

Producing Reactive Species on Si(100), Ge(100), and Si(111) Surfaces by Attachments of Diacetylenes

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Received: January 6, 2004; In Final Form: February 12, 2004

Formation of a bilayer or a multilayer organic thin film on semiconductor surfaces is promising for the manufacture of new-generation microelectronic/nanoelectronic materials. A prerequisite for realization of such a goal is the formation of monolayer organic thin films with reactive functional groups exposed as a template for further chemical manipulations. We report herein a theoretical prediction that attachments of diacetylenes on Si(100)- 2×1 , Ge(100)- 2×1 , and Si(111)- 7×7 surfaces could produce monolayers of reactive [3]cumulenenic or/enynic surface species. Our density-functional cluster-model calculations revealed the following: (i) Diacetylene can undergo either stepwise [4 + 2]-like or stepwise [2 + 2]-like cycloadditions onto a X=X dimer of X(100)- 2×1 surfaces (X = Si and Ge) via a common singlet-diradical intermediate. (ii) On Si(100), the [2 + 2]-like pathway is kinetically favored over the [4 + 2]-like one, preferentially giving rise to enynic adspecies. (iii) On Ge(100), both pathways are competitive, resulting concomitantly in [3]cumulenenic and enynic adspecies. (iv) On Si(111)- 7×7 , diacetylene can undergo either 1,4 addition or 1,2 addition onto a rest atom-adatom pair with the former process being favored over the latter both thermodynamically and kinetically and leading preferentially to the formation of [3]cumulenenic adspecies on the surface. It is noteworthy that the [4 + 2]-like cycloaddition of diacetylene on Ge(100) 2×1 is among the few examples of [4 + 2] cycloaddition with a 1,3-diyne acting as a four-electron component affording six-membered cyclic [3]cumulenenes.

1. Introduction

In recent years, growing interest is focused on the organic functionalization of semiconductor surfaces owing to their important applications in microelectronic technology.^{1–5} Quite interesting organic/silicon surface chemistry has been so far disclosed.⁵ For example, the [2 + 2] cycloaddition of alkenes and [4 + 2] cycloaddition of conjugated dienes and the allied aromatic compounds on X(100) (X = Si and Ge) was found to result in rather strong X–C bonds,^{5–7} which facilitates the design and construction of monolayer organic thin films on semiconductor surfaces. Yet, it is nontrivial to produce a bilayer or a multilayer organic thin film on semiconductor surfaces; a prerequisite for realization of such a goal is the formation of monolayer organic thin film with reactive functional groups exposed as a template for further chemical manipulations. Such a challenge has motivated the recent investigations on the attachment of multifunctional organic compounds on these semiconductor surfaces.^{3–5,8} In this paper, we report the results of density-functional cluster-model calculations on the cycloaddition chemistry of diacetylene (C₄H₂) on three representative surfaces of silicon and germanium, i.e., Si(100)- 2×1 , Ge(100)- 2×1 , and Si(111)- 7×7 . The calculations revealed that reactive [3]cumulenenic or/enynic species could be readily formed on these semiconductor surfaces upon attachments of diacetylenes, providing precursors highly promising for further chemical functionalization.

Diacetylenic molecules containing a C₄ fragment (i.e., a C≡C–C≡C– group) are commonly used as precursors for the synthesis of carbon-rich π -conjugated networks⁹ and are subject to either 1,4-addition or 1,2-addition reactions.¹⁰ On the other hand, the reconstructed X(100)- 2×1 (X = Si and Ge) surfaces (Figure 1a) consist of rows of buckled X=X dimers that have concomitantly π -bond, zwitterionic, and diradical characters (Chart 1).^{5d} Such intriguing electronic structure of the X=X dimers enables them to be prone to undergo either [4 + 2] (Diels–Alder reaction) or [2 + 2] cycloadditions with incoming conjugated dienes such as 1,3-cyclohexadienes and butadienes.⁷ Also it has been shown that the attachment of simple alkenes (e.g., C₂H₄)⁶ and alkynes (e.g., C₂H₂)¹¹ on these X=X dimers gives rise to [2 + 2] cycloaddition products, probably following stepwise, diradical reaction pathways.^{6c,11a} In light of these chemical precedents, two possible reaction pathways are proposed for the attachment of a 1,3-diyne (e.g., diacetylene) onto a X=X dimer of X(100) surfaces, i.e., a [4 + 2]-like route yielding a [3]cumulenenic adspecies and a [2 + 2]-like route producing an enynic adspecies (Scheme 1). Both cumulenenic and enynic groups that are reactive organic groups well documented in synthetic organic chemistry can be precursors for further chemical modification to form bilayer or even multilayer organic thin films on these semiconductor surfaces. Furthermore, although [4 + 2] cycloadditions that generally involve conjugated dienes as four-electron components and simple alkenes as two-electron components have been well documented and widely exploited in synthetic organic chemistry,¹² so far only two examples have been reported of [4 + 2] cycloaddition with a 1,3-diyne acting as a four-electron component,¹³ in which the

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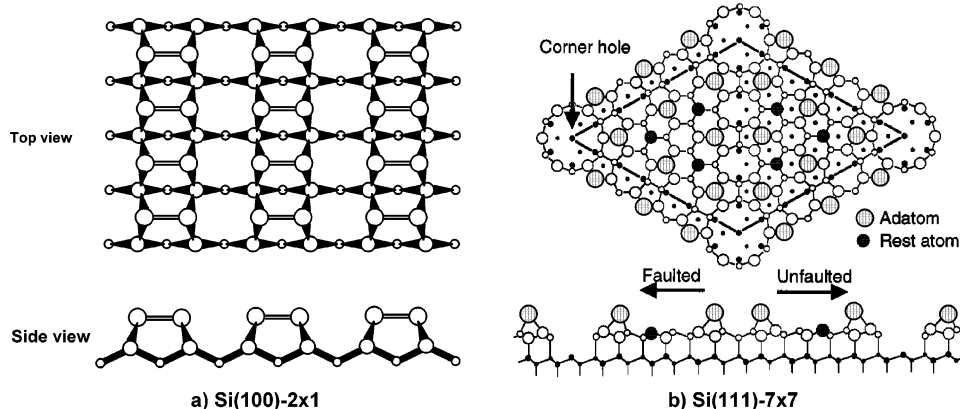
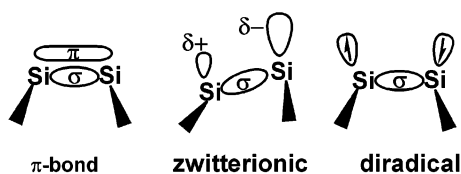
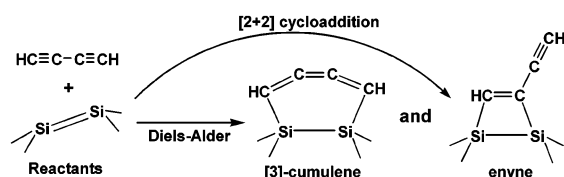


Figure 1. Atomic arrangements of (a) Si(100)-2 \times 1 and (b) Si(111)-7 \times 7 surfaces.

CHART 1. Three Models Describing the Bonding within a Buckled X=X Dimer (X = Si and Ge)



SCHEME 1. Possible Pathways for the Attachment of a Diacetylene on a X=X Dimer of X(100) Surface (X = Si and Ge)

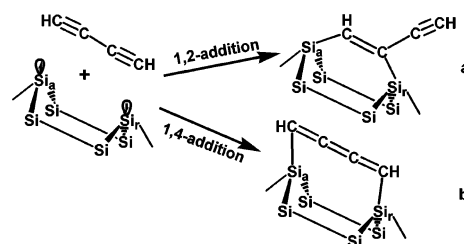


produced cyclic [3]cumulenenic species are strongly strained, unstable, and subject to further isomerization. Meanwhile, such 1,3-diyne-involving [4 + 2] cycloadditions are always sterically hindered.¹⁴ In this respect, if [4 + 2] cycloaddition of diacetylene on X(100) surfaces (X = Si and Ge) is plausible and affords stable [3]cumulenenic adspecies, this would be the first example of [4 + 2] cycloaddition with a 1,3-diyne acting as a four-electron component affording stable cyclic [3]cumulenes.

The Si(111)-7 \times 7 surface adopts the dimer–adatom–stacking fault structure (Figure 1b); each 7 \times 7 unit has 19 dangling bonds.¹⁵ Adjacent adatom–rest atom pairs exposed on Si(111)-7 \times 7 were found to be diradical-like^{8c} and readily undergo 1,2 additions with simple alkenes (e.g., ethylene) and alkynes (e.g., acetylene) and 1,4 additions with conjugated dienes (e.g., 1,3-butadiene) and allied aromatics (e.g., benzene and thiophene), producing di- σ -bonded adspecies by following diradical mechanisms.¹⁶ Similarly, it is possible for diacetylenic molecules to undergo 1,2-addition (pathway a in Scheme 2) and/or 1,4-addition (pathway b in Scheme 2) onto an adatom–rest atom pair site, giving rise to enynic adspecies and/or [3]cumulenenic adspecies on Si(111)-7 \times 7, respectively.

The purpose of the present theoretical work is to explore the regioselectivities and mechanisms for the cycloaddition reactions of diacetylene with Si(100)-2 \times 1, Ge(100)-2 \times 1, and Si(111)-7 \times 7 surfaces. It should be mentioned that neither experiment nor theoretical calculation has been reported on the adsorption of diacetylene on Ge(100)-2 \times 1 and Si(111)-7 \times 7 surfaces. A very recent HREELS (high-resolution electron energy loss spectroscopy) study conducted by Xu et al. revealed the

SCHEME 2. Possible Pathways for the Attachment of a Diacetylene on a Si(111)-7 \times 7 Surface



preferential formation of enynic adspecies on Si(100)-2 \times 1 upon the adsorption of diacetylene.¹⁷ Such an experimental observation is confirmed by our calculations reported herein.

2. Computational Details

For the study of diacetylene adsorption on X(100)-2 \times 1 surfaces (X = Si and Ge), we used X₉H₁₂ clusters to model the X=X dimers.^{6c,7b–e,11a} Calculations were done at the (U)B3LYP/6-31G* level¹⁸ of theory. The cluster models as well as the computational method have been widely employed in a previous study of the chemistry of X(100) surfaces (X = Si and Ge).^{6c,7b–e,19} At the B3LYP/6-31G* level of theory, the X₉H₁₂ (X = Si and Ge) cluster adopts a closed-shell ground state with an asymmetric X=X dimer; the buckling angle of the Ge=Ge dimer in the Ge₉H₁₂ cluster is estimated to be 15.7°, whereas for the Si₉H₁₂ case, the buckling angle of the Si=Si dimer is quite small (~1.7°). Such a prediction is in qualitative agreement with the experimental observations that dimers on both Ge(100) and Si(100) surfaces are buckled at low temperatures.^{5d} It should be noted that more significant dimer buckling had been predicted when larger cluster models that contain two or three dimers were used to model Si(100).^{7e,19d}

For the study of the adsorption of diacetylene on a Si(111)-7 \times 7 surface, we used a Si₁₆H₁₈ cluster model^{16,20} to represent the adjacent adatom–rest atom pair on a faulted half of a Si(111)-7 \times 7 surface unit cell. The hybrid density functional (U)B3LYP method,¹⁸ together with the effective-core-potential LANL2DZ basis set for Si atom,²¹ the standard 6-31+G* basis set for C atom,²² and the D95 basis set for H atom,²³ was used to investigate the energetics of the reactions. Such a combination of cluster model and computational method had been used in our previous theoretical investigations of the adsorptions of some unsaturated hydrocarbons, methanol, and ammonia on the same surface.^{16,20}

All calculations were performed with the Gaussian 98 package.²⁴ For all cases, geometry optimizations with no

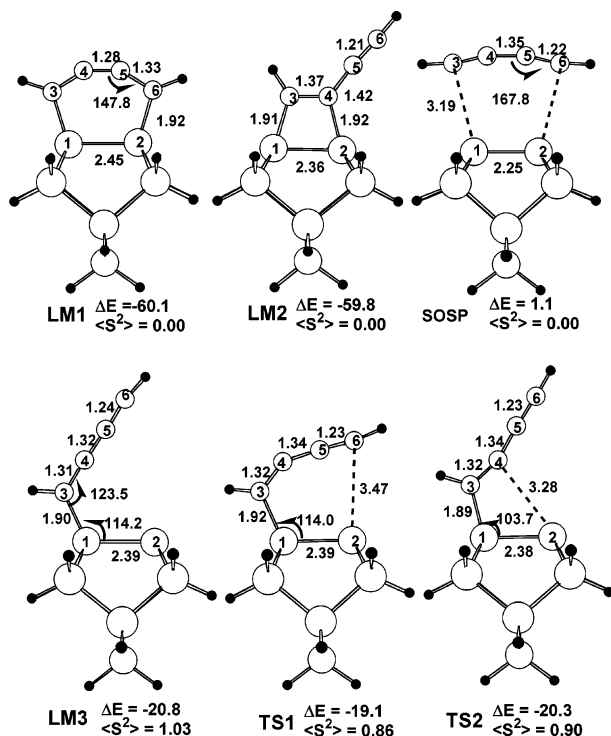


Figure 2. (U)B3LYP/6-31G*-optimized products (**LM1** and **LM2**), saddle points (**TS1**, **TS2**, and **SOSP**), and intermediate (**LM3**) for the cycloaddition of diacetylene on Si_9H_{12} cluster model. The $\langle S^2 \rangle$ values for the wave functions of these stationary points and energies (ΔE , kcal/mol) relative to isolated diacetylene and Si_9H_{12} are also given.

constrained degrees of freedom were performed using analytical gradients and the Berny algorithm. Reported energies are ZPE (zero-point energy) corrected, unless otherwise specified.

3. Results and Discussion

Attachment of Diacetylene on $\text{Si}(100)\text{-}2 \times 1$. Figure 2 depicts the predicted intermediates, saddle points, and products for the cycloaddition of diacetylene with the $\text{Si}=\text{Si}$ dimer of the Si_9H_{12} cluster model. Both $[4 + 2]$ and $[2 + 2]$ additions of diacetylene with the $\text{Si}=\text{Si}$ dimer are found to be highly exothermic (predicted exothermicities around 60 kcal/mol), giving rise to a cyclic [3]cumulene (**LM1**) and an enyne (**LM2**), respectively. Noteworthy, the $\text{C}=\text{C}=\text{C}=\text{C}$ group in the as-formed [3]cumulenic adspecies (**LM1**) is not collinear with two equivalent $\text{C}=\text{C}=\text{C}$ angles of 147.8° , implying substantial steric strain within it.

$[4 + 2]$ Pathway. Effort to search for the transition state along a concerted pathway for the heterogeneous $[4 + 2]$ reaction has been made by using the RB3LYP (spin-restricted B3LYP) method that has been proven reliable in the study of classic $[4 + 2]$ cycloaddition reactions.²⁵ A second-order saddle point (**SOSP**) is found to be only 1.1 kcal/mol higher than the isolated reactants in energy, implying that such a heterogeneous $[4 + 2]$ reaction would adopt an asymmetric pathway. Detailed potential energy surface (PES) calculations revealed no transition state for the asymmetric $[4 + 2]$ pathway; selected points along the PES are given in Figure 3. The high asynchrony of such a barrierless process is obvious; e.g., the selected point **P4** within such a barrierless pathway has a short $\text{Si}-\text{C}1$ bond ($\sim 2.02 \text{ \AA}$) but a rather large $\text{Si}-\text{C}4$ distance of 3.54 \AA . In addition, the specific geometry of **P4** suggests that it might be inherently diradicaloid. Accordingly, the stability of the close-shell RKS (restricted Kohn–Sham) wave function for **P4** has been carefully checked at the UB3LYP/6-31G* level of theory. The

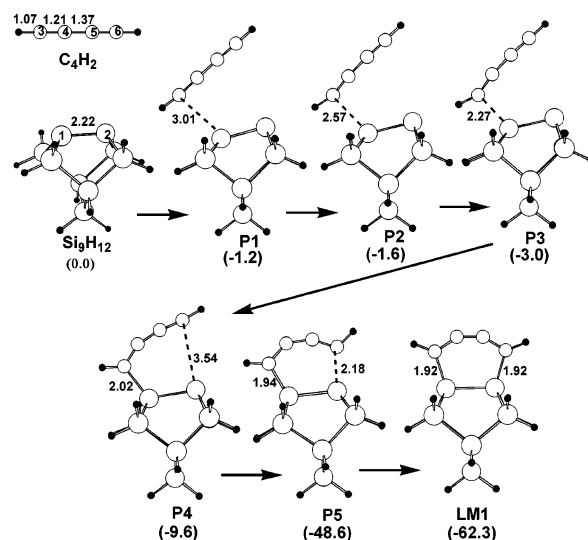


Figure 3. Selected points along the asymmetric $[4 + 2]$ cycloaddition pathway for the attachment of diacetylene on the Si_9H_{12} cluster model predicted by the RB3LYP/6-31G* calculations. Relative energies (not corrected for ZPE, in kcal/mol) are given in parentheses.

calculation revealed that **P4** is diradicaloid with the corresponding open-shell singlet UKS (unrestricted Kohn–Sham) wave function being stable by 3.4 kcal/mol relative to the closed-shell RKS wave function. This means the asymmetric one-step $[4 + 2]$ pathway shown in Figure 3 might be artificial due to the use of closed-shell RKS wave functions in the PES calculations. We thus employed the spin-unrestricted B3LYP (UB3LYP) method to re-explore the $[4 + 2]$ pathway. A singlet-diradical intermediate (**LM3**), in which the adsorbed diacetylene is mono- σ bonded to an end of the $\text{Si}=\text{Si}$ dimer, is located 20.8 kcal/mol lower than the isolated reactants. Interestingly, formation of such a diradical intermediate is found to be barrierless, probably due to the rather weak π bonding (bond strength of 5–10 kcal/mol)²⁶ within the $\text{Si}=\text{Si}$ dimer. Further ring closure (radical–radical combination) within this diradical intermediate (**LM3**) can lead to the $[4 + 2]$ cycloaddition product **LM1** by overcoming an activation barrier of 1.7 kcal/mol (relative to **LM3**) at the transition state **TS1**. Accordingly, the $[4 + 2]$ cycloaddition of diacetylene with the $\text{Si}=\text{Si}$ dimer available on $\text{Si}(100)$ follows inherently a stepwise and diradical mechanism, as schematically shown in Figure 4. Such unusual $[4 + 2]$ cycloaddition of diacetylene with the $\text{Si}=\text{Si}$ dimer is barrierless and highly exothermic, readily affording a cyclic [3]cumulene. This differs largely from the molecular $[4 + 2]$ reaction of diacetylene with ethylene, which follows a symmetric reaction pathway with moderate endothermicity and a high activation energy.^{13a}

$[2 + 2]$ Pathway. The $[2 + 2]$ cycloaddition appears to follow a diradical mechanism, somewhat similar to the previously revealed diradical mechanisms for the $[2 + 2]$ cycloaddition of simple alkenes and alkynes on $\text{Si}(100)$.^{6c,11a} The $[2 + 2]$ cycloaddition product (**LM2**) can be formed from the singlet-diradical intermediate **LM3** by overcoming a rather small barrier (only 0.5 kcal/mol with respect to **LM3**) at the transition state **TS2**. Thus, by following the diradical mechanisms (Figure 4) via a common singlet-diradical intermediate (**LM3**), both $[2$

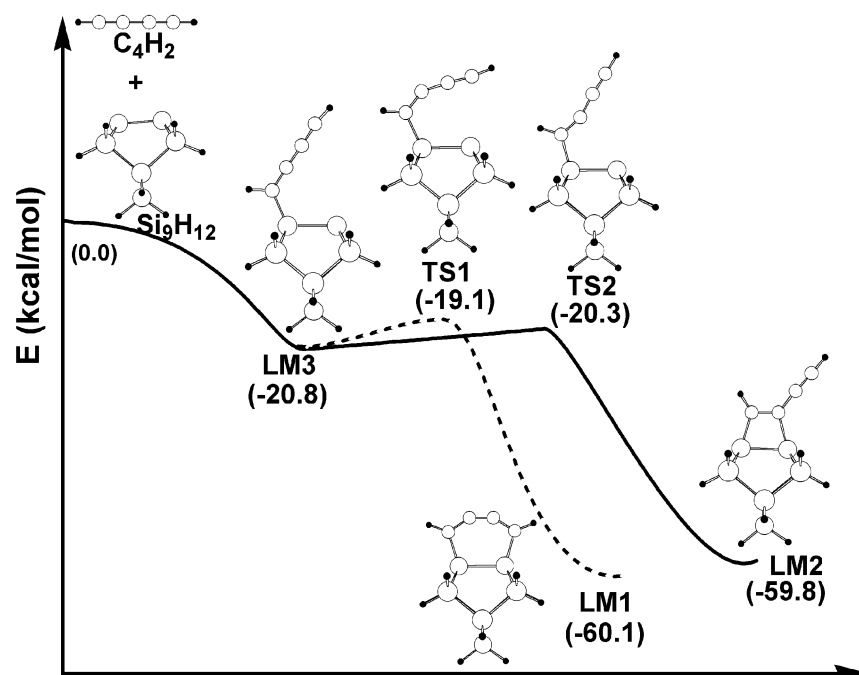


Figure 4. Profile of energy surface for the attachment of diacetylene on Si(100) predicted by (U)B3LYP/6-31G* calculations (dashed line for the [4 + 2] pathway and solid line for the [2 + 2] pathway). Relative energies are given in parentheses.

TABLE 1: Predicted Vibrational Frequencies (cm⁻¹) for Diacetylene in the Gas Phase and Adsorbed on Si(100)-2 × 1

mode	gas phase		chemisorbed on Si(100) ^a	
	calcd ^a	exp ^b	enynic	[3]cumulenitic
C≡C-H bend	260	220		
C≡C-H bend	696	630	585, 588	
C-C stretch	884	844	1010 ^c	
=CH off-plane bend			841	646, 814
=CH in-plane bend			1157	1098(asym) 1175(sym)
C=C stretch			1459	1535(asym) 1975(sym)
C≡C asymmetric stretch	2031	2020	2099 ^d	
C≡C symmetric stretch	2198	2184		
=C-H stretch			3007	3041, 3041
≡C-H stretch	3338, 3340	3332	3338	

^a Present work. A scaling factor of 0.955 is used in the calculations of the frequencies. ^b Data from ref 27. ^c =C-H inplane bend + C-C stretch (with very low IR absorption intensity).

+ 2] and [4 + 2] cycloaddition products can be formed; the formation of the enynic adspecies (i.e., [2 + 2] product) is kinetically preferential. This prediction agrees well with the recent HREELS experiment that only enynic adspecies were observed after adsorption of diacetylene on Si(100) surface.¹⁷ The HREELS spectrum of the diacetylene/Si(100) chemisorption system¹⁷ shows a series of vibrational modes with frequencies at 3336, 3033, 2100, 1638, 1253, 842, and 629 cm⁻¹, respectively. These experimental data are in line with the vibrational frequencies of the enynic adspecies predicted at the B3LYP/6-31G* level of theory (cf. Table 1).

Despite the fact that both diacetylene and ethylene have been shown to undergo [2 + 2] cycloaddition onto a Si=Si dimer of Si(100)-2 × 1, substantial differences in their diradical mechanisms should be noted. In the adsorption of diacetylene, the formation of the diradical intermediate from isolated reactants is direct and barrierless, whereas the adsorption of ethylene proceeds from a dative-bonded π complex through a barrier of 3.7 kcal/mol toward a diradical intermediate.⁶ Such a difference reflects the higher reactivity of diacetylene.

While the present study focuses on the reaction of diacetylene on a single dimer, we could not exclude such a possibility that interdimer reactions may also occur. Note that, in addition to single dimer reactions, interdimer reactions were recently observed for the adsorption of acetylene^{11b} and 1,3-cyclohexadiene^{7f} on Si(100).

Attachment of Diacetylene on Ge(100)-2 × 1. The predicted intermediates, saddle points, and products for the cycloaddition of diacetylene with the Ge=Ge dimer of the Ge₉H₁₂ cluster are depicted in Figure 5. The profile of energy surface for the reaction pathways is schematically shown in Figure 6. Similar to the adsorption of diacetylene on Si(100)-2 × 1, the adsorption of diacetylene on the Ge(100)-2 × 1 surface also follows stepwise (diradical) mechanisms. The [4 + 2]- and [2 + 2]-like additions are predicted to be exothermic by 49.8 and 47.9 kcal/mol, giving rise to the [4 + 2] product **LM1b** and [2 + 2] product **LM2b**, respectively. The lower exothermicities for the adsorption on Ge(100) than the adsorption on Si(100) can be ascribed to the fact that a Ge-C single bond is generally weaker than a Si-C single bond. A common singlet-diradical intermediate **LM3b** by 14.3 kcal/mol than the isolated reactants is found to be responsible for the stepwise [4 + 2]-like and [2 + 2]-like pathways. In contrast to the adsorption on Si(100) where the stepwise [2 + 2] pathway is favorable over the stepwise [4 + 2] pathway, the stepwise [4 + 2] pathway is highly competitive with the stepwise [2 + 2] pathway on Ge(100). Note that the transition state **TS1b** preceding the [2 + 2] product **LM2b** is only by 0.1 kcal/mol lower than the transition state **TS2b** that leads to the [4 + 2] product **LM1b**. This means both enynic and [3]cumulenitic adspecies can be readily and concomitantly formed on Ge(100). The different selectivities for the attachments of diacetylene on Ge(100) and Si(100) surfaces can be attributed to the fact that a Ge-Ge bond (~2.49 Å in **LM3b**) is longer than a Si-Si bond (~2.39 Å in **LM3**); the longer X-X bond facilitates the [4 + 2] pathway.

Apart from the stepwise diradical [4 + 2] and [2 + 2] pathways, we have also considered the concerted [4 + 2] pathway that is symmetry allowed. By maintaining a C_{2v}

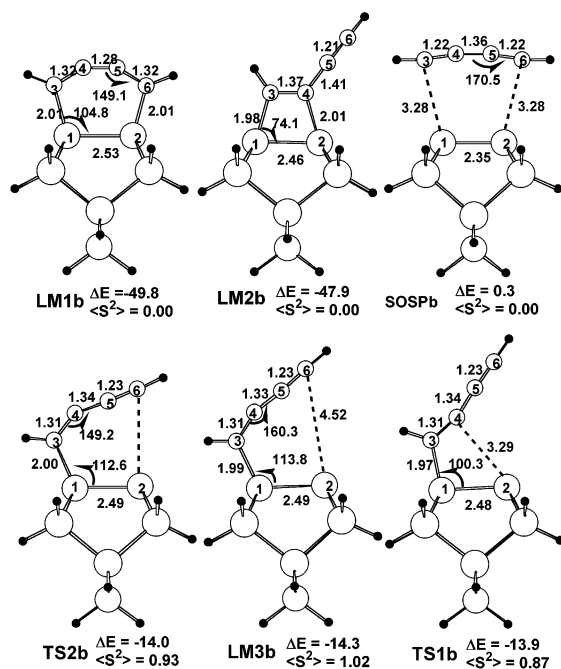


Figure 5. (U)B3LYP/6-31G*-optimized products (LM1b and LM2b), saddle points (TS1b, TS2b, and SOSpb), and intermediate (LM3b) for the cycloaddition of diacetylene on Ge_9H_{12} cluster model. The $\langle S^2 \rangle$ values for the wave functions of these stationary points and energies (ΔE , kcal/mol) relative to isolated diacetylene and Ge_9H_{12} are also given.

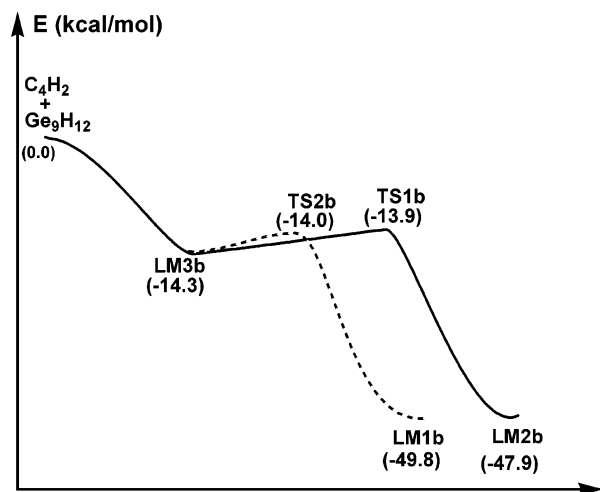


Figure 6. Profile of the energy surface for the attachment of diacetylene on $\text{Ge}(100)$ represented by the single-dimer Ge_9H_{12} cluster model (dashed line for the $[4 + 2]$ pathway and solid line for the $[2 + 2]$ pathway). Relative energies are given in parentheses.

symmetry for the $\text{C}_4\text{H}_2 + \text{Ge}_9\text{H}_{12}$ system, a second-order saddle point **SOSpb** is located by only 0.3 kcal/mol higher than the isolated reactants. Further elaborate PES calculations at the RB3LYP/6-31G* level revealed that the concerted $[4 + 2]$ pathway (Figure 7) is highly asymmetric, analogous to the asymmetric $[4 + 2]$ pathway (Figure 3) for the $\text{C}_4\text{H}_2/\text{Si}_9\text{H}_{12}$ system which has been shown to be artificial. Re-exploration of such a highly asynchronous pathway at the UB3LYP/6-31G* level of theory gives rise to the stepwise, diradical $[4 + 2]$ pathway shown in Figure 6. Thus similar to $\text{C}_4\text{H}_2/\text{Si}(100)$ case, the $[4 + 2]$ cycloaddition of diacetylene on $\text{Ge}(100)$ follows intrinsically the stepwise diradical $[4 + 2]$ pathway.

Attachment of Diacetylene on $\text{Si}(111)-7 \times 7$. The predicted intermediates, transition states, and products for the attachment

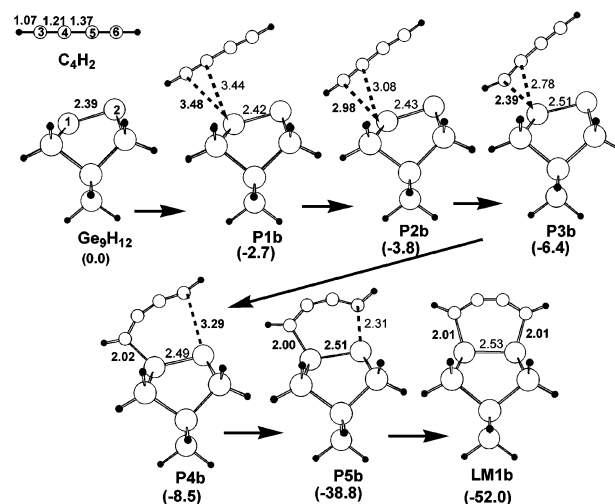


Figure 7. Selected points along the asymmetric $[4 + 2]$ cycloaddition pathway for the attachment of diacetylene on the Ge_9H_{12} cluster model predicted by RB3LYP/6-31G* calculations. Relative energies (not corrected for ZPE, in kcal/mol) are given in parentheses.

of diacetylene on the $\text{Si}_{16}\text{H}_{18}$ cluster model are depicted in Figure 8. The profile of energy surface for the reaction pathways is given in Figure 9. The adsorption of diacetylene on $\text{Si}(111)-7 \times 7$ is initiated by the barrierless formation of a singlet-diradical intermediate **LM1c**, which is 24.4 kcal/mol lower than the isolated reactants in energy. In **LM1c**, the diacetylene moiety is mono σ bonded onto the Si adatom with a C–Si bond length of 1.89 Å. From **LM1c**, ring closing (radical–radical recombination) may occur either between the C4 atom and the Si rest atom or between the C2 atom and the Si rest atom, resulting in 1,4-addition product **LM2c** or 1,2-addition product **LM3c**, respectively. The predicted formation energies for **LM2c** and **LM3c** are -76.6 and -63.4 kcal/mol, showing that 1,4 addition is thermodynamically favorable over 1,2 addition. Furthermore, two transition states, **TS1c** and **TS2c**, were located preceding the 1,4 addition and 1,2 addition products, respectively. The predicted activation energy for the elementary step, **LM1c** \rightarrow **LM2c**, is only 0.6 kcal/mol, whereas a value of 4.4 kcal/mol is predicted for the elementary step **LM1c** \rightarrow **LM3c**. Hence, the stepwise 1,4-addition process is kinetically preferential, giving solely rise to [3]cumulenic adspecies on $\text{Si}(111)-7 \times 7$. It should be pointed out that on a real $\text{Si}(111)-7 \times 7$ surface, the substrate Si atoms, especially those within the second, third, and fourth layers, should be much more constrained than those in the $\text{Si}_{16}\text{H}_{18}$ cluster model. Thus the present cluster model calculations may somewhat overestimate the reactivity of surface reactions, especially in the 1,2-addition case that demands significant surface relaxation. If certain constraints were exerted on the substrate Si atoms of the $\text{Si}_{16}\text{H}_{18}$ cluster model, the activation barrier for the formation of a 1,2-addition product from the singlet-diradical intermediate would be higher than the present value (4.4 kcal/mol) and the selectivity to the 1,4-addition product would be more significant.

As shown in Figure 8e, the C_4 fragment ($-\text{C}=\text{C}=\text{C}=\text{C}-$) in the as-formed [3]cumulenic adspecies (**LM2c**) is not collinear with a $\text{C1}=\text{C2}=\text{C3}$ bond angle of 158.7° and a $\text{C2}=\text{C3}=\text{C4}$ bond angle of 171.3° , implying substantial strain within the $\text{C}=\text{C}=\text{C}$ skeleton. Some characteristic vibrational frequencies of [3]cumulenic adspecies are predicted to be 3048 and 3004 cm^{-1} for the C–H stretching modes, 2025 and 1564 cm^{-1} for $\text{C}=\text{C}=\text{C}$ stretching modes, and 1184 and 1129 cm^{-1} for the C–H bending modes.²⁸ These values can be fingerprints for future experimental detection of the [3]cumulenic adspecies.

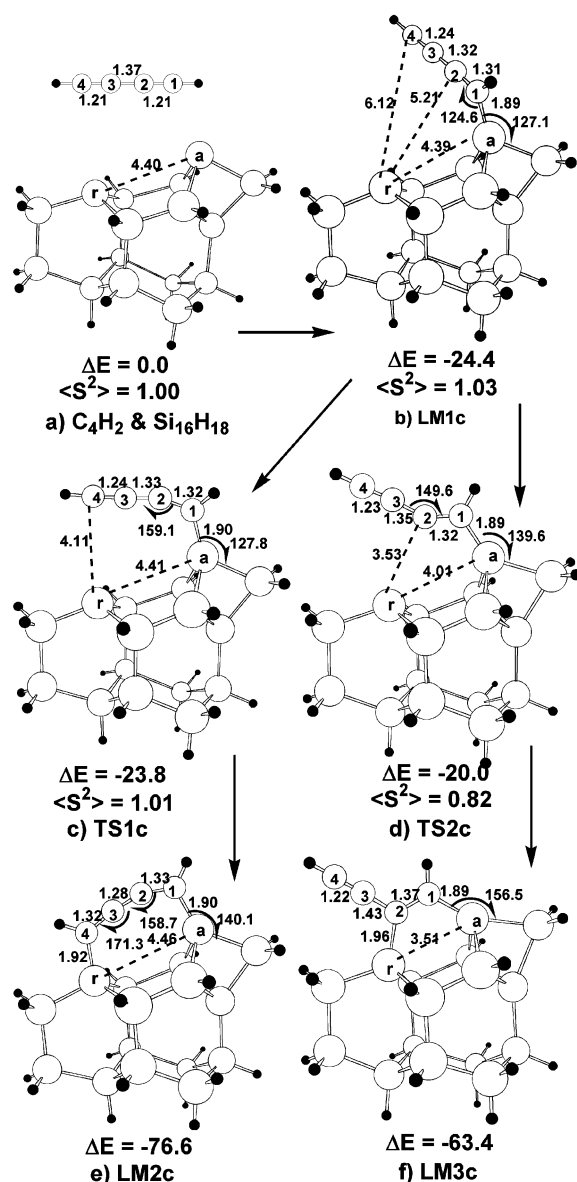


Figure 8. (U)B3LYP-optimized intermediates, transition states, and products for the attachment of diacetylene on the $Si_{16}H_{18}$ cluster modeling a rest atom–adatom pair on Si(111)- 7×7 . Relative energies (ΔE in kcal/mol) and $\langle S^2 \rangle$ values are also given.

4. Concluding Remarks

In summary, we provided theoretical predictions on the selectivities and mechanisms for the attachments of diacetylene on Si(100)- 2×1 , Ge(100)- 2×1 , and Si(111)- 7×7 surfaces. It is shown that the adsorption of diacetylene gives rise to enynic adspecies on Si(100)- 2×1 , [3]cumulenic adspecies on Si(111)- 7×7 , and both [3]cumulenic and enynic adspecies on Ge(100)- 2×1 . All these cycloaddition-like chemisorptions follow diradical mechanisms. The diradical mechanisms disclosed here advocate the diradical characters of the $X=X$ dimers available on $X(100)-2 \times 1$ ($X = Si$ and Ge). More significantly, the diradical mechanisms reported herein and elsewhere^{6c,11a,16} should be of great help in our understanding of the intriguing new chemistry of more complex, multifunctional unsaturated organic molecules on the semiconductor surfaces that may be mediated by dangling bonds available on the surfaces. Furthermore, it should be noted that the [4 + 2] cycloaddition of diacetylene on Ge(100) that affords cyclic [3]cumulenic adspecies can be regarded as the third so-far-reported example of [4

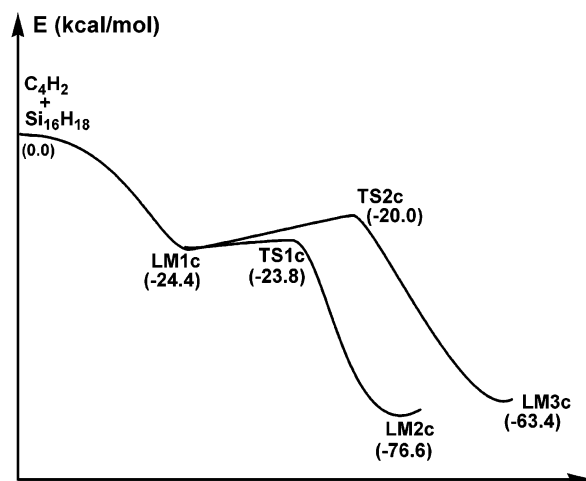


Figure 9. Profile of the energy surface (unit in kcal/mol) for the attachment of diacetylene on the $Si_{16}H_{18}$ cluster modeling a rest atom–adatom pair on the Si(111)- 7×7 surface.

+ 2] cycloaddition with a 1,3-diyne acting as a four-electron component.¹³ Finally, the as-formed [3]cumulenic or/and enynic surface species can be templates (or precursors) for further synthetic construction of bilayer or even multilayer organic thin films on the semiconductor surfaces. In this regard, the well-documented chemistry¹⁴ of [3]cumulenes and enynes can be exploited.

Acknowledgment. This work was sponsored by NSF of China (Grants Nos. 20021002, 20203013, 90206038, and 20023001), Fok Ying-Tung Education Foundation, Ministry of Education of PRC (Grant No. 20010384005), Ministry of Science and Technology (Grants Nos. G1999022408 and 2002CCA01600), and NSF of Fujian Province (Grants Nos. E0210001 and 2002F010).

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