乙炔在 Ge(001) 表面吸附的反应路径

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摘要: 采用第一性原理方法研究了乙炔分子在 Ge(001) 表面的吸附反应. 通过系统考察 0.5 和 1.0 ML 覆盖度时形成 di- σ 和 end-bridge 构型的反应路径, 研究在表面形成 di- σ 和 paired-end-bridge 构型的反应几率. 除了表面反应以外, 本文还涉及了亚表层 Ge 原子参与的吸附反应, 乙炔在亚表层原子上吸附形成的亚稳态结构 sub-di- σ , 是形成 end-bridge 结构的第二条途径, 此反应机理对于表面吸附结构的形成起重要的作用. 与乙炔分子不同的是, 表面以下原子参与时乙炔分子的吸附反应为吸热反应. 综合热力学和动力学的分析表明, paired-end-bridge 构型是乙炔分子吸附的主要构型, 此结论解释了乙炔分子在 Ge(001) 表面吸附构型的实验结果. 对于乙烯和乙炔两分子在 Ge(001) 表面吸附的分析比较揭示了导致两者之间差异的原因.

关键词: 密度泛函理论; Ge(001) 表面; 乙炔分子; 形成反应; 亚表层; 热力学; 动力学
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Reaction Pathways of Acetylene Adsorption on the Ge(001) Surface

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Abstract: The adsorption reaction of acetylene on the Ge(001) surface is investigated by first-principles calculations. In order to understand the relative populations of the di- σ and paired-end-bridge structures, we calculated the adsorption reaction paths leading to their formation at 0.5 and 1.0 ML coverage. More importantly, we studied the adsorption channel involving sublayer Ge atoms by forming a metastable sub-di- σ structure. This sub-di- σ structure represents second reaction pathway that results in the end-bridge structure, which plays an important role in the formation of the adsorption configurations. In contrast to C₂H₂, the adsorption of C₂H₄ on the Ge(001) surface involving subsurface Ge atoms, is endothermic. Our calculations show from both kinetic and thermodynamic standpoints that the paired-end-bridge structure is the primary adsorption configuration that explains the experimental observations. Our work also helps to understand the fundamental differences between the adsorption of C₂H₂ and C₂H₄ on the Ge(001) surface.

Key Words: Density functional theory; Ge(001) surface; Acetylene molecule; Formation reaction; Sublayer; Thermodynamics; Kinetics

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1 Introduction

The adsorption of unsaturated hydrocarbon molecules on the elemental semiconductor surface has attracted great interest because of its potential in technological applications such as non-linear optical devices, molecular electronic devices, and chemical sensors.^{1–4} Comparing to the intensive studies on the interaction of hydrocarbon molecules on Si(001) surface, the devotion to the Ge(001) surface is much less. In order to study the potential of the assemble hydrocarbon layer on Ge(001) surface in production of molecular microelectronic and optoelectronic devices fabrication and stability, the interaction of unsaturated hydrocarbon molecules with Ge(001) surface has received more attention recently.^{5–7}

Ge dimer is the reactive center on the Ge(001) surface, thus, both the intradimer and interdimer adsorptions are possible for $C_2H_4/Ge(001)$. The intradimer di- σ model has the two C atoms of the C_2H_4 bonded to the two Ge atoms of a single surface dimer, and the interdimer end-bridge model has the two C atoms bonded to the two Ge atoms on one side of two adjacent dimers along the dimer axis. Kim *et al.*⁵ observed two distinct desorption features by their temperature-programmed desorption (TPD) measurements. According to their observed scanning tunneling microscopy (STM) features, these respective features were assigned as the di- σ and paired-end-bridge configurations in which an additional C_2H_4 molecule adsorption makes the end-bridge structure to be paired. The STM images show that the di- σ structure dominates over the paired-end-bridge structure. Recently, we⁸ studied the di- σ and end-bridge configurations for C_2H_4 adsorption on Ge(001) surface at 0.5 and 1.0 ML coverages using first-principles calculations. Our calculated total energies indicate that di- σ and paired-end-bridge structures are energetically favorable, i.e., the adsorption is exothermic. Furthermore, our calculations of the formation paths show that the reaction rate of di- σ structure is higher, and the end-bridge structure is easy to be paired.

In addition to the di- σ and end-bridge models in which two C atoms are bonded to two Ge atoms, two additional adsorption models of the p-bridge and r-bridge configurations are believed to be probable for $C_2H_2/Ge(001)$. In both the r-bridge and p-bridge configurations, the two C atoms of C_2H_2 molecule are bonded to the four Ge atoms of the two adjacent surface dimers by forming four σ bonds. The C—C axis is parallel to the Ge-Ge dimer bond in the p-bridge configuration and perpendicular to the C-C dimer bond in the r-bridge configuration. The previous STM and TPD investigation by Kim *et al.*⁹ observed two adsorption configurations for C_2H_2 on Ge(001) surface labeled as “Feature A” and “Feature B”, which were assigned to the di- σ and p-bridge configurations, respectively. However, as listed in Table 1, according to our total energy calculation,¹⁰ as well as the theoretical calculations of Cho and Kleinman,¹¹ p-bridge configuration is much less stable than the paired-end-bridge configuration. Both calculations confirm that the two bonding features are actually the di- σ and paired-end-bridge

Table 1 Calculated adsorption energies (unit in eV) per C_2H_2 molecule on Ge(001) surface

	di- σ		end-bridge		r-bridge	p-bridge
	0.5 ML	1.0 ML	0.5 ML	1.0 ML		
this GGA	1.59	1.57	1.52	1.88	0.07	−0.23
Cho and Kleinman ¹¹	1.78	1.81	1.64	1.87	0.24	−0.03

configurations, respectively.

Moreover, theoretical calculations of Cho and Kleinman¹¹ found that the reaction rate to form the end-bridge structure was smaller than that of the di- σ structure. Nevertheless, the well-measured STM images indicates that Feature B dominates at all C_2H_2 coverage, and at the saturated coverage, the appearance ratio of Feature B to Feature A is 0.62:0.38. This indicates the reaction rate to form the end-bridge and paired-end-bridge adsorptions should be larger than the rate to form the di- σ adsorptions, which is conflicting with Cho and Kleinman's calculation results. On the other side, the experimental results on the two molecules are in contrast to each other: paired-end-bridge structure has been observed to be dominant over the di- σ structure in the present case of C_2H_2 ,⁹ and the population of di- σ structure is larger than that of the paired-end-bridge structure in the case of C_2H_4 ,⁵ which is indeed consistent with our calculation results on $C_2H_4/Ge(001)$.⁸

In the present work, we re-study the adsorption and desorption kinetics of $C_2H_2/Ge(001)$ by employing our experience in using the first-principles method based on the density functional theory (DFT) to examine small molecules on Si and Ge systematically, to understand the discrepancy between the experiment observation and theoretical calculation, and to dig out the root cause to the difference between the adsorptions of C_2H_2 and C_2H_4 on Ge(001) surface.

2 Calculation methods

The Ge(001) surface was simulated by a slab containing eight Ge atomic layers and a vacuum region of 1.294 nm spacing. Ge(001) surface has the similar reconstruction as the Si(001) surface. Four different reconstructions, symmetric (2×1), bucked (2×1), $p(2 \times 2)$, and $c(4 \times 2)$, have been investigated. Among them $c(4 \times 2)$ and $p(2 \times 2)$ are the most stable geometries. The energy difference between the two geometries is less than $0.003 \text{ eV} \cdot \text{dimer}^{-1}$, which agrees well with two previous studies^{12,13} in this topic. Thus, the Ge(001) surface was modeled by a repeated $p(2 \times 2)$ unit cell, while the dangling bonds of the bottom Ge atoms were saturated by H atoms. The structure optimization was performed using the calculated bulk lattice constant of 0.575 nm in the total energy calculation, the Ge atoms in the bottom layer of the slab, as well as the terminating hydrogen atoms were fixed to the bulk position. The Brillouin zone was sampled by a Monkhorst-Pack scheme with $4 \times 4 \times 1$ k -point grids.

The geometry optimization in the present study was performed on the basis of density functional theory with applying the Vienna *ab initio* simulation package (VASP).^{14–17} The total

energy calculations were carried out using the Vanderbilt ultrasoft pseudopotential^{18–20} and plane-wave method with cutoff energy of 350 eV. The generalized gradient approximation (GGA)^{21,22} of Perdew-Wang (PW91) was used for the electronic exchange-correlation potential. The minimum energy paths for the adsorption reactions were mapped out using the nudged elastic band (NEB) method developed by Jónsson and co-workers.^{23,24}

3 Results and discussion

3.1 Reaction pathways at 0.5 ML

According to previous studies^{8,25–27} for $C_2H_4/Si(001)$, $C_2H_2/Si(001)$, and $C_2H_4/Ge(001)$, the concerted [2+2] cycloaddition reaction is actually allowed based on the calculated reaction barrier and the analysis of the symmetry. The relative importance between the symmetric concerted [2+2] addition mechanism and the two-step asymmetric addition mechanism has been investigated further. It turns out that the asymmetric addition starting from a three-atom complex state in which the two C atoms of the adsorbed molecule are bonded to the “down”-Ge atom of a Ge-Ge dimer with a π dative bond is the more accessible route because the “down”-Ge atom of a Ge-Ge dimer is known to be electron deficient, and because the adsorbed molecule can access to this π precursor state with no strict alignment requirement of the molecular axis in its arrival trajectory relative to the Ge-Ge dimer. In contrast, the concerted addition mechanism is less important because the incoming molecular axis must align in parallel to the surface dimer. Thus, statistically, the significance of concerted addition pathways is much less than that of the asymmetric addition pathways and the role of concerted addition can be ignored.

In another consideration of reaction kinetics, we study the asymmetric addition pathways including their intermediate precursor states. By using the NEB method, we have found the minimum energy paths from the precursor states to the di- σ and end-bridge structures. Path I describes the formation of the di- σ configuration from the P_I state and Path II leads to the formation of the end-bridge configuration from the P_{II} state, the corresponding atomic geometries of the precursor (P), transition (T), and the chemisorptions (C) states on the reaction paths I and II are displayed in Fig.1, and the corresponding adsorption energies are given in Table 2. Along Path I, the respective adsorption energies of the P_I and T_I states are 0.27 and 0.08 eV; thus the reaction barrier from the P_I state to the di- σ configuration is 0.19 eV. In comparison, along Path II, the corresponding adsorption energies for the P_{II} and T_{II} are 0.28 and 0.05 eV, and the reaction barrier to form the end-bridge structure is 0.23 eV. It indicates that both the di- σ and end-bridge configurations are energetically favorable over the precursor states by about 1.2–1.3 eV. Thus, if the energy released by the formation of the precursor state is not dissipated away quickly, it is enough to drive the chemisorptions through the transition state. In other words, both the di- σ and end-bridge configurations can be formed *via* the precursor state in common experimental conditions, their formation rates are decided by the reaction barriers.

Our calculated adsorption energies for P_I and P_{II} states are consistent with the previous first-principles study by Cho and Kleinman,¹¹ as listed in Table 2. According to their calculations, the barriers are 0.09 and 0.13 eV for the di- σ and end-bridge structures, respectively. Although our calculations raise both respective values to 0.19 and 0.23 eV, the difference be-

Fig.1 Atomic geometries of the π -complex precursor (P), transition (T), and chemisorption (C) states for the adsorption of C_2H_2 on Ge(001) surface along different paths

(a) path I: asymmetric addition reaction leading to the di- σ structure from P_I state; (b) path II: asymmetric addition reaction leading to the formation of the end-bridge structure from the P_{II} state

Table 2 Comparison between the adsorption of C_2H_2 and C_2H_4 on Ge(001) surface, calculated adsorption energies (E_{ads}) of the π -complex precursor (P), transition (T), and the chemisorption (C) states, and energy barriers (E_b) from the P to the C

Configuration	$C_2H_2/Ge(001)$				$C_2H_4/Ge(001)^b$			
	E_{ads}/eV			E_b/eV	E_{ads}/eV			E_b/eV
	P	T	C		P	T	C	
di- σ	0.27	0.08	1.59	0.19	0.40	0.17	1.00	0.23
	0.25 ^a	0.16 ^a	1.78 ^a	0.09 ^a				
end-bridge	0.28	0.05	1.52	0.23	0.35	0.16	0.90	0.19
	0.26 ^a	0.13 ^a	1.64 ^a	0.13 ^a				
paired-di- σ	0.24	0.05	1.57	0.19	0.23	0.06	0.97	0.17
			1.81 ^a					
paired-end-bridge	0.29	0.16	1.88	0.13	0.25	0.13	1.13	0.12
	0.31 ^a	0.29 ^a	1.87 ^a	0.02 ^a				

$E_{ads}=E(\text{mole})+E(\text{Ge}(001))-E(\text{mole}/\text{Ge}(001))$, where $E(\text{mole})$ and $E(\text{Ge}(001))$ represent the energies of the C_2H_2 (C_2H_4) molecule and the bare Ge(001) surface, respectively; $E(\text{mole}/\text{Ge}(001))$ represents the total energy of the adsorbed

C_2H_2 (C_2H_4)/Ge(001) system. ^aReference¹¹, ^bReference⁸

tween the two barriers is again 0.04 eV. As reported by Cho and Kleinman,¹¹ the ratio of the reaction rate R_1 to form the di- σ configuration to the reaction rate R_2 to form the end-bridge configuration, represented as R_1/R_2 , is 1.2 if all the adsorption energy of the precursor state is retained. Using the Arrhenius-type activation process with a typical value ($\sim 10^{14}$ s⁻¹) for the pre-exponential factor which has been adopted by Cho and Kleinman, we have calculated the reaction rate R_2 from the precursor state P_{II} to the end-bridge structure; the resultant R_2 is 1.3×10^{10} s⁻¹. We also find that the reaction rate R_1 to form the di- σ structure is 4.7 times larger than R_2 . The factor R_1/R_2 becomes 1.1 if all the adsorption energies of the precursor state are retained. Therefore, our calculations are again consistent with the reported results of Cho and Kleinman, with both predicting that the formation rate of di- σ structure is larger than that of the end-bridge structure.

3.2 Reaction pathways at 1.0 ML

After studying the adsorption of one single molecule to form the di- σ and end-bridge structures, we have further calculated the respective reaction pathways of adding one more C_2H_2 molecule to form the actual paired-di- σ and paired-end-bridge structures. As listed in Table 2, comparing the formation of the paired-di- σ structure and the first di- σ structure, one sees that the adsorption energy of the precursor state to form the paired-di- σ structure is slightly lower by 0.03 eV, and the formation energy of the second di- σ structure is also lower by 0.02 eV. In contrast, the adsorption energy of the precursor state to form the paired-end-bridge structure is slightly higher, and the formation energy of the second end-bridge structure is higher by about 0.4 eV. These comparisons indicate that the di- σ structure is energetically favorable over the paired-di- σ structure; in contrast, the end-bridge structure will be eventually paired up.

Along the reaction pathway to form the paired-di- σ structure, the energy barrier is 0.19 eV. In comparison, the reaction barrier is 0.13 eV along the formation path of the paired-end-

bridge structure. Comparing the formation reaction of the paired-end-bridge structure and the first end-bridge structure, the reaction barrier is lower by 0.10 eV. In the case of the di- σ structure, the reaction barrier to form the paired-di- σ structure does not change from the barrier of the first di- σ structure. All these comparisons from both thermodynamics and kinetics indicate that the adsorption of a second di- σ C_2H_2 is impeded; in contrast, the formation of the paired-end-bridge structure is easy and the formation rate is higher once the end-bridge structure is formed.

In order to demonstrate the above comparisons more explicitly, we estimate the reaction rate to form the paired-end-bridge structure by adopting an Arrhenius-type rate formula again and the value turns out to be 6.4×10^{11} s⁻¹, which is 11 times larger than the formation rate of the paired-di- σ structure. The factor R_1/R_2 becomes 1.3 if all the adsorption energies of the precursor states are retained. According to the STM experiment, the ratio of "Feature A" image which is assigned as di- σ structure to the "Feature B" image which is now assigned as paired-end-bridge structure was obtained as 0.38:0.62 at saturation coverage. Hence, a factor of 1.3 is not enough to make up the deficiency in the formation rates of the end-bridge structure. Consistent with our calculations, the formation of the paired-end-bridge structure is also easier as shown in the report by Cho and Kleinman,¹¹ which cannot help the appearance ratio of paired-end-bridge structure to the di- σ structure to rise to the experimental value of 0.62:0.38.

3.3 Reaction pathways involving the sublayer Ge atom

The calculated adsorption energies of the precursor state and the reaction barriers to form the intradimer di- σ and interdimer end-bridge structures for C_2H_4 molecule on Ge(001) surface are also listed in Table 2. The energy released by the formation of the precursor state is not dissipated away quickly when the surface temperature is high, which is the common experimental condition. Since the adsorption energy of the P_{II} state is larger than that of the P_I state, the reaction rate to form the di- σ structure will be larger than the reaction rate to form the end-bridge structure. This is consistent with the present case for the adsorption of C_2H_2 on Ge(001) surface. Also, the adsorption energies of the precursor states and reaction barriers to form the paired-di- σ and paired-end-bridge structures are consistent between the two molecules, both shows the end-bridge structure will be easily paired up.

According to the experimental studies,⁵ on the other side, the di- σ structure dominates over the paired-end-bridge structure on the C_2H_4 adsorbed Ge(001) surface, while in the present case of $C_2H_2/Ge(001)$, as mentioned above, the appearance ratio of paired-end-bridge structure to di- σ structure is 0.68:0.32. In other words, in contrast to the theoretical studies, the relative population between the di- σ structure and paired-end-bridge structure in the case of $C_2H_2/Ge(001)$ is opposite to that in the case of $C_2H_4/Ge(001)$. In our previous study²⁷ for the ad-

sorptions of C_2H_2 and C_2H_4 molecule on Si(001) surface, we found one more important reaction site besides the surface dimer, the sublayer adsorption site, which plays a crucial role in understanding the different adsorption of C_2H_2 and C_2H_4 on Si(001) surface. Here, in order to dig out the root cause to the difference between the adsorptions of the two molecules on Ge(001) surface, and to understand the discrepancy between the experiment observation and theoretical calculation, we study the sublayer adsorption again.

The formation of the sub-di- σ structure from the P_{II} state is described as Path III displayed in Fig.2(a). The formation process involves the breaking of the Ge1—Ge3' bond and the formation of two C—Ge σ bonds, C2—Ge1 and C1—Ge3'. The adsorption energy for the transition state T_{III} is 0.10 eV as listed in Table 3, thus the reaction barrier to form the sub-di- σ structure is 0.18 eV. The more stable end-bridge structure can be formed through this sub-di- σ structure in the reaction along Path IV. The atomic structures involved in this path are shown in Fig.2(b). During the conversion from the sub-di- σ structure to the transition state T_{IV} , the Ge3—Ge3' and C1—Ge3' bonds are broken, and the C1—Ge3 and Ge1—Ge3' bonds are formed. As listed in Table 3, the adsorption energy of the sub-di- σ structure is 0.54 eV, and the reaction barrier from it to the more stable end-bridge structure is 0.31 eV. In common experimental conditions, the released energy of 0.54 eV by the formation the sub-di- σ structure can push the system to climb through the transition state T_{IV} to the product of the end-bridge structure.

Based on our calculations, there are two possible routes starting from the P_{II} precursor state to form the end-bridge structure: one is through the transition state T_{II} , and the second one

Table 3 Calculated adsorption energies of the precursor, transition chemisorptions states, and energy barrier from the P to the C states for the $C_2H_2/Ge(001)$ along the formation paths of the sub-di- σ structure from the P_{II} state, and the formation of the end-bridge structure through sud-di- σ structure

Configuration	E_{ads}/eV			E_b/eV
	P	T	C	
sub-di- σ	0.28	0.10	0.54	0.18
end-bridge	0.54	0.23	1.52	0.31

is through the meta-stable sub-di- σ structure. Meanwhile, the reaction barrier to form the sub-di- σ structure from the P_{II} state is a little bit smaller than the barrier to form the di- σ structure from the P_I state. Plus, the adsorption energy of the P_{II} state is a little bit larger than the adsorption energy of the P_I state. Thus, the reaction rate to form the sub-di- σ structure is a little higher than the reaction rate to form the di- σ structure. This sub-di- σ structure will be converted to the more stable end-bridge structure eventually in the reaction along the second route from the P_{II} state. Consequently, with this sublayer reaction channel in addition to the reaction channel through the transition state T_{II} to form the end-bridge structure, the population of the end-bridge structure can be larger than the population of the di- σ structure. Our calculations provide a new and more sensible explanation to the population ratio of end-bridge structure over di- σ structure beyond Cho and Kleinman's consideration for the possibility of the end-bridge structure being formed in either direction.

In contrast to the adsorption of C_2H_2 , the adsorption energy for C_2H_4 adsorbed between a sublayer Ge atom and a dimer Ge atom is about -0.20 eV, indicating that the sublayer adsorption channel for C_2H_4 molecule is unlikely since the adsorption

Fig.2 Atomic geometries of the π -complex precursor, transition, and chemisorption states for the adsorption of C_2H_2 on Ge(001) surface along different paths

(a) path III: asymmetric addition reaction leading to the formation of the sub-di- σ structure from the P_{II} state; (b) path IV: proceed reaction leading to the formation of the end-bridge structure from sub-di- σ structure

Fig.3 Atomic geometries of the sub-di- σ structure for the adsorption of C_2H_4 on the Ge(001) surface

turns out to be endothermic.⁸ It is thus reasonable to conclude that the sublayer adsorption channel plays an important role in the different behavior between C_2H_2 and C_2H_4 adsorptions on Ge(001) surface. Actually, this sublayer reaction channel also plays an important role in differentiating the behavior of the two molecules on Si(001) as we have shown in our previous report.²⁷ The C_2H_4 is less active than C_2H_2 because there is only one π bond in C_2H_4 compared to two π bonds in C_2H_2 . Additionally, in the C_2H_4 sub-di- σ structure shown in Fig.3, the two HC-Ge angles on one C atom are 105.9° and 99.6°, indicating the distortion from the ideal value of 109.5° for a sp^3 C. This also contributes to the instability.

4 Conclusions

The addition reaction pathways indicate that the di- σ structure appears on alternate dimer sites, and the end-bridge structure appears in the paired model. More importantly, the reaction channel involving the sublayer Ge atoms has been identified, with the channel leading to the formation of an intermediate sub-di- σ structure in common experiment conditions. The formation rate of this sub-di- σ structure is higher than the reaction rate of the di- σ structure. The end-bridge structure can thus be formed through this meta-stable intermediate structure. But for $C_2H_4/Ge(001)$, the adsorption of C_2H_4 involving the sublayer Ge atoms is endothermic. With the identification of this sublayer adsorption channel, it is easier for one to understand the difference between $C_2H_2/Ge(001)$ and $C_2H_4/Ge(001)$.

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