Applied Surface Science 335 (2015) 198–207

Contents lists available at ScienceDirect

Applied Surface Science

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

# The process of dissociation of $Cl_2$ molecule on the Ge(0 0 1)-p(1 × 2) surface

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ARTICLE INFO

*Article history:*
Received 6 January 2015
Received in revised form 8 February 2015
Accepted 8 February 2015
Available online 16 February 2015

*Keywords:*
Germanium
Chlorine
Adsorption
Dissociation
Surface relaxation and reconstruction
Density functional calculations

ABSTRACT

In this paper, we analyze theoretically four possible reaction paths during dissociative adsorption of chlorine molecule at the germanium surface. We have calculated the temporary atomic structures, local density of states and spatial distributions of charge density during the processes of dissociation and adsorption. Depending on the reaction path the properties of the system in the process can differ significantly from the final state.

## 1. Introduction

The question how halogens react with semiconductor surfaces is of fundamental interest. This reaction also plays an essential role in such technologically important processes as semiconductor device fabrication. The chemisorption of halide molecules on semiconductor surfaces is an important initial stage in many surface reactions. Chemisorption of $Cl_2$ on Ge surfaces provides an example of such a process. At the (0 0 1) surface of Si and Ge, halide molecules can dissociate, and atoms usually will be adsorbed at the substrate dimer dangling bonds without breaking bonds between surface dimer atoms. Scanning tunneling microscopy (STM) experiments indicate that adsorption of atoms resulting from dissociated molecule is possible on both sides of the same dimer or on neighboring dimers. The first configuration is observed more frequently [1,2].

There are fewer studies of adsorption of halogens on Ge surfaces than of adsorption on Si or GaAs. Hence it is important to verify, if the phenomena at surfaces of different semiconductors are similar. The (0 0 1) surfaces of Ge and Si reconstruct in a similar way [3]. The p(1 × 2) structure is known to be found at the room temperature for both Ge(0 0 1) and Si(0 0 1). Adsorption of $Cl_2$ on Si(0 0 1) was examined theoretically in [5–8]. The adsorption of $Cl_2$ on germanium surface was investigated in Refs. [9,10]. The effect of isolated halogen atoms on the Ge(0 0 1) surface was discussed by Shah et al. [4]. Okada et al. [5] studied the process of dissociation of chlorine molecule on Si surface in detail.

The aim of the present investigation is to consider the properties of the $Cl_2$ molecule and the substrate surface during the time of dissociative adsorption on Ge(0 0 1)-p(1 × 2) surface.

## 2. Method of calculation

In this paper, we present calculations performed using the local-orbital minimal-basis technique [11,12] based on the density functional theory. The FIREBALL code [13,14] was used for computations. The ion cores were simulated by norm-conserving pseudopotentials, calculated using the FHI98PP package [15]. The Ge and Cl pseudopotentials were constructed using the scheme of Troullier and Martins [16] and Hamann [17], respectively. Exchange-correlation contributions were introduced within the local-density approximation (LDA) [18]. Atomic orbitals of the $sp^3$ basis used in FIREBALL computations for Ge were confined to the regions limited by atomic radii of 3.80 a.u. for *s* orbitals, and 5.25 a.u. for *p* orbitals. This approach yielded the lattice constant of 5.638 Å, bulk modulus of 70 GPa, and the main energy gap of 0.45 eV for Ge crystal. Respective experimental values are 5.657 Å for lattice

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http://dx.doi.org/10.1016/j.apsusc.2015.02.055

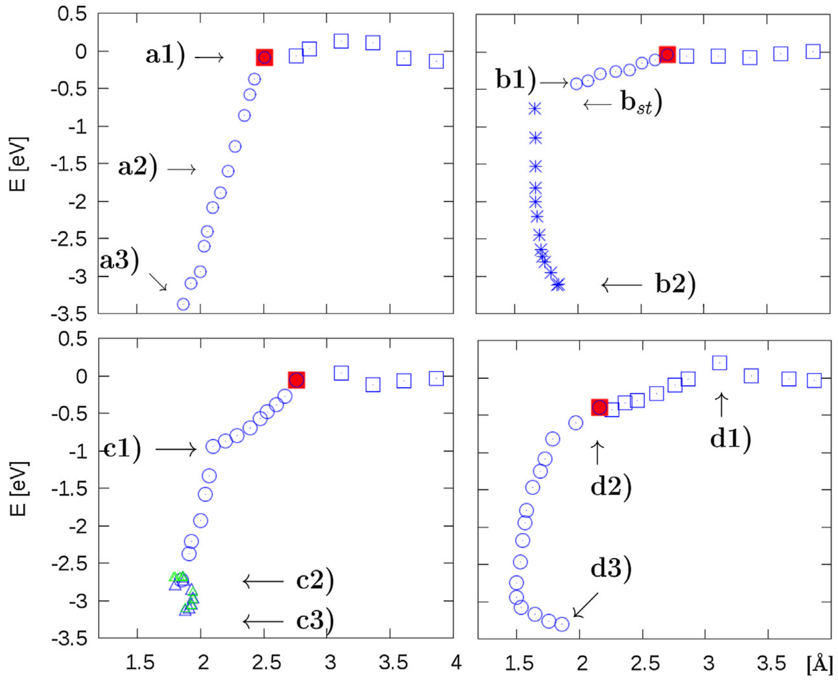

**Fig. 1.** Energy of $Cl_2$ and the substrate versus height of the molecule above the surface related to a sum of energies of an isolated molecule and the substrate. Panels a, b, c, and d present different paths of reaction illustrated in Figs. 3, 6, 8 and 10.

constant, 68.87 GPa for bulk modulus, and 0.664 eV for main energy gap. The Cl orbitals fireball radii were taken equal to 3.0 a.u. for *s* orbitals, and 4.0 a.u. for *p* orbitals. This allows to reproduce the length of chlorine molecular bond of 1.98 Å. All the presented surface-structure calculations were performed for a p(4 × 4) super-cell.

In our calculations, we used a slab built of 12 atomic layers of Ge. The dangling bonds of the bottom Ge layer were saturated by H atoms, and the number of atoms in the p(4 × 4) super-cell was 226 (including 2 atoms of chlorine molecule). The eight lowest Ge layers and H atoms were fixed in the course of MD simulations. In FIREBALL calculations, 18 special k-points were used for molecular dynamics tests of $Cl_2$ molecule stability above Ge(0 0 1) surface and also for relaxation. The dissociation process was simulated with time step of 0.5 fs.

## 3. Results

In order to investigate of behavior of chlorine molecule at germanium surface we performed initially molecular dynamics calculations at room temperature. They have shown that $Cl_2$ molecule dissociated only in few geometrical orientations with respect to the substrate surface: parallel and above the dimer (further case a), perpendicular to the dimers and above lower dimer atoms (case b), diagonally between lower and upper atoms of neighboring dimers (case c), and parallel and between the dimers from alternative rows (case d). The other orientations, suggested by others for chlorine molecule dissociation at silicon surface [2,7], were not detected in our molecular dynamics tests. After finding the orientations allowing to initiate the process of dissociation, the Cl/Ge(0 0 1) system has been relaxed in order to determine minimum-energy configurations. The adsorption energy value of ordering which depends on molecule orientation is *E-a* >*E-d* >*E-b* ≥ *E-c*. This differs from results obtained in [2,7] for Cl/Si(0 0 1) system where is *E-a* >*E-b* >*E-d* >*E-c*. for chlorine adsorption on silicon. There exists a slight energy barrier preventing chlorine molecules to approach the germanium surface (from ∼ 0.1 eV in case b, to ∼ 0.3 eV in case d). If a $Cl_2$ molecule overcomes this energy barrier (Fig. 1, a–d, circle in square), it moves closer to the surface, but it will not necessarily dissociate (case b). The existence of this energy barrier is similar to that obtained for adsorption at silicon surface [7]. However some studies imply, there is no energy barrier for the reaction of dissociation of $Cl_2$ and $F_2$ on Si(0 0 1) [5]. It is also possible, that the molecule with little kinetic energy would physisorb at the surface (case b), too high over the surface to dissociate (see Fig. 2).

The process of dissociation can start if the molecule reaches the position near enough to the surface, no more than 0.8 Å above final position of adsorbed chlorine atoms and in contact with at least one dangling bond. When the molecule is so near to the surface, its density of states appear to be substantially modified by the influence on the surface. At the same time the surface atomic and electronic structure is changed. Finally, after dissociation and adsorption of chlorine ions the Cl/Ge(0 0 1) system relaxes and reconstruction of the substrate surface layer is observed, very likely as in case of adsorption of single chlorine atom [4]. The tilting angle of the dimer on which at least one atom is adsorbed is reduced. Hence, the changes in the density of states of the surface layer can be observed.

The dimers without adsorbed Cl atom are not noticeably changed. The tilting angle of non-adsorbed dimers changes less than 1° and electronic structure of these dimers does not change visibly (Figs. 3–5). This means a little gap in the surface density of states at the Fermi level is preserved, as in case of clean Ge(0 0 1)-p(1 × 2) surface [19,20].

In what follows we describe different possible reaction paths of $Cl_2$ to the surface. Presented are simulated possible atomic and

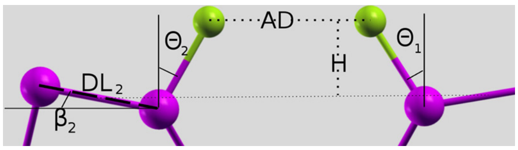

**Fig. 2.** The side view of atomic structure of the Ge(0 0 1)-p(1 × 2) surface with dissociatively adsorbed $Cl_2$ molecule. Parameters of atomic structure are indicated.