

Diradical Mechanisms for the Cycloaddition Chemistry of Ethylene on X(100) Surfaces (X = C, Si, and Ge)

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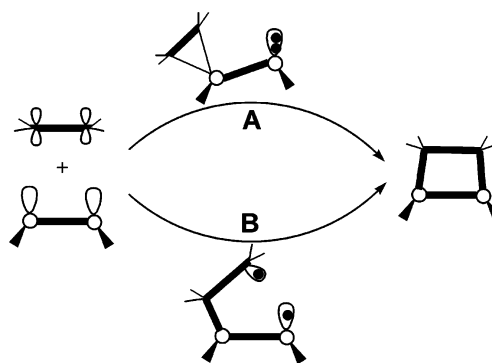
Systematic density functional cluster model calculations reveal that the [2 + 2] cycloadditions of ethylene on the (100) surfaces of group IV semiconductors (silicon, germanium, and diamond) follow diradical mechanisms. Details of the reaction pathways vary subtly with the bonding nature of the surface dimers, including their zwitterionicity, weakness of their π -bond, and readiness to react as a diradical.

1. Introduction

Organic functionalization of the surfaces of group IV semiconductors (diamond, silicon, and germanium) is of great interest recently, owing to its potential applications in microelectronics technology.^{1–5} A large number of organic compounds have been investigated experimentally regarding their availability to form uniform, strong organic–semiconductor interfaces. Much abundant and fascinating organic–semiconductor surface chemistry has been revealed, especially on the (100) surfaces of single-crystalline diamond, silicon, and germanium, which adopt the 2×1 reconstruction with the first-layer atoms dimerizing to form rows of X–X dimers (X = C, Si, Ge).⁵ The chemical bonding in the surface X–X dimers features a σ bond and a much weaker π bond, analogous to the C=C double bond within a simple alkene, and thus should be better denoted as X=X.^{5e} Accordingly, the X=X dimers of the X(100)- 2×1 surfaces (X = C, Si, Ge) have been found to be subject to [4 + 2] cycloaddition (Diels–Alder reaction) with conjugated dienes,^{6–8} 1,3-dipolar cycloaddition with 1,3-dipolar molecules,⁹ and [2 + 2] cycloaddition with simple alkenes.^{10–12}

Among the above-mentioned interesting cycloaddition chemistry of the X(100) surfaces, the [2 + 2] cycloaddition of simple alkenes is of particular interest for two reasons. First, the [2 + 2] cycloaddition of simple alkenes was found to form uniform organic adlayers on the Si(100) surface and was suggested to be stereospecific and highly stereoselective, i.e., the stereochemistry of the incoming alkenes is retained during the reaction.^{10a} This point is very important for finely controlling and designing organic–semiconductor interfaces for further specific applications. Second, such surface reaction seemingly conflicts with the Woodward–Hoffmann rules,¹³ according to which the concerted [2 + 2] cycloaddition between two double bonds should be symmetry-forbidden. To account for such an intriguing surface reaction, two possible mechanisms have been proposed, as shown in Scheme 1. The low-symmetry pathway A was supposed to be initiated by a nucleophilic attack of the incoming alkenic π -bond onto the electron-deficient, buckled-down atom of the surface dimer [for Si(100) and Ge(100)], forming a π -complex intermediate followed by “a smooth progression” toward the final [2 + 2] product without C–C

SCHEME 1



bond rotation. Accordingly, it was believed that the stereochemistry of the incoming alkenes is retained by following such a reaction pathway, accounting for the stereospecificity of the [2 + 2] cycloaddition of 1,2-deuterioethylene on Si(100) observed in Fourier transform infrared (FTIR) experiments.^{10a} On the other hand, the radical mechanism, pathway B, was suggested to proceed via a diradical intermediate followed by ring closing. This latter mechanism should not be stereospecific as C–C bond rotation may occur within the diradical intermediate, which was supported by the recent scanning tunneling microscopy (STM) observation that the [2 + 2] cycloaddition of *trans*-2-butene on the Si(100) surface is not stereospecific but highly stereoselective, with a small degree of isomerization.^{10b}

Another noteworthy feature of the [2 + 2] cycloaddition chemistry of alkenes on the X(100) surfaces is that such surface reactions have rather different reactive sticking probabilities on C(100), Si(100), and Ge(100); for example, for the adsorption of cyclopentene, the sticking coefficients are approximately unity on Si, 0.1 on Ge, and on the order of 10^{-3} on diamond.^{12a} It was suggested that all these [2 + 2] cycloadditions should follow the low-symmetry pathway A, and the subtle structural and electronic difference of the X=X dimers of the three surface—i.e., the dimer of C(100) surface is symmetric with a π bond strength of ~ 28 kcal/mol^{14a} and the dimers of Si(100) and Ge(100) are buckling with the much weaker π bond strengths of 5–10 kcal/mol^{14b,15}—should account for the different reactivities of the [2 + 2] cycloadditions.^{5e}

Despite the large number of experimental investigations on the [2 + 2] cycloaddition chemistry of alkenes on the X(100)

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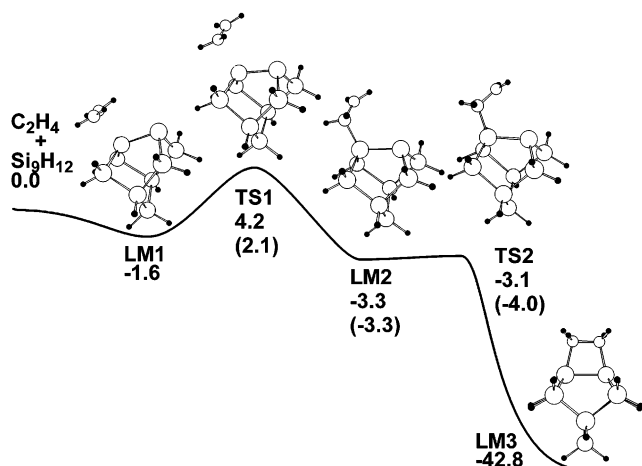


Figure 1. Profile of energy surface for the [2 + 2] cycloaddition of ethylene on Si(100)-2 \times 1 surface predicted at the (U)B3LYP/6-31G* level of theory. For singlet-diradical stationary points, spin-projected energies are given in parentheses (ref 10d).

surfaces ($X = \text{C}, \text{Si}, \text{Ge}$), few theoretical investigations can be found in the literature concerning the reaction mechanism.^{10c,d,11d,12b} Recent density functional slab model calculations by Cho and Kleinman^{10c,11d} predicted that the [2 + 2]-like adsorptions of cyclopentene on Si(100) and Ge(100) surfaces follow the low-symmetry pathway A with little or no barrier, and they argued that on C(100) the [2 + 2]-like adsorption of simple alkenes is catalyzed by a few hydrogen impurities.^{12b} On the contrary, the most recent density functional cluster model calculations^{10d} demonstrated that the [2 + 2] cycloaddition of ethylene on Si(100) follows a diradical mechanism, proceeding via a π -complex precursor and a singlet diradical intermediate (Figure 1). Such a diradical mechanism accounts well for the nonsterospecificity of the reaction observed in STM experiments.^{10b} We further envision that a similar mechanism would work for the [2 + 2] cycloaddition of simple alkenes on the (100) surfaces of diamond and germanium and, herein, report the results of a systematic density functional investigation on the reaction pathways of ethylene with the X(100) surfaces ($X = \text{C}, \text{Si}, \text{Ge}$).

2. Computational Details

We used X_9H_{12} clusters to model the $\text{X}=\text{X}$ dimers of X(100) surfaces. All calculations were performed with the GAUSSIAN98 package.¹⁶ The hybrid density functional method, including Becke's three-parameter nonlocal-exchange functional¹⁷ with the correlation functional of Lee–Yang–Parr¹⁸ (B3LYP) as well as analytical gradients, was employed. The basis set used is the standard all-electron split-valence basis set 6-31G*. Geometry optimizations and vibrational analyses were performed with no constraints of freedom. Final energy parameters include the unscaled zero-point energy (ZPE) corrections calculated at the B3LYP/6-31G* level of theory, unless otherwise specified. All the stationary points (transition states and adjacent local minima) along the reaction paths have been connected by using the intrinsic reaction coordinate (IRC) calculations.¹⁹ The cluster models as well as the computational method have been widely employed in previous investigations on the chemistry of X(100) surfaces ($X = \text{C}, \text{Si}$, and Ge).^{6b,e,7c,d,9,10d} Especially the spin-unrestricted B3LYP method, i.e., UB3LYP, has been used for the study of the stationary points that are singlet diradical; spin-projected energies were calculated with the approximate spin correction procedure proposed by Yamaguchi et al.²⁰

At the B3LYP/6-31G* level of theory, the Si_9H_{12} , Ge_9H_{12} , and C_9H_{12} ($X = \text{Si}, \text{Ge}$) clusters are predicted to have closed-shell ground states. Geometry optimizations reveal that the $\text{X}=\text{X}$ dimers in the former two clusters are asymmetric, whereas the one in the C_9H_{12} cluster is symmetric. The predicted buckling angle of the $\text{Ge}=\text{Ge}$ dimer in the Ge_9H_{12} cluster is much larger than that of the $\text{Si}=\text{Si}$ dimer in the Si_9H_{12} cluster, i.e., $\sim 1.7^\circ$ for the Si_9H_{12} case versus 15.7° for the Ge_9H_{12} case. The results are in qualitative agreement with the experimental observation that at low temperatures dimers on Ge(100) and Si(100) surfaces are buckled, whereas those on the C(100) surface are symmetric.^{5e}

3. Results

3.1. $\text{C}_2\text{H}_4/\text{Si}(100)$. Our predicted reaction pathway and energetics for the [2 + 2] addition of ethylene on the Si_9H_{12} cluster model are given in Figure 1. Details of the geometries of the stationary points can be found in our previous report.^{10d} At a first glance, the [2 + 2]-like adsorption is predicted to be exothermic by 42.8 kcal/mol at the B3LYP/6-31G* level of theory, in good agreement with the experimental estimation of ~ 42 kcal/mol reported by Fink et al.^{11c} This justifies our choice of cluster model and computational method for the study of the ethylene/Si(100) chemisorption system. It should be pointed out that ZPE correction is essential here for a reasonable prediction of the exothermicity, since the ZPE-uncorrected value for the exothermicity predicted in our cluster model calculations is 44.9 kcal/mol, 2.8 kcal/mol higher than the experimental estimation. Note that an even higher exothermicity (~ 48.3 kcal/mol) for the 0.5 ML coverage adsorption of ethylene on Si(100) was predicted by Miotto et al.^{10e} using a slab model and a different density functional.

From Figure 1, we could conclude briefly that the [2 + 2] cycloaddition of ethylene on Si(100) proceeds through a weakly bound π -complex (LM1) and mono- σ -bonded, singlet diradical intermediate (LM2). The rate-determining step is the formation of LM2 from LM1, giving rise to an overall activation energy of 4.2 kcal/mol. Upon spin correction, a value of 2.1 kcal/mol is obtained for the overall activation energy.

3.2. $\text{C}_2\text{H}_4/\text{C}(100)$. The predicted reaction pathway and energetics for the [2 + 2] cycloaddition of ethylene onto the dimer site of the C_9H_{12} cluster model are shown in Figure 2. Different from the mechanism predicted for $\text{C}_2\text{H}_4/\text{Si}_9\text{H}_{12}$, no π -complex precursor has been located for the addition of C_2H_4 to the $\text{C}=\text{C}$ dimer site on C(100). A singlet diradical intermediate LM1C is formed from isolated reactants by overcoming an energy barrier of 14.5 kcal/mol at the transition state TS1C. Upon spin correction, the barrier reduces to a value of 9.2 kcal/mol. TS1C is partially diradical-like with a $\langle S^2 \rangle$ value of 0.53; the forming C_3-C_2 bond in TS1C is 2.071 Å in length. LM1C is lower by -2.6 kcal/mol than isolated reactants. In LM1C, the ethylene moiety is mono- σ -bonded onto an end of the $\text{C}=\text{C}$ dimer with a C_2-C_3 bond length of 1.54 Å; the radical-end $-\text{CH}_2$ group in the ethylene moiety is far away from unreacted C_4 atom of the $\text{C}-\text{C}$ dimer with a $\text{C}_1\cdots\text{C}_4$ distance of 3.142 Å. Spin density analysis on the wave functions of LM1C reveals that the unreacted C_4 and C_2 atoms have spin densities of +1.07 and -0.94 , respectively, indicating that the two unpaired electrons are mainly localized on these two carbon atoms. Radical–radical combination within LM1C appears to be quite facile with a small barrier of 0.5 kcal/mol (at TS2C) relative to LM1C and leads to the formation of the final [2 + 2] product LM2C. In this element reaction, the transition state TS2C is rather early; the forming C_4-C_2 bond (2.923 Å) in TS2C is shorter by only ~ 0.2 Å than the C_4-C_2 distance (3.142 Å) in

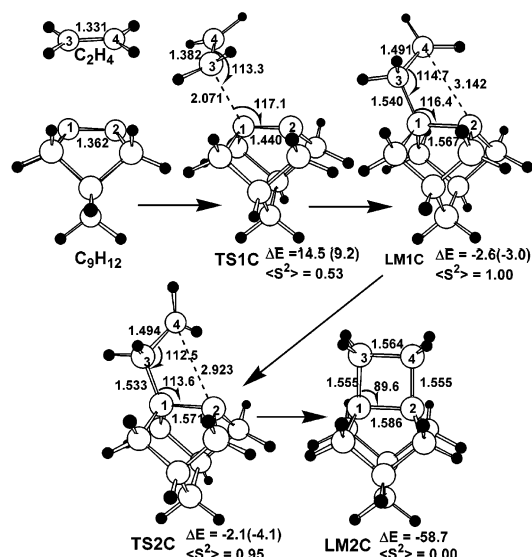


Figure 2. Reaction pathway and energetics (relative to isolated reactants) for the [2 + 2] cycloaddition of ethylene on C(100)-2×1 surface predicted at the (U)B3LYP/6-31G* level of theory. For singlet-diradical stationary points, spin-projected energies are given in parentheses. Units are kilocalories per mole for energy, angstroms for bond lengths, and degrees for bond angles.

LM1C but much longer than the C4–C2 bond (1.555 Å) in LM2C. The small barrier of this step diminishes upon correction of spin contamination. Formation of the [2 + 2] product LM2C is predicted to be exothermic by 58.7 kcal/mol with respect to isolated reactants, C₂H₄ and C₉H₁₂ cluster. Thus the [2 + 2] cycloaddition of ethylene on C(100) is more exothermic than on Si(100). The higher exothermicity on C(100) than on Si(100) can be ascribed to the much higher bond strength of a C–C bond than that of a Si–C bond, as the [2 + 2] cycloaddition gives rise to two C–C bonds on C(100) but two Si–C bonds on Si(100).

In summary, our density functional cluster model calculations revealed that the [2 + 2] cycloaddition of ethylene on C(100) follows a diradical mechanism. The predicted overall activation of only 9.2 kcal/mol for this surface reaction suggests that the [2 + 2]-like adsorption of ethylene on C(100) can occur at room temperature without the help of surface defects and impurities, but the reaction probability would be low under UHV (ultrahigh vacuum) conditions.

3.3. C₂H₄/Ge(100). As shown in Figure 3, the reaction mechanism predicted for the cycloaddition of ethylene on Ge(100) is essentially analogous to, but with different energetics from, that predicted for the C₂H₄/Si(100) system.

The reaction is initiated by the barrierless formation of a π -complex (LM1G), which is lower by 7.2 kcal/mol than isolated reactants. The stronger dative bonding of ethylene onto the buckled Ge=Ge dimer of Ge(100) than that onto the Si=Si dimer of Si(100) hints at a stronger zwitterionic character of the Ge=Ge dimer than of the Si=Si dimer.

The second step is the formation of a singlet-diradical intermediate (LM2G) from the π -complex precursor. A transition state (TS1G) that connects LM1G and LM2G is located 10.2 kcal/mol higher than LM1G (or 3.0 kcal/mol higher than the original reactants). TS1G is partially singlet-diradicaloid as evidenced by the $\langle S^2 \rangle$ value (0.60) of its wave functions; the singlet-diradicaloid nature of LM2G is characterized by the $\langle S^2 \rangle$ value of its wave functions as well as the nearly unity spin densities localized at the C2 and C4 atoms.

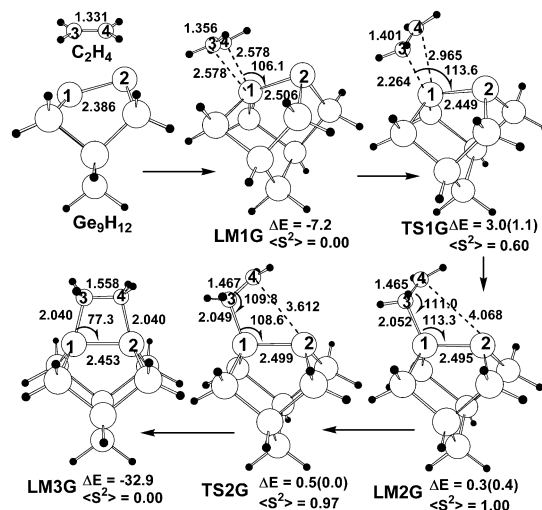


Figure 3. Reaction pathway and energetics (relative to isolated reactants) for the [2 + 2] cycloaddition of ethylene on Ge(100)-2×1 surface predicted at the (U)B3LYP/6-31G* level of theory. For singlet-diradical stationary points, spin-projected energies are given in parentheses. Units are kilocalories per mole for energy, angstroms for bond lengths, and degrees for bond angles.

The final step is the formation of the [2 + 2] product LM3G from the diradical intermediate LM2G via the transition state TS2G. TS2G is found to be only 0.2 kcal/mol higher than LM2G in energy. Among the three steps, the second one is the rate-determining step, giving rise to an overall activation energy of 3.0 kcal/mol. After correction for spin contamination, an overall activation energy of 1.1 kcal/mol is predicted for the [2 + 2]-like adsorption of ethylene on Ge(100).

The exothermicity predicted for ethylene adsorption on Ge(100) is 32.9 kcal/mol at the B3LYP/6-31G* level of theory, lower by 10 kcal/mol than the predicted value of 42.8 kcal/mol for ethylene adsorption on Si(100). Such a prediction is in qualitative agreement with the TPD experiments^{11c} that revealed lower adsorption energy for ethylene on Ge(100) than on Si(100). However, it appears that the B3LYP/6-31G* calculations tend to overestimate the Ge–C bond strength, as the B3LYP/6-31G* predicted adsorption energy of 32.9 kcal/mol is 7.5 kcal/mol higher than the experimental estimation of 25.4 kcal/mol^{11c} based on TPD spectra of C₂H₄/Ge(100). Such a deviation implies an overestimation of ~3.7 kcal/mol for each Ge–C bond formed. Accordingly, for the transition states (TS1G and TS2G) and intermediate (LM2G) that have explicit Ge–C bonding interaction(s), their energies relative to the isolated reactants have all been overestimated. By taking into account the 3.7 kcal/mol overestimation for a Ge–C bond, the energies of TS1G, LM2G, TS2G, and LM3G relative to isolated reactants are empirically estimated to be 2.9,²¹ 2.2, 1.8, and –25.4 kcal/mol, respectively. Thus our estimated overall activation energy for the [2 + 2] cycloaddition of ethylene on Ge(100) is 2.9 kcal/mol, higher by 0.8 kcal/mol than that of ethylene adsorption on Si(100).

The present prediction differs substantially from that reported by Miotto et al.^{10e} and by Cho and Kleinman.^{11d} Employing a slab model with periodic boundary conditions in two dimensions and a different density functional, Miotto et al.^{10e} proposed that the [2 + 2] addition of C₂H₄ to Ge(100) follow a low-symmetry pathway (i.e., pathway A in Scheme 1), and estimated the activation energy and exothermicity for the addition reaction to be ~5.5 and ~20.7 kcal/mol, respectively. However, it appears that no ZPE has been accounted for in these figures. In our cluster model calculations, the ZPE-uncorrected values for

the activation energy is 3.2 kcal/mol, lower by 2.3 kcal/mol than Miotto's prediction. Besides the different model and density functional used in their study, the lack of spin polarization in their density functional calculations might also be a cause of such a discrepancy. Cho and Kleinman^{11d} employed a similar computational technique that lacks spin polarization to investigate the reaction pathways for cyclopentene addition to Si(100) and Ge(100) surfaces and approached analogous low-symmetry pathways.

4. Discussion

It is well-known that [2 + 2] cycloaddition between two ethylene molecules is symmetry-forbidden and thermally unapproachable even if a low-symmetry, diradical pathway was allowed. However, our density functional calculations presented above clearly demonstrated that ethylene can undergo [2 + 2] cycloaddition onto the X=X dimers of the X(100) surfaces (X = C, Si, Ge) by following diradical mechanisms. The opening of diradical pathways for the [2 + 2] cycloadditions of ethylene with the X=X dimers can be ascribed to the much weaker π -bonds within the X=X dimers of X(100) surface than that of an ethylene. Note that the surface dimer π -bond strength is \sim 28 kcal/mol for C(100)^{14a} and 5–10 kcal/mol for Si(100)¹⁵ and Ge(100),^{14b} much smaller than the π -bond strength of 56 kcal/mol²² in ethylene. The weaker π -bond a surface dimer has, the more diradicaloid is it and the easier is it for the surface dimer to undergo a diradical reaction. Thus our predicted order of reactivity for the [2 + 2] cycloaddition of ethylene onto the X(100) surfaces, C(100) \ll Ge(100) < Si(100), correlates negatively with the order of dimer π -bond strengths.

Our calculations also disclosed subtle difference among the diradical mechanisms of the [2 + 2] reactions on the three surfaces. On Si(100) and Ge(100), π -complex precursors can be formed from ethylene and a buckled dimer, whereas no π -complex has been found on C(100). This reflects the zwitterionicity of the asymmetric dimers on Si(100) and Ge(100) as well as the nonzwitterionicity of the symmetric dimers on C(100).

In short, the [2 + 2] cycloadditions of a simple alkene, such as ethylene, onto the X=X dimers of X(100) follow diradical pathways; details of reaction pathways vary subtly with the bonding nature⁵ of the surface dimers, including their zwitterionicity, weakness of the dimer π -bond, and readiness to react as a diradical.

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Supporting Information Available: Cartesian coordinates of all reported stationary points, as well as the total electronic and zero-point vibrational energies (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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