

Cycloaddition Reactions of 1-Pyrazoline on the Si(100) 2×1 Surface: A Possible Route to an Si=N Interfacial Double Bond

Chultack Lim and Cheol Ho Choi*

Department of Chemistry, College of Natural Sciences, Kyungpook National University,
Taegu 702-701, South Korea

Received: March 13, 2003; In Final Form: April 20, 2003

Multiconfigurational and density functional theories are adopted to study the potential energy surface along the possible reaction mechanisms of 1-pyrazoline on the Si(100) 2×1 surface. According to the computed potential energy surfaces, the Si–N single bonded product is initially formed without a reaction barrier due to the strong Lewis base of the nitrogen lone pair electrons. With a mild internal activation barrier, the most stable $[2 + 2]$ cycloaddition product is formed. The surface Si–Si σ bond broken product was found to be stable, which requires 4.4 kcal/mol of overall activation barrier, making it kinetically quite accessible. The surface isomerization reaction product, which has two Si=N double bonds as a result of breakage of both the surface Si–Si σ bond and the N–N σ bond, is found to be thermodynamically as well as kinetically stable, suggesting a possible route to multiple interfacial Si=X bond.

Introduction

As the size of semiconductor devices shrinks, the surface characteristics in comparison to the bulk properties are increasingly important. Thus, the understanding and precise control of the interfacial surface reactions become crucial for the proper functioning of semiconductor devices. In addition to the traditional modifications of the silicon surface such as etching, doping, and film deposition, a great deal of effort has been devoted to developing molecular based electronics by synthetically attaching organic molecules to the semiconductor surface. Such interfacial chemical reactions not only mean new types of surface chemical bonds, but they can also provide new functional groups to the semiconductor surface. These modifications can then be used to provide new electronic, optical, and biological properties to the plain semiconductor.¹

Many saturated and unsaturated organic and organometallic compounds are actively being tested for the creation of new types of interfacial chemical bonds.

Interfacial Si–C bonds have been created mostly by surface cycloaddition reactions using unsaturated hydrocarbon compounds. Although $[2_s + 2_s]$ cycloadditions are formally orbital symmetry forbidden,² experimental^{3,4} and theoretical^{5,6} studies have shown that ethylene, propylene, and acetylene can easily chemisorb on the Si(100) 2×1 surface, yielding $[2 + 2]$ products, and are able to resist temperatures of up to 600 K. Diene systems have also been actively studied. In the case of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene, theoretical and experimental studies have shown⁷ that the surface dimer can act as a good dienophile, yielding Diels–Alder or $[4 + 2]$ cycloaddition products. Subsequent experimental⁸ and theoretical⁹ studies indicate that there is strong competition between the $[2 + 2]$ and $[4 + 2]$ products. Aromatic systems, such as benzene, appear to rather easily undergo addition reactions on the Si(100) surface. Such reactions create new C–Si bonds, thereby removing aromatic stability.^{10,11} While adsorption of

simple alkenes and dienes on Si(100) is essentially irreversible due to the formation of strong C–Si bonds, benzene has been shown to adsorb reversibly¹⁰ and even exhibit redistributions of surface products.¹¹

Interfacial Si–N bonds have been created mostly by nucleophilic surface reactions. It has been known that NH_3 ¹² adsorbs molecularly on the “down” atom of the presumed buckled silicon dimer with no activation barrier. The molecularly adsorbed species dissociates to form NH_2 and H. The NH_2 fragment is thermally stable and decomposes only at high temperatures around 700 K. Other nitrogen containing compounds¹³ such as pyrrolidine, *N*-methylpyrrolidine, trimethylamine, dimethylamine, pyrrole, aniline, 3-pyrroline, pyrrolidine, HCN, and acrylonitrile have been studied. These studies have shown that the electron donation of the lone pair electrons of nitrogen to the silicon surface is likely the initial stage of the addition reaction. Therefore, this type of surface reaction has been described as nucleophilic addition, a dative bond reaction, or a Lewis base/acid reaction.

Interfacial Si–O bonds have been created by nucleophilic surface reactions as well as cycloaddition reactions. Water^{14,15} molecules undergo dissociative adsorption on the Si(100) surface. Methanol,¹⁶ ethanol,¹⁷ and formic acid^{18,19,20} have been shown to dissociatively adsorb. In the case of glyoxal-, methylglyoxal-, and biacetyl carbonyl-containing molecules,²¹ the carbonyl group can adsorb onto the surface by a $[2 + 2]$ cycloaddition with negligible activation barrier. 1,2-Dicarbonyls, such as glyoxal, may also react by means of a $[4 + 2]$ addition to form a hetero-Diels–Alder product. Other organic interfacial bonds such as Si–S²² have been created.

Despite a great deal of synthetic effort, to our knowledge, attempts to create multiple interfacial bonds have not yet been reported. A possible route to multiple interfacial bonds may be surface isomerization reactions via pericyclic reactions of the $[2 + 2]$ product of acetylene as shown in Figure 1. Acetylene has one C–C π bond left after chemisorption. The remaining Si–Si σ bond and the C–C π bond may undergo further pericyclic reaction, releasing four-membered ring strain energy

* E-mail: cchoi@knu.ac.kr. Telephone: +82-53-950-5332. Fax: +82-53-950-6330.



Figure 1. Possible route of the silicon surface isomerization reactions via pericyclic reaction of the [2 + 2] product of acetylene.

and making two new Si=C double bonds. This reaction resembles the electrocyclic ring opening reaction, in which cyclobutene, on heating, gives 1,3-butadiene. Theoretical^{5a,b} and experimental^{23,24} studies on this system suggest sp^2 hybridization of carbon atoms. Using Auger spectroscopy and temperature-programmed desorption (TPD), Taylor et al.^{3c} proposed that the Si-Si dimer bond is cleaved when the acetylene molecule adsorbs on top of a dimer. The structure with this complete cleavage of the Si-Si dimer bond was subsequently confirmed²³ by scanning tunneling microscopy (STM) to be the major product. However, independent experimental studies concluded that no direct evidence regarding the structure of the Si-Si σ bond was observed.²⁵

Except for early studies,²⁶ the majority of theoretical studies support the unbroken Si-Si dimer structure.²⁷ The most recent slab model DFT study by Sorescu and Jordan⁶ showed that the broken Si-Si dimer structure is about 30 kcal/mol less stable than the unbroken structure. A Si_9H_{12} cluster study of the same system²⁸ predicts that the Si-Si cleaved structure is not a minimum on the potential energy surface.

It appears that the product of surface pericyclic reactions which has Si=C interfacial bonds may not be a minimum, and even if it is, it may not be kinetically stable.

Molecular examples of the Si=X (X=C, N, etc.) bond are rare. None of the multiple bonded systems that involve Si had been isolated until 1966, when Gusel'Nikov proved the existence of dimethylsilene.²⁹ Only recently has the monomeric form of silanimines, which has a Si=N bond, been characterized³⁰ by photoelectron spectroscopy.

However, the highly reactive Si surface may provide a unique environment for the existence of Si=X multiple bondings. The search for new routes that lead to new types of interfacial chemical bondings ultimately provides new dimensions to the properties of the synthetically modified semiconductors. By studying the factors that govern the reactivity of these routes, precise control of these surface reactions can be possible. In this paper, theoretical study of the potential energy surface of the reaction mechanisms of 1-pyrazoline on the Si(100) 2×1 surface is performed to search for a possible route to the stable multiple Si=X interfacial bond.

Computational Details

An all electron 6-31(d)³¹ basis set was used for the entire calculation. The minimum energy reaction paths were determined by first optimizing the geometries of the minima and transition states. Then, each stationary point was characterized by computing and diagonalizing the Hessian matrix (matrix of energy second derivatives). To follow the minimum energy path (MEP), the Gonzalez-Schlegel second-order method³² was used with a step size of 0.3 amu^{1/2} bohr.

Various points on the reaction paths, particularly the transition states and intermediates, are often inherently multiconfigurational. Therefore, CASSCF (complete active space SCF)³³ wave functions were primarily used to properly describe these species. The selected orbitals for the active space will be discussed in

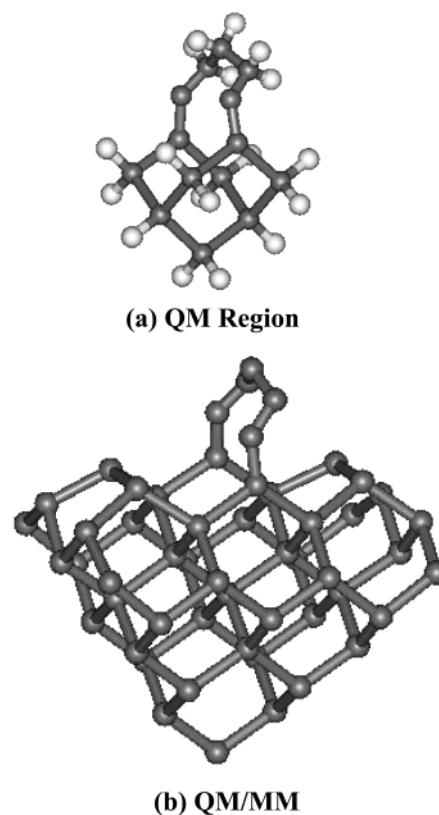


Figure 2. (a) $C_3N_2Si_9H_{18}$ quantum region embedded in (b) the $C_3N_2Si_{48}H_{46}$ SIMOMM cluster.

detail. To consistently describe the reaction paths leading to all surface products, an (8,8) active space was used which is composed of four electrons in the two sets of σ , σ^* and π , π^* of the 1-pyrazoline N=N double bond and four electrons in the two sets of σ , σ^* and π , π^* of the surface Si dimer.

To recover the dynamic electron correlation and to ensure that all parts of the reaction path are treated consistently, the multireference second-order perturbation theory was used. The level of accuracy for such a method is at least comparable to that of MP2^{34,35} when single reference methods are appropriate. The particular version of this method used in the present work is referred to as MRMP2³⁶ (multireference second-order perturbation theory). For comparison, single-reference density function theory (DFT) has also been adopted using the B3LYP³⁷ exchange-correlation functional. The GAMESS (general atomic and molecular electronic structure system)³⁸ program was used for all of the computations.

To take into account the surface size effect, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called SIMOMM (surface integrated molecular orbital molecular mechanics)³⁹ was used. The SIMOMM cluster is composed of a $C_3N_2Si_9H_{18}$ quantum region embedded in a $C_3N_2Si_{48}H_{46}$ cluster. MM3⁴⁰ parameters were used for the molecular mechanics optimization part of the computation (see Figure 2). The SIMOMM method turned out to be useful, since some of the surface products are accompanied by a large change of surface structure that cannot be properly described by the 9-Si cluster model. All of the computations were done without imposing symmetry unless otherwise specified.

Results and Discussions

Surface Products. Full geometry optimization was performed with SIMOMM:CASSCF and SIMOMM:DFT theories. SIMOMM:MRMP2 single-point energies were evaluated at

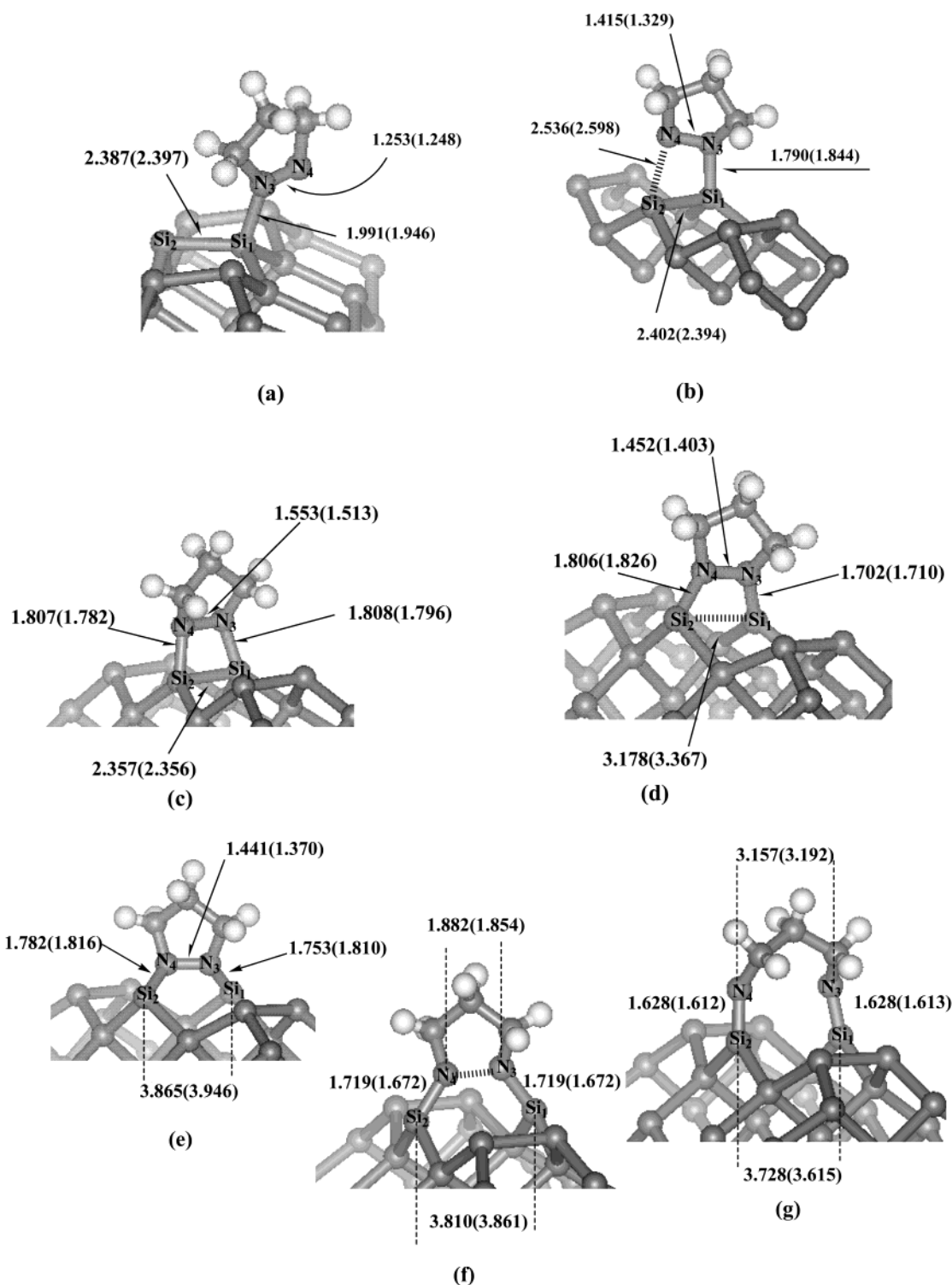


Figure 3. Intermediates and transition states along the surface reaction. A portion of the cluster model is shown for readability: (a) **I** intermediate; (b) $\text{TS}_{\text{I} \leftrightarrow [2+2]}$, transition state that connects the products in parts a and c; (c) **[2+2]**, $[2+2]$ cycloaddition product; (d) $\text{TS}_{[2+2] \leftrightarrow \text{broken-[2+2]}}$, transition state that connects the products in parts c and e; (e) **broken-[2+2]**, $[2+2]$ cycloaddition product with broken $\text{Si}_1\text{--Si}_2$ σ bond; (f) $\text{TS}_{\text{broken-[2+2]} \leftrightarrow \text{open-[2+2]}}$, transition state that connects the products in parts e and g; (g) **open-[2+2]**, surface pericyclic reaction product with $\text{Si}_1=\text{N}_3$ and $\text{Si}_2=\text{N}_4$ double bonds. The geometric parameters are obtained with SIMOMM:CASSCF/6-31G*, and the values in parentheses are calculated with SIMOMM:B3LYP/6-31G*.

SIMOMM:CASSCF geometries. The results are presented in both Figure 3 and Table 1. All energies of calculated intermediates and transition states are given relative to that of separated reactants, which is referred to as a reference point.

Four minima were located with SIMOMM:DFT and SIMOMM:CASSCF theories. The DFT and MRMP2 calculations consistently predict that the $[2+2]$ cycloaddition product

[2+2] (Figure 3c) is the most stable surface product followed by **I** (Figure 3a), **open-[2+2]** (Figure 3g), and **broken-[2+2]** (Figure 3e) with the relative MRMP2/6-31G* energies of 5.7, 10.6, and 23.0 kcal/mol for the latter three. DFT overestimates the relative stabilities of these minima by about 3–10 kcal/mol as compared to those of MRMP2. One of the main reasons for such a discrepancy is the single-configurational nature of DFT

TABLE 1: Geometric Data (Å) and Energetics (kcal/mol) of Products, Intermediates, and Transition States

		bond length				dihedral angle (θ)	ΔE^a
		Si ₁ –Si ₂	Si ₁ –N ₃	N ₃ –N ₄	Si ₂ –N ₄	\angle Si ₂ –Si ₁ –N ₃ –N ₄	
reactant	SIMMOM:B3LYP/6-31G(d)	2.224		1.239			0.0
	SIMMOM:CASSCF(8×8)/6-31G(d)	2.299		1.257			0.0
	MRMP2(8×8)/6-31G(d)						0.0 ^b (25.2) ^c
I	SIMMOM:B3LYP/6-31G(d)	2.397	1.946	1.248	3.792	36.5	–22.1
	SIMMOM:CASSCF(8×8)/6-31G(d)	2.387	1.991	1.253	4.625	141.1	–13.0
	MRMP2(8×8)/6-31G(d)						–19.5 ^b (5.7) ^c
TS_{I→[2+2]}	SIMMOM:B3LYP/6-31G(d)	2.394	1.844	1.329	2.598	31.4	–15.1
	SIMMOM:CASSCF(8×8)/6-31G(d)	2.402	1.790	1.415	2.536	27.6	3.1
	MRMP2(8×8)/6-31G(d)						–15.0 ^b (10.2) ^c
[2+2]	SIMMOM:B3LYP/6-31G(d)	2.356	1.796	1.513	1.782	0.15	–36.9
	SIMMOM:CASSCF(8×8)/6-31G(d)	2.357	1.808	1.553	1.807	0.03	–18.8
	MRMP2(8×8)/6-31G(d)						–25.2 ^b (0.0) ^c
TS_{[2+2]→broken-[2+2]}	SIMMOM:B3LYP/6-31G(d)	3.367	1.710	1.403	1.826	17.4	1.6
	SIMMOM:CASSCF(8×8)/6-31G(d)	3.178	1.702	1.452	1.806	19.8	20.9
	MRMP2(8×8)/6-31G(d)						4.4 ^b (29.6) ^c
broken-[2+2]	SIMMOM:B3LYP/6-31G(d)	3.946	1.810	1.370	1.816	38.5	–11.0
	SIMMOM:CASSCF(8×8)/6-31G(d)	3.865	1.753	1.441	1.782	39.2	5.5
	MRMP2(8×8)/6-31G(d)						–2.2 ^b (23.0) ^c
TS_{broken-[2+2]→open-[2+2]}	SIMMOM:B3LYP/6-31G(d)	3.861	1.672	1.854	1.672	11.9	12.1
	SIMMOM:CASSCF(8×8)/6-31G(d)	3.810	1.719	1.882	1.719	7.2	25.6
	MRMP2(8×8)/6-31G(d)						15.6 ^b (40.8) ^c
open-[2+2]	SIMMOM:B3LYP/6-31G(d)	3.615	1.613	3.192	1.612	0.62	–21.1
	SIMMOM:CASSCF(8×8)/6-31G(d)	3.728	1.628	3.157	1.628	0.008	–18.1
	MRMP2(8×8)/6-31G(d)						–14.6 ^b (10.6) ^c

^a Values are energies relative to separated reactants (1-pyrazoline + bare silicon surface). ^b Values calculated with single-point energy. ^c Values are energies relative to [2+2].

TABLE 2: Active Space Natural Orbital Occupation Number (NOON) of the Surface Products, Intermediates, and Transition States^a

orbital number	a	b	c	d	e	f	g
85	1.9870	1.9818	1.9844	1.9814	1.9808	1.9741	1.9685
86	1.9769	1.9738	1.9748	1.9778	1.9769	1.9740	1.9677
87	1.9562	1.9678	1.9727	1.9679	1.9707	1.8888	1.9201
88	1.9148	1.6718	1.9580	1.9671	1.2562	1.4271	1.9011
89	0.0850	0.3382	0.0431	0.0362	0.7481	0.5705	0.0972
90	0.0332	0.0327	0.0247	0.0300	0.0312	0.1142	0.0814
91	0.0241	0.0209	0.0241	0.0221	0.0195	0.0270	0.0332
92	0.0228	0.0131	0.0182	0.0175	0.0167	0.0242	0.0310

^a The corresponding structures are presented in Figure 3.

theories that cannot properly describe multiconfigurational systems. The reference point which is the separated 1-pyrazoline and pure Si surface possesses more multiconfigurational character than the four minima. As a result, any single-configurational method should fail to consistently describe the entire potential energy surface. The multiconfigurational nature can be easily measured by the analysis of the natural orbital occupation numbers (NOONs). The NOONs of the important points along the surface reaction are presented in Table 2. Although some of the points are single-configurational, many important points are highly multiconfigurational. So it is clear that, to consistently describe the entire potential energy surface, a multiconfigurational wave function is essential. The same failure of single-configurational methods was seen in the similar systems.^{13j}

SIMOMM:MRMP2 energetics and SIMOMM:CASSCF geometries shall be mainly referred to for the rest of the discussion, unless otherwise noted.

The bond lengths of Si₁–Si₂, Si₁–N₃, and N₃–N₄ of the most stable surface product [2+2] are calculated to be 2.36, 1.81, and 1.55 Å, respectively. These values represent the typical single bond lengths. The Si₁–N₃ bond length of the single bonded surface product **I** is 1.99 Å, which is slightly elongated from the value of [2+2]. The N₃–N₄ bond length of **I** is 1.25

Å, showing that it still has double bond character. **Broken-[2+2]** is an interesting structure where the remaining surface Si₁–Si₂ σ bond is broken by creating a diradical. The distance between Si₁ and Si₂ is calculated to be 3.87 Å, indicating that there is no net bonding interaction between them. The bond lengths of Si₁–N₃ and N₃–N₄ are calculated to be somewhat shorter than those of [2+2]. As discussed in the Introduction, the possibility of the cleavage of the Si–Si σ bond is controversial in the case of acetylene chemical adsorption on the Si(100) 2 × 1 surface. Also, no theoretical cluster model calculation predicted its existence. However, according to our calculations, by replacing the carbon multiple bond with the N=N double bond such as in 1-pyrazoline, the broken Si–Si σ bond structure can be stabilized. **Open-[2+2]** is also an interesting product where both the Si₁–Si₂ and the N₃–N₄ σ bonds are broken while the unique Si₁=N₃ and Si₂=N₄ double bonds with the bond length 1.63 Å are formed. As discussed earlier, **open-[2+2]** is 10.6 kcal/mol less stable than the most stable [2+2], which is not too high an energy. Therefore, energetic results strongly indicate its existence. In order for these species to exist, kinetic stability as well as kinetic accessibility is also required. In the following section, the potential energy surface along a possible route to these species is explored.

Reaction Mechanism to the [2 + 2] Cycloaddition Product.

According to our potential energy search, the initial surface product of 1-pyrazoline on the Si(100) 2 × 1 surface turned out to be **I**, which has one Si₁–N₃ chemical bond without any reaction barrier. The high reactivity of **I** may be due to the lone pair electrons of nitrogen that can act as a strong Lewis base. As shown in Figure 3a, the other nitrogen N₄ of **I** is located at the opposite side of Si₂. The dihedral angle Si₂–Si₁–N₃–N₄ is 141.1° or 36.5° at the SIMMOM:CASSCF or SIMOMM:B3LYP level, respectively, indicating that the rotation barrier with respect to the Si₁–N₃ bond is mild. Such a large dihedral angle indicates that the adsorbed 1-pyrazoline needs to significantly rotate before making another Si₂–N₄ bond. The first transition state, **TS_{I→[2+2]}** (Figure 3b), in which N₄ is making a

bond with Si₂, connects intermediate **I** and the $[2 + 2]$ cycloaddition product **[2+2]** with the forward activation energy of 4.5 kcal/mol. However, the overall stability of **TS_{I→[2+2]}** with respect to the reference point (the separated systems) is -15.1 kcal/mol, indicating that it is merely an internal barrier. The CASSCF geometry shows that the dihedral angle (Si₂-Si₁-N₃-N₄) and length between Si₂ and N₄ of **TS_{I→[2+2]}** are 27.6° and 2.536 Å. As a result of the mild transition state, the surface reactions to the global minimum **[2+2]** product occur easily. Therefore, **[2+2]** is not only thermodynamically the most stable but also kinetically highly accessible.

Although **[2+2]**, the $[2 + 2]$ cycloaddition product, is thermodynamically stable, it can further undergo surface isomerization reactions. One possible reaction is the surface pericyclic reaction that is discussed below.

Surface Isomerization Reaction Mechanism to the Open-[2+2] Product. The transition state **TS_{[2+2]→broken-[2+2]}** (Figure 3d), in which the Si₁-Si₂ σ bond is being broken, connects the $[2 + 2]$ cycloaddition product, **[2+2]**, and another surface product, **broken-[2+2]** (Figure 3e), with the forward activation energy 29.6 kcal/mol. However, the overall stability of **TS_{[2+2]→broken-[2+2]}** with respect to the reference point is 4.4 kcal/mol, which is not prohibitively high. Therefore, with some mild thermal energies, this barrier can easily be overcome, making the existence of the **broken-[2+2]** surface product possible. Another transition state, **TS_{broken-[2+2]→open-[2+2]}** (Figure 3f) in which the remaining N₃-N₄ σ bond is being broken, connects **broken-[2+2]** and **open-[2+2]** with the forward activation energy 17.8 kcal/mol. The overall activation energy is 15.6 kcal/mol, which is still quite high. Therefore, at low surface temperature, **TS_{broken-[2+2]→open-[2+2]}** effectively prevents isomerization to **open-[2+2]**. However, this barrier can be overcome at high surface temperature. It is noted that the reverse activation barrier from **open-[2+2]** is 30.2 kcal/mol, indicating that once **open-[2+2]** is formed, it is kinetically stable. A way to further activate this channel would be to introduce substituents that can stabilize **TS_{broken-[2+2]→open-[2+2]}**. Experimental studies exploring the existence of these species are highly expected.

Conclusions

Multiconfigurational wave functions and density functional methods were adopted to study the potential energy surface along the possible surface reaction mechanisms of 1-pyrazoline on the Si(100) 2×1 surface in the pursuit of new interfacial chemical bonds. The overall reactions occur via a stepwise radical mechanisms. According to the computed potential energy surfaces, initially, a Si-N single bonded product is formed without any reaction barrier due to the strong Lewis base of nitrogen lone pair electrons. After that, with a mild internal activation barrier, the most stable $[2 + 2]$ cycloaddition product is formed. The Si-Si σ bond broken product was found to be stable, which requires 4.4 kcal/mol of overall activation barrier, making it kinetically quite accessible. A surface product which has two Si=N double bonds as a result of breakage of both the surface Si-Si σ bond and the N-N σ bond is found to be thermodynamically as well as kinetically stable. However, it requires 15.6 kcal/mol of overall activation barrier, making it only accessible in a high-temperature environment. Nonetheless, kinetic stability makes its existence possible, once it is formed at high temperature, suggesting a possible route to a multiple interfacial Si=X bond. These last two surface configurations were not reported to be stable in earlier studies using carbon compounds.

A way to further activate this channel would be to introduce substituents that can stabilize **TS_{broken-[2+2]→open-[2+2]}**. Experimental confirmation of our conclusions is highly expected.

Unlike the case of our previous study,^{13j} surface isomerization reactions among possible surface products may be possible.

While single-configurational methods may be useful for studying the relative energies of the products, they are not appropriate to study the entire potential energy surface of dissociation/adsorption reactions. This is due to the highly multiconfigurational nature of the reactants, as well as some of the intermediates and transition states, necessitating the use of multiconfigurational descriptions to obtain reliable kinetic predictions.

Acknowledgment. This work was supported by Korea Research Foundation Grant KRF-2002-070-C00048.

References and Notes

- (1) (a) Buriak, J. M. *J. Chem. Soc., Chem. Commun.* **1995**, 95, 1589. (b) Yates, J. T., Jr. *Science* **1998**, 279, 335. (c) Lopinski, G. P.; Moffatt, D.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **1998**, 392, 909.
- (2) Woodward, R. B.; Hoffmann, R. *The conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.
- (3) (a) Nishijima, M.; Yoshinobu, J.; Tsuda, H.; Onchi, M. *Surf. Sci.* **1987**, 192, 383. (b) Yoshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *J. Chem. Phys.* **1987**, 87, 7332. (c) Taylor, P. A.; Wallace, R. M.; Cheng, C. C.; Weinberg, W. H.; Dresser, M. J.; Choyke, W. J.; Yates, J. T., Jr. *J. Am. Chem. Soc.* **1992**, 114, 6754. (d) Li, L.; Tindall, C.; Takaoka, O.; Hasegawa, Y.; Sakurai, T. *Phys. Rev. B* **1997**, 56, 4648.
- (4) (a) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1995**, 50, 413. (b) Mezheny, S.; Lyubintsky, L.; Choyke, W. J.; Wolkow, R. A.; Yates, J. T., Jr. *J. Chem. Phys. Lett.* **2001**, 344, 7.
- (5) (a) Imamura, Y.; Morikawa, Y.; Yamasaki, T.; Nakasuji, H. *Surf. Sci.* **1995**, 341, L1091. (b) Liu, Q.; Hoffmann, R. *J. Am. Chem. Soc.* **1995**, 117, 4082.
- (6) Sorescu, D. C.; Jordan, K. D. *J. Phys. Chem. A* **2000**, 104, 8259.
- (7) (a) Konecny, R.; Doren, D. *J. Am. Chem. Soc.* **1997**, 119, 11098. (b) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, 119, 11100. (c) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. **1998**, 108, 4599.
- (8) Hovis, J. S.; Liu, H. B.; Hamers, R. J. *J. Phys. Chem. B* **1998**, 102, 6873.
- (9) (a) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1999**, 121, 11311. (b) Choi, C. H.; Gordon, M. S. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z.; Apeloig, Y., Eds.; John Wiley & Sons: New York, 2001; Vol. 3, Chapter 15, p 821.
- (10) Taguchi, Y.; Fujisawa, M.; Takaoka, T.; Okasa, T.; Nishijima, M. *J. Chem. Phys.* **1991**, 95, 6870.
- (11) (a) Lopinski, G. P.; Fortier, T. M.; Moffatt, D. J.; Wolkow, R. A. *J. Vac. Sci. Technol. A* **1998**, 16, 1937. (b) Lopinski, G. P.; Fortier, T. M.; Moffatt, D. J.; Wolkow, R. A. *J. Chem. Phys. Lett.* **1998**, 282, 305.
- (12) (a) Widjaja, Y.; Mysinger, M. M.; Musgrave, C. B. *J. Phys. Chem. B* **2000**, 104, 2527. (b) Widjaja, Y.; Musgrave, C. B. *Surf. Sci.* **2000**, 469, 9. (c) Riganese, G.-M.; Pasquarello, A. *Appl. Phys. Lett.* **2000**, 76, 553. (d) Queeney, K. T.; Chabal, Y. J.; Raghavachari, K. *Phys. Rev. Lett.* **2001**, 86, 1046. (e) Miotto, R.; Srivastava, G. P.; Miwa, R. H.; Ferraz, A. C. *J. Chem. Phys.* **2001**, 114, 9549. (f) Miotto, R.; Srivastava, G. P.; Ferraz, A. C. *Phys. Rev. B: Condensed Matter Mater. Phys.* **2001**, 63, 125321/1. (g) Miotto, R.; Srivastava, G. P.; Ferraz, A. C. *Surf. Sci.* **2001**, 482-485, 160. (h) Hartmann, J. M.; Gallas, B.; Ferguson, R.; Fernandez, J.; Zang, J.; Harris, J. *J. Semicond. Sci. Technol.* **2000**, 15, 362. (i) Widjaja, Y.; Musgrave, C. B. *Phys. Rev. B: Condensed Matter Mater. Phys.* **2001**, 64, 205303/1.
- (13) (a) Wang, G. T.; Mui, C.; Musgrave, C. B.; Bent, S. F. *J. Phys. Chem. B* **2001**, 105, 3295. (b) Cao, X.; Hamers, R. J. *J. Am. Chem. Soc.* **2001**, 123, 10988. (c) Cao, X.; Coulter, S. K.; Ellison, M. D.; Liu, H.; Liu, J.; Hamers, R. J. *J. Phys. Chem. B* **2001**, 105, 3759. (d) Luo, H.; Lin, M. C. *J. Phys. Chem. B* **2001**, 105, 4368. (e) Bacalzo-Gladden, F.; Lu, X.; Lin, M. C. *J. Phys. Chem. B* **2001**, 105, 4368. (f) Tao, F.; Wang, Z. H.; Qiao, M. H.; Liu, Q.; Sim, W. S.; Xu, G. Q. *J. Chem. Phys.* **2001**, 115, 8563. (g) Tao, F.; Wang, Z. H.; Xu, G. Q. *J. Phys. Chem. B* **2002**, 106, 3557. (h) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: London, 1976. (i) Tao, F.; Sim, W. S.; Xu, G. Q.; Qiao, M. H. *J. Am. Chem. Soc.* **2001**, 123, 9397-9403. (j) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **2002**, 124, 6162.
- (14) (a) Irene, E. A. *J. Electrochem. Soc.* **1978**, 125, 1708. (b) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, 1, 211. (c) Schmeisser, D.; Himpel, F. J.; Hollinger, G. *Phys. Rev. B* **1983**, 27, 7813. (d) Fujiwara, K. *Surf. Sci.*

- 1981, 108, 124. (e) Nishijima, M.; Edamoto, K.; Kubota, Y.; Tanaka, S.; Onchi, M. *J. Chem. Phys.* **1986**, *84*, 6458. (f) Chabal, Y. J.; Christman, S. B. *Phys. Rev. B* **1984**, *29*, 6974. (g) Oellig, E. M.; Butz, R.; Wagner, H.; Ibach, H. *Solid State Commun.* **1984**, *51*, 7. (h) Larsson, C. U. S.; Flodstrom, A. S.; Nyholm, R.; Incoccia, L.; Senf, F. *J. Vac. Sci. Technol., A* **1987**, *5*, 3321. (i) Fives, K.; McGrath, R.; Stephens, C.; McGovern, I. T.; Cimino, R.; Law, D. S.-L.; Johnson, A. L.; Thornton, G. *J. Phys.: Condens. Matter* **1989**, *1*, SB105. (j) Johnson, A. L.; Walczak, M. M.; Madey, T. E. *Langmuir* **1988**, *4*, 277. (k) Gao, Q.; Dohnalek, Z.; Cheng, C. C.; Choyke, W. J.; Yates, J. T., Jr. *Surf. Sci.* **1994**, *312*, 261. (l) Bu, H.; Rabalais, J. W. *Surf. Sci.* **1994**, *301*, 285. (m) Wee, A. T. S.; Huan, C. H. A.; Thong, P. S. P.; Tan, K. L. *Corrosion Sci.* **1994**, *36*, 9. (n) Ranke, W.; Xing, Y. R. *Surf. Sci.* **1985**, *157*, 339. (o) Schröder-Bergen, E.; Ranke, W. *Surf. Sci.* **1990**, *236*, 103. (p) Chander, M.; Li, Y. Z.; Patrin, J. C.; Weaver, J. H. *Phys. Rev. B* **1993**, *48*, 2493. (q) Larsson, C. U. S.; Johnson, A. L.; Flodstrom, A. S.; Madey, T. E. *J. Vac. Sci. Technol., A* **1987**, *5*, 842. (r) Ciraci, S.; Wagner, H. *Phys. Rev. B* **1983**, *27*, 5180. (s) Katircioglu, S. *Surf. Sci.* **1987**, *187*, 569. (t) Russo, N.; Toscano, M.; Barone, V.; Lelj, F. *Surf. Sci.* **1987**, *180*, 599. (u) Barone, V. *Surf. Sci.* **1987**, *189/190*, 106.
- (15) (a) Thiel, P. A.; Madey, T. E. *Surf. Sci. Rep.* **1987**, *1*, 211. (b) Ong, C. K. *Solid State Commun.* **1989**, *72*, 1141. (c) Konecny, R.; Doren, D. J. *J. Chem. Phys.* **1997**, *106*, 2426. (d) Jung, Y.; Gordon, M. S. (in preparation). (e) Cho, J.; Kim, K. S.; Lee, S.; Kang, M. *Phys. Rev. B* **2000**, *61*, 4503. (f) Gurevich, A. B.; Stefanov, B. B.; Weldon, M. K.; Chabal, Y. J.; Raghavachari, K. *Phys. Rev. B* **1998**, *58*, R13434. (g) Jung, Y.; Choi, C. H.; Gordon, M. S. *J. Phys. Chem. B* **2001**, *105*, 4039. (h) Zhou, X.-L.; Flores, C. R.; Whilte, J. M. *Appl. Surf. Sci.* **1992**, *62*, 223. (i) Schulze, R. K.; Evans, J. F. *Appl. Surf. Sci.* **1994**, *81*, 449. (j) Andersohn, L.; Köhler, U. *Surf. Sci.* **1993**, *284*, 77.
- (16) (a) Glass, J. A.; Wovchko, E. A.; Yates, J. T., Jr. *Surf. Sci.* **1995**, *338*, 125. (b) Lu, X.; Zhang, Q.; Lin, M. C. *J. Chem. Phys.* **2001**, *3*, 2156.
- (17) (a) Eng, J. R. J.; Raghavachari, K.; Struck, L. M.; Chabal, Y. J.; Bent, B. E.; Flynn, G. W.; Christman, S. B.; Chaban, E. E.; Williams, G. P.; Rademacher, K.; Mantl, S. *J. Chem. Phys.* **1997**, *106*, 9889. (b) Casaletto, M. P.; Zanon, R.; Carbone, M.; Piancastelli, M. N.; Abelle, L.; Weiss, K.; Horn, K. *Surf. Sci.* **2000**, *447*, 237.
- (18) Tanaka, S.; Onchi, M.; Nishijima, M. *J. Chem. Phys.* **1989**, *91*, 2712.
- (19) Ikeura-Sekiguchi, H.; Sekiguchi, T. *Surf. Sci.* **1997**, *390*, 214.
- (20) Ikeura-Sekiguchi, H.; Sekiguchi, T. *Surf. Sci.* **1999**, *549*, 433.
- (21) Barriocanal, J. A.; Doren, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 7340.
- (22) (a) Ellison, M. D.; Hamers, R. J. *J. Phys. Chem. B* **1999**, *103*, 6243. (b) Coulter, S. K.; Schwartz, M. P.; Hamers, R. J. *Phys. Chem. B* **2001**, *105*, 3079. (c) Lu, X.; Xu, X.; Wang, N.; Zhang, Q.; Lin, M. C. *J. Phys. Chem. B* **2001**, *105*, 10069.
- (23) (a) Yates, J. T., Jr. *J. Phys.: Condens. Matter* **1991**, *3*, S43. (b) Bozack, M. J.; Taylor, P. A.; Choyke, W. J.; Yates, J. T., Jr. *Surf. Sci.* **1986**, *177*, L933. (c) Clemen, L.; Wallace, R. M.; Taylor, P. A.; Dresser, M. J.; Choyke, W. J.; Weinberg, W. H.; Yates, J. T., Jr. *Surf. Sci.* **1992**, *268*, 205. (d) Cheng, C. C.; Wallace, R. M.; Taylor, P. A.; Choyke, W. J.; Yates, J. T., Jr. *J. Appl. Phys.* **1990**, *67*, 3693. (e) Cheng, C. C.; Choyke, W. J.; Yates, J. T., Jr. *Surf. Sci.* **1990**, *231*, 289.
- (24) Li, L.; Tindall, C.; Takaoka, O.; Hasegawa, Y.; Sakurai, T. *Phys. Rev. B* **1997**, *56*, 4648.
- (25) Hovis, J.; Lee, S.; Liu, H.; Hamers, R. J. *J. Vac. Sci. Technol., B* **1997**, *15*, 1153.
- (26) (a) Craig, B. I.; Smith, P. V. *Surf. Sci.* **1992**, *276*, 174. (b) Cramer, C. S.; Weiner, B.; Frenklach, M. *J. Chem. Phys.* **1993**, *99*, 1356.
- (27) (a) Fisher, A. J.; Blochl, P. E.; Briggs, G. A. D. *Surf. Sci.* **1997**, *374*, 298. (b) Pan, W.; Zhu, T.; Yang, W. *J. Chem. Phys.* **1997**, *107*, 3981.
- (28) Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169.
- (29) Nametkin, N. S.; Vdovin, V. M.; Gusel'nikov, L. E.; Zav'yalov, V. E. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1966**, 584.
- (30) Metail, V.; Joanteguy, S.; Chrostowska-Senio, A.; Pfister-Guillouzo, G.; Systemans, A.; Ripoll, J. L. *Inorg. Chem.* **1997**, *36*, 1482.
- (31) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
- (32) (a) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853.
- (33) (a) Sunberg, K. R.; Ruedenberg, K. In *Quantum Science*; Calais, J. L., Goscinski, O., Linderberg, J., Ohrn, Y., Eds.; Plenum: New York, 1976. (b) Cheung, L. M.; Sunberg, K. R.; Ruedenberg, K. *Int. J. Quantum Chem.* **1979**, *16*, 1103. (c) Ruedenberg, K.; Schmidt, M.; Gilbert, M. M.; Elbert, S. T. *Chem. Phys.* **1982**, *71*, 41. (d) Roos, B. O.; Taylor, P.; Siegbahn, P. E. *Chem. Phys.* **1980**, *48*, 157. (e) Schmidt, M. W.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233.
- (34) Möller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.
- (35) (a) Werner, H.-J. *Mol. Phys.* **1996**, *89*, 645. (b) Schmidt, M. S.; Gordon, M. S. *Annu. Rev. Phys. Chem.* **1998**, *49*, 233. (c) Glaesemann, K. R.; Gordon, M. S.; Nakano, H. *Phys. Chem. Chem. Phys.* **1999**, *1*, 967.
- (36) (a) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983. (b) Nakano, H. *Chem. Phys. Lett.* **1993**, *207*, 372.
- (37) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Stephens, P. J.; Devlin, F. J.; Chabowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623. (c) Hertwig, R. H.; Koch, W. *Chem. Phys. Lett.* **1997**, *268*, 345.
- (38) (a) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comput. Chem.* **1993**, *14*, 1347. (b) Fletcher, G. D.; Schmidt, M. W.; Gordon, M. S. *Adv. Chem. Phys.* **1999**, *110*, 267.
- (39) Shoemaker, J. R.; Burgraff, L. W.; Gordon, M. S. *J. Phys. Chem. A* **1999**, *103*, 3245.
- (40) (a) Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551. (b) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566. (c) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.