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

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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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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, 4×4×4 and 2×2×1 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.

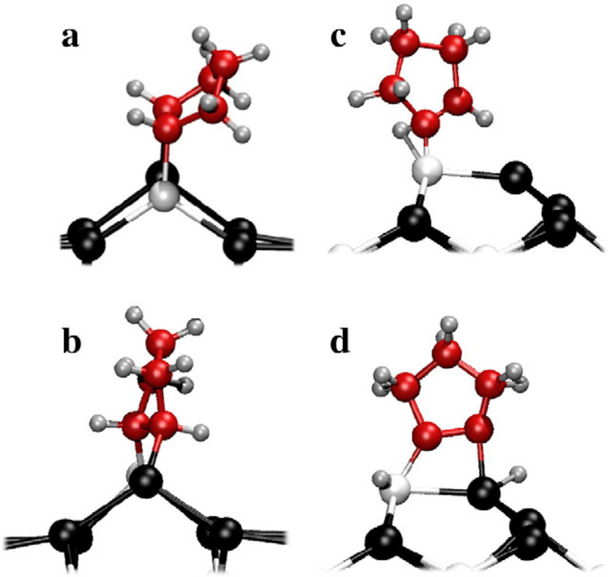

Fig. 1. Schematic representation of the (a) cis type, (b) trans type, (c) single bonded and (d) dissociated adsorption models for cyclopentene on InP(001). Black, gray (light gray) and red (dark gray) large spheres correspond to In, P and C atoms, while small spheres correspond to H atoms.

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