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The process of dissociative adsorption of fluorine on Ge(001) surface

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ABSTRACT

The process of dissociation of a fluorine molecule on the (001) surface of germanium has been analyzed using density functional theory. Initial orientations of the F_2 molecule with respect to the substrate leading to its dissociative adsorption have been identified. Reaction paths at p(1 × 2) and c(2 × 4) reconstructed Ge(001) surfaces are different, but final configurations of the adsorbate/substrate system are found qualitatively the same. Adsorption energy of around 5 eV per molecule depends on the final arrangement of adatoms, being always higher for the p(1 × 2) substrate reconstruction. The energy barrier for dissociative adsorption of F_2 on Ge(001) is always less than 0.2 eV. The structural and electronic properties of distinct final adsorbate configurations have been examined, indicating that the surface density of states is metallic at Ge dimers with one adsorbed F atom and non-metallic at Ge dimers with two F adatoms.

1. Introduction

The dissociative chemisorption of halide molecules at surfaces is an important step in many surface reactions. It is a part of the technological process of semiconductor device fabrication. In particular, fluorine may be used to passivate germanium surface before deposition of a dielectric layer [1]. This makes the knowledge of how the halogens react with semiconductor surfaces of practical interest. Results of such processes depend on the specific semiconductor surface reconstruction. It is also important to recognize the differences in reaction parameters for distinct halogen molecules.

The (001) surfaces of silicon and germanium are known to exhibit a variety of reconstructions, related to the different ordering of surface dimers [2]. At the Ge(001) surface, the c(2 × 4) ordering is the one of the lowest energy, but the p(1 × 2) reconstruction is often utilized as the substrate in adsorption experiments. On the other hand, both the c(2 × 4) and p(1 × 2) reconstructions can be simultaneously observed on the same (001) surface of Ge at room temperature [2].

Halide molecules dissociate at the (001) surfaces of silicon and germanium. Consequently, the halide atoms adsorb at the dangling bonds of the substrate atoms. The adsorbate-covered surface still exhibit dimers, but their tilting angles change. As a result, the local density of states changes. Scanning tunneling microscopy (STM) experiments indicate that adsorption of halide atoms originating from the dissociated molecule may take place either on both sides of the same dimer or at the dangling bonds of neighboring dimers. Configurations with two halide atoms adsorbed on both sides of the same dimer are observed more frequently [3,4].

Most of theoretical studies of halide deposition on semiconductor surfaces concern chlorine adsorption on silicon [5–8]. The chlorine-covered surface of germanium was discussed in Refs. [9–11]. The isolated halogen atom on the Ge(001)-c(2 × 4) surface was discussed by Shah et al. [12]. Okada et al. [5] studied in detail the process of dissociation of the fluorine molecule on the silicon surface. Likewise, the process of dissociation of the chlorine molecule on the Ge(001)-p(1 × 2) surface was studied in Ref. [11].

The aim of the present investigation is to compare the process of dissociation of the F_2 molecule and the consequent adsorption of fluorine atoms at the p(1 × 2) and c(2 × 4) reconstructed Ge(001) surfaces.

2. Method of calculation

Calculations were performed using a local-orbital minimal-basis technique, based on the density functional theory (DFT) [13,14]. The FIREBALL code [15,16] was utilized. The pseudopotentials for germanium and fluorine were constructed according to the schemes of Troullier and Martins [17] and Hamann [18], respectively, using the FHI98PP package [19]. Exchange–correlation contributions were introduced within the local-density approximation (LDA) [20]. In the framework of the FIREBALL code, the sp^3 basis was used. Atomic

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orbitals of germanium were limited by atomic radii of 3.80 a.u. for *s* orbitals and 5.25 a.u. for *p* orbitals. These values yielded the lattice constant of 5.638 Å, the bulk modulus of 70 GPa, and the main energy gap of 0.45 eV for the bulk Ge crystal, as compared to the experimental values of 5.657 Å for the lattice constant, 68.87 GPa for the bulk modulus, and 0.664 eV for the main energy gap. The fluorine orbitals radii equal to 2.4 a.u. for *s* orbitals and 3.5 a.u. for *p* orbitals were taken, which reproduces the F_2 molecular bond length of 1.41 Å.

Throughout the calculations, the system was modeled by the (001)-oriented slab consisting of 12 atomic layers of germanium (to assure convergent electronic characteristics of the considered Ge(001) surface) and a layer of H atoms saturating the dangling bonds of the bottom Ge layer, assuming a (4 × 4) surface unit cell. The total number of atoms in such a supercell was equal to 226, including 2 fluorine atoms of the F_2 molecule. The 8 bottom layers of germanium and all hydrogen atoms were fixed in the course of simulations. Eighteen special k-points were used for molecular dynamics simulations and relaxation of the F/Ge(001) system. The time step in the dissociation process simulations was taken to be 0.5 fs.

3. Results

The F_2 molecule dissociates only in a few initial orientations with respect to the substrate surface. Orientations leading to the dissociative adsorption were obtained from preliminary molecular dynamics calculations. The F_2 molecule can dissociate only in a few specific positions relative to the substrate, otherwise it keeps moving and rotating above the surface as a whole. The molecule orientations leading to dissociative adsorption occur not to be the same for the p(1 × 2) and c(2 × 4) reconstructed surfaces. On the other hand, similar orientations at the p(1 × 2) or c(2 × 4) surfaces do not necessarily lead to the same dissociation paths. However, the final configurations of F-adsorbed Ge dimers appear to be almost identical, with just a slight difference in the dimer tilt angles.

There have been found four possible final configurations of fluorine atoms with respect to substrate dimers: (A) both F atoms adsorb at the dangling bonds of the same Ge dimer (configuration *A* in Fig. 1); (B) F atoms adsorb at the dangling bonds of the lower Ge atoms of neighboring dimers on the opposite sides of the same dimer row (configuration *B* in Fig. 1); (C) F atoms adsorb at the dangling bonds of the lower Ge atoms of neighboring dimers on the same side of the dimer row (configuration *C* in Fig. 1); (D) F atoms adsorb at the dangling bonds of the lower Ge atoms of dimers from adjacent dimer rows (configuration *D* in Fig. 1).

The adsorption process starts when F_2 molecule reaches the position ≈2 Å above the average height of surface Ge atoms. Further, the course of dissociation and adsorption processes depends on the initial molecule orientation. We note that different initial configurations may lead to the same final configuration. The distinct final configurations (cf. Fig. 1) can be reached in the following ways.

3.1. *Configuration* A

Configuration *A* occurs at the p(1 × 2) reconstructed surface in a simple and expected manner. At the beginning, the F_2 molecule is placed parallel to the dimer in contact with Ge dangling bonds (cf. Fig. 2c for A_pi). The dissociation process starts when the molecule is located ≈1 Å above the final vertical position of adsorbed F atoms (cf. Fig. 2a and b for A_pi). To reach this position, F_2 molecule overcomes the energy barrier of 0.2 eV (see below). Already at this distance, the surface density of states is influenced by the molecule and becomes metallic in character (cf. Fig. 2d for A_pi). The adsorbed dimer becomes flat, as expected in the case of two halide atoms adsorbed at the same Ge dimer (cf. Fig. 2b and c for A_pf). In spite of the reduced dimer tilt, the local density of states at F-adsorbed dimer exhibits a slight energy gap in the vicinity of the Fermi level and takes lower values near this gap, especially above the Fermi level (cf. Fig. 2d for A_pf).

In contrast to the p(1 × 2) reconstructed surface, at the c(2 × 4) one the F_2 molecule does not dissociate from the initial position A_ci parallel to the surface dimer, but becomes physisorbed as a whole in position A_cp above the Ge dimer (cf. Fig. 2 for A_ci and A_cp). This equilibrium position corresponds to a shallow energy minimum (see Fig. 7 below). However, there exists another reaction path eventually leading to the final configuration of type *A*, namely, configuration A_cf in Fig. 2. The F_2 molecule located above the dimer row and oriented towards upper atoms of the neighboring Ge dimers (cf. Fig. 3 for B_ci) can dissociate to a meta-stable configuration (cf. Fig. 3 for B_ct). In this transition configuration one

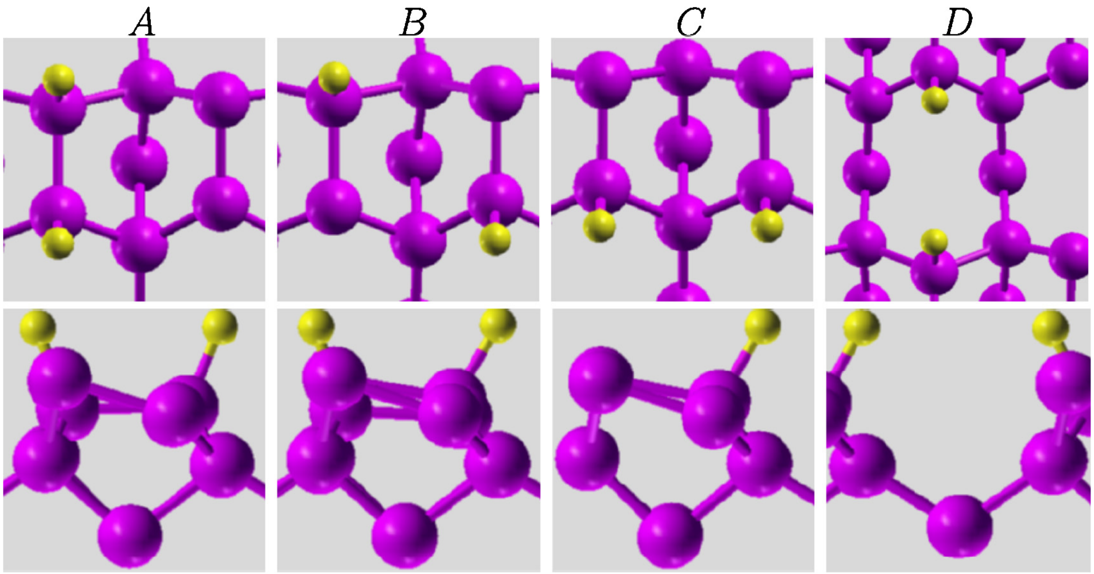

Fig. 1. Possible final locations of fluorine atoms adsorbed on Ge(001) surface as a result of F_2 molecule dissociation, illustrated for the case of p(1 × 2) reconstruction. Top panel: top view; bottom panel: side view along the surface dimer row.