Surface Science 605 (2011) 824–830

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/ locate/susc

Driving forces for the adsorption of cyclopentene on InP(001)

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ARTICLE INFO

Article history:
Received 12 October 2010
Accepted 24 January 2011
Available online 1 February 2011

Keywords:
Organic molecules
InP(001)
III–V semiconductors
Adsorption

ABSTRACT

In this work the interaction of cyclopentene with a set of InP(001) surfaces is investigated by means of the density functional theory. We propose a simple approach for evaluating the surface strain and based on it we have found a linear relation between bond and strain energies and the adsorption energy. Our results also indicate that the higher the bond energy, the more disperse the charge distribution is around the adsorption site associated to the high occupied state, a key feature that characterizes the adsorption process. Different adsorption coverages are used to evaluate the proposed equation. Our results suggest that the proposed approach might be extended to other systems where the interaction of the semiconductor surface and the molecule is restricted to first neighbor sites.

1. Introduction

The study of the adsorption and surface reaction mechanism of organic molecules on semiconductor surfaces has attracted a great deal of interest as they are considered a key issue in the development of advanced electronic devices and sensors for various uses, such as biotechnology, nanoelectronics, high density data storage and medical diagnostics. The variety of organic molecular structures, functionalities and electronic properties is the main reason for the great number of novel applications that might be obtained by the modification of semiconductor surface [1–3]. The production of such devices requires the development of a well defined organic layer on the substrate surface. As such organic layers are basically formed by exposing the substrate surface to organic compounds, the understanding of first stages of the surface-organic interaction is crucial in order to improve the quality of deposited layers. Following the pioneer works by Hamers and co-workers [1], the majority of theoretical and experimental works on this field have addressed the so-called [2+2] cycloaddition reactions of several carbon based molecules and the silicon (001) surface.

For III–V compounds, on the other hand, little is known about the interaction of organic molecules and their bare surface. This is in contrast to the number of possible applications that might be obtained by the proper functionalization of III–V semiconductors. In principle, it is desirable to establish a general rule to help isolate and predict the most probable configuration of a given surface. This was (at least partially) accomplished for bare surfaces with the electron counting rule [4] or other simple approaches, such as the one proposed by Mirbt and co-workers [5].

In this work we investigate the interaction of cyclopentene (C_5H_8) with the indium phosphide (001) surface. Cyclopentene was chosen as it is considered a very good prototype for the study of the organic molecules adsorption, and in particular hydrocarbons, on semiconductor surfaces. This is because cyclopentene has both double and single carbon–carbon bonds. Therefore, it is possible to study changes induced by the molecule on the surface electronic properties upon its adsorption and extend their conclusions to similar systems. Indeed, this is the main reason why the cyclopentene interaction with Si—Si dimers on the Si(001) surface is a well known process. It is well established that this process is characterized by a cycloaddition [2+2] reaction [6–8], i.e., two π bonds from C C and Si Si are broken and two new σ Si—C are created. Indeed, it was recently shown by Ferraz and Miotto [8] that the mechanism observed for the cyclopentene adsorption on Si(001) might be extended to other hydrocarbons like cyclohexene and 1,4-cyclohexadiene. InP(001) surface is an interesting case study as it is known to be a model case for III–V semiconductors. In addition, the surface stoichiometric of the InP surface allows the formation of many different reconstructions and can be explored in order to achieve the required properties [9]. As it is clear from the phase diagram that correlates the surface energy to the chemical potential energy obtained by Schmidt [9], the reconstructions known as (2×2)-1D and (2×2)-2D are the most likely to be observed under P-rich conditions [9]. For In-rich samples, on the other hand, the α, β2 and mixed-dimer reconstructions are found to be the most favorable ones [9].

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doi:10.1016/j.susc.2011.01.027

It is fair to say that InP(001) is interesting in the present context because (i) it shows (like many III–V(001) surfaces) a rich variety of surface reconstructions [9] and (ii) it is one of the few surfaces the interaction of which with organic molecules (namely cyclopentene) has already been well characterized for at least one specific surface structure [10]. In this sense, predictions of what is going to happen on the other surface structures should help to understand chemical trends which might also hold for adsorption on other compound semiconductor surfaces. As many experimental and theoretical works [9,11–13] suggest that InP(001) presents a variety of surface reconstructions, we have extended our studies to the other possible reconstructions, namely the 2×2-1D, 2×2-2D, β2 and α as changes on experimental synthesis might lead to different final states. In addition, the cyclopentene interaction might induce changes in the surface that could result in different order reconstructions. Our aim in this study is to contribute in the understanding of cyclopentene interaction with InP(001). Pursuing this goal, we have obtained a function that governs the adsorption energy of the system and a quantitative evaluation of driving forces for the adsorption process. As this function can be extended to other systems, we understand that it might be used as a general rule for predicting the most probable adsorption configuration of a given molecule on a semiconductor surface.

2. Theoretical modeling

Our calculations are based on density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) [14]. In detail, the surface was modeled in a super-cell geometry, with an atomic slab of nine layers and a vacuum region equivalent to seven atomic layers. On the top side of the slab we placed the cyclopentene molecules and the back surface dangling bonds were saturated with fractionally charged pseudohydrogen atoms. The gas-phase calculations for cyclopentene were made using a cubic unit cell with a lattice constant of 15 Å. The electron–ion interaction between In, P, C and H atoms is described by Projector Augmented Wave (PAW) potentials [15,16] and the electron–electron exchange-correlation interactions were simulated using the generalized gradient approximation (GGA) [17]. The single-particle orbitals were expressed in a plane-wave basis up to the kinetic energy of 450 eV. For the Brillouin-zone summation, $4\times4\times4$ and $2\times2\times1$ Monkhorst–Pack [18] meshes were used for the electronic structure calculations for the bulk and surface, respectively. The atoms were assumed to be in their fully relaxed positions when the forces acting on the ions were smaller than 0.01 eV/Å. The interaction between cyclopentene and the InP(001)surface is investigated considering different adsorption configurations, namely: (a) cis type (hydrogens at the same molecule side), (b) trans type (hydrogens at opposite molecule sides), (c) single bonded and (d) dissociated (hydrogens are dissociated from the molecule and transferred to the mixed-dimer), as schematically shown in Fig. 1.

The most probable adsorption configuration from the energetical point of view was obtained by a direct comparison of the calculated adsorption energies $E(ads)$. The adsorption energy ($E(ads)$) is defined as the difference between the total energy for a given configuration ($E(conf)$) and the energy for the free InP(001) surface plus the total energy for a gas-phase cyclopentene molecule ($E(ref)$), according to the equation: $E(ads)=E(conf)-E(ref)$. We have also estimated the bond energy ($E(bond)$) as a measure of the how strongly the molecule is bonded to the surface. In this work, ($E(bond)$) is defined as the total energy of a given configuration minus the total energy of its constituents (i.e. the free surface and the gas phase molecule) arranged in the same geometry of the adsorbed structure: $E(bond)=E(sys)-E(surf.ads.geom)-E(mol.ads.geom)$. For both $E(ads)$ and $E(bond)$ a negative sign indicates an exothermic process while positive values an endothermic process. Charge difference image plots are obtained as follow: the total charge density of the bare surface and the gas phase molecules (at the adsorbed geometries) are subtracted from the total charge density for a given configuration. This image method allows an investigation of the charge transfer process upon the adsorption of a given molecule.

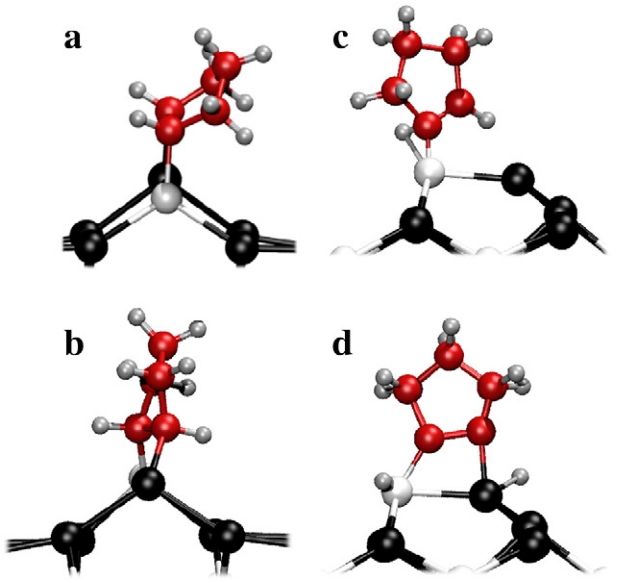

Fig. 1. Schematic representation of the (a) cis type, (b) trans type, (c) single bonded and (d) dissociated adsorption models for cyclopentene on InP(001). Black, gray (light gray) and red (dark gray) large spheres correspond to In, P and C atoms, while small spheres correspond to H atoms.

3. Results

Our density functional calculations indicate that the only exothermic process for the adsorption of cyclopentene on the InP(001)-(2×4) is observed when the mixed dimer structure (Fig. 2(a)) is considered. A complete study of cyclopentene adsorption on mixed-dimer InP surface was recently presented by Passman et al.'s work [10]. In this joint theoretical–experimental work, a series of adsorbed structures are evaluated in order to be compared to reflectance anisotropy spectra and core level shift data. In the following, only a brief comment on the main results is made. For a more detailed discussion, refer to Ref. [10] and references therein. According to the total energy simulations, the most probable configuration from the energetical point of view is represented by a cis type molecule adsorbed on the mixed-dimer (Fig. 2(a)), with an adsorption energy of −0.28 eV. The calculated adsorption energy is relatively low when compared to the cyclopentene adsorption on Si(001), which was found to be around −1.9 eV [8]. This is mainly because of the different nature of the bonds formed upon adsorption of cyclopentene on Si and InP. In the first case (Si) the [2+2] cycloaddition involves the formation of two σ bonds originated from the broken π C C and Si Si bonds. Such σ bonding formation would involve the breaking of the In—P mixed dimer, which was not observed in our calculations. In order to access this possibility, we have considered different values for the In—P mixed dimer bond length. However, we found that the structures produced by increasing or decreasing the In—P mixed dimer length are either energetically unstable or evolve to the final standard mixed dimer structure. In a similar manner, when the dimer cleaved structure was obtained upon hydrogenation of the In and P components of the dimer, the final structure was found to be energetically unfavorable. Therefore our data clearly suggests that the cis type adsorption on the mixed-dimer reconstruction is the most probable structure. This is in agreement with the experimental temperature desorption measurements by Passman and co-workers

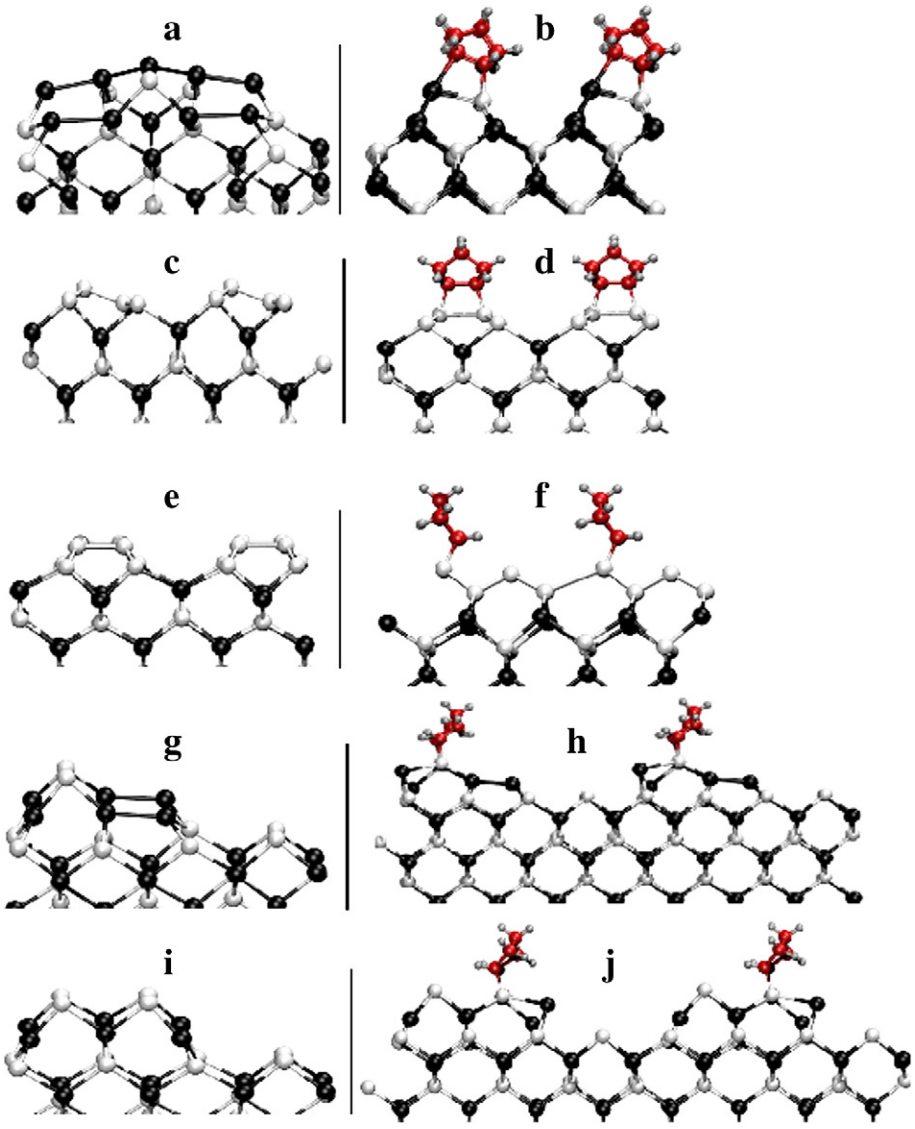

Fig. 2. Schematic view of the (a) InP(001)-(2×4) mixed-dimer surface, (b) cyclopentene adsorption on InP(001)-(2×4) mixed-dimer, (c) InP(001)-(2×2).1D surface, (d) cyclopentene adsorption on InP(001)-(2×2).1D surface,(e) InP(001)-(2×2).2D surface, (f) cyclopentene adsorption on InP(001)-(2×2).2D surface,(g) InP(001)-(2×4) α surface, (h) cyclopentene adsorption on InP(001)-(2×4) α surface,(i) InP(001)-(2×4) β2 surface, (h) cyclopentene adsorption on InP(001)-(2×4) β2 surface. Black, gray (light gray) and red (dark gray) large spheres correspond to In, P and C atoms, while small spheres correspond to H atoms.

[10] suggesting that cyclopentene desorbs around 300–400 K, while a much higher temperature is observed in the case of silicon [2]. This small adsorption energy is also consistent with the low sticking coefficient observed experimentally [10].

Upon adsorption, the main characteristics of the cyclopentene molecule remain unchanged. The bond lengths of C—H and C—C keep its 1.1 Å and 1.5 Å value respectively. On the other hand, the double bonded C C increases its length after adsorption from 1.3 Å to 1.5 Å due to the π bond breaking process. In addition, the plane cyclopentene in the gas phase deforms its $P\hat{C}C$ angle from 180° to around 115° due to the adsorption as can be seen in Table 1.

Besides the mixed dimer structure, we have also considered the (2×2).1D, (2×2).2D, α(2×4) and the β2(2×4) reconstructions. The (2×2).1D surface is characterized by one P—P dimer in a (2×2) reconstruction, as in Fig. 2(c). Similarly to the Si—Si dimer on the Si (001) surface, P—P dimers present a tilt angle that as result of the charge transfer process from the down P atom to the up one and presents, making it a good candidate to investigate the role of tilted dimers on the adsorption of cyclopentene on semiconductor surfaces. The 2×2.2D reconstruction has the same structure, with an extra P—P dimer, but all surface dimers are now flat at the surface (Fig. 2(e)). The α(2×4) reconstruction corresponds to a geometry combining two In dimers in the uppermost atomic layer with P—P bonds in the layer underneath (Fig. 2(g)). Finally, in the β2(2×4) reconstruction one P dimer is added to the α structure, as in Fig. 2(i). For the surface phase diagrams of all these structures, please refer to Ref. [9] and references therein.

Table 1
Adsorption energy and structural parameters for the adsorption of cyclopentene on different InP(001) reconstructions. Adsorption energies E_{ads} are in eV, bond lengths in Å, and bond angles in °. $X\hat{Y}Z$ stands for the angle formed by the X–Y–Z structure, centered in Y.

Structure	E_{ads}	Dimer	P—C	In—C	$P\hat{C}C$	$In\hat{C}C$	$P\hat{P}C$
Mixed dimer	−0.28	2.68	1.9	2.3	114.8	117.1	68.6,80.7
2×2.1D	−1.76	2.46	1.9	–		118.7	76.3,76.3
2×2.2D	−0.83	2.30	1.9		113		78.7,78.9
β2(2×4)	−0.42	2.23	1.9		116.9		78.3,81.1
α(2×4)	−0.21	2.22	1.9		118.6		80.5, 79.1
Si—Si	−1.94	2.36	1.9		120.5		77.7, 77.7

Upon adsorption of cyclopentene on the (2×2).1D (Fig. 2(d)), the P—P dimer gets symmetric, exactly as observed for silicon. The P—C bond lengths indicate the presence of a σ bond and the In—P bond length suggests strength in the P—P bond when compared to the mixed-dimer system. Table 1 summarizes the most important structural and energetic properties for the following discussion. The bond energies obtained following the scheme described on Section 2 for both the adsorption on InP and Si(001) surfaces indicate −1.76 eV for P—P and −1.94 eV for Si—Si, respectively. The similarity between the adsorption energy values might suggest that cyclopentene adsorption on both P—P and Si—Si dimers follows the same reaction paths. However, as discussed above, the adsorption of cyclopentene on Si—Si is characterized by a cycloaddition reaction process whereas the P—P adsorption is related to P charge transfer from the surface to the adsorbate.

A comparison between the dimer bond length at the adsorbed 2×2.1D (2.46 Å) and 2×2.2D (2.30 Å) structures, suggests that the P—P interaction is not just dependent on the dimer's and molecule's chemical elements but also on the dimer's neighborhood. In contrast to symmetric dimers observed for both 2×2.1D and 2×2.2D bare surfaces, the adsorption of cyclopentene on the 2×2.2D structure induces an asymmetry on the back bonds: two of them present a bond length of 3.46 Å, while the remaining two have only 2.22 Å. The presence of an extra dimer results in charge redistribution mainly around the P—P dimer bond and on the adsorption site (as seen on Fig. 3). The P—C bond length of 1.9 Å is not changed upon adsorption, in all considered structures suggesting that the σ type bond is probably unaffected by local changes in the environment. It is interesting to emphasize that the adsorption and bond energies for cyclopentene adsorption on the 2×2.2D are 0.93 eV and 1.25 eV lower than those observed for the adsorption on the 2×2.1D reconstruction.

Upon adsorption of cyclopentene on the α(2×4) (Fig. 2(h)) one of the In atoms recovers its tetrahedral coordination with respect to the neighboring atoms. As the other In atom does not have its charge state changed, they keep the trigonal symmetry. Although we have obtained a high bond energy for the adsorption of cyclopentene on the α reconstruction, the calculated adsorption energy is very low. We believe that these can be attributed to the surface relaxation, as changes in bond lengths and bond angles for the adsorbed molecule are negligible.

In a similar manner, In atoms undergo a sp2–sp3 transition when cyclopentene adsorbs on the β2(2×4) reconstruction. Finally, it is worth pointing out that we have also tried other configurations, where hydrogen atoms are closer to the In dimers. In all considered cases, the In movement towards the sublayer is observed. We believe that this is clear evidence that this relaxation process is governed not only by the electrostatic attraction between the atoms, but it is mainly related to the charge transfer effect discussed above.

Our total energy calculations indicate a much higher adsorption energy for the (2×2)-2D (−1.76 eV) and (2×2)-1D (−0.83 eV) adsorption models when compared to the other considered structures (typically around −0.20 to −0.4 eV). These two reconstructions were already pointed out by Pulci and co-workers [19] as exceptions from the typical semiconductor surface in the sense that they do not obey the electron counting rule. In order to check if the strong adsorption energy of (2×2)-2D and (2×2)-1D arises to the extent from the fact that these surfaces are not really passivated, we present in Fig. 4 the density of states (DOS) of all considered adsorption models. In this figure black (dark) and red (gray) lines correspond to the bare surface and the final adsorption configuration DOS, respectively. Although for some adsorption models, such as β2(2×4), (2×2)-2D (2×2)-1D new surface states in the main gap region are induced upon adsorption, the semiconductor character is evident in all considered models. In this sense, it is fair to say that none of the considered adsorption models present a metallic character.

3.1. Driving forces for the adsorption process

The adsorption energies and structural properties for all considered reconstructions (mixed dimer, (2×2).1D, (2×2).2D, α(2×4) and the β2(2×4)) are summarized on Table 1. Our results show no clear correlation between the adsorption energy and the evaluated geometric properties. It is also clear that the P—C bond length and P$\hat{C}$C bond angles are not affected by the chosen reconstruction, suggesting that regardless the original structure, the molecule interacts with a similar substrate environment. These observations are further supported by the charge

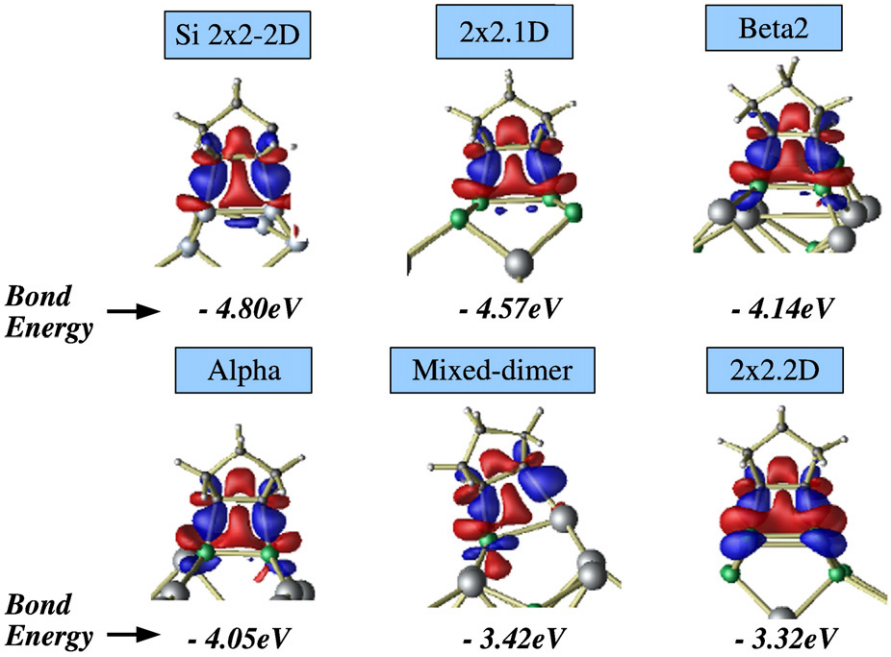

Fig. 3. Charge density difference after cyclopentene adsorption to several InP(001) surface reconstructions. The red regions correspond to charge depletion and the blue ones to charge enhancement. Black, gray (light gray) and red (dark gray) large spheres correspond to In, P and C atoms, while small spheres correspond to H atoms.

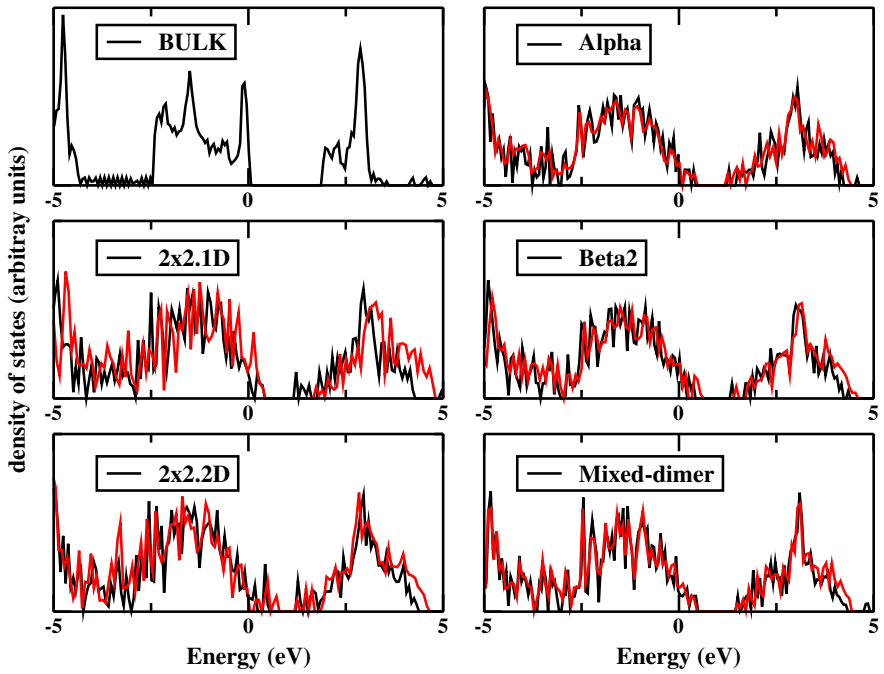

Fig. 4. Density of states (DOS) for bulk InP (top left panel) and cyclopentene adsorption on InP(001)-(2×4) mixed-dimer, InP(001)-(2×2).1D, InP(001)-(2×2).2D, InP(001)-(2×4) α, and InP(001)-(2×4)β2 surfaces. Black (dark) and red (gray) lines correspond to the bare surface and the final adsorption configuration DOS, respectively.

difference image plots presented on Fig. 3. These charge difference images (3) suggest that the charge density distribution above the dimer is very similar for every structure. While the red images over the C C bond, representing the breaking of the π bond are clear in all images, changes in the sublayer charge distributions are noticeable. Our data suggest that the higher the bond energy (as indicated in Fig. 3) the higher the charge density below the dimer is.

As discussed previously, the main difference between 2×2.1D and 2×2.2D adsorbed reconstruction is the P—P dimer back bond asymmetry. This asymmetry induces a charge redistribution and in the final state the charge is mainly concentrated over P atoms. In symmetric structures, such as the 2×2.1D, the charge is concentrated between the dimers. In this sense, our data might be an indication that the bond energy is proportional to the dimer symmetry in relation to the four bonds to the sublayer. It is also clear from Fig. 3 that the charge density transfer is very similar regardless of the considered structure. This is a clear indication that the molecule geometry is little affected by the adsorption process, and hence its remaining groups can be used for further functionalization. We believe that this is also an indication that the present discussion can be extended to similar organic molecules with different chain lengths. In Fig. 5, we present the calculated bond and adsorption energies for each studied reconstruction. Although the bond energy is a key element in the adsorption process, no clear correlation between bond and adsorption energy can be depicted.

It is well known that the thermodynamic concepts of surface energy, surface stress and surface strain are intimately connected, as pointed out by Shuttleworth [20]. Further approximations were introduced by Wolf [21] in order to allow a quantitative estimation of those quantities. More recently, Chang and Hing [22] suggested that the surface strain is proportional to the force on the bond direction. Therefore, in principle it is possible to numerically estimate this quantity. However, the relaxation process during the interaction of the molecule with the surface is not clearly known. We understand that it is not possible to correlate the ionic movement during the minimization process and the real relaxation of the system. Therefore we propose a simple model, which is basically an extension of the original work by Wolf [21], that qualitatively express the surface strain without really calculating it. This simplified model assumes that the lowering of the excess free energy is the ultimate driving force for the relaxation and reconstruction processes [23]. As processes of creation of a surface (by bond breaking) and deformation (by straining) are identical [20], we assume that the higher the number of dangling bonds in a given surface, the higher the strain energy will be. If this is the case, the surface strain for the considered reconstructions should follow the sequence: (2×2).2D, (2×2).1D, mixed dimer, β2(2×4), and α(2×4). We have found that considering the simple relation $\Delta\ E(Sup) = E(sup.livre) - E(sup.geom.Ads.)$, where $\Delta\ E(Sup)$ represents a quantity that is proportional to the surface strain. $E(sup.livre)$ is the total energy of the reconstructed bare InP(001) surface, and $E(sup.geom.Ads.)$ is the bare InP(001) surface with the structure observed after the adsorption of the molecule. Considering this simple approach, the expected trend is observed. This is illustrated in Fig. 6, where it is clear that $\Delta\ E(Sup)$ is not directly correlated to the adsorption energy.

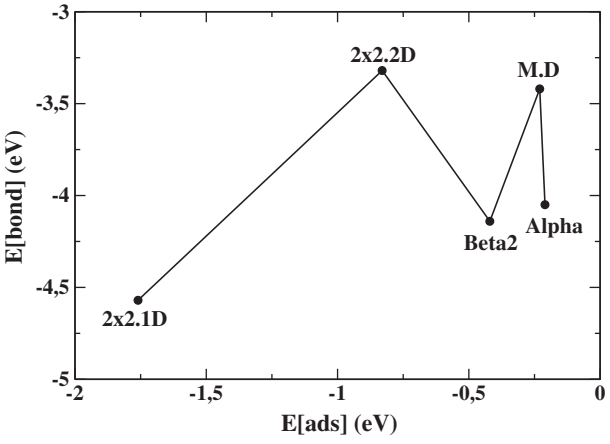

Fig. 5. Relation between the bond energy adsorption energy.

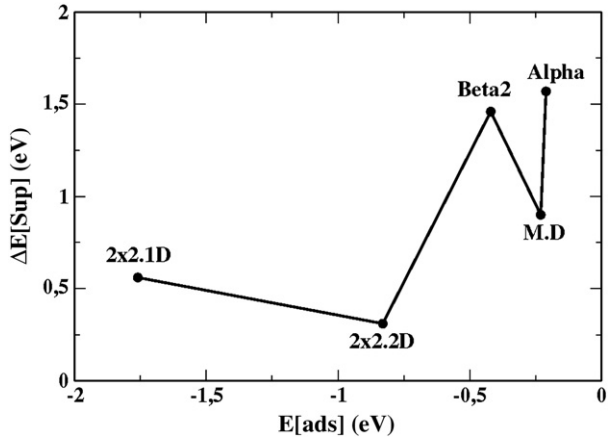

Fig. 6. Relation between $\Delta\ E(Sup)$ (a quantity that is proportional to the surface strain) and the adsorption energy.

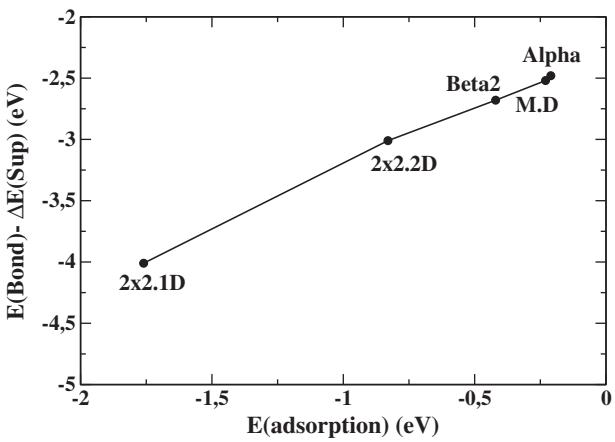

Fig. 7. $\Delta\ E(Sup)$ minus bond energy dependence on the adsorption energy.

As discussed above, the bond energy is directly related to how strong a given molecule is bonded to the surface. In a similar manner, the strain energy, and hence $\Delta\ E(Sup)$, can be thought as the amount of energy that is "expended" in order to allow the adsorption of the molecule. This quantity might play a decisive role in the decreasing of the adsorption energy of a given configuration. When the bond energy is subtracted from $\Delta\ E(Sup)$ this new quantity has an approximately linear behavior with the adsorption energy, as clearly seen on Fig. 7.

A linear fit leads to:

$$(E(bond) - \Delta\ E(Sup)) = a + bE(ads), \quad (1)$$

with $a = -2.26eV$ and $b = 1$.

An exothermic process for the studied system must comply with the condition $(E(ads)) < 0$ and hence $(E(bond) - E(Sup)) < -2.26eV$. Therefore, the difference between the energy gain by the system upon adsorption of the molecule and the strain energy (or its related quantity $\Delta\ E(Sup)$) should be higher than a. For the adsorption of cyclopentene on InP(001) $a = -2.26$ eV. However, there is still one missing point in the picture: the structural changes observed for the adsorbed molecule. Although in the present case the cyclopentene molecule does not experience big structural changes, it is clear that part of the energy gain upon adsorption is also used to deform the molecule. In the present case, the molecule adopts a cis type configuration. Following similar arguments, we propose that the quantity $\Delta\ E(mol) = E(gas.molecule) - E(gas.geom.Ads.)$, i.e. the difference between the total energy of the gas phase molecule and the gas phase molecule with the same geometry observed upon adsorption is proportional to the contribution of the molecule to the surface strain. In the present case, $\Delta\ E(mol)$ was found to be constant, and equal to -2.26 eV. This is in agreement with the fact that the final molecular structure is little influenced by the substrate reconstruction. Therefore, the quantity a in Eq. (1) can be directly identified as $\Delta\ E(mol)$.

From the above discussion, we propose that the function that governs the adsorption energy of any organic molecule in a semiconductor surface is:

$$E(ads) = E(bond) - \Delta\ E(Sup) - \Delta\ E(mol) \quad (2)$$

It is also interesting to note that the differences on charge redistribution observed in Fig. 3 upon cyclopentene adsorption can now be correlated with Eq. (2). The higher the bonding energy, the higher is the charge distribution. This is further evidence of the general character of our proposal.

In order to further explore the general character of this function, we have considered the adsorption of a second cyclopentene molecule on the InP(001) surface, as higher monolayer coverages were observed experimentally [10]. Not surprisingly, for the adsorption of the second molecule, we have found $\Delta\ E(mol) = -2.26eV$. However, as expected, $E(bond)$ and $\Delta\ E(Sup)$ have different values as the adsorption site and the charge distribution are different. In this case $\Delta\ E(Sup)$ is defined as the energy of surface with the geometry observed after the adsorption of the first molecule minus the energy of the surface with the geometry observed after the adsorption of the second molecule. Eq. (2) can be used without restrictions as in the considered case involves the subsequent (and not simultaneous) adsorption of two molecules. In the case of simultaneous adsorption, Eq. (2) has to be re-written as: $E(ads) = E(bond)(site) + E(bond)(site) - \Delta\ E(Sup) - 2\Delta\ E(mol)$, where $2\triangle Emol$ expresses the fact that both adsorbed molecules are little affected by the substrate.

4. Summary

In summary, in this work, the driving forces for the adsorption process of cyclopentene on the InP(001) surface are investigated by first-principle calculations. A series of different adsorption structures are tested. Our calculations suggest that the most probable adsorbed system is the cis type molecule on the InP(001), in agreement with recent experimental results [10]. We propose a simple approach for evaluating the surface strain and based on it we have found a linear equation that governs the adsorption process: $E(ads) = E(bond) - \Delta\ E(Sup) - \Delta\ E(mol)$ Particularly, for cyclopentene adsorption on InP(001), we have obtained a constant value for $\Delta\ E(mol)$, suggesting that indeed the molecule is little influenced by the substrate, and hence its remaining groups can be used for further functionalization. The charge density difference images indicate that the charge distribution is related to bond energy and characterizes the adsorption processes. The evaluation of a second molecule adsorption generalizes the equation for higher surface coverages. This conclusion and the observation of constant $\Delta\ E(mol)$ value qualify the studied equation as general and applicable to different systems.

Acknowledgments

The authors acknowledge financial support from the Brazilian agencies FAPESP, CNPq and CAPES.

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[23] We are aware of other approximations, such as the one proposed by Cammarata (Thermodynamic model for surface reconstruction based on surface stress effects, by R. C. Cammarata, Surface Science, Volume 273, Issues 1-2, 15 June 1992, Pages L399-L402 where the total surface stress (and not the difference between the surface stress and surface energy) is considered to be the driving force for the surface reconstruction. However, we choose to follow the original approach of Dieter Wolf.