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Ab-initio study of SiF₂ molecule adsorption on Si(001)-p(2 × 2) reconstructed surface

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Abstract

First-principles calculations are performed to investigate the relaxation and electronic properties of SiF₂ molecule deposited on surface. The reconstructed Si(001)-p(2 × 2) surface, modeled using density functional theory method, forms the basis for our molecule adsorption study. Several adsorption configurations corresponding to different orientations of the molecule have been investigated. Both stable dissociative and non-dissociative adsorption are found. For the most stable configuration, the adsorption takes place without dissociation of the molecule whose silicon atom binds two atoms of the surface. The progressive decomposition process of SiF₂ is also explored using the nudged elastic band (NEB) method. An important energy barrier is obtained for the SiF₂ molecule decomposition as compared to that of the SiF molecule. This could explain the high percentage of the SiF₂ volatile molecule observed experimentally during the fluoride plasma etching process on the Si(001) surface.

1. Introduction

The mechanisms study of the active plasma particles interaction with the treated surface is an important condition for the optimization of the existing and development of new technological plasma chemical processes for Si surface. Plasma etching using halogen based plasma such as CF₄, XeF₂ and SF₆, etc...[1–3] is a well known technique providing anisotropic profile and smooth surfaces. The reaction of silicon with atomic fluorine is the basis of ion-plasma and plasma-chemical etching which produces volatile compounds SiF_x ($x = 1 - 4$) that can easily be removed from the surface at low temperatures. It is generally agreed that SiF₄ is the major etching product [2,4]. However, the relative abundance of intermediate reactions and other etch products (SiF₃, SiF₂, SiF and polysilyl species) are still controversial.

The fundamental understanding of the mechanism by which SiF_x ($x=1-4$) species are produced in the fluorosilyl layer has been the focus of many experimental and theoretical works [5–8]. Engstrom et al. [5] have found that exposure of Si(001) to an F₂ or mixed F and F₂ beam produces only SiF₂ at low coverage and a mixture of SiF₂ and SiF₄ at higher coverage.

Experimentally, Wen et al. [9] have found that the initial adsorption of SiF₄ at 30 K on Si(111)(7 × 7) surface results in the formation of SiF and SiF₃. Similar results have been observed in the XeF₂/Si(111) system where XeF₂ interacts with the silicon surface by releasing fluorine atom and sequentially fluorinating the surface. A theoretical studies of atomic layer etching of silicon in SF₆ plasma have shown that chemisorption of F atoms on the surface is the etching-rate limiting process at low pressure, while with the increase in pressure, the formation of SiF₂ molecules becomes the etching-rate limiting process. Using molecular dynamic simulations, Gou et al. [10–13] have studied consecutive impacts of SiF₃, SiF₂ and SiF on the Si(001) surface. They have found that, a

Si_xF_y interfacial layer is formed and the SiF specie is dominant. Other *ab-initio* and molecular dynamic simulations, pointed out that many different reaction paths are competing e.g., fluorination of dangling bonds, breaking of dimer bonds and attack of subsurface Si atoms, leading to the concurrent formation of adsorbed SiF, SiF₂ and SiF₃ [14–21].

In their recent study, R. Knizikevičius et al. [22] have found that chemisorption of F atoms on the silicon surface does not occur instantly. At room temperature, at least 96% of F atoms incident to the atomically clean silicon surface are reflected. The nonlinear regression analysis of the experimental data indicates that the reaction of F atoms with silicon is a second overall order reaction. The volatile reaction product is formed during the reaction $2\text{SiF} \rightarrow \text{SiF}_2 + \text{Si}$. Kinetic reaction order monotonically decreases with the increase in partial pressure of F atoms due to the increased surface coverage. Winters et al. [4,23] showed that the primary volatile product of XeF₂ reaction with Si(111) is SiF₄(85%), with a small amount of SiF and SiF₂ radicals (15%). So, during etching, some fluorosilane products (SiF_x, $x=1-4$) may be dissociated and ionized in the plasma. These resulting fluorosilane may diffuse to the surface and interact with silicon surface. The redeposition of fluorosilane may significantly influence surface chemistry during etching. Relatively, few studies have examined this reverse process. In our recent study of SiF molecule adsorption on Si(001)-p(2 × 2) reconstructed surface [24], we have found that the dissociative adsorption of the SiF molecule is energetically the most stable configuration. The comparison between the energy barriers calculated for the different decomposition paths of the SiF molecule on the surface Si(001) shows that the on-dimer decomposition is kinetically favored over the inchannel process during the SiF molecule dissociation. The experiment about infrared spectrum of SiF_x ($x = 1-4$) showed that the SiF₂ gas appears in the sequential difluorination reaction on Si(111) surface. Because of the instability of SiF and SiF₃, their lifetimes are too short to be detected. However, SiF₂ was detected in the experiment, and it is the first molecule desorbed under real conditions [25].

The role of SiF₂ in the etching of silicon by fluorine atoms is still to be under debate. In this work we aim to understand how SiF₂ molecule interact with Si(001)-p(2 × 2) reconstructed surface and elucidate the role of this molecule in the chemical etching of silicon. First, we study the SiF₂ molecule adsorption on the Si(001)-p(2 × 2) surface by exploring its different adsorption sites, as well as the physical properties induced on the surface by the molecule. Subsequently, a detailed study of SiF₂ molecule decomposition on the Si(001) surface is discussed.

2. Computational method

These present calculations are based on density functional theory (DFT) using Vienna Ab-initio Simulation Package code (VASP) [26]. The frozen ionic cores are described by the projector augmented wave (PAW) method [27], and the Kohn–Sham valence states are expanded in the plane wave basis sets up to 380 eV. The p(2 × 2)-Si(001) surface was modeled as periodically repeated slabs with eight atomic layers and eight Si atoms on each layer, forming two dimer rows. For the surface calculations, slabs were separated by a vacuum spacing greater than 18 Å, being large enough to suppress any interaction between the periodically repeated images of the slabs. The three top layers are allowed to relax for all geometry optimizations, while the bottom layers are fixed to the experimental bulk lattice constant (5.43 Å) [28]. At the bottom layer of the slab, the Si atoms are fixed in their bulk positions and every dangling bond is passivated by an H atom (two H atoms per Si atom) and the positions are kept fixed during the structure optimization. The surface Brillouin zone is sampled with the Monkhorst–Pack scheme [29] using a (9 × 9 × 1) k-points mesh converging with respect to the electronic energy. The conjugate-gradient (CG) method was used for geometry

optimization and the minimum energy structure was identified when the change in the total energy and the forces acting on each atom were less than 10^{-5} and 0.01 eV/\AA , respectively.

The adsorption energy of SiF_2 molecule is calculated using the following equation :

$$E_{ads} = E_{ref} - E,$$

where E is the total energy of chemisorbed SiF_2 molecule and E_{ref} is the total energy of reference system, in which the free SiF_2 molecule is placed far from the $\text{Si}(001)$ surface.

Climbing image-nudged elastic band (CI-NEB) method [30] is employed to search the minimum energy paths (MEP) and/or locate the transition state structures (TS). Each TS was confirmed to have only one imaginary vibrational mode.

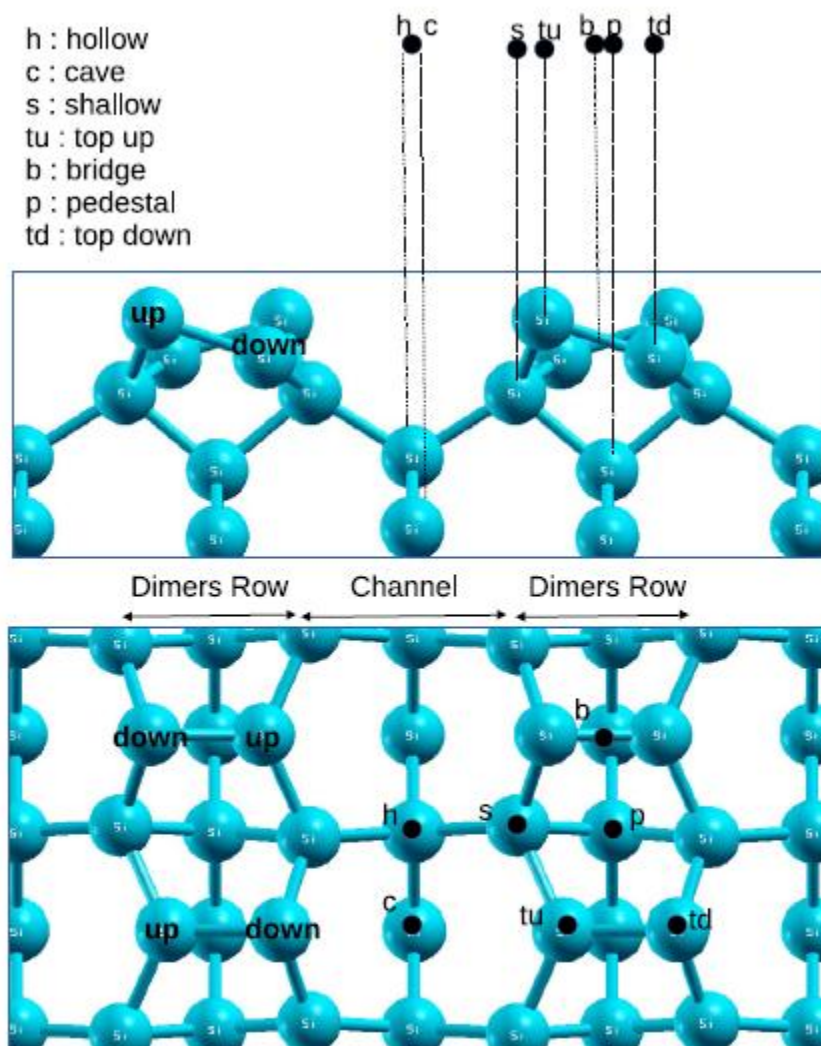


Fig. 1. Schematics of starting sites of the SiF_2 molecule adsorption on $\text{Si}(001)$ - $p(2 \times 2)$ surface from two different views (side and top views).

3. Results and discussion

3.1. SiF_2 free molecule and $\text{Si}(001)$ - $p(2 \times 2)$ reconstructed surface

The total energy of the SiF₂ gas-phase molecule was calculated in a box with dimensions of 20 Å on each side, large enough to ensure negligible interactions between neighboring supercells. Our calculations show that the most stable geometry for the SiF₂ molecule is an *C*2*v* isosceles triangle with a bonding energy of 6.83 eV. The calculated Si-F, F-F bond lengths and F-Si-F angle are of 1.61 Å, 2.63 Å and 100.58°, respectively. These results are in good agreement with the experimental and others theoretical values [16,31].

The Si(001)-p(2 × 2) reconstruction is characterized by a buckling along the dimer rail and reversing from one dimer to another (Fig. 1). The dimer bond length and the tilt angle of the dimer are of 2.33 Å and 18.98°, respectively. Our results are similar to those found in the literature [32].

3.2. SiF₂ molecule adsorption on Si(001)-p(2 × 2) surface

To investigate the adsorption behavior of SiF₂, the molecule is initially placed at 5 Å above the silicon surface on the high symmetry adsorption sites, namely, top-up (t-u), bridge (b), pedestal (p), top-down (t-d), shallow (s), hallow (h) and cave (c) (Fig. 1).

From the different initial orientations of the molecule and by targeting different sites on the surface, several stable adsorption configurations were obtained through geometric optimization of high precision criteria. All converged atomic configurations are shown on panel 1 of Fig. 2. The corresponding adsorption energy and the geometric parameters of the stable adsorption configuration are listed in Table 1.

For all converged configurations, the SiF₂ gives rise to a geometry with surface atoms qualitatively similar to that obtained for the SiF molecule on Si(001) surface with an adsorption energies smaller than those of the SiF molecule on the Si(001)-p(2 × 2) surface [24]. For the non-dissociative adsorption configurations (Fig. 2), we find that the SiF₂ molecule adsorbs by its silicon atom (*Si**) on bridged sites (“bridge”) by forming two bonds with two Si surface atoms (A, B, C, D and F configurations) or by forming two different bonds *Si**-*Si* and *F*-*Si* (G and H configurations). In the top site (I and J configurations), the SiF₂ molecule is adsorbed by forming a single bond with a surface atom. Furthermore, the position of the Si* atom on bridge sites makes it possible to classify the non-dissociative adsorption configurations of SiF₂ into three different categories: Si* forms two bonds with Si surface atoms of either (i) the same dimer (on-dimer), (ii) the adjacent dimers of the same row (inter-dimer) or (iii) the adjacent rows (inter-row) of the first layer.

Table 1

Adsorption energy (E_{ads}) and the geometrical parameters of the different sites. d_{Si-F} denote the Si-F bond lengths. d_{Si^*-Si} , d_{Si-Si} , θ and β refer to the bond lengths between Si atom of the molecule (Si*) and Si surface atoms, the Si surface dimers lengths, the buckling angle and the molecule angle, respectively. “ref” and “disso” notations denote the reference and dissociative configurations, respectively.

Sites	E_{ads} (eV)	d_{Si-F} (Å)	d_{Si^*-Si} (Å)	d_{Si-Si} (Å)	θ°	β°
ref	0.00	1.60, 1.60	5.00, 5.00	2.33, 2.33	18.98, 18.98	100.58
A	2.45	1.61, 1.60	2.38, 2.40	2.42, 2.36	10.05, 11.88	104.93
B	2.26	1.59, 1.59	2.30, 2.30	2.46, 2.30	18.38, 4.16	107.12
C	1.71	1.61, 1.60	2.48, 2.52	2.47, 2.62	6.43, 18.04	106.19
D	1.51	1.60, 1.60	2.45, 2.47	2.40, 2.35	20.95, 20.87	104.5
E (disso)	1.43	1.63, 1.62	2.39	2.33, 2.39	2.86, 18.82	/
F	1.40	1.63, 2.02	2.48	2.28, 2.31	18.42, 7.97	90.52
G	1.33	1.64	2.55	2.40, 2.35	13.70, 13.18	91
H	1.27	1.63	2.54	2.35, 2.40	14.11, 10.29	89.27
I	0.92	1.64, 1.64	2.53	2.33, 2.34	12.37, 18.75	89.43
J	0.88	1.61, 1.61	2.42	2.34, 2.32	14.95, 19.4	103.5

3.3. Non-dissociative adsorption

For the inter-dimer category (A, D, G and H), the A arrangement is energetically the most favorable with an adsorption energy of 2.45 eV. The D, G, and H configurations are found to be higher in energy by 0.94 eV, 1.12 eV and 1.18 eV, respectively. In the A configuration, the Si* atom binds *Siup* and *Sidown* atoms of two adjacent dimers, while in the D configuration, the Si* atom binds two *Siup*

surface atoms. In the G and H configurations, the SiF₂ molecule is bonded with its Si* and F atoms. In the two obtained on-dimer B and F configurations, the SiF₂ molecule is adsorbed with an energies adsorption of 2.66 and 1.05 eV, respectively. In the B configuration, the molecule is adsorbed via its Si* atom by forming two chemical bonds of length 2.30 Å with the two atoms of the same dimer. However, in the F configuration, the molecule is adsorbed on the same dimer by forming two different bonds (Si*-Si and F-Si). In the inter-row configuration (C solution) the Si* atom of the molecule binds with two silicon atoms *Si_{up}* of 2.5 Å belonging to two adjacent dimers with an adsorption energy of 1.71 eV. In the I and J configurations, where the adsorption energy is lower than 1 eV, the SiF₂ molecule adsorbs on the top site via its atom Si* by forming a single bond with a surface atom.

We can also see that after adsorption, the Si*-F bond lengths of SiF₂ in A-D and J configurations remains unchanged with respect to its free molecule bond (1.6 Å). However, in the F-I configurations, only one of two Si*-F bond length is stretched to about 1.64 Å. It is also important to notice that, in A-D and J configurations, the calculated SiF₂ bond angles are increased (> 100.58°) and they are reduced to about 90° in the F-I adsorption configurations as compared with that of SiF₂ free molecule. The SiF₂ molecule adsorption on Si(001)-p(2 × 2) surface has also an important effect on the dimer bond lengths and on the buckling angle between the *Si_{up}* and *Si_{down}* atoms. In fact, the dimer lengths for all adsorption sites are in the range of 2.30–2.40 Å except for the case of C configuration where the two dimers were stretched to rather long values of 2.47 and 2.62 Å, respectively. In addition, we have found that in all obtained configurations, the surface dimers get partially symmetrized after SiF₂ molecule adsorption (only one dimer in which the Si* atom is bonded becomes symmetric with a tilt angle less than 10°, while the others one are still tilted).

3.3.1. Electronic properties

In the following, the electronic properties of the adsorbed SiF₂ molecule on Si(001)-p(2 × 2) surface are studied. The nature of the bonding of the molecule on the Si(100) surface is visualized by the electronic distribution charge density in Fig. 2. The charge densities illustrate the formation of chemical bonds between the Si* molecule atom and Si surface atoms. The interaction of SiF₂ molecule with the Si(001) surface atoms is followed by charge transfer from the surface to the Si* atom when bonding with the surface. This charge transfer is of 0.12 *e*⁻ in the most stable ineter-dimer configuration. It is very low in the case of the on-dimer (0.08 *e*⁻) and the inter-row (0.02 *e*⁻) configurations. We note that this charge transfer is lower for the SiF molecule adsorption on Si(100) surface; they are of 0.26, 0.24 and 0.02 *e*⁻ in the inter-dimer, inter-row and on-dimer configurations, respectively [24]. This result can explain the lower adsorption energy of the adsorbed SiF₂ molecule as compared to that of SiF which goes from 3.97 to 2.75 eV. We have also performed an analysis of the local (projected) density of states (L(P)DOS) onto the SiF₂ molecule and Si surface atoms before and after adsorption for the most stable configuration. From Figs. 3-a and 3-b, it is clear that after adsorption, the localized energy states of the SiF₂ free molecule are continuously redistributed over an energy range of 10 eV. By analyzing the LPDOS of Si surface atoms and Si* atom after adsorption (3-c and 3-d), we note a strong Si*-Si atoms interaction. A lowering in the intensity of LPDOS of the surface atoms and the disappearance of the peaks around Fermi level is due to the saturation of the dangling bonds of the surface atoms. This saturation is a consequence of the hybridization between the *p*(Si*) – *p*(Si) and *p*(F) – *p*(Si*) orbitals.

3.4. Dissociative configuration

Among all tested initial configurations, only the one in which the SiF₂ molecule is placed perpendicularly with respect to the channel of the surface leads to a spontaneous dissociation

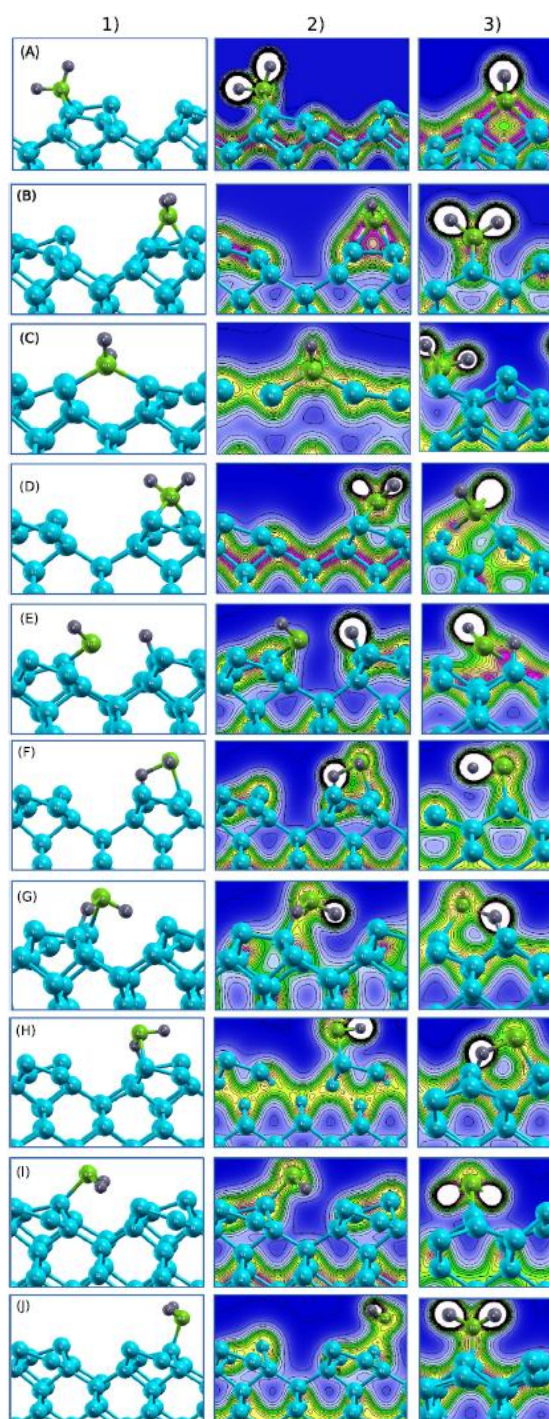


Fig. 2. Different adsorption configurations of the SiF₂ molecule on the optimized $p(2 \times 2)$ structure of the Si(001) surface. The first panel shows the binding structures of the molecule. The second and third panels present the 2D spatial distributions of the electron charge density, in the plane perpendicular to the surface and in the plane parallel or perpendicular to the dimers rows.

(E configuration). Contrary of the SiF molecule adsorption on Si(001)- $p(2 \times 2)$ where the dissociative adsorption is the most stable configuration [24], the dissociative adsorption of SiF₂ molecule is less favorable than the non dissociative adsorption with an important energy difference of 1.02 eV. In this

configuration, the molecule dissociates to F atom and SiF molecule. The distance between F atom and SiF molecule is 3.65 Å. As in F adatom and SiF molecule adsorption on Si(100) surface [24], the detached F atom from the SiF₂ molecule is adsorbed in the top site with a bond length of 1.62 Å, while the dissociated SiF molecule forms one Si* – Si bond in the adjacent row. It is important to note that Si* and Si subsurface inter-atomic distance is only 2.55 Å.

The SiF₂ dissociation is clear from Fig. 2 in which we can see that the distributions of the electronic charge densities of F atom and the SiF molecule are note merged. The Bader population analysis shows a significant charge transfer from Si to the dissociated F atom (0.8e⁻), which may be interpreted in terms of the higher electronegativity of F compared to that of Si. In addition, a high charge transfer of 0.64 e⁻ from Si surface atoms to the detached fragment SiF indicates a strong interaction between Si and SiF molecule obtained after the SiF₂ molecule dissociation.

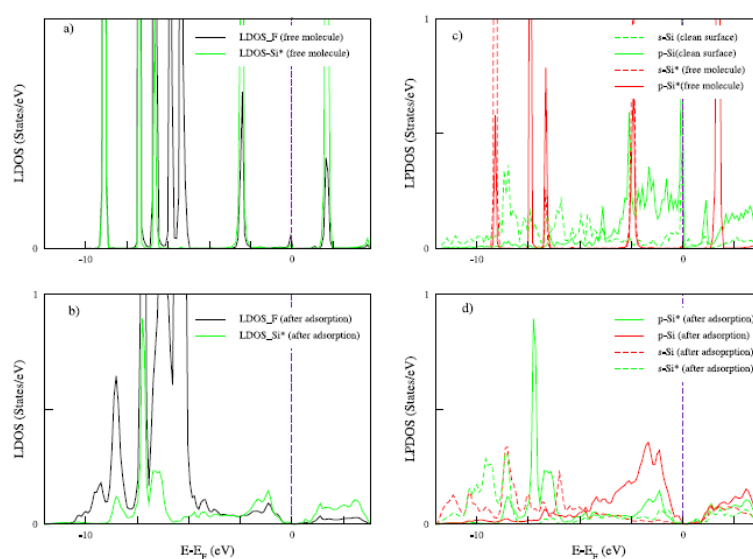


Fig. 3. Local Density (projected) states (LPDOS) of Si* and F molecule atoms as well as adjacent surface Si atoms of the most stable configuration and the reference system : (a) LDOS of the free molecule SiF₂. (b) LDOS of the molecule after the adsorption in the A configuration. (c) LPDOS of Si* and the surface atoms in the system without interaction. (d) LPDOS of Si* atom and Si surface atom after adsorption. In all DOS plots, the Fermi energy is set to zero.

3.5. SiF₂ molecule decomposition on Si(001)-p(2 × 2) surface

In this part, we explore the reaction paths of the SiF₂ molecule dissociation using the Nudged Elastic band (NEB) algorithm by considering only the most stable configuration (Fig. 2-A) as the initial state (IS). Fig. 4 depicts the initial, intermediate and dissociation adsorption steps of SiF₂ molecule on Si(001) surface. The progressive decomposition process of SiF₂ can be described as, SiF₂ → F+SiF → Si+F+F. The intermediate state (INS) of the dissociation is represented by the F atom and the SiF molecule jointly adsorbed on their most favorable adsorption site of the same row : the fluorine atom is adsorbed on an “up-top” site of the surface with a bond of 1.6 Å and the SiF molecule is adsorbed on a “bridge” site forming two bonds with two atoms of two different dimers (bond length of 2.37 Å) [24]. The final state (FS) is a complete dissociation of the molecule in which the F atom of the SiF adsorbed molecule diffuses to the adjacent row. During the dissociation process, only the fluorine atom diffuses across the surface to the nearest dangling bond, while the silicon atom of the molecule prefers to keep its initial site.

From the potential Energy Surface (PES) curve shown in Fig. 4, one can see that the energy difference between the final state and the initial state is very small, so the dissociative reactions of SiF₂ on Si(001) surface is thermoneutral. In the first decomposition process (Fig. 4-a), the F atom of SiF₂ molecule moves to the top-up surface site with a rather small energy barrier of 0.8 eV (TS1) and

which is higher than that obtained for the F diffusion from SiF molecule to the surface (0.6 eV) [24]. This result indicates that Si-F bond is easily formed on the Si(001) surface. So, the difference between the calculated barrier energy of F diffusion from SiF and SiF₂ molecules to the surface can be explained by the longer hopping distance in the first step of SiF₂ decomposition (3.7 Å) as compared to that of the SiF dissociation (2.9 Å). In the presence of the Si-F bond on the surface (second process decomposition, Fig. 4-b), the second F atom of SiF₂ molecule continues to cross through an high barrier of 1.64 eV (TS2) in order to break its Si-F bond and to adsorb on the “top-up” site surface atom of the adjacent row.

By comparing our results with those of F adatom diffusion on the Si(001) surface (fluorine adatom can diffuses into the surface with migration barriers of 1.23–1.75 eV [24]), we can conclude that energetically it is easier for the fluorine atom to diffuse from the molecule toward the surface than the diffusion from a surface site to another. This result is in good agreement with the experimental results showing that the fluorine diffusion assisted by extra silicon atoms is diffused freely on the surface [20]. The comparison between the energy barriers calculated for the SiF₂ decomposition at the Si(001) surface with those of SiF molecule shows that the high values of the calculated activation energies greater than 0.6 eV indicates a difficult dissociation of the SiF₂ as compared to the SiF molecule dissociation on the Si(001) surface. These results may also confirm the experimental observations showing SiF₂ as a primary product, with a higher percentage than the SiF molecule during fluoride plasma etching of silicon [2,25].

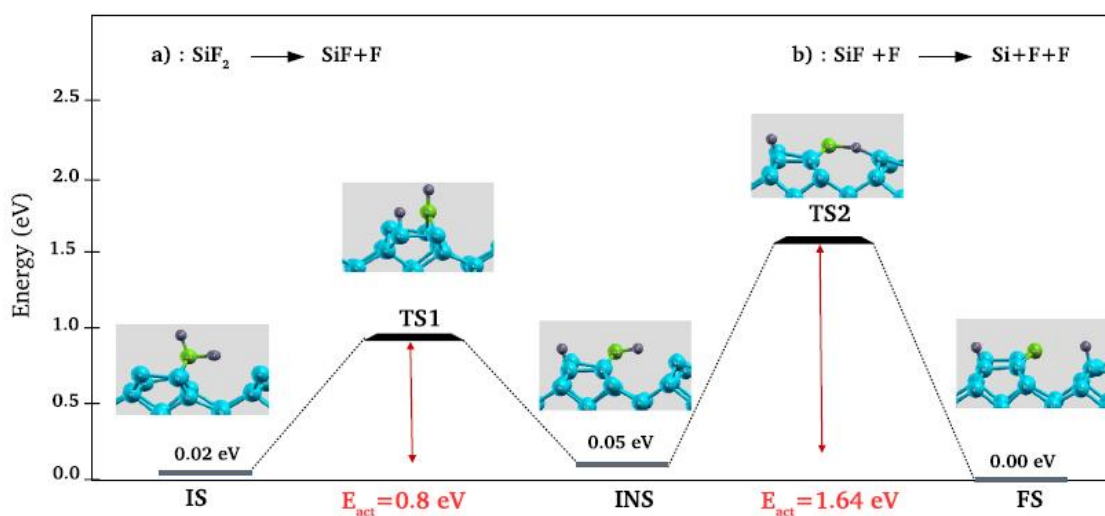


Fig. 4. Potential energy surface for the progressive decomposition process of SiF₂ on Si(001)p(2 × 2) surface: SiF₂ → F+SiF → Si+F+F.

4. Conclusion

We have investigated the adsorption and dissociation reactions of SiF₂ molecule on Si(001)-p(2 × 2) reconstructed surface using density functional theory calculations. From a geometric optimization with full relaxation, several types of adsorption configuration were obtained. The most stable corresponds to an adsorption without dissociation of the molecule, whose silicon atom forms a bridge connexion between two surface atoms. Charge density plots and density of states were presented to identify the charge transfer and the bonding of the molecule to the surface. We have found that the adsorption of SiF₂ molecule on the silicon surface has a significant influence on the

surface chemistry. It affects surface coverage and changes the reactivity of silicon substrates. The Nudged Elastic band (NEB) algorithm is used to explore the reaction paths of the molecule SiF₂ dissociation by evaluating potential energy surface. We have found that the decomposition of SiF₂ molecule into SiF and F is kinetically more favorable than its complete dissociation (Si+2F). The high activation energy values calculated (greater than 0.6 eV) lead to less favorable dissociation of this molecule, as compared to SiF molecule dissociation. This could explain the high percentage of the SiF₂ volatile molecule observed experimentally during the fluoride plasma etching process on the Si(001) surface. The redeposition of this molecule on the silicon surface becomes the etching-rate limiting process.

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