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A theoretical study of c-C_5H_8 adsorption on Ge (0 0 1)-2 × 1 and on dimer vacancies on the surface: Electronic structure and bonding

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ABSTRACT

In this work we analyzed the geometry and the chemical interactions for c-C_5H_8 adsorption on Ge (0 0 1), using density functional theory calculations (DFT). We examined the changes in the atomic interactions using a slab model. We considered two cases, the cyclopentene adsorption on Ge(0 0 1) and on dimer vacancies on the surface. We found an average distance H–Ge, –C–Ge and =C–Ge of 1.50, 1.70 and 1.65 Å, respectively, on dimer vacancies; and an average =C–Ge distance of 2.05 Å on Ge–Ge dimer. We also computed the density of states (DOS) and the DOS weighted overlap populations (OPDOS) corresponding to C–C, C–Ge, C–H, and Ge–Ge bonds. During adsorption the main contribution are the C=C double bond in both cases, and the next C and the H's belonging to this bonds in the case of adsorption on dimer vacancies. The orbital contribution includes participation of the $2p_y$ and $2p_z$ orbitals corresponding to unsaturated C atoms, $2p_z$ corresponding to side saturated C, and the 4p orbitals of Ge for the adsorption on dimer vacancies; 2s and $2p_z$ orbitals corresponding to double bond C atoms, 4s and $4p_z$ orbitals of Ge for the adsorption on Ge(0 0 1).

1. Introduction

There is interest in the surface chemistry of Ge(0 0 1) for its use in microelectronics and for comparisons with the (0 0 1) surface of silicon. Recent experiments examined the formation of organic layers by cycloaddition chemistry involving molecules with four or more carbon atoms on Si(0 0 1), C(0 0 1) and, to a lesser extent, on Ge(1 0 0) surfaces [1].

Sixty years passed since the invention of the point contact transistor by Bardeen and Brattain [2]. The invention of the transistor was a significant event in itself, but it also served to inspire a much larger revolution in the realm of electronics, which continues today. The use of these semiconductor-based electronic devices directed a large number of investigations with the goal of trying to understand the chemical and physical properties of semiconductor interfaces [3].

The microelectronics revolution that was started 60 years ago has grown into an industry that drives much of the world's technology today. Microelectronics use semiconductor materials as their basic building block. These semiconducting solids – such as silicon, gallium arsenide, and germanium – have become ubiquitous. Semiconductor-based devices can now be found in everything from automobiles and home appliances, to means of communication and equipment in our office [4–6].

In the late 1950s, based on LEED measurements, Schlier and Farnsworth [7] proposed that the surface atoms of Si(0 0 1) and Ge(0 0 1) will dimerize resulting in a (2 × 1) reconstruction. The driving force for this dimerization is the reduction in the number of dangling bonds from two to one per surface atom between the unreconstructed and reconstructed surfaces. Along with the dimerization comes the development of an anisotropic surface stress tensor; the surface is under compressive stress along the substrate dimer row direction and under tensile stress perpendicular to the substrate dimer rows.

The dimerization of surface atoms was first imaged on Si(0 0 1) in real-space with STM by Tromp et al. [8] and Hamers et al. [9] in the mid 1980s. Both buckled (asymmetric) and non-buckled (symmetric) dimers were observed in these images. After three decades of intense research activity, the original idea put forth by Schlier and Farnsworth – the reduction of dangling bonds by dimerization – was finally verified by a few real-space images of Si(0 0 1) [10].

Over the past several years the adsorption of unsaturated hydrocarbon molecules on semiconductor surfaces has attracted much attention because of the technological interest of combining the wide range of functionality of organic molecules with the existing semiconductor-based infrastructure [11–14]. Especially the Si(0 0 1) surface has been extensively employed for the investigation of hybrid organic-silicon systems [15–27] whereas only little

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work addressed hydrocarbon adsorbates on the Ge(0 0 1) surface [1,28–30]. There is a general consensus that the reaction of unsaturated hydrocarbons (e.g., alkenes) with Si(0 0 1) takes place via a precursor state, finally forming a [2 + 2] product in which the π bond of alkene and the π bond of a surface dimer interact to produce two σ bonds [18,20,24,25,31].

A clean substrate holder and keeping the pressure of the vacuum system in the low 10^{-10} Torr range during annealing are essential for achieving a well-ordered and properly clean Ge(0 0 1) surface. Most of the defects that remain fall in the category of dimer-vacancy (DV) defects. These dimer vacancies can be found in isolation (A-type DV defects), in neighboring pairs of dimer vacancies within in the same substrate dimer row (B-type DV defects), or in more complicated structures such as the (1 + 2) DV configuration [32]. The (1 + 2) DV defects consist of a single dimer vacancy followed by a normal dimer and a pair of dimer vacancies, respectively. This defect is sometimes denoted in the literature as a "split-off dimer" and exhibits a rather peculiar feature. STM line scans across the (1 + 2) DV defects on both Si and Ge(0 0 1) surfaces reveal that the apparent depth of these defects (∼2 Å) is actually deeper than a single layer (1.4 Å) [32]. The explanation for this observation might be electronic in nature or simply topographic [33]. However, it clearly shows that this type of defect differs distinctively from the A- and B-type DV defects. The large variation in the density of dimer vacancies after cleaning suggests that these types of defects are probably not thermodynamically generated. It is much more likely that the origin of the majority of the dimer vacancies lies in the presence of a small amount of foreign atoms in the subsurface region. Another possibility is that some residual gases such as O_2, H_2, and H_2O etch the germanium top layer during annealing.

Yang studied the clean Ge(0 0 1)-(2 × 1) surface by STM [32] and many different dimer-vacancy (DV) defects and complexes were seen on the surface. Among them the complex consisting of a missing dimer, a twin missing-dimer, and a dimer between them, i.e., the (1 + 2)-DV complex, comprises a great majority.

There are several theoretical and experimental studies about germanium surfaces. Hwang et al. studied chiral adsorption on semiconductor surfaces of diamond, silicon, and germanium, which reconstruct to form similar surface X=X dimmers (X = C, Si, Ge). They investigated the chiral adsorption configurations of styrene on Ge(1 0 0) using STM, thus they showed that dimerization of styrene molecules on germanium produces the enantiomeric (R,R) and (S,S) configurations [34].

Lee et al. used a combination of surface-sensitive techniques to examine the surface reactions of cyclopentene and cyclohexene with the Ge(0 0 1) surface. Bonding configurations were determined by XPS, IR and STM. The strength of surface interactions was also monitored by temperature-programmed desorption. Cyclopentene and cyclohexene react with surface germanium-dimer bonds to yield reaction products that are consistent with a [2 + 2] cycloaddition reaction. This reaction generates rows of the surface complex oriented along the dimer-bond direction of the Ge(0 0 1) surface, which is observed by scanning tunneling microscopy [1].

Cho et al. investigated the adsorption of acetylene, ethylene, and benzene on the Si(0 0 1) and Ge(0 0 1) surfaces by first-principles DFT calculations. They found that the adsorption energies of the three hydrocarbons containing a triple bond, a double bond, and a π-conjugated aromatic ring decrease as the sequence of $C_2H_2 > C_2H_4 > C_6H_6$. They also found that the bondings of acetylene, ethylene, and benzene to Ge(0 0 1) are much weaker than those to Si(0 0 1). As a result, benzene is weakly bound to Ge(0 0 1) while it is chemisorbed on Si(0 0 1), consistent with temperature-programmed desorption data [35].

Miotto et al. compared the interaction processes involved in the adsorption of ethylene on the silicon and germanium surfaces using a first-principles pseudopotential method. Their calculated surface band structure suggests that the adsorption of ethylene does not passivate the surface, with the presence of a surface state due to the adsorbate system in the fundamental gap region [36].

The adsorption and reaction of 1,3-cyclohexadiene with the Ge(1 0 0)-(2 × 1) surface were investigated by Lee et al. [3]. The surface reactions were followed by UPS and HREELS. They found that adsorption of this molecule at 300 K results in the formation of a cycloaddition surface adduct.

Prayongpan et al. investigated the adsorption and reaction of 1,5-cyclooctadiene with the Ge(1 0 0) surface. The subsequent surface reactions were followed by XPS and TPD. The bonding configuration was compared with ab initio calculations. 1,5-Cyclooctadiene reacts with surface Ge dimers to form a four-membered ring structure at the surface at room temperature [37].

Cho and Kleinman performed a detailed DFT study for the adsorption geometry of cyclopentene on non-defect containing Ge (0 0 1) surface at different coverages [31].

Ge deposited on Si(1 0 0) initially forms heteroepitaxial layers, which grow to a critical thickness of ∼3 MLs before the appearance of three-dimensional strain relieving structures. Experimental observations reveal that the surface structure of this Ge wetting layer is a dimer-vacancy line (DVL) superstructure of the unstrained Ge(1 0 0) dimer reconstruction [38].

Li et al. presented tight binding calculations of various aspects of Ge growth on Si(0 0 1) for coverages between one and three monolayers (ML) of Ge [39]. This work follows naturally from their previous paper [40], where they studied the (2 × N) reconstruction which forms at sub-monolayer coverages using first-principles electronic structure techniques.

As the coverage of Ge on Si(0 0 1) approaches 1 ML, it forms the well-known (2 × N) reconstruction, where regularly spaced missing dimers appear in the surface; experimental observations of N show that it typically lies between 8 and 12, with the spacing dependent on growth source (gas source, e.g., GeH_4, or a solid source) and conditions (growth rate and temperature) [41,42]. As the thickness of the deposited layer increases, various further effects are seen on this reconstruction, again depending on growth source and conditions for their onset: the value of N decreases [42–44]; the missing dimers align in neighbouring dimer rows to form straight trenches [43,44]; a new, patch-like reconstruction with a double periodicity (called the (M × N) reconstruction) [41,45–46]; the roughness of step edges changes (with the different step types eventually becoming equally rough, leading to steps running along the elastically soft (1 0 0) and (0 1 0) directions) [43]; and finally three-dimensional structures such as "hut" pits and clusters form [47,48].

The objective of the present work is to compare the adsorption of cyclopentene (c-C_5H_8) on Ge(0 0 1) reconstructed surface ([2 + 2] cycloaddition) and on a dimer vacancies on the same surface. The selected DFT methodology allows us to study the changes in atomic orbitals, chemical bonding and electronic structure.

2. The adsorption model and the computational methods

The adsorption geometries and the electronic densities were calculated by means of the ADF-BAND2000 program (Amsterdam Density Functional) [49] program using the Kohn–Sham Hamiltonian with the gradient-corrected Becke exchange [50] potential together with the correlation potential of Perdew [51] and the unrestricted scheme to obtain spin-polarized wave functions. BAND contains a method for calculations on periodic systems in which all aspects of numerical precision are efficiently controlled [52]. Full electron Slater basis sets of triple-ξ quality contained in the ADF-BAND package were used. The basis set of Ge consisted of

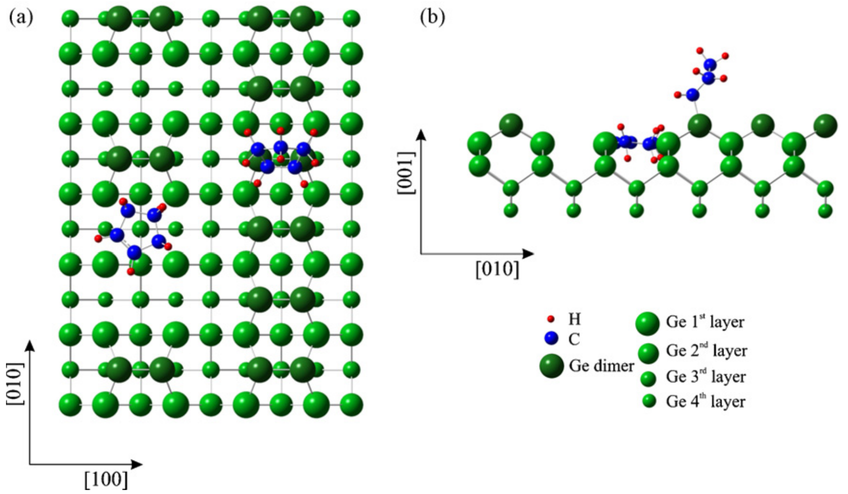


Fig. 1. (a) Top and (b) Side view of cyclopentene [2 + 2] adsorption on Ge(0 0 1) and on a 1 + 2 DV.

4p- and 4s-orbitals. The *k*-points set were generated according to the geometrical method of Ramirez and Böhm [53,54]. In order to increase the computational efficiency, the innermost atomic shells of electrons are kept frozen for every atom except hydrogen, since the internal electrons do not contribute significantly to the bonding. We used a supercell containing 42 atomic sites in a diamond like lattice to model the Ge surface by a two dimensional slab of finite thickness, so as to better simulate the semi-infinite nature of the semiconductor surface. A four-layer slab was employed as a compromise between computational economy and reasonable accuracy. To test the effect of slab thickness on the electronic structure, we performed several calculations considering 4–12 Ge layers. The small cell used here was capable of properly describing the system and the use of more layers does not add a considerable improvement in the results. We also included pseudo hydrogen's for passivating the down Ge atom. The molecule was adsorbed on

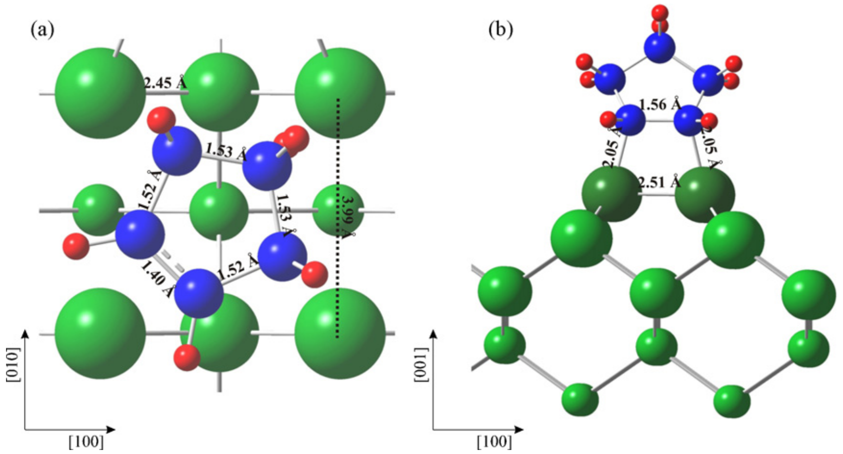


Fig. 2. (a) Bond distances in c-C_5H_8 adsorption on Ge(0 0 1) with DV. (b) Bond lengths in cyclopentene [2 + 2] cycloaddition adsorption on Ge(0 0 1).

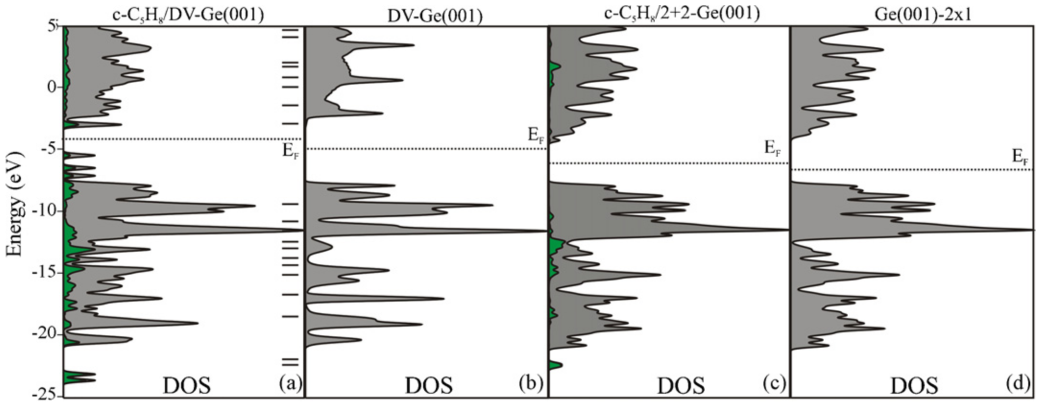


Fig. 3. (a) Total DOS of c-C_5H_8 on Ge(0 0 1) with DV. (b) Total DOS of bare DV containing Ge(0 0 1) surface. (c) Total DOS of c-C_5H_8 on Ge(0 0 1) 2 × 1. (d) Total DOS of bare 2 × 1 reconstructed Ge(0 0 1). The tick marks show the electronic levels of a monolayer of c-C_5H_8.

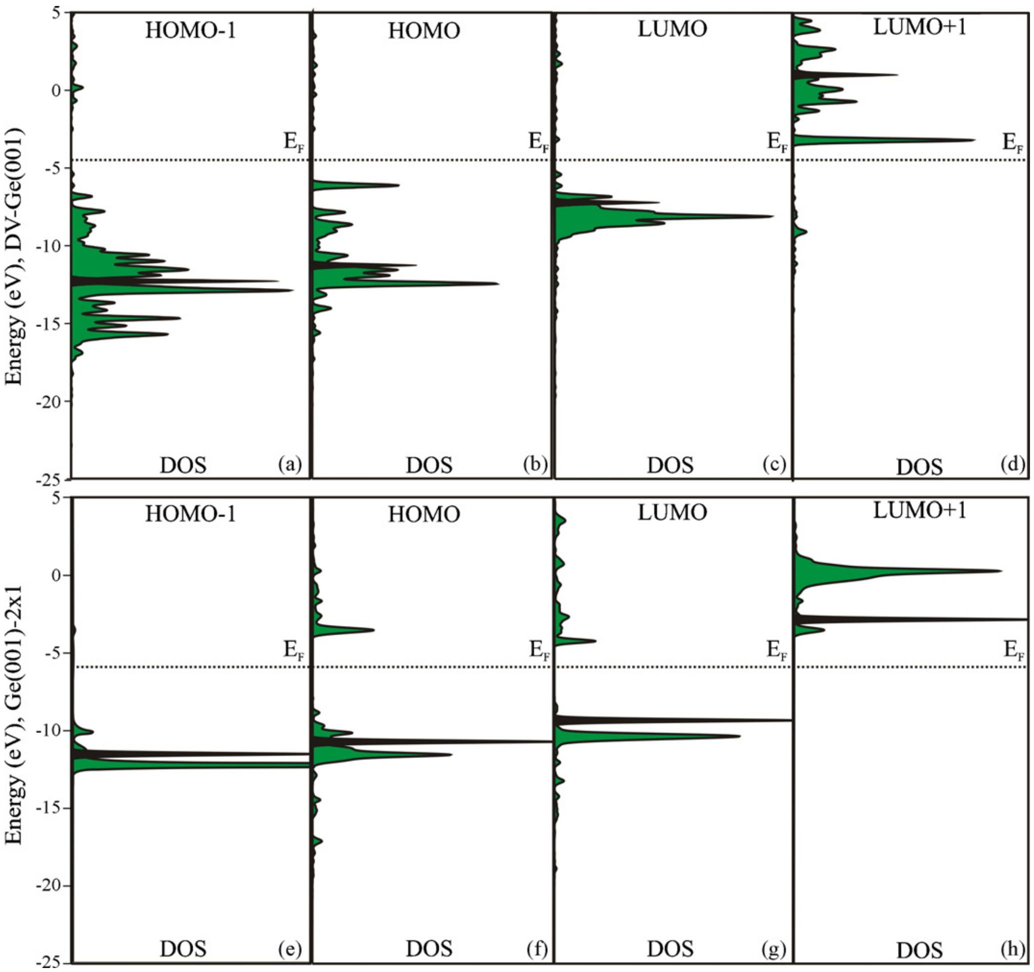


Fig. 4. Frontier orbitals contribution to DOS curves of adsorpted c-C_5H_8. (a) HOMO − 1, (b) HOMO, (c) LUMO and (d) LUMO + 1 for adsorption on DV. (e) HOMO − 1, (f) HOMO, (g) LUMO and (h) LUMO + 1 for [2 + 2] adsorption.

one side of the slab with a 4 × 4 × 4 reciprocal space grid in the supercell Brillouin zone [55–57].

We considered two cases, the cyclopentene adsorption on a (1 + 2) DV consisting of a missing dimer, a twin missing-dimer, and a dimer between them where the molecule is adsorbed parallel to the surface, and the adsorption following a [2 + 2] cycloaddition in which c-C_5H_8 locates above the Ge–Ge dimer interacting with them.

The adsorption energies were calculated with the following total energy difference:

$$\Delta E_{\mathrm{ads}} = \left| E\left(\frac{C_5H_8}{\mathrm{Ge}}\right) - E(C_5H_8) - E(\mathrm{Ge}) \right|$$

where $E(C_5H_8/\mathrm{Ge})$, $E(C_5H_8)$ and $E(\mathrm{Ge})$ are the molecular energy on the slab, the molecular energy and the bare slab total energy, respectively [58].

The density of states (DOS) of both c-C_5H_8 and Ge surface and the orbital overlap population (OPDOS) curves between atoms and orbitals were calculated in order to analyze the adsorbate–substrate interactions. The DOS curve is a plot of number of orbitals per unit volume per unit energy. The OPDOS curve is a plot of the overlap population weighted DOS versus energy. Integration of the OPDOS curve up to the Fermi level (E_F) gives the total overlap population of the bond specified [59]. Looking at the OPDOS, we may analyze the extent to which specific states contribute to a bond between atoms or orbitals. The overlap population (OP) shows the degree of bonding of two specified atoms. A positive number means a bonding interaction, while a negative number means an antibonding interaction. When computing the DOS and OPDOS the system is divided into two fragments, consisting of the surface and adsorbate, respectively. This enables us to compare the changes between the bare surface, the adsorbate, and the composite adsorbed system [60]. Integration of the OPDOS curve up to the Fermi level gives the total OP.

3. Results and discussion

The electronic structure of an isolated c-C_5H_8 molecule can be described taking into account 15 valence orbitals, 14 of them normally occupied. All the occupied molecular orbitals are of closed-shell structure [61].

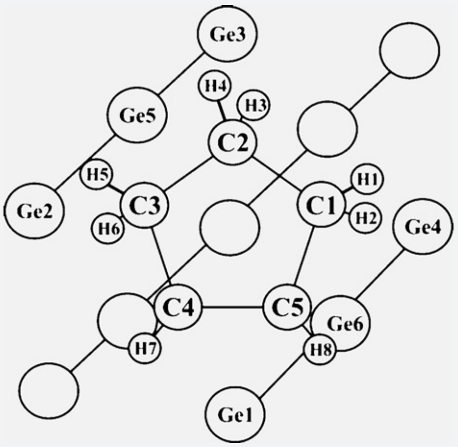
The molecule-surface distance and the molecule geometry were optimized to get the minimum total energy in both c-C_5H_8 on Ge(0 0 1) and c-C_5H_8 on dimer vacancies. In Fig. 1 the studied sur-

Table 1
Orbital electron occupation.

	Adsorption on DV		[2 + 2] Cycloaddition	
	Isolated c-C_5H_8	c-C_5H_8/Ge(0 0 1)	Isolated c-C_5H_8	c-C_5H_8/Ge(0 0 1)
HOMO − 1	2	1.504	2	1.974
HOMO	2	1.362	2	1.372
LUMO	0	0.152	0	1.172
LUMO + 1	0	0.058	0	0.004

Table 2
Overlap populations.

Bond	C_5H_8/DV-Ge(0 0 1)	C_5H_8 monolayer	Surface Ge	Inner Ge	Bulk Ge
C1–C2	0.661	0.737			
C2–C3	0.699	0.737			
C3–C4	0.762	0.777			
C4–C5	0.956	1.260			
C5–C1	0.704	0.777			
C1–H1	0.523	0.803			
C1–H2	0.565	0.803			
C2–H3	0.424	0.816			
C2–H4	0.448	0.816			
C3–H5	0.477	0.802			
C3–H6	0.325	0.803			
C4–H7	0.633	0.812			
C5–H8	0.445	0.812			
Ge1–Ge2	0.000		0.040	0.000	0.000
Ge1–Ge6	0.188		0.645	0.645	0.633
Ge4–Ge6	0.363				
Ge2–Ge3	0.133				
C4–Ge1	0.266				
C5–Ge1	0.390				
H8–Ge1	0.266				
H7–Ge1	0.209				
C5–Ge6	0.378				
H8–Ge6	0.078				
C1–Ge4	0.544				
H1–Ge4	0.245				
C2–Ge3	0.126				
H3–Ge3	0.238				
C3–Ge3	0.151				
C3–Ge2	0.537				
H5–Ge2	0.322				
H6–Ge3	0.328				
H6–Ge2	0.229				



face and the adsorbed molecules are shown. A detailed view of the adsorption geometries and bond lengths is shown in Fig. 2(a) and (b) for both situations. When cyclopentene is adsorbed on reconstructed Ge(0 0 1) the molecule is placed tilted up on the Ge–Ge dimer with a =C–Ge distance of 2.05 Å. On dimer vacancies the molecule adopts a semi planar ring location, with an average H–Ge, –C–Ge and =C–Ge distances of 1.50, 1.70 and 1.65 Å, respectively, these results agree with experimental and DFT studies [35,37,62,63]. The computed adsorption energy was 1.97 eV for cyclopentene on dimer vacancies being the [2 + 2] adsorption 0.94 eV more stable which is close to the values reported by Lee et al. [1].

3.1. The chemisorption system

Fig. 3 shows the DOS plots for c-C_5H_8/Ge (0 0 1) systems. The tick marks (Fig. 3a) show the electronic levels of a hypothetical two dimensional monolayer of planar c-C_5H_8 and perpendicular c-C_5H_8. All the levels lie at the same energy as they have in the isolated molecular specie. We found no adsorbate–adsorbate interaction in this hypothetical network. Upon adsorption the substrate might mediate this interaction and hence a non-interacting system in the vacuum turns into interacting. Such long-range interaction was considered for the adsorption of phenylglycine on metallic Cu(1 1 0) [64] where the adsorbates were separated 10 Å. In our case, with a semiconductor surface and an average distance between adsorption sites of about 20 Å (that means the distance between 1 + 2 DV sites), this long-range interaction was not considered.

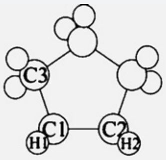
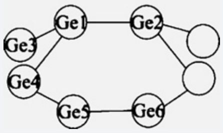
Fig. 3(a) and (c) shows the whole system after chemisorptions, c-C_5H_8 on the Ge (0 0 1) slab for both cases. The shaded curve shows the contribution of the states of the chemisorbed molecule. To discard the interactions between adsorbates we performed additional calculations using half of the original c-C_5H_8 coverage, obtaining similar results. Fig. 3(b) and (d) shows the DOS curve of the bare Ge surface slab model with and without dimer vacancies. Comparing DOS curves between −25 and 5 eV in Fig. 3(a) and (c), we can see the bands corresponding to c-C_5H_8 spreads out after adsorption due to the interaction between orbitals from the molecule and the surface.

3.2. Adsorbate frontier orbitals analysis

More information is obtained when we look at what happens to each molecular orbital of c-C_5H_8 upon adsorption. The contributions to the DOS of each of the c-C_5H_8 frontier orbitals are shown in Fig. 4. The horizontal sticks display the energy of the molecular orbitals in the isolated planar species, from HOMO − 1 orbital to LUMO + 1 orbital.

Almost all the molecular orbitals of c-C_5H_8 interact with the semiconductor surface, except those lying lower in energy. After adsorption, the whole HOMO band is spread over ca. 10 eV and approach 30% of its DOS is pushed up above the Fermi level in the case of adsorption on Ge–Ge dimer. We can clearly see the dispersion corresponding to the bands, these are due to an important interaction with the Ge surface. Table 1 contains the main frontier orbitals electronic occupation for isolated and adsorbed cyclopentene. The more visible effects for both cases are the HOMO electronic depopulation and partial LUMO electronic occupation after chemisorption, initially empty for the isolated molecule. The c-C_5H_8 interacts strongly with this surface.

Table 3
Percent change in OP and OP of bonds formed after [2 + 2] cycloaddition on Ge(0 0 1).

Bond	c-C_5H_8/[2 + 2]-Ge(0 0 1)	
C1=C2	−27.8%	
Ge1-Ge2	−18.8%	
Ge1-Ge3	−1.5%	
Ge4-Ge5	1.2%	
Ge5-Ge6	−1.8%	
C1-Ge1	0.580	
C2-Ge2	0.574	

3.3. Bonding analysis

Tables 2 and 3 collect the OP values for selected bonds following the numbering in the inserted scheme in the cases of DV (dimer vacancies) and [2 + 2] cycloaddition adsorption on the reconstructed Ge surface.

In the case of adsorption on DV of the Ge(0 0 1) surface, we collected the OP values in Table 2; thus, we can clearly see that c-C_5H_8 is adsorbed to the surface bonded mainly by its lateral saturated carbons (C1 and C3) and its hydrogen atoms H3, H4, H5, H6 and H8. The OP value of the C2–H3, C2–H4, C3–H5, C3–H6 and C5–H8 bonds decrease approximately 50% after adsorption, indicative of a weakening of these bonds that interacts directly with Ge atoms. The OP for other C–C, C=C and C–H bonds, decrease less significantly (less than 35%).

The strong adsorbate–surface bonding requires that both molecular and Ge–Ge intrinsic bonding strength decrease. The Ge–Ge surface bonds are weakened between 50 and 80% approximately (see Table 2).

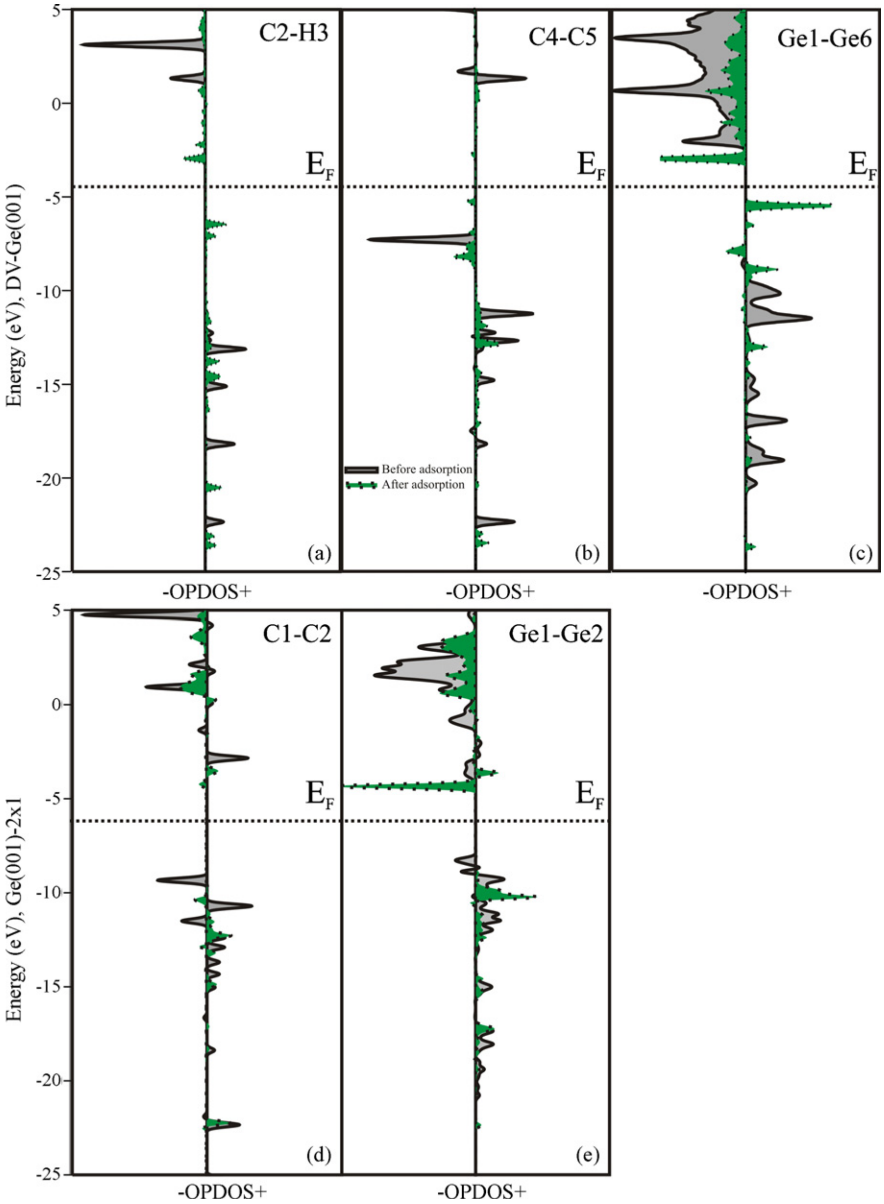


Fig. 5. OPDOS curves for selected bonds before and after adsorption. (a) C4–H3 bond, (b) C4–C5 bond, (c) Ge1–Ge6 bond, for adsorption on DV; (d) C1=C2 bond, (e) Ge1–Ge2 bond, for [2 + 2] adsorption on Ge(0 0 1).

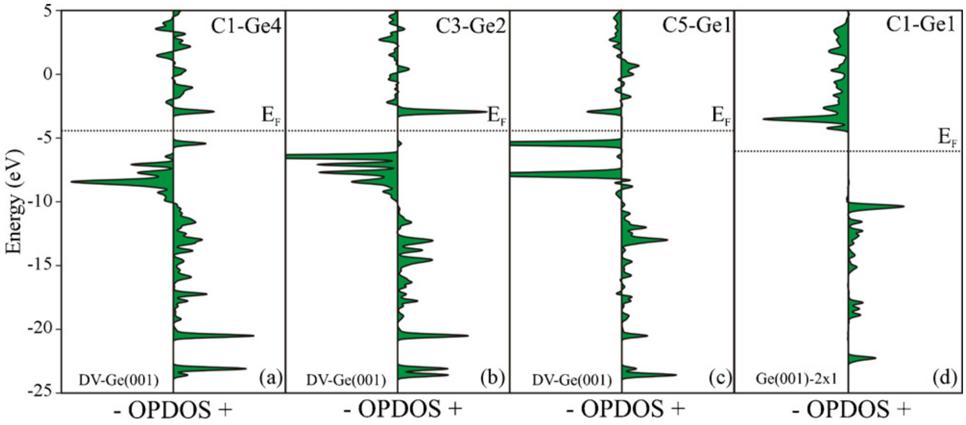


Fig. 6. (a) OPDOS curve for C1–Ge4 bond, (b) OPDOS curve for C3–Ge2 bond (c) OPDOS curve for C5–Ge1 bond, for adsorption on DV. (d) OPDOS curve for C1–Ge1 bond, for [2 + 2] adsorption on Ge(0 0 1).

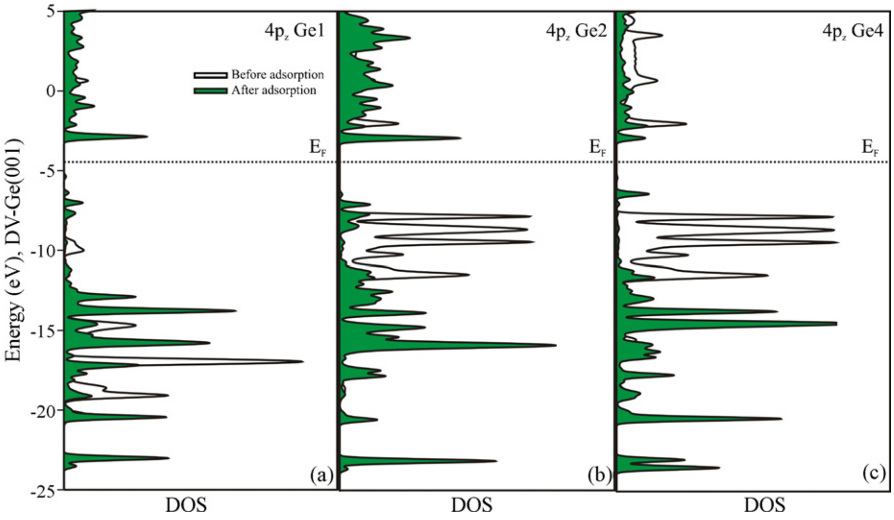


Fig. 7. Orbitals contributions to DOS before and after adsorption on DV of Ge(0 0 1). (a) $4p_z$ orbital contribution for Ge1. (b) $4p_z$ orbital contribution for Ge2. (c) $4p_z$ orbital contribution for Ge4.

Table 4

Percent change in atomic orbital occupations for the c-C_5H_8/DV-Ge(0 0 1) chemisorption system and for the c-C_5H_8/[2 + 2]-Ge(0 0 1) chemisorption system.

DV	s (%)	p_x (%)	p_y (%)	p_z (%)
H1	−22.28			
H2	−27.28			
H3	−28.70			
H4	−22.97			
H5	−20.50			
H6	−32.65			
H7	−15.27			
H8	−26.75			
C1	−2.90	−10.22	−15.74	−12.43
C2	−3.41	−15.78	−20.90	−34.07
C3	−5.52	−21.57	−14.61	−31.23
C4	−1.95	−6.02	−16.69	−21.96
C5	−5.12	−12.45	−25.56	−19.19
Ge1	−31.25	−54.93	−23.13	−57.15
Ge2	−30.67	−16.55	−39.80	−67.12
Ge3	−21.08	0.25	58.00	−35.24
Ge4	−21.43	−18.31	−3.21	−62.63
Ge5	−19.25	−39.18	−24.25	−24.24
Ge6	−12.16	−17.02	−44.03	−31.13
[2 + 2] Cycloaddition				
C1	−5.51	−2.37	−1.24	4.17
C2	−5.55	−7.52	3.91	4.28
Ge1	−7.20	4.58	−2.55	8.37
Ge2	−6.95	4.57	−2.51	8.22

In the case of [2 + 2] adsorption, analyzing the data in Table 3, we can see that cyclopentene is adsorbed to the Ge(0 0 1) surface bonded mainly to the Ge–Ge dimer by its unsaturated carbon atoms (C1 and C2). The OP value of the C═C bond decrease approximately 28% and the Ge1–Ge2 bond decrease about 19% after adsorption process.

The OPDOS curves before and after the adsorption for: C2–H3, C4═C5 and Ge1–Ge6 on DV of the Ge(0 0 1) surface; and C1═C2 and Ge1–Ge2 on the Ge(0 0 1) surface are shown in Fig. 5. The contributions to the right of the vertical axis are bonding between the specified atoms, and to the left are antibonding. In Fig. 6 the OPDOS curves for C–Ge and H–Ge formed bonds are shown. The C–Ge OPDOS curves present two sharp peaks below the Fermi Level (between −25 and −15 eV) corresponding to the s orbitals of c-C_5H_8 interacting with the surface. We can also notice that C1–Ge4 and C1–Ge1 are the stronger bonds because the OPDOS curves present almost bonding contributions.

3.4. Orbital by orbital contribution to the bonds

To obtain further information about the adsorbate–surface interaction, we studied the contribution to chemisorption of the individual atomic orbitals of the H, C and Ge atoms. The corresponding atomic orbital occupations are displayed in Table 4 for

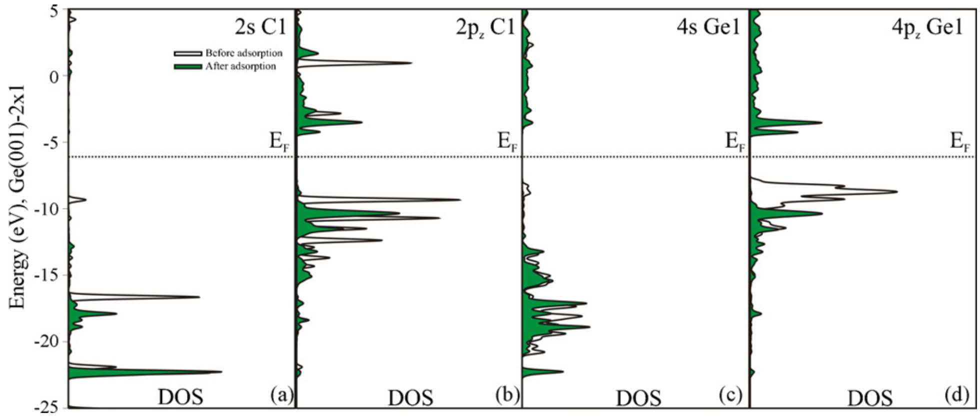


Fig. 8. Orbitals contributions to DOS before and after [2+2] adsorption on Ge(0 0 1). (a) 2s orbital contribution for C1. (b) $2p_z$ orbital contribution for C1. (c) 4s orbital contribution for Ge1. (d) $4p_z$ orbital contribution for Ge1.

adsorption on DV and on reconstructed surface. In adsorption on dimer vacancies we can see a significant decrease of Ge $4p_z$ and $4p_x$ orbitals OP values after c-C_5H_8 adsorption. Fig. 7 confirms this behavior where $4p_z$ orbitals contributions to total DOS of Ge1, Ge2 and Ge4 are also shown. We must emphasize that intensity $4p_z$ orbital band decrease due its participation in the adsorption process.

In [2 + 2] cycloaddition, we can see an important participation of the 4s and $4p_z$ orbitals corresponding to Ge–Ge dimer, the olefinic carbon atoms interact with 2s and $2p_z$ orbitals, Fig. 8 shows the partial DOS contribution of this orbitals before and after c-C_5H_8 adsorption.

4. Conclusions

In this work we analyzed the electronic structure changes and bonds formations during c-C_5H_8 adsorption on Ge(0 0 1) surface with and without DV using DFT calculations. On DV, the c-C_5H_8 adsorbs with its ring parallel to the surface while on Ge–Ge dimers the adsorption geometry is tilted up. The molecule binds to the surface mainly through unsaturated carbons, and in the case of the adsorption on dimer vacancies its hydrogen atoms too. A decrease in the C═C, C–H and Ge–Ge bonds strength is detected, and the formation of ═C–Ge and H–Ge bonds is observed, describing the basic interactions during chemisorption. We also found that $2p_y$ and $2p_z$ orbitals corresponding to unsaturated C atoms, $2p_z$ corresponding to side saturated C, and the 4p orbitals of Ge for the adsorption on dimer vacancies; 2s and $2p_z$ orbitals corresponding to double bond C atoms, 4s and $4p_z$ orbitals of Ge for the adsorption on Ge(0 0 1) play an important role in the bonding between c-C_5H_8 and the surface.

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