see 4.2.2.).

For bromine and iodine the bonds to the surface P atoms are so weak that the recombinative X_2 desorption is more probable
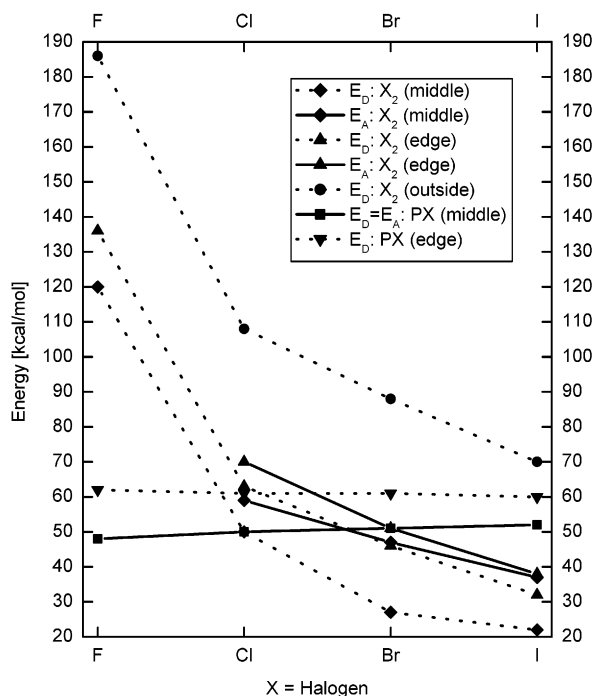
Figure 7. Desorption energies E_D and related barrier heights E_A (kcal/mol) for the P-rich surface with monohalogenation of the surface P atoms (middle and edge) and the second layer In atoms at the edge (outside) (see Figure 1f).
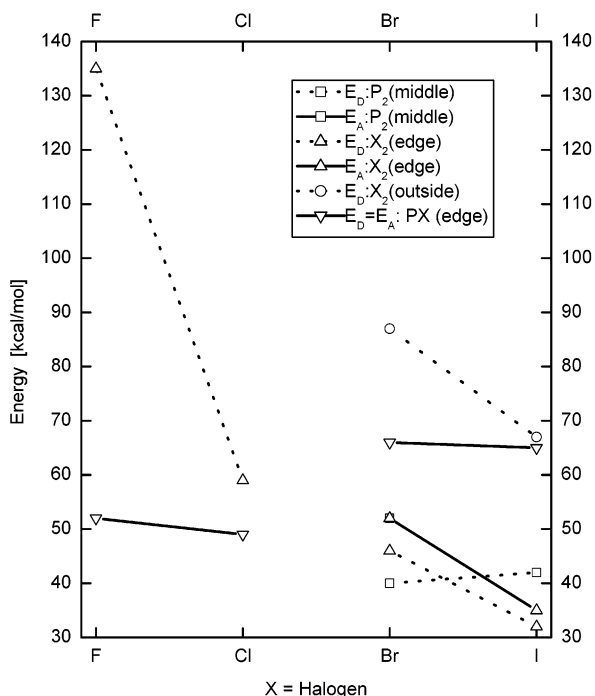

Figure 8. Desorption energies E_D and related barrier heights E_A (kcal/mol) for structures resulting from the most probable reactions of structure (f) (Figures 1 and 7).

than the PX desorption. Barriers of 47 (Br_2) and 37 (I_2) kcal/mol have to be overcome (middle). The consecutive reaction is the X_2 desorption from the edge (Figure 8 $E_A(Br_2)$: 52 and $E_A(I_2)$: 35 kcal/mol). The halogen-free P-dimer surface is obtained as discussed in section 4.1.2.1. For bromine the barriers are so high that higher temperature or higher bromination is required. However, the PI removal is possible by I_2 and P_2 desorption.
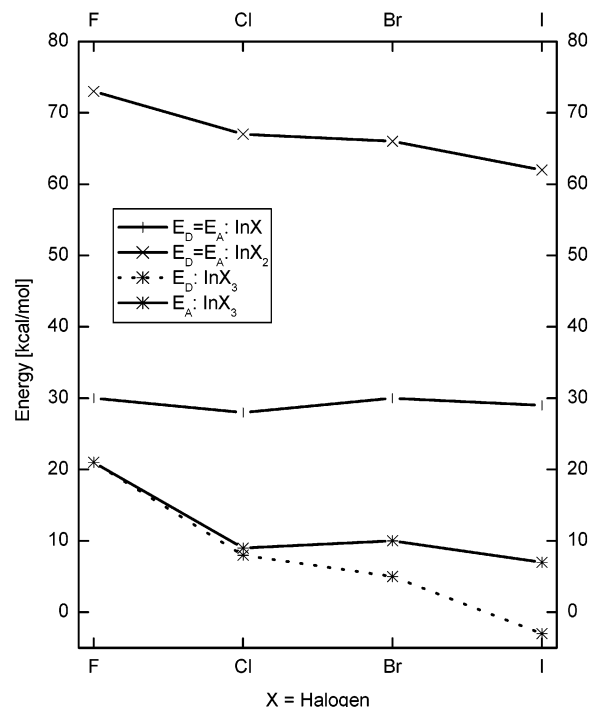

Figure 9. Desorption energies E_D and related barrier heights E_A (kcal/mol) for the plane In-rich surface with higher halogenation (see Figure 1g).

4.2. High Halogenation: InX_m and PX_m Desorption (X = F, Cl, Br, I; $m = 1-3$). *4.2.1. In-Rich Surface (Figure 1g and 9).* The InX are bound to the surface by $28-30$ kcal/mol. The InX_2 are very strongly bonded at the surface ($73-62$ kcal/mol). For both species the desorption energies are close to the barrier heights (no additional barriers). InX_3 surface species can be formed from InX surface species by dissociative chemisorption of X_2 (chemisorption energies: F: -146, Cl: -62, Br: -39, and I: -16 kcal/mol). The InX_3 are weakly bound at the surface. The bond strength decreases and the difference between desorption energy and barrier height increases from F to I. $InCl_3$, $InBr_3$, and InI_3 are the weakest bound species (E_A: $7-10$ kcal/mol). InF_3 requires a higher energy expense for the desorption (E_A: 21 kcal/mol).

The experiments for Cl_2 etching find that a corrosion phase composed preferentially of $InCl_3$ is formed on the surface [1-6, 16]. Figure 11 shows two investigated dimer InX_3 arrangements. The binding energies of the coordinatively bound molecules (Table 1) demonstrate that the stability of $(InX_3)_n$ aggregates decreases with the halogen mass. All the InX_3 molecules are more strongly bound between themselves (II) than with the surface (Figure 9).

4.2.2. P-Rich Surface (Figure 1h and 10). The PX are strongly bound to the surface (E_A: $50-63$ kcal/mol). The PX_2 have desorption energies between 26 and 31 kcal/mol. For both species the desorption energies agree with the barrier heights. The PX_3 species have large differences between desorption energies and barrier heights. The desorption is always exothermic. The barrier heights vary between 20 and 24 kcal/mol. A maximum is found for chlorine. The chlorine value is close to the activation energy of the experiment (26 kcal/mol).[5]

5. Mechanisms and Summary

Reaction energies and related barrier heights of halogenated InP(001) surface structures are calculated using the density functional theory and molecular models for typical local surface
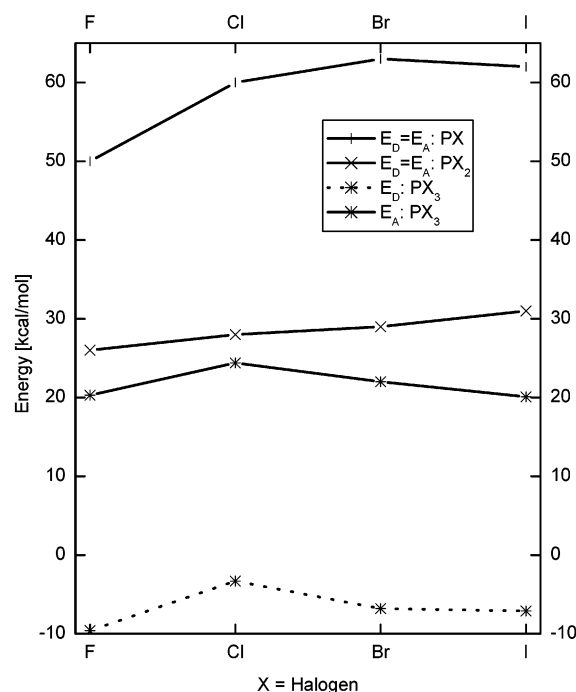
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Figure 10. Desorption energies E_D and related barrier heights E_A (kcal/mol) for the plane P-rich surface with higher halogenation (see Figure 1h).
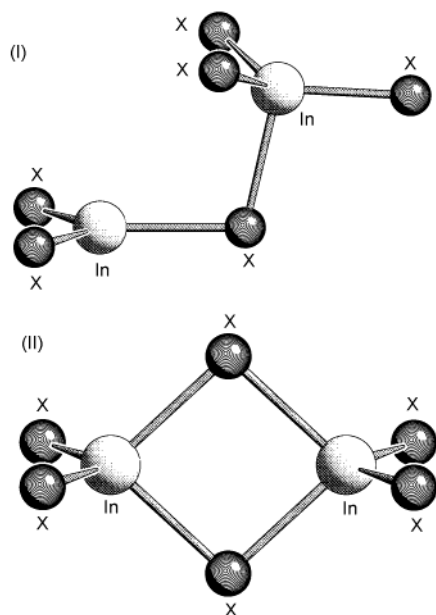

Figure 11. InX_3 dimer structures.

structures. The obtained data allow the generation of elementary mechanisms for chemical etching depending on the used halogen (X = F, Cl, Br, I). Two reaction regimes are found. (i) under low halogenation the In atoms leave the surface as InX (19−35 kcal/mol). The P atoms are removed as P_2 (about 37 kcal/mol) or after combination as P_4 independently of the used halogen. The desorption of formed PF, PCl, PBr, and InX_2 surface species requires a higher energy expense (>50 kcal/mol) or a higher halogenation. The PI removal from the surface by recombinative I_2 and P_2 desorption is more favorable (37

TABLE 1: Binding Energies (kcal/mol) of InX_3 Dimer Structures

X	structure I	structure II
F	33	45
Cl	8	22
Br	3	17
I	1	12

kcal/mol). (ii) Under high halogenation In atoms could leave the surface as InX_3 (F: 21 kcal/mol; Cl, Br, I: 10−7 kcal/mol). However, a relatively stable corrosion phase composed of InX_3 molecules is formed on the surface. P atoms can be removed as PX_3 (20−24 kcal/mol) or PX_2 (26−31 kcal/mol).

Considering only the energetics of surface reactions one could work under high halogen exposure and low temperatures. However, the transport of the etch gas molecules to the surface and the reaction products from the surface is restricted under low temperatures by a corrosion phase composed of InX_3 molecules.[4−6,16] The necessary higher temperatures lead to higher etch rates, a higher halogen consumption, a lower halogen availability, and, finally, a lower surface halogenation. Under low halogenation one should better work with I_2. This halogen requires a lower energy expense for the PI removal. Experimental investigations are necessary for verification of the results.

Supporting Information Available: Dissociation energies of relevant diatomic molecules and basis set superposition errors. This material is available free of charge via the Internet at http://pubs.acs.org.

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