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Electric field induced hydrogenation of silicene

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An alternative approach for hydrogenation of silicene is proposed through applying an external electric field in order to reduce the reaction energy barrier based on density functional theory calculations. It is found that a positive perpendicular electric field *F* can act as a catalyst to reduce the energy barrier of H_2 dissociative adsorption on silicene, which facilities the hydrogenation of silicene. In addition, it is found that the barrier decreases as *F* increases, and when *F* is above 0.05 au (1 au = 5.14×10^{11} V/m), the barrier is quite low and hydrogenation of silicene can go through efficiently at room temperature. The catalyst effect of the electric field on

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hydrogenation of silicene is induced by the redistribution of atomic charge under the electric field, which would change the chemical activity of slicene significantly.

1. Introduction

Graphene has a two-dimensional honeycomb structure with unique electronic, mechanical and thermodynamic properties, which has been attracting great attention since it was fabricated in 2004.[1-3] It is known that intrinsic graphene is a semiconductor with zero band gap, the band gap can be opened and the width of the gap is controllable through different ways.[4-7] Hydrogenation is one of the effective methods that can be used to control the electronic properties of graphene.[8-11] For example, graphene can undergo full hydrogenation and become a wide gap semiconductor with a band gap of around 3.5 eV.[8] This hydrogenated graphene—graphane is stable at room temperature.[12] Furthermore, it has been reported that through hydrogenation graphene can be switched from metallic to semiconducting, and from nonmagnetic to magnetic.[13] These discoveries bring vital perspectives for the possible applications of graphene-based devices. For instance, graphene is found to be a promising material for hydrogen storage with high hydrogen storage capacity and revisable hydrogen storage and release.[14,15]

These remarkable achievements on graphene have attracted more and more attention to the other elements in the IV group in order to find the similar properties. Newly reported silicene, a two-dimensional honeycomb network of silicon atoms, is the hottest one of this type.[16-20] This special silicon component does not exist in nature and was first predicted as an aromatic stage of two-dimensional Si with a buckled structure in 1994 through first-principles calculations.[21] The authors claimed that there was a linear dispersion around the Dirac cone at the Fermi level at the K point like in graphene. Several years later, the single layer sheet of Si was obtained on a substrate via the chemical exfoliation of calcium disiliside[22] and single-wall silicon nanotubes were achieved on Ag (110) or Ag (100) substrates.[23] It is known that the electronic configurations of silicon are similar to those of carbon. However, in silicon the sp^3 hybridization is more stable than the sp^2 hybridization,[24] which is opposite to that of carbon. Therefore, silicon cannot spontaneously form honeycomb structure as carbon but low buckled structure instead. Although isolated silicene has not been reported experimentally yet, different theoretical works have proven that this isolated two-dimensional buckled honeycomb network of silicon atoms is a stable structure when it was firstly reported in 1994.[21] For example, phonon dispersion calculations[19] and first-principles calculations based on density functional theory (DFT)[25] have clearly confirmed that freestanding silicene is stable and energetically degenerate. In addition, many studies on silicene are based on freestanding silicene including its hydrogenation.[24,26,27] Therefore, freestanding silicene will be studied in this work.

Recently, several works confirmed that silicene is a zero band gap semiconductor.[20,24] This discovery brings the same challenge to silicene as for graphene that is controlling the band gap in order to vary the properties of silicene for future potential applications. With these expectations and the routes used for graphene, the hydrogenation of silicene has become a topic of great interests[28-35] and various breakthroughs in this area have been reported. When silicene is hydrogenated on a substrate, generally only the top side of Si atoms are hydrogenated, which makes the system show ferromagnetic properties.[36] While half hydrogenated silicene without substrates turns out to be a ferromagnetic semiconductor with an indirect band gap (about 0.84 eV) based on generalized gradient approximation (GGA) calculation[26]. While fully hydrogenated silicene, named silicane, generates about 2 eV indirect band gap by local density approximation (LDA) calculation and becomes an insulator.[37] Furthermore, it is also found that by applying a proper hydrogenation ratio the band structure of silicene can be tuned to produce metallic, semiconducting, or insulating properties.[24,26] These results open a door to widen the applications of silicene-based devices.

However, according to the study of binding energy on low buckled silicene based on DFT-GGA calculations,[37] it is found that the energy barrier of hydrogen atom adsorption on silicene is too high compared to that of gaseous hydrogen molecules, which indicates that the dissociative adsorption of hydrogen on silicene would be difficult due to the passive surface of silicene. The possibility of the dissociation can be understood by the energy barrier of this reaction, which is defined as the energy difference between the initial state and the highest energy along the minimum energy reaction paths (transition state). With high energy barrier, reactions would not go effectively or not even happen.[38,39] It is reported that the chemical reactions can be modified by an electric field, which would induce the electron redistribution, thus change the chemical activity.[40] For example, the dissociation activation energy of molecular oxygen on Pt (111) is changeable with an applied electric field.[41] More recently, the energy barrier of the hydrogenation of graphene was reported to reduce to zero by applying an electric field with a proper intensity and the hydrogenation could go smoothly and efficiently.[42] For silicene, it is also found that an external electric field could control the band gap of silicene[43] and at the silicene/(0001) ZnS interface.[44] Therefore, an electric field is considered in this work to modify the electric properties and chemical acitivity of silicene as a catalyst.

In order to reduce the energy barrier of silicene hydrogenation, a perpendicular electric field is applied and its effect on hydrogenation is investigated through DFT calculation in this work. The hydrogenation of silicene can be understood through the calculation of the reaction pathway of one H_2 molecule dissociative adsorption on silicene in the presence of the external electric field. The mechanism of the energy barrier reduction induced by the external electric field can be analyzed through partial density of states (PDOS). In addition, the effect of hydrogenation on the electronic properties of silicene is also discussed.

2. Simulation methodology

The DFT calculations are performed by the DMol3 code. The local density approximation (LDA) with the Perdew and Wang (PW91) functional is employed as the exchange-correlation functional. A double numerical plus polarization (DNP) stays basis set. The convergence tolerance of energy is taken as 10^{-5} Ha (1 Ha = 27.21 eV). The maximum allowed force and displacement are 0.002 Ha and 0.005 Å, respectively. Linear synchronous transition/quadratic synchronous transit (LST/QST)[21] and nudged elastic band (NEB)[45] tools in DMol3 are employed to investigate the minimum energy pathway for hydrogen dissociative adsorption on silicene. Three-dimensional periodic boundary conditions are taken in the simulation. A 3×3×1 supercell is adopted for all the structures in the present simulations with a vacuum width of 18 Å above the layer to minimize the interlayer interaction, as shown in Figure 1. The *k*-point is set to 6×6×1 and all atoms are allowed to relax in all the calculations.

The adsorption energy of an H_2 molecule onto silicene E_{ad} is defined as,

$$E_{ad} = E_{H2+silicene} - (E_{silicene} + E_{H2}) \tag{1a}$$

where the subscripts H_2+silicene, silicene, and H_2 denote the silicene with a H_2 molecules adsorbed, bare silicene, and a H_2 molecule respectively. After hydrogenation, the binding energy of H atoms on silicene $E_{Si\text{-}H}$ can be determined as,

$$E_{Si\text{-}H} = E_{2H+silicene} - (E_{silicene} + 2E_H) \tag{1b}$$

where subscripts 2H+silicene and H denote the silicene with 2 H atoms chemically adsorbed and a free H atom respectively.

3. Result and discussion

Before hydrogenation, the H_2 molecule is weakly physically adsorbed on silicene. There are 4 possible adsorption positions as indicated in Figure 1(a): positions 1 and 3 on the top of a silicon atom in the higher or lower plane of the buckled structure, position 2 over the middle of a Si-Si bond or position 4 the center of a Si ring. In order to determine the most stable structure, we calculate all the four possible positions. The results in Table 1 show that the total energy and adsorption energy of a H_2 molecule on silicene at position 1-3 are almost the same but those at position 4 are lower, *i.e.* the H_2 molecule is favorable to adsorb at the hollow site of the Si ring. This configuration is also considered to be the reactant for the silicene hydrogenation reaction. Note that the distance between H_2 molecule and the silicene layer at position 4 is calculated to be 2.454 Å, which is shorter than that in the other structures due to the stronger binding energy. In the subsequent atomic hydrogen adsorption, there are three possible positions for the two hydrogen atoms, which are ortho, meta and para positions shown as the second H atom at positions 1-3 in Figure 1(b). All the three possible configurations are calculated, the corresponding results are listed in Table 1. It is found that the hydrogenated silicene with two hydrogen atoms in ortho position, *i.e.* the second H atom at position 3, has the lowest energy, the corresponding structure is shown in Figure 2 (b). In the hydrogenated silicene, the Si-H bond length $l_{\text{Si-H}}$ is 1.50 Å and the Si-Si bond length $l_{\text{Si-Si}}$ is 2.355 Å, which agrees with reported results $l_{\text{Si-H}}$ = 1.50 Å, $l_{\text{Si-Si}}$ = 2.36 Å[30] and $l_{\text{Si-H}}$ = 1.519 Å, $l_{\text{Si-Si}}$ = 2.359 Å[24] in fully hydrogenated silicene. In addition, the Si atoms bonded with the two H atoms moved up about 0.78 Å towards the H atoms as shown in the side view of the hydrogenated silicene of Figure 2(b). Figure 2 also shows the band structures of silicene before and after hydrogenation. As shown in the bottom panel of Figure 2(a), before hydrogenation, silicene is a zero bandgap semiconductor similar to graphene, and the physical adsorption of a H_2 molecule does not change the band structure of silicene.

However, after hydrogenation, the band gap of silicene opens about 110 meV as shown in the bottom panel of Figure 2(b), which is similar to the reported result when silicene is hydrogenated by 25% and band gap was calculated to be 148 meV.[24] This means partial hydrogenation could also open a band gap in silicene, and its band gap depends on the ratio of hydrogenation, where half hydrogenated silicene turns out to be a semiconductor with a band gap about 0.84 eV[25] and fully hydrogenated silicene, named silicane, generates about 2 eV band gap.[37]

Due to the importance of hydrogenation of silicene, it is vital to understand the chemical reaction of the hydrogenation process. For a H_2 molecule dissociative adsorption on silicene, the structures of reactant and production are shown in Figures 2 (a) and 2 (b). After LST/QST and NBE calculations, the energy minimum dissociative absorption pathway is shown in Figure 3. From this figure, the dissociative adsorption reaction energy barrier $E_{\mathrm{bar}} = E_{\mathrm{TS}} - E_{\mathrm{IS}}$ is 1.75 eV where E_{TS} and E_{IS} are respectively the energies of transition state (TS) and initial state (IS). Before TS, the H_2 molecule is dissociated into two free H atoms with a small energy barrier around 0.1 eV, then one of the H atoms binds with a Si atom nearby at the top layer while the other H atom keeps free, as shown as the TS in Figure 3. In addition, the Si atom that is going to bind with the free H atom has also shifted upwards, but the two H atoms are still closed to each other with strong interaction, which prevents the binding between the free H atom and the Si atom. At the final state FS, the distance of the two H atoms increases, and thus the other free H atom also binds with the nearest Si atom as shown in Figure 3. Therefore, this reaction can be separated into two steps: the H_2 molecule is first dissociated into two H atoms, and then one of them binds with a Si atom nearby while the other one is free; at the second step, the two H atoms adjust their positions and the other H atom also binds with its nearest Si atom. Although this reaction releases energy about 0.25 eV in total (total energy of the final state E_{FS} - E_{IS}), there is a high energy barrier of ~1.75 eV for the first step. Consequently, the first step becomes a rate-limiting step because of a large energy needed.

It is reported that a reaction is difficult to happen at room temperature if the reaction energy barrier is higher than 0.75 eV.[46] Due to the high energy barrier of 1.75 eV for this hydrogenation process, the reaction is difficult to go through at room temperature, high reaction temperature or other external energy source is required. Therefore, it is desirable to reduce the hydrogenation energy barrier. Applying external electric field is an alternative way to alter the electronic distribution of silicene, thus changing its chemical potential. In addition, electric field is found be a catalyst to reduce the reaction barriers for the dissociative adsorption of H_2O on graphene,[47] and H_2 on graphene as well.[42] Therefore, an external electric field is considered here to investigate the possibility of reducing the hydrogenation energy barrier of silicene.

To investigate the effect of an electric field, electric fields with different directions and intensities are considered, the electric field along the arrow in Figure 1 is defined as the positive electric field. It is found that the positive electric field can reduce the energy barrier for the hydrogenation reaction, while the negative electric field has opposite effect on the hydrogenation reaction, increasing the energy barrier. Therefore, only the result of energy barrier under positive electric fields is shown in Figure 4. It is clearly shown that the electric field can reduce the energy barrier of a H_2 molecule dissociative adsorption on silicene remarkably. The energy barrier decreases with the intensity of the electric field increasing. Noted that E_{bar} is lower than 0.75 eV when F above 0.05 au. *i.e.*, the H_2 molecule can be dissociated and adsorbed on silicene automatically at room temperature in the presence of the electric field of 0.05 a.u. If further increasing the intensity of the electric field until to 0.06 a.u., the barrier can be reduced further. However, when $F \geq 0.06$ a.u., the structure of silicene would be destroyed, which should be avoided in applications.

To better understand the effect of electric fields, the hydrogenation pathways of silicene under different electric fields are shown in Figure 5. As shown in the figures, the configurations before and after hydrogenation reconstructed as expected when the electric field is strong enough. When $F \geq 0.03$ a.u., after geometry optimization, the reactants transferred from IS to an energy minimum state, State 1. At state 1, the H_2 molecule slightly adjusts its position and orientation over silicene layer. Then the H_2 molecule is dissociated into 2 H atoms at TS, while one of the H atoms binds with a Si atom in the upper layer for the cases in Figures 5(a)-5(c). When $F = 0.05$ a.u. as shown in Figure 5(d), different from other cases, the two H atoms bind with a same Si atom at TS. This special binding is probably caused by the strongly upward force on the positively charged silicon atom and downward force on the negatively charged hydrogen atom under the positive electric field. Similar to the case without an electric field, the two H atoms are still closed to each other with relatively strong interaction. After the binding of the second H atom with a Si atom, the H-H interaction is reduced and their distance is increased remarkably as shown in State 2 of Figure 5(d). As expected, the structure of the hydrogenated silicene would be reconstructed as well in the presence of an electric field, which is shown as the State 2 in Figure 5 except the case at F = 0.01 a.u., which is considered to be too weak to change the structure. Therefore, under strong positive electric field, the reaction would stop at State 2. Once the electric field is removed, the structure of State 2 would reconstruct into the structure of FS. In addition, the reaction energy E_R decreases as F increases, which would further benefit the hydrogenation process. Therefore, silicene can be hydrogenated spontaneously under the electric field of 0.05 a.u. with low energy barrier of 0.38 eV.

As mentioned above, we also investigated this reaction in the presence of a negative electric field, but it is found that the energy barrier increases to 1.92 eV under an electric field of -0.02 a.u.. If further increasing the electric field, the silicene structure would be destroyed, which is similar to the investigation of the effects of an electronic field on the atomic structure of graphene/α-SiO_2 (0001) interface,[48] where the structure of graphene was destroyed and covalent bonds between graphene and SiO_2 substrate are formed under a strong negative electric field. It is known from Figure 2 that H atoms are negatively charged and the Si atoms bonded with the H atoms are positively charged. In the presence of a negative electric field, the distance between Si and H atoms would increase due to the upward force on H atoms while downward force on Si atoms. Therefore, the negative electric field prevents the formation of covalent bonds between Si and H atoms and results in higher hydrogenation energy barrier. On the contrary, in the presence of a positive electric field, the negatively charged H atoms are attracted downward and the positively charged Si atoms are pushed upward by the electric field, which facilitates the formation of Si-H bonds. Therefore, the positive electric field can reduce the hydrogenation energy barrier of silicene.

The effect of electric fields on hydrogenation energy barrier of silicene can be also understood through analyzing PDOS of the configuration at TS under different electric field as shown in Figure 6. The bands of *s* orbital of the two H atoms and the *p* orbital of the two corresponding Si atoms binding with the two H atoms at TS are provided. It is clear that the interaction of the lowest Si-H interaction band (the weight of the overlap between the bands of *s* orbital of H and *p* orbital of Si) between (-0.2) ~ (- 0.4) eV is enhanced when F increases, while the interaction band near Fermi level does not change much under positive electric fields. Under a negative electric field, the lowest band is weakened and the band near Fermi level is enhanced. It is known that the interaction of the lowest band determines the interaction of Si-H, and thus determines the energy barrier. Therefore, when F = 0.05 a.u., the Si-H atom interaction is the strongest, thus it’s easier for the H_2 molecule to dissociate and form covalent bond with Si, and the corresponding hydrogenation barrier is the lowest, which agrees with the result in Figure 5.

As mentioned above, the electronic properties of silicene could be tuned by the ratio of hydrogenation.[24,26,27] For the hydrogenation of graphene, it is reported that large ratio of hydrogenation is difficult due to H frustration based on DFT and molecular dynamic (MD) calculations[49] and experiments also showed that the extensive hydrogenation is hard to achieve.[50] Nevertheless, silicene has a buckled structure unlike planar structure of graphene because the *sp*^{3} hybridization is more stable than the *sp*^{2} hybridization in silicon.[24] This may make a difference on the hydrogenation between silicene and graphene. In addition, hydrogenation is believed to be easier near defects,[51] which are unavoidable in actual situations. Therefore, different from graphene, large ratio of hydrogenation of silicene may be possible, which will be studied in our following works.

4. **Conclusion**

The dissociative adsorption of a H_2 molecule on silicene in the presence of different electric fields is investigated by DFT calculations. It is found that the energy barrier of dissociative adsorption of a H_2 molecule on silicene can be reduced by applying a positive perpendicular electric field, which can act as a catalyst to facility the silicene hydrogenation reaction, while negative electric fields have converse effect on this reaction to increase the reaction energy barrier. In addition, the energy barrier decreases as the electric field increases. When the intensity of the positive electric field is 0.05 a.u. or larger, the barrier is lower than 0.75 eV, and the hydrogenation would happen smoothly and efficiently at room temperature. Therefore, we propose an alternative method to hydrogenate silicene, which is essential to open its band gap for its application in electronic devices.

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Table 1 The total energy, binding energy, and the distance between H_2 molecule and the silicene layer of all the possible structures before (Reactants) and after hydrogenation (Products). For total energy, the energy of the most stable structure is set to be zero for comparison.

	Reactants				Products		
Position	1	2	3	4	1	2	3
Total energy (eV)	0.066	0.061	0.068	0	0.52	0.08	0
Binding energy (eV)	-0.1	-0.1	-0.1	-0.166	-5.39	-4.96	-5.46
$D_{H\text{-}Si}$ (Å)	3.2	3.1	3.6	2.45			

Captions:

Fig. 1 (a) The four possible positions for a H_2 molecule physically adsorbed in silicene, (b) the three possible positions of the second H atom when 2 H atoms chemically adsorbed on silicene. The direction of positive electric field is denoted by the arrow.

Fig. 2 The initial and final structures and the corresponding band structures for a H_2 molecule on silicene before and after dissociative adsorption and atomic charge near the adsorbed hydrogen. The numbers at the top panel of the figure denote the atomic charge of the atoms.

Fig. 3 The reaction pathway of the dissociative adsorption of a H_2 molecule on silicene. The energy of reactant IS is taken to be zero. IS, TS and FS denote initial structure, transition structure, and final structure, respectively. E_{bar} is the energy barrier and E_{R} is the reaction energy.

Fig. 4 Energy barrier of the dissociative adsorption of a H_2 molecule on silicene under the positive perpendicular electric fields. The units of E_{bar} and F are eV and a.u., respectively.

Fig. 5 The pathway of dissociative adsorption of a H_2 molecule on silicene in the presence of positive electric fields. Transition structure and energy minimum states 1 and 2 are represented by TS, 1 and 2 respectively. The initial structure IS and the final structure FS are already shown in Figure1. The energy in IS is set to be zero. The E_{bar} and E_{R} are energy barrier and reaction energy respectively and their units are eV.

Fig. 6 The PDOS analysis of the two H atoms and the two corresponding Si atoms at TS under different electric fields. The black curve is the PDOS of the two silicon atoms and the purple one indicates that of the two hydrogen atoms. The red dash line stands for the Fermi level.

Fig. 1

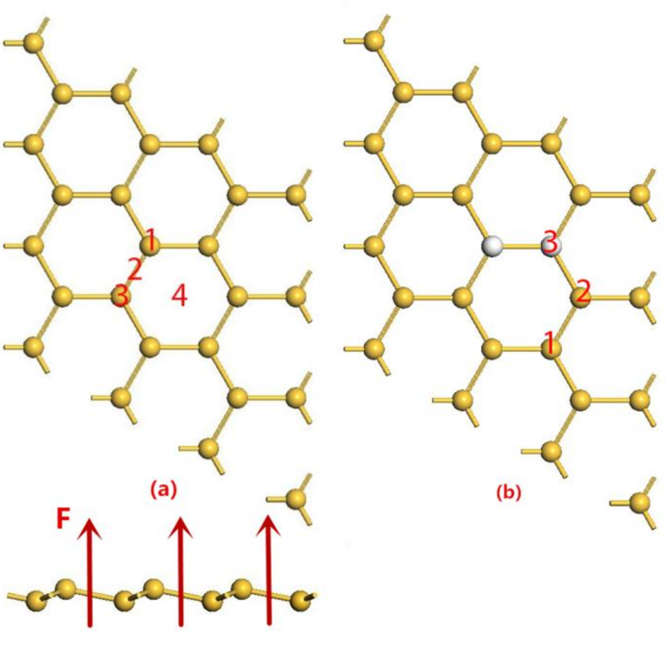

1
2
3
4
(a)
F
3
2
1
(b)

Fig. 2

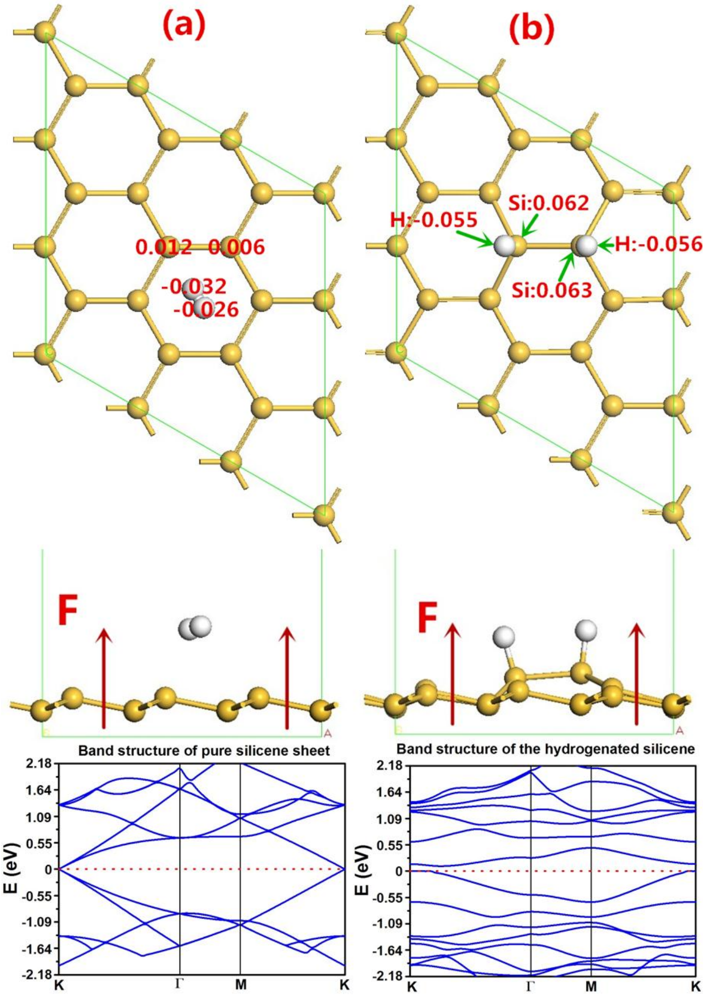

(a)
(b)
0.012
0.006
-0.032
-0.026
H:-0.055
Si:0.062
H:-0.056
Si:0.063
F
F
Band structure of pure silicene sheet
Band structure of the hydrogenated silicene
E (eV)
2.18
1.64
1.09
0.55
0
-0.55
-1.09
-1.64
-2.18
K
Γ
M
K

Fig. 3

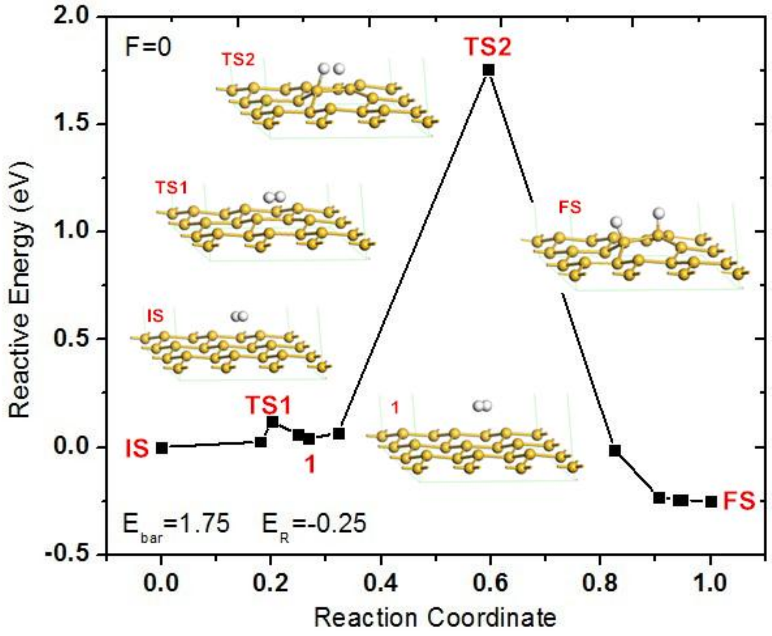

F=0
TS2
TS1
IS
FS
1
TS2
TS1
IS
1
FS
E$_{bar}$=1.75 E$_R$=-0.25
Reactive Energy (eV)
2.0
1.5
1.0
0.5
0.0
-0.5
0.0
0.2
0.4
0.6
0.8
1.0
Reaction Coordinate

Fig. 4

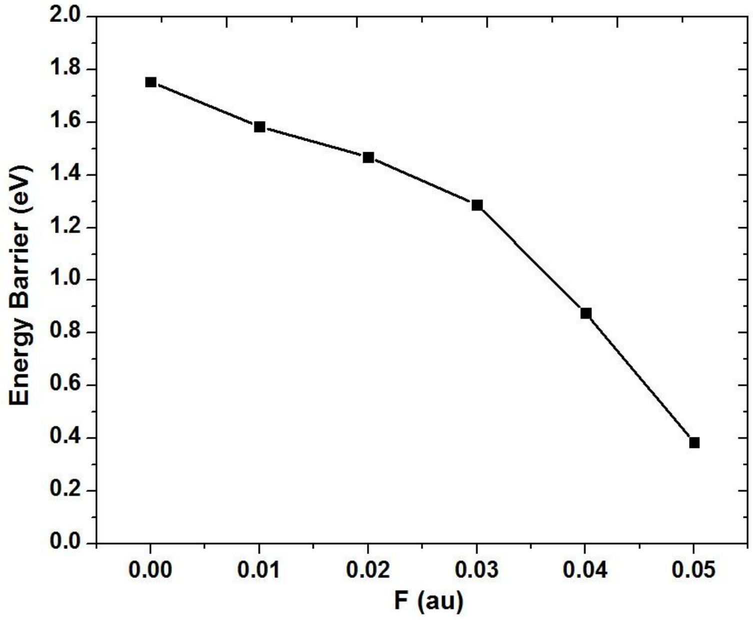

Energy Barrier (eV)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0.00
0.01
0.02
0.03
0.04
0.05
F (au)

Fig. 5

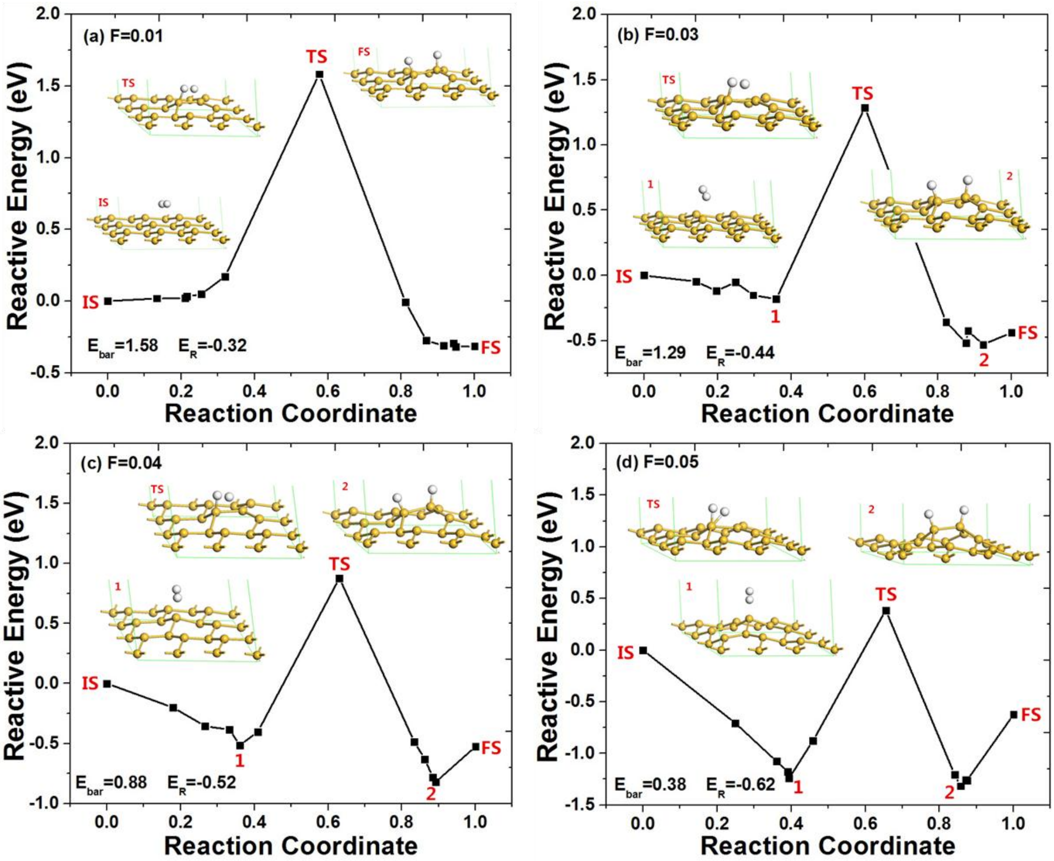
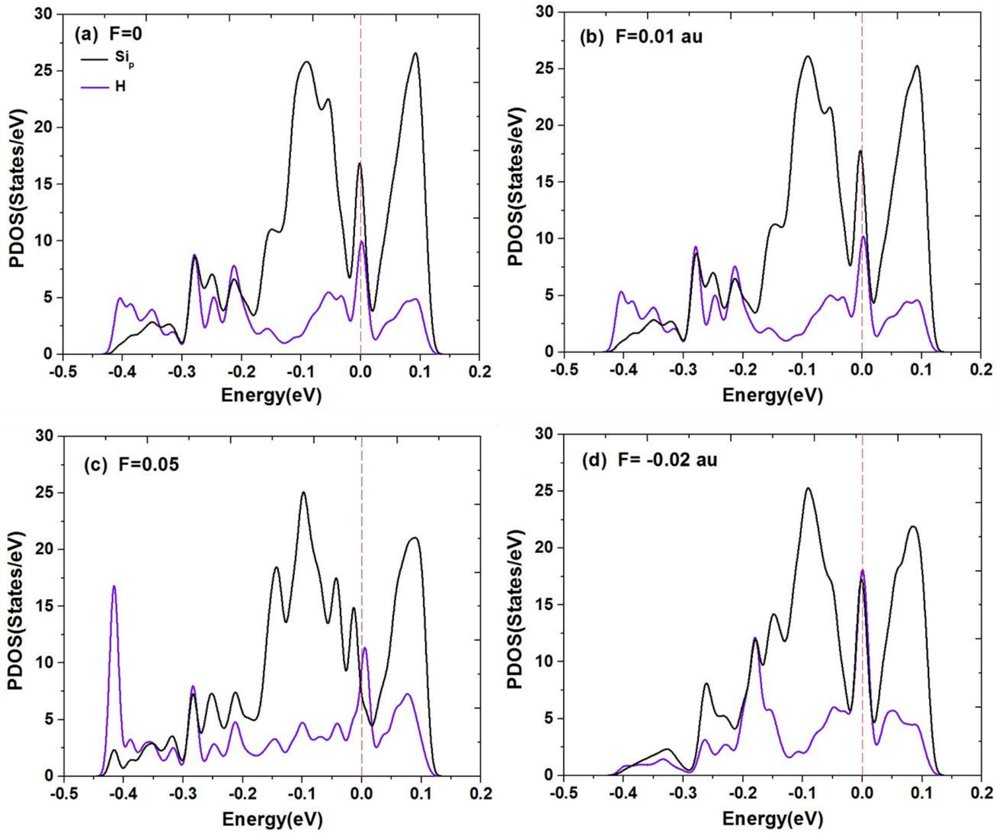

(a) F=0.01
TS
FS
IS
TS
IS
FS
E_bar=1.58 E_R=-0.32
(b) F=0.03
TS
1
2
TS
IS
1
2
FS
E_bar=1.29 E_R=-0.44
(c) F=0.04
TS
2
1
TS
IS
1
2
FS
E_bar=0.88 E_R=-0.52
(d) F=0.05
TS
2
1
TS
IS
1
2
FS
E_bar=0.38 E_R=-0.62
Reactive Energy (eV)
Reaction Coordinate
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
0.0
0.2
0.4
0.6
0.8
1.0

Fig. 6


(a) F=0
Si_p
H
(b) F=0.01 au
(c) F=0.05
(d) F= -0.02 au
PDOS(States/eV)
Energy(eV)
30
25
20
15
10
5
0
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2