Dry Synthesis of Triple Cumulative Double Bonds (C=C=C=N) on Si(111)-7 × 7 Surfaces

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The interactions of cyanoacetylene and diacetylene with a Si(111)-7 × 7 surface have been studied as model systems to mechanistically understand the chemical binding of unsaturated organic molecules to diradical-like silicon dangling bonds. Vibrational studies show that cyanoacetylene mainly binds to the surface through a diradical reaction involving both cyano and C≡C groups with an adjacent adatom–rest atom pair at 110 K, resulting in an intermediate containing triple cumulative double bonds (C=C=C=N). On the other hand, diacetylene was shown to the covalently attached to Si(111)-7 × 7 only through one of its C≡C groups, forming an enynic-like structure with a C=C−C≡C skeleton. These chemisorbed species containing triple cumulative double bonds (C=C=C=N) and C=C−C≡C may be employed as precursors (or templates) for further construction of bilayer organic films on the semiconductor surfaces.

I. Introduction

The covalent binding of organic molecules on semiconductor surfaces has recently become an increasingly important vehicle of surface modification and functionalization for potential application in molecular electronics.[1−3] The present focus is to understand the reaction mechanisms of organic molecules on semiconductor surfaces. In particular, the reactivity and selectivity of multifunctional organic molecules on semiconductor surfaces are extensively studied, providing functionalized surface for specific applications as well as templates for further chemical manipulations, such as the formation of bilayer or multilayer organic thin films on the semiconductor surface.[4−6]

Si(111)-7 × 7, the so-called dimer-adatom-stacking (DAS) faulted model,[7,8] can be regarded as a model template for understanding the interaction between organic molecules and silicon surface due to its multiple reactive sites with different electronic structures and spatial distributions in one unit cell. Nineteen dangling bonds in every unit cell are located at 12 adatoms, 6 rest atoms, and 1 corner hole. The charge transfer occurs preferentially from adatoms to rest atoms, thereby resulting in completely occupied dangling bonds at rest atoms and the corner hole as well as partially or empty dangling bonds at adatoms. The great difference in electron density and the spatial separation (∼4.5 Å) between the adjacent adatom and rest atom make them an efficient diradical in the covalent attachment of unsaturated organic molecules.[9−11]

Previous studies in this area mainly focused on the binding of simple alkenes (e.g., ethylene),[12,13] alkynes (e.g., acetylene),[14−16] nitriles (e.g., acetonitrile),[17,18] and allied aromatics (e.g., benzene and thiophene).[19−23] Experimental and theoretical calculations suggest the [2 + 2]-like cycloaddition mechanism for molecules containing one C=C/C≡C (N) bond and [4 + 2]-like cycloaddition pathway for diene-like molecules.

Currently, attention is directed toward the reactivity and selectivity of multifunctional molecules on Si(111)-7 × 7 where different functional groups in the molecule may compete for active sizes on the surface. It is also possible that more than one functional group in the molecule simultaneously bind to the surface. We have shown that acrylonitrile containing conjugated C=C and C≡N groups can be bound to Si(111)-7 × 7 through a [4 + 2]-like cycloaddition reaction, creating a cyclic, six-membered ketenimine (C=C=N).[10] Although recent density functional theory (DFT) calculations showed the feasibility of the formation of [3]-cumulenic adspecies in the reaction of diacetylene on Si(111)-7 × 7,[24] experimental evidence has yet to be established.

Cyanoacetylene (CH≡C−C≡N) and diacetylene (CH≡C−C≡CH) are two conjugated molecules made of C≡C and C≡N(C) groups. Investigating their interactions with Si surfaces will provide the correlation of reaction selectivity and binding configuration with the functional groups in the molecule, to offer the necessary flexibility in the functionalization and modification of silicon surfaces.

In this paper, HREELS was used to characterize the vibrational properties of cyanoacetylene and diacetylene on Si(111)-7 × 7. DFT calculations (pBP/DN** in Spartan 5.1) were carried out to optimize the chemisorption geometries and obtain their adsorption energies and vibrational frequencies. Our experimental results together with DFT calculations show that (a) cyanoacetylene is chemically attached to Si(111)-7 × 7 through both cyano and C≡C groups, producing molecular templates containing triple cumulative double bonds at the organic/silicon interface, and (b) diacetylene is covalently bonded to Si(111)-7 × 7 through an addition reaction of a C≡C group with the neighboring adatom–rest atom pair, forming an enynic-like intermediate.

II. Experimental Section

The experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of <2 × 10⁻¹⁰ Torr, achieved with turbo-molecular and sputter-ion pumps. The chamber is equipped with a high-resolution electron energy loss spectrometer (HREELS, LK-2000-14R) and a quadrupole mass spectrometer (UTI-100). The HREELS spectrometer is equipped with a double-pass 127° cylindrical deflector analyzer (CDA)

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TABLE 1: Vibrational Modes Assignment for Physisorbed and Chemisorbed Cyanoacetylene (CA) on Si(111)-7 × 7[a]

vibrational assigns	CA gas-phase IR[28]	gas-phase calculation[b]	physisorbed CA on Si(111)−7 × 7[b]	vibrational assigns	chemisorbed CA on Si(111)−7 × 7[b]	calcd vibrational freq for CA on Si(111)−7 × 7[b]
C≡C−C≡N bend	220	247		Si−N stretch	569	584
C−C≡N bend	499	550	525	Si−C stretch	649	667
C≡C−H bend	663	634	741	C=C=C=N torsion	821	805
C−C stretch	955	912	941	C=C=C=N bending	1205	1189
C≡C stretch	2079	2081	2100	C=C=C=N symmetric stretch	1570	1566
C≡N stretch	2274	2273	2289	C=C=C=N asymmetric stretch	2010	2022
≡C−H stretch	3339	3304	3313	−CH = stretch	3035	3040

[a] IR data[28] for vapor cyanoacetylene (the vibrational frequencies are given in cm⁻¹). [b] Present work.

as the monochromator and a single-pass 127° CDA for energy analysis. For HREELS experiments, the electron beam with an energy of 5.0 eV impinges on Si(111)-7 × 7 at an incident angle of 60° with a resolution of 6−7 meV (fwhm, 50 cm⁻¹).

The samples of dimension 8 × 18 × 0.35 mm³ were cut from n-type Si (111) wafers (phosphors-doped, with a resistivity of 1−30 Ω·cm, 99.999%, Goodfellow). The samples can be cooled to 110 K with liquid nitrogen and heated to 1400 K. The clean Si(111)-7 × 7 surfaces were prepared by cycles of Ar ion bombardment (500 eV, 30 min, 20 µA cm⁻²) and final annealing at 1200 K for 10 min in UHV.

Cyanoacetylene was synthesized by the method of Colos and Waluk.[25] In short, the starting compound, methyl propiolate (Aldrich, 99.0%), was transformed into an amide, HCCCONH₂, in the presence of excess liquid ammonia. The amide eliminated a molecular of water to yield the nitrile when mixed with P₂O₅ and heated in a vacuum. Diacetylene was prepared by dehydrochlorination of 1,4-dichloro-2-butyne (Aldrich, 98.0%).[26] Cyanoacetylene and diacetylene were all trapped with an acetone/liquid nitrogen slush. The final products were measured by FTIR spectroscopy (Nicolet Nexus 870) and purified in several freeze−pump−thaw cycles before being dosed onto the silicon surface through an adjustable leak valve.

III. Results and Discussion

III.A. Cyanoacetylene Binding on Si(111)-7 × 7. Figure 1 shows the high-resolution electron energy loss spectra of Si-(111)-7 × 7 exposed to cyanoacetylene at 110 K as a function of exposure. The vibrational frequencies and their assignments for physisorbed and chemisorbed molecules are listed in Table 1. For physisorbed multilayer, vibrational features at 525, 741, 941, 2100, 2289, and 3313 cm⁻¹ are unambiguously resolved. Table 1 clearly shows that the vibrational features of physisorbed cyanoacetylene (Figure 1d) are in excellent agreement with the IR spectrum of gaseous cyanoacetylene.[27,28] Among these vibrational signatures, the peak at 3313 cm⁻¹ is assigned to the Csp−H stretching mode. Other features at 2289, 2100, and 941 cm⁻¹ are correlated to the C≡N, C≡C, and C−C stretching modes, respectively.

The vibrational features of chemisorbed cyanoacetylene at low exposures (Figure 1a) or obtained by annealing the multilayer cyanoacetylene-covered sample to 300 K to drive away all the physisorbed molecules and only retain the chemisorbed molecules (Figure 2b), however, are significantly different. Losses at 569, 649, 821, 1205, 1570, 2010, and 3035 cm⁻¹ can be readily resolved. The disappearance of the C≡N stretching vibration around 2289 cm⁻¹ in chemisorbed molecules strongly suggests its involvement in the surface binding. A new feature at 3035 cm⁻¹ is noticed, which is assigned to (sp²) C−H stretching vibration. This result shows the rehybridization of the C¹ atom of the C²≡C¹H group from sp to sp² due to its
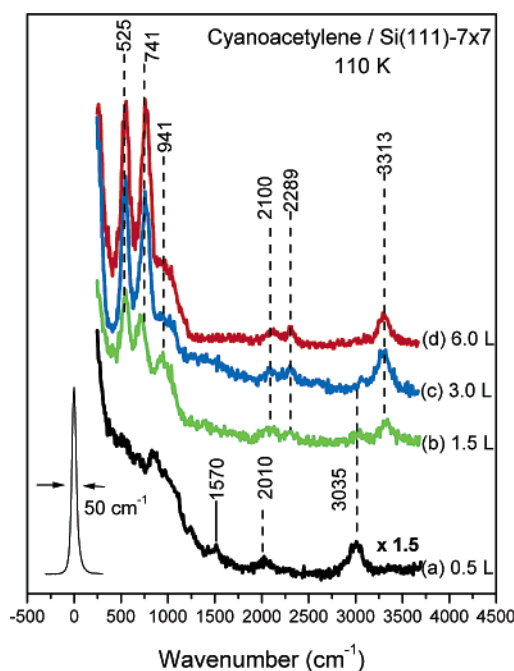

Figure 1. HREELS spectra of cyanoacetylene on Si(111)-7 × 7 as a function of exposure at 110 K.

binding with the Si-dangling bond. This is further confirmed by the absence of the (sp)C−H (at 3313 cm⁻¹) and C≡C (at 2100 cm⁻¹) stretching modes in the vibrational signatures of chemisorbed cyanoacetylene. The major spectroscopic change is the appearance of a new peak at 2010 cm⁻¹, ascribed to the characteristic vibration of a C=C=C=N skeleton (asymmetric stretching mode).[29,30] This assignment is further supported by the concurrent observation of the symmetric stretching, bending, and torsion modes of C=C=C=N at 1570, 1205, and 821 cm⁻¹, respectively. The formation of a C=C=C=N skeleton is also consistent with the absence of the C−C stretching mode (at 941 cm⁻¹) in the vibrational features of chemisorbed molecules. Furthermore, the other new features at 569 and 649 cm⁻¹ are ascribed to the Si−N and Si−C stretching modes,[21] respectively. The detailed assignments are given in Table 1, which also lists the main vibrational frequencies of the Si−CH=C=C=N−Si structure from our DFT calculations, further confirming our assignment for chemisorbed cyanoacetylene on Si(111)-7 × 7. The details of DFT theoretical modeling will be given in section III.C.

Figure 3 presents three possible binding modes of cyanoacetylene on Si(111)-7 × 7. Binding via a [2 + 2]-like cycloaddition through the cyano group will form a surface intermediate of CH≡C−C(Si)=N(Si) (Figure 3a), where the C≡C group is retained. However, the disappearance of the ≡CH (3313 cm⁻¹) and C≡C (2100 cm⁻¹) stretching modes in our
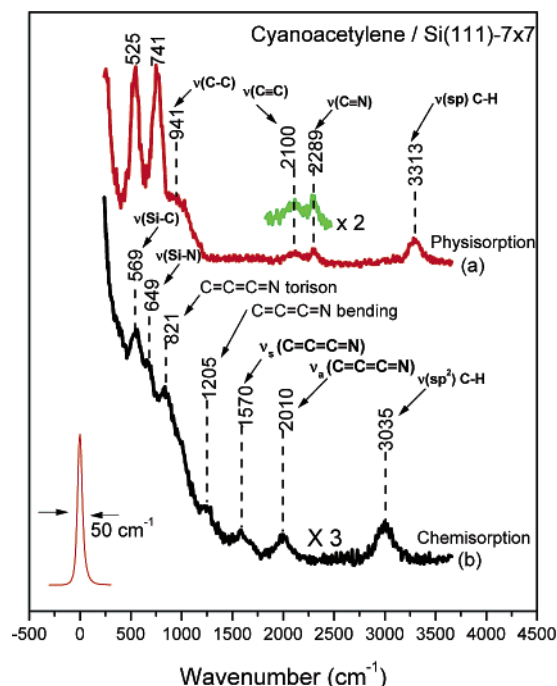
Figure 2. HREELS spectra of the physisorbed cyanoacetylene on Si-(111)-7 × 7 at 110 K (a) and saturated chemsorption monolayer prepared after annealing the surface in (a) to 300 K (b).
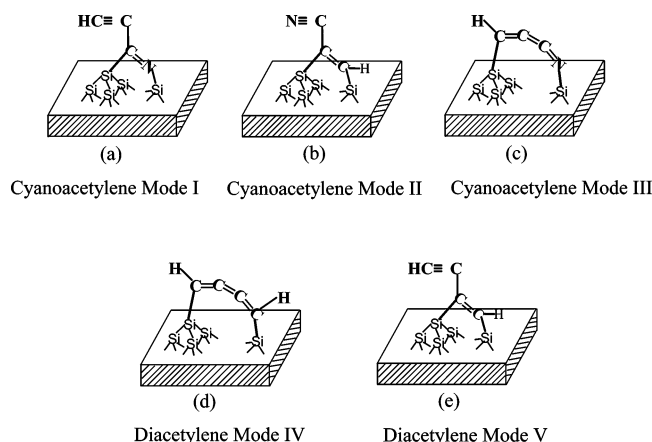

Figure 3. Schematic diagrams of the possible modes for covalent bonding of cyanoacetylene and diacetylene to Si(111)-7 × 7.

HREELS results rules out this possiblility. Alternatively, the [2 + 2]-like reaction through the C≡C group to a neighboring adatom−rest atom pair would give a chemisorbed species of (Si)CH=C(Si)-C≡N (Figure 3b) with a C=C−C≡N conjugated structure. In this cycloadduct, the two C atoms in C≡C group rehybridize from sp into sp^2, together with the retention of the cyano group. The disappearance of C≡N stretching mode at 2289 cm^{-1} in the chemisorbed molecules also excludes this mode.

In fact, our results are consistent with the [4 + 2]-like cycloaddition reaction mechanism, forming a product containing a −CH=C=C=N− skeleton (Figure 3c). In this structure, the disappearance of C≡N is expected, together with the conversion of C≡C to C=C upon cycloaddition. The characteristic C=C=C=N skeleton of the surface intermediate is characterized by the detected asymmetric stretching mode at 2010 cm^{-1}, together with its symmetric stretching (at 1570 cm^{-1}), bending (at 1205 cm^{-1}), and torsion (at 821 cm^{-1}) modes. Hence, these results allow us to conclude that cyanoacetylene covalently bonds to the Si surface principally through breaking both $\pi_{C≡N}$
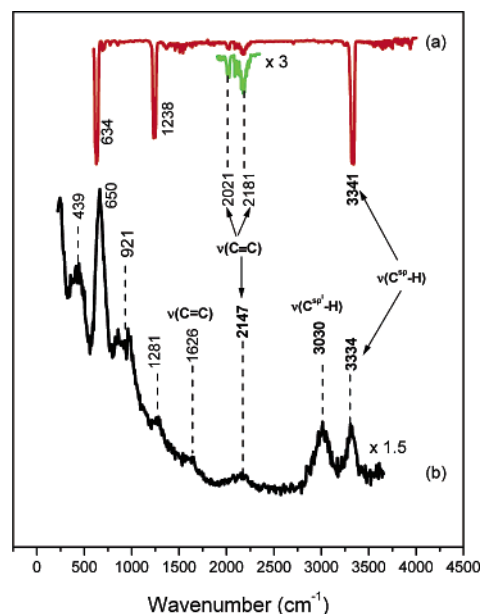

Figure 4. IR spectrum (scanning range 4000−600 cm^{-1}) for gaseous diacetylene (a) and the high-resolution electron energy loss spectrum of Si(111)-7 × 7 exposed to diacetylene (b) at room temperature.

TABLE 2: Vibrational Modes Assignment for Gas-Phase Diacetylene and Chemisorbed Diacetylene on Si(100)-2 × 1 (Vibrational Frequencies Given in cm^{-1})

vibrational assigns	diacetylene gas phase		chemisorbed diacetylene on Si(111)−7 × 7[a]
	IR[a,b]	previous IR[c]	HREELS
C≡C−H bend		220	
C≡C−C bend		483	439
Si−C stretch			650
C≡C−H bend	634	626	
C−C stretch			921
≡CH bend	1238	1241	1216
C=C stretch			1638
C≡C stretch	2021(a), 2181(s)	2019(a), 2189(s)	2100
=CH stretch			3033
≡C−H stretch	3341	3332	3336

[a] Present work. [b] IR spectra scanned from 4000 to 600 cm^{-1}. [c] Reference 31.

and $\pi_{C≡C}$ bonds to react with the dangling bonds located on the adjacent adatom−rest atom pair via the [4 + 2]-like process.

III.B. Diacetylene Binding on Si(111)-7 × 7. Figure 4 shows the IR spectrum (scanning range 4000−600 cm^{-1}) for gaseous diacetylene (Figure 4a) and the high-resolution electron energy loss spectra of Si(111)-7 × 7 exposed to diacetylene at room temperature (Figure 4b). Similar results were obtained for chemisorbed diacetylene on Si(111)-7 × 7 at 110 K (not shown). The vibrational frequencies and their assignments for gas-phase diacetylene and chemisorbed molecules on Si(111)- 7 × 7 are listed in Table 2. Vibrational signatures at 634, 1238, 2021, 2181, and 3341 cm^{-1} can be clearly identified in the IR spectra for gaseous molecules, which are in excellent agreement with previous studies.[26,31] The features at 3341 and 2021, 2181 cm^{-1} are correlated to the ≡C$^{(sp)}$−H and C≡C stretching modes, respectively.

The vibrational features of chemisorbed diacetylene are significantly different from the IR spectra of gaseous molecules. Losses at 439, 650, 921, 1281, 1626, 2147, 3030, and 3334 cm^{-1} are readily resolved. The coexistence of the ≡C^{sp}−H (at 3334 cm^{-1}) and =C^{sp2}−H (at 3030 cm^{-1}) stretching modes in the chemisorbed molecules strongly demonstrates the rehybrid-

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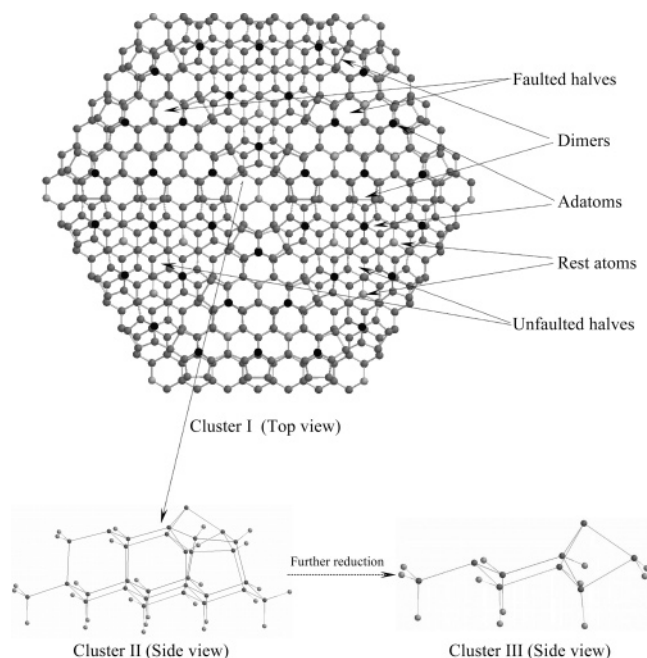
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Figure 5. A large cluster of the top five silicon layers constructed based on the DAS model to present three Si(111)-7 × 7 surface unit cells surrounding a corner hole. Cluster I has 973 atoms including the capping H atoms (not displayed for clarity).

Figure 6. Optimized C_3NH/Si_9H_{12} and C_4H_2/Si_9H_{12} clusters corresponding to the five possible attachment configurations through the [4 + 2]-like and [2 + 2]-like cycloadditions.

TABLE 3: Adsorption Energies of the Local Minima in the Cyanoacetylene/Si_9H_{12} Model System from PBP/DN

functional group	$C\equiv N$	$C\equiv C$	$C\equiv C-C\equiv N$
binding model	I	II	III
reaction model	[2 + 2]	[2 + 2]	[4 + 2]
adsorption energy[a]	22.8	51.1	64.9

[a] Adsorption energy: $\Delta E = [E(Si_9H_{12}) + E(C_3HN)] - E(C_3HN/Si_9H_{12})$. All energies are in kcal mol^{-1}.

ization of one of the $C\equiv C$ groups on binding to the surface. This is further supported by the concurrent observation of the $C\equiv C$ and $C=C$ stretching modes at 2147 and 1626 cm^{-1}, respectively. These results clearly demonstrate that diacetylene covalently binds to Si(111)-7 × 7 through a [2 + 2]-like cycloaddition between one of its $C\equiv C$ groups and surface reactive sites.[32] The formation of two new Si−C linkages is confirmed by the appearance of a new peak at 650 cm^{-1} (Si−C stretching mode).[19] In addition, the absence of the Si−H stretching vibration around 2055 cm^{-1} [33] suggests the nature of molecular chemisorption for diacetylene on Si(111)-7 × 7 at room temperature.

Figure 3 shows two possible routes for the covalent attachment of diacetylene on Si(111)-7 × 7, namely, a [4 + 2]-like reaction (Figure 3d) and a [2 + 2]-like pathway (Figure 3e), producing a [3]-cumulenic and an enynic-like adspecies, respectively. In reality, our main experimental evidence of (1) the coexistence of $\equiv C^{sp}-H$ and $=C^{sp2}-H$ stretching modes and (2) the concurrent observation of the $C\equiv C$ and $C=C$ stretching modes unambiguously excludes the possibilities of the [4 + 2]-like cycloaddition. Thus, our vibrational studies of chemisorbed diacetylene strongly suggest the formation of an enynic-like surface intermediate containing a (Si)CH=C(Si)−C≡CH skeleton through the reaction of one of the $C\equiv C$ groups with an adatom−rest atom pair via a [2 + 2]-like process.

III.C. DFT Calculations. Because of the high reactivity of $C\equiv C$ and $C\equiv N$ groups on Si(111)-7 × 7,[14−18] various competitive reaction pathways are possible over the same surface binding sites (the neighboring adatom−rest atom pair) for both cyanoacetylene and diacetylene. Thus, we have theoretically modeled some of the possible configurations to aid the understanding of the reactivity and selectivity of these π-conjugated systems on Si(111)-7 × 7.

As shown in the left-bottom panel of Figure 5, cluster model II ($Si_{30}H_{28}$) is cut from the central part of MMFF94[34]-optimized cluster I (the top panel of Figure 5) containing 973 atoms including the capping hydrogen atoms, where the precision of atomic positions suffers the least from boundary effects. It
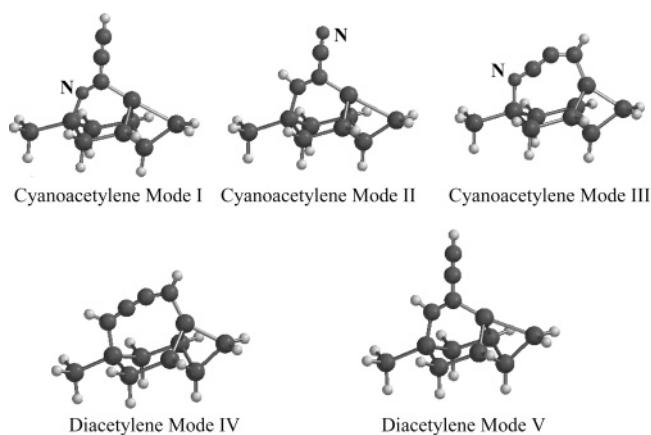
contains an adatom and an adjacent rest atom from an unfaulted subunit, serving as a "diradical" binding site for the attachment of one cyanoacetylene or diacetylene molecule. Capping H atoms at the cluster boundaries are kept frozen. Silicon atoms in the bottom double layers are placed at bulk lattice positions prior to the geometry optimization process, with each Si−Si bond length set to 2.3517 Å and all bond angles adjusted to 109.4712°. Cluster III (Si_9H_{12}) was obtained from further reduction of cluster II ($Si_{30}H_{28}$). Similarly, all capping H atoms were frozen during geometry optimization. Clusters I−III were used in successful prediction of the adsorption energy of benzene on Si(111)-7 × 7[35] and the most stable binding configurations of acrylonitrile,[10] benzonitrile,[36] styrene,[37] pyrazine,[38] and acetylethyne[39] on Si(111)-7 × 7.

The possible binding modes were constructed by cyanoacetylene/diacetylene adsorption onto the mother cluster (cluster III of Figure 5). Calculations were performed using the SPARTAN package.[40] The energies of chemisorbed configurations were calculated at the DFT theory level using perturbative Beck-Perdew functional (pBP86) in conjugation with a basis set of DN** (comparable 6-31 G**).[40] Geometric optimizations were conducted under SPARTAN default criteria. Adsorption energies, synonymous to formation heat, are quoted here as the difference between the energy of the adsorbate/substrate complex and the total sum of the substrate and gaseous molecule. Figure 6 presents the optimized geometries of the local minima for the $C_3NH(C_4H_2)Si_9H_{12}$ model systems. Table 3 reveals that the reaction for cyanoacetylene on Si(111)-7 × 7 involving both $C\equiv C$ and $C\equiv N$ groups is thermodynamically favored compared to other possible reactions. This process is exothermic by 64.9 kcal mol^{-1}. In addition, the calculated vibrational frequencies (Table 1) for the cluster corresponding to mode III are very consistent with the experimental observation.

For diacetylene on Si(111)-7 × 7, DFT calculation results are shown in Table 4. The binding configuration of mode IV (Figure 6) through the [4 + 2]-like cycloaddition (76.6 kcal mol^{-1}) is more stable compared to mode V (Figure 6) through the [2 + 2]-like cycloaddition (63.4 kcal mol^{-1}). Similar results

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TABLE 4: Adsorption Energies of the Local Minima in the Diacetylene/Si₉H₁₂ Model System from PBP/DN

functional group	C≡C	C≡C−C≡C
binding model	IV	V
reaction model	[2 + 2]	[4 + 2]
adsorption energy[a]	63.4	76.6

[a] Adsorption energy: $\Delta E = [E(Si_9H_{12}) + E(C_4H_2)] - E(C_4H_2/Si_9H_{12})$. All energies are in kcal mol^{-1}.

are presented in the recent theoretical prediction of diacetylene on Si(111)-7 × 7 by Lu et al.[24] Apart from the larger adsorption energy, their calculations also revealed that the formation of mode IV (0.6 kcal mol^{-1}) has a lower activation barrier compared to mode V (4.4 kcal mol^{-1}). Thus, the formation of [3]-cumulenic adspecies (mode IV) was suggested in the reaction of diacetylene on Si(111)-7 × 7.[24] This is indeed in contrast to our experimental findings that diacetylene binds on Si(111)-7 × 7 through a [2 + 2]-like cycloreaction (mode V) between one of its C≡C groups and the neighboring adatom−rest atom pair. Further detailed theoretical modeling is desired to completely understand the adsorption dynamics of diacetylene/Si-(111)-7 × 7.

IV. Conclusions

We have successfully prepared the molecular templates containing a stable triple cumulative double bond (C=C=C=N) and an enynic-like structure at the organic/silicon interface under UHV conditions. The resulting chemisorbed species containing C=C=C=N or C=C−C≡C can serve as precursors (or templates) for further construction of bilayer organic films on the semiconductor surfaces.

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