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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