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Acetylene reaction with the Si(111) surface: A semiempirical quantum chemical study

B. Weiner
Department of Physics, The Pennsylvania State University, DuBois, Pennsylvania 15801

C. S. Carmer and M. Frenklach
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802
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The interaction between the acetylene molecule and the Si(111) surface was modeled using the geometry optimization pathway of the Zerner intermediate neglect of differential overlap semiempirical quantum chemical program. The surface was represented by a 49-atom cluster containing four layers of silicon atoms. To determine the effect of the interaction upon the silicon surface, 12 central atoms from the top two layers were allowed to move to stable positions. The geometry of the silicon surface was initially optimized without acetylene, resulting in a significant rearrangement of the mobile atoms. Nine separate calculations were then performed, differing in the initial position and orientation of the acetylene molecule above the surface. The geometry of the resulting surface structures was found to be highly dependent upon the initial placement and orientation of the acetylene. In each case, the acetylene was found to react with the silicon surface by the formation of Si—C bonds. An analysis of the Wiberg bond indices revealed that the initial triple bond between carbon atoms was reduced to approximately a single bond, the exact bond order varying slightly from case to case. It was also found that Si—Si bonds surrounding the reaction site were weakened, and in some cases broken, due to the strain induced by the Si—C bond formation. The degree to which the surfaces were rearranged was found to correlate with the final energies, indicating that the most distorted surfaces were the most energetically favorable.

I. INTRODUCTION

The reaction of hydrocarbons with silicon surfaces is of interest in several areas. Recent advances in the chemical vapor deposition (CVD) of cubic silicon carbide (β-SiC) have made possible the growth of high-quality single-crystal films suitable for electronic applications.[1–3] β-SiC films are grown on silicon substrates by a two-step process. In the first step, a hydrocarbon (typically C_2H_2, C_2H_4, or C_3H_8) diluted with H_2 flows over a silicon surface as the temperature is increased from 300 to approximately 1673 K. The products of hydrocarbon decomposition react with the surface to form an initial layer of poorly crystallized SiC, roughly 10 nm thick. Homoepitaxial growth of β-SiC then proceeds as SiH_4 is added to the reaction mixture and the temperature held constant. Large-area films with low defect densities are only formed when the temperature ramping technique is employed. It is believed that the initial layer acts as a "buffer" to accommodate the large lattice mismatch between silicon and SiC, and as a barrier to prevent rapid evaporation and outward diffusion of silicon.[4] A related area that has received attention is the low-pressure synthesis of diamond from hydrocarbon precursors.[5,6] A wide variety of materials have proven successful as substrates for the growth of polycrystalline diamond films. When silicon wafers are used as substrates, SiC has often been identified as an interlayer material.[7] To date, the synthesis of high-quality single-crystal diamond films has not been achieved, but is much desired due to diamond's outstanding thermal, electronic, and optical properties. In order to optimize the CVD process of both β-SiC and diamond films a better understanding of the initial surface reaction is needed.

Of particular interest to us is the formation of ultrafine (smaller than 1 μm) silicon carbide powders used in sintered ceramics, composite materials, and as catalyst supports. When gaseous mixtures of SiH_4 and various hydrocarbons are pyrolized at temperatures above 1400 K, silicon particles 20–50 nm in diameter are formed and subsequently converted to SiC. It is unclear by what mechanism this conversion takes place. One possibility is that carbon condenses from the gas phase onto the surface of the silicon particles, and through solid-state diffusion of either silicon or carbon, a product layer of SiC is built up.[8] Another possibility is that after the silicon particles are formed, products of the hydrocarbon pyrolysis attack the silicon surface. Silicon-carbon bonds are formed causing Si—Si bonds to rupture because of the strain induced by the greater strength of the Si—C bonds.[9] In this way, cluster size groups of silicon and carbon atoms would be able to break away from the silicon particle surface and contribute to the nucleation and growth of β-SiC. The net result of this process would be growth of SiC particles, while silicon particles are etched away.

A determination of how the structure of a silicon surface is affected by reaction with C_2H_2 constitutes the main objective of this work. Acetylene was chosen for this study as it is one of the primary decomposition species in the thermal breakdown of hydrocarbons.[10] In addition, acetylene has been suggested to be an important

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precursor to the growth of β-SiC films[11] and powders[12] as well as to the low-pressure growth of diamond.[13] We consider the (111) surface as it is widely used in film growth studies and has been well characterized.[14,15] Previous quantum chemical studies of the interaction between C_2H_2 and a silicon surface have concentrated on the nature of bond formation between silicon and carbon.[16,17] Chu and Anderson[17] applied the atom-superposition and electron-delocalization molecular-orbital (ASEDMO) theory and found that acetylene is adsorbed on a silicon surface with the formation of σ bonds between silicon and carbon at twofold sites. On adsorption, the carbon-carbon triple bond of acetylene changed to between a single and double bond, in reasonable agreement with electron energy loss spectroscopy.[18,19] In their study, however, the silicon surface was modeled by saturating dangling surface bonds with hydrogen and holding the silicon atoms in their ideal crystalline positions so that the silicon surface structure was not allowed to change. In the present study dangling bonds were not saturated nor were the surface silicon atoms held fixed. The computational strategy of this study is presented in Sec. II and results presented in Sec. III. The results are consistent with the etching model of SiC particle formation.

II. COMPUTATIONAL PROCEDURE

Figure 1 shows the structure used to model a silicon (111) surface. Four layers of silicon atoms, totaling 49 atoms, were initially placed at ideal crystal lattice positions. The bottom two layers and the edge atoms of the top layers were held fixed while the remaining top central atoms, shown in Fig. 2, were subjected to structural optimization. Stable positions were found by using the geometry optimizer pathway of the Zerner intermediate neglect of differential overlap (ZINDO) semiempirical method.[20] An acetylene molecule, with an optimized structure, was then placed 3.0 Å above the top atomic layer at three different locations, marked as 0, 1, and 2 in Fig. 2. Three orientations of the linear acetylene molecule, corresponding to alignment with the x, y, and z axes, were used at each position for a total of nine initial starting points. Each case will be referred to by the initial placement of the acetylene molecule. For example, X_0 corresponds to the C_2H_2 being parallel to the x axis at position 0. These structures were then optimized giving various final geometries.

The reaction of acetylene with the surface was modeled by finding stationary points on the potential energy surface obtained by varying the positions of the silicon, carbon, and hydrogen nuclei. Local minima correspond to stable structures and saddle points between these minima are transition states between these configurations. The 49-atom silicon cluster is treated as a large molecule as we are interested in local structural changes, i.e., formation and breaking of chemical bonds rather than bulk properties. Only s and p basis functions were used to describe silicon atoms. It has been demonstrated for the second-row atoms, in computations with the SINDO1 method,[21-24] that more accurate results are obtained by

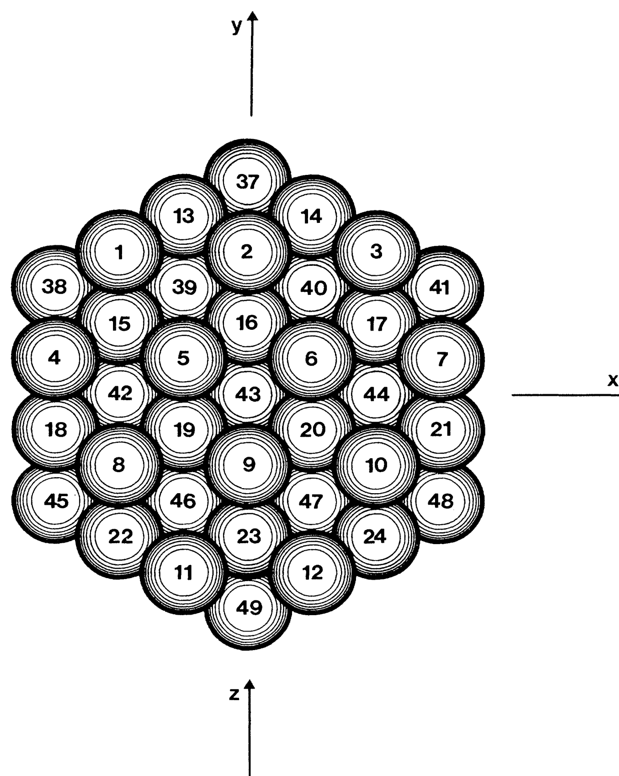

FIG. 1. Schematic illustration of the 49-atom silicon cluster used to model the Si(111) surface. Both a top view (top) and side view (bottom) are shown. The z axis is parallel to the [111] direction. Atoms 25–36 are in the third layer and cannot be seen in the top view.

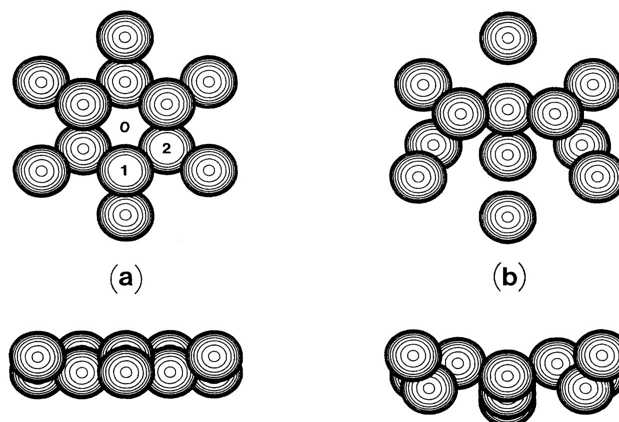

FIG. 2. Schematic illustration of the 12 atoms that were not held fixed during the geometry optimization calculations. (a) prior to optimization. Positions 0, 1, and 2 indicate initial positions of acetylene. (b) After optimization.

neglecting d functions. Since the method used in the present work, ZINDO, is similar to SINDO1, d basis functions were not included in the description of silicon atoms. A binding energy of 4.98 eV/atom was calculated for the unoptimized silicon *cluster,* in good agreement with the experimentally determined cohesive energy of *bulk* silicon, $E_{\mathrm{coh}}=4.63$ eV/atom. Carbon atoms were described by s and p functions while only s functions were used to describe the hydrogen atoms.

The geometry optimizer in the ZINDO program uses the Broyden-Fletcher-Golfarb-Shanno (BFGS) update method. Because of the size of the problem we did not examine the matrix of second derivatives of the energy functional at the stationary points. However, stationary points found with this method are usually local minima as the approximate updated Hessian is constrained to be positive definite at all times. The ZINDO program is based on a variant of the intermediate neglect of differential overlap (INDO) method.[25] The form of the approximate Hamiltonian used and the chosen values of the semiempirical parameters give molecular geometries as accurately as the modified INDO (MINDO) method.[26] Geometry optimization programs based on the local density approximation, although more accurate than the INDO method, are prohibitively expensive in terms of computer time and memory when dealing with the number of atomic centers that are of interest in the present study (more than 50). This is of course even more true for quantum chemical *ab initio* codes.

In this study, Wiberg atomic bond orders were used to characterize changes in chemical bonding. The bond order is a measure of overlap electron density between two atoms and was calculated by

$$B_{ab}=\sum_{1\le i\le j\le N}\rho_{ij}^2 ,$$

where B_{ab} is the bond order between atoms a and b; i and j are restricted to atomic orbitals on atoms a and b, respectively; and N is the total number of atomic orbitals. The bond order matrix ρ is defined in terms of the molecular-orbital coefficients c_{ik} of the n occupied molecular orbitals by

$$\rho_{ij}=\sum_{1\le k\le n} c_{ik}c_{jk} .$$

A bond order of 1 indicates a single bond, a bond order of 2 indicates a double bond, and a bond order of 3 indicates a triple bond.

III. RESULTS AND DISCUSSION

A significant restructuring of the ideal (111) surface occurred when optimized prior to the placement of acetylene, as shown in Fig. 2. The optimized surface became slightly concave as the center atoms moved downward, by several tenths of an angstrom, toward the lower fixed layer (not shown in Fig. 2). Silicon surfaces are known to reconstruct by the rearrangement of surface atoms into structures that differ from the ideal crystal lattice. A 2×1 reconstruction is observed when a Si single crystal is cleaved to expose the (111) surface. Upon annealing at temperatures above 675 K an irreversible transformation to a 7×7 reconstruction takes place. The 7×7 reconstruction is stable up to 1100 K at which point the Si(111) surface returns to the unreconstructed state. A large body of experimental and theoretical evidence supports these reconstructions and is reviewed by Haneman.[14] The structure shown in Fig. 2(b) does not correspond to any of these well-characterized Si(111) surfaces as it is a relaxation of the ideal surface at 0 K. Note, however, that a precise structural determination of the surface is not of concern in the present study, but rather changes in the bonding that occurs when acetylene reacts with it.

The energy of the relaxed surface was found to be 0.22 eV/atom lower than that of the unoptimized surface, which is reasonable in comparison with calculated reconstruction energies.[27] The HOMO-LUMO gap (highest occupied molecular orbital–lowest occupied molecular orbital) for the optimized surface was calculated to be 3.18 eV using the spectroscopic parametrization of the ZINDO program. This is larger than the 1.1-eV band gap of bulk silicon, but is a reasonable value given that it was calculated within the Hartree-Fock approximation. In addition, the cluster consists of only 49 atoms and is not expected to display bulklike properties.[28] The surface shown in Fig. 2(b), optimized prior to the addition of acetylene, will be referred to as the initial silicon surface throughout the remainder of the text.

The final structures resulting from the geometry optimization of the acetylene added cases are shown in Fig. 3. In most cases, acetylene is not merely adsorbed on the silicon surface, but appears to penetrate the first layer of silicon atoms, as seen in the side views of Fig. 3. The final bond orders for the carbon-carbon and carbon-hydrogen bonds are listed in Table I. All the carbon-carbon bond orders are approximately equal to 1, indicating that the initial triple bond of acetylene was broken to form a nearly single bond. The bonding between carbon and hydrogen was only slightly weakened during the reaction, however it is interesting that the hydrogen atoms remain fairly strongly bound to the carbon atoms, even when located deep in the surface and surrounded by silicon atoms. An analysis of silicon-carbon bond formation and the changes in silicon-silicon bonding is given later in the text.

It can be seen by simple inspection of the surfaces in Fig. 3 that the reaction with acetylene can cause major rearrangement of surface silicon atoms. This is particularly evident when acetylene was placed at position 1, where gaps were formed in the surface and it appears as though a group of silicon atoms was "pulled" toward the acetylene. The surface rearrangement was less dramatic, but still significant, when acetylene was placed at other positions. The final geometry was clearly dependent on the initial placement and orientation of the acetylene molecule. The energy of reaction ΔE_r is defined as the energy of the final structure minus the energies of the optimized silicon surface and acetylene, and is reported for each case in Table I. The difference between the highest and lowest calculated energies, corresponding to X_2 and Z_1, respectively, was quite large, equal to 15.3 eV.

In an effort to better understand the rearrangement of

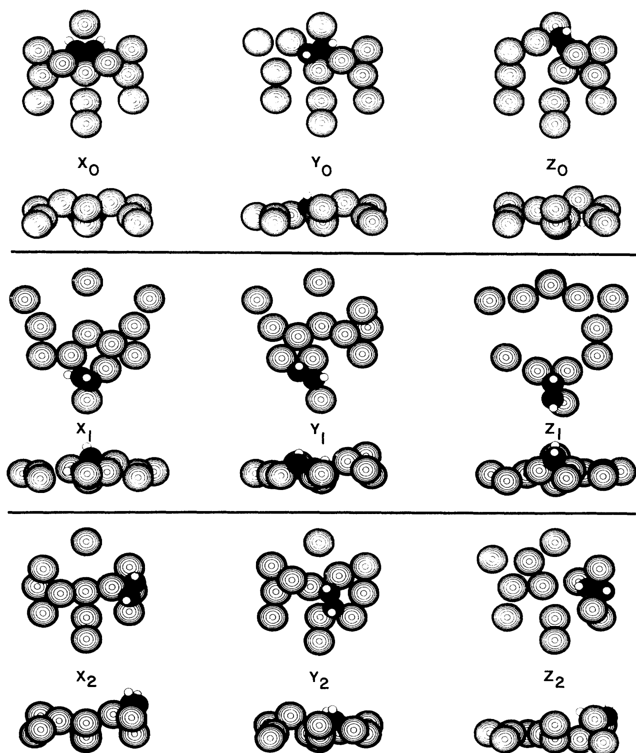

FIG. 3. Top and side views of the nine surfaces resulting from the geometry optimization of the acetylene added cases. Each case is specified by the initial placement and orientation of the C_2H_2 molecule. Concentric circles designate silicon atoms, solid circles designate carbon atoms, and small open circles designate hydrogen.

the surface due to the reaction with acetylene we have analyzed the change in bond order of Si—Si bonds surrounding each reaction site. The specific question of interest to the present study was to determine if Si—Si bonds were broken as a result of the interaction between silicon and carbon. The notation 1_N Si will be used to indicate the first nearest neighbors of carbon atoms. The bonds of interest are those between 1_N Si and their nearest neighbors in the initial silicon surface, which will be indicated by the notation 2_N Si. In Table II we list the bond orders between 1_N Si and carbon atoms, as well as the initial and final values of the 1_N Si–2_N Si bond orders. In all cases, as 1_N Si atoms form bonds with carbon they become less strongly bound to their neighboring silicon atoms. In most of the cases there were some 1_N Si atoms that became entirely separated from 2_N silicon atoms, as evidenced by the final bond orders being nearly equal to zero. Even in the X_0 case, which appears to be the least distorted by the interaction with acetylene, there was significant weakening of the Si—Si bonding. This result lends credence to the proposed mechanism of SiC particle growth which is based on the breaking of Si—Si bonds and the resultant etching of silicon particle surfaces, as described in Sec. I.

The rearrangement of silicon atoms can be explained on the basis of the bond strength differences. The reported dissociation energy of a Si—C bond is 4.68 eV,[29] while that of a Si—Si bond is 3.38 eV.[30] Because of its greater strength, a Si—C bond is more thermodynamically stable and of shorter length than a Si—Si bond. Thus, as an acetylene molecule approaches the surface, it is energetically preferable for the nearest silicon atoms to bond with the incoming carbon atoms. This places a strain on the bonds between the silicon atoms interacting with the carbon atoms, and their nearest silicon neighbors (1_N Si—2_N Si bonds). Because the surface silicon atoms are ultimately connected to the relatively immobile bulk atoms, simulated by the fixed layers in this study, the induced strain can cause the Si—Si bonds to weaken, or break entirely. It should be noted that the quantum chemical calculations employed were carried out at the temperature 0 K, and the thermal motion of atoms was not taken into account. When one considers the effect of elevated temperature, it is reasonable to expect that the thermal energy would provide an additional contribution to the breaking of weakened Si—Si bonds, allowing a group of silicon and carbon atoms to break free from the silicon surface.

In order to quantify the rearrangement of the silicon surface, for purposes of comparison, we have calculated a surface "disturbance" value D, defined as

$$D=\sum_{i,j=1}^{N_{\mathrm{Si}}}(d_{ij(F)}-d_{ij(I)}) , \tag{1}$$

where d_{ij} is the interatomic distance between silicon atoms i and j, N_{Si} is the number of silicon atoms in the model, and the subscripts F and I indicate the final and initial (optimized) structures. The disturbance value

TABLE I. Parameters resulting from the optimization of the nine acetylene added surfaces.

Acetylene position	C—C bond order	C—H bond orders	ΔE_r (eV)	Disturbance value (Å)
X_0	1.31	0.86,0.86	−28.16	−33.54
Y_0	1.13	0.70,0.94	−32.44	17.39
Z_0	0.96	0.78,0.86	−28.93	−16.08
X_1	1.16	0.66,0.93	−38.53	117.47
Y_1	0.89	0.87,0.94	−34.59	37.56
Z_1	0.91	0.93,0.95	−40.74	243.74
X_2	1.22	0.95,0.95	−25.47	−29.44
Y_2	1.16	0.91,0.94	−26.23	−58.39
Z_2	0.95	0.84,0.94	−30.01	2.33

takes into account the change in separation of all the silicon atoms, not just that between nearest neighbors. Summing the change in the interatomic separation of the silicon atoms between the final and initial structures provides a measure of how much the surface has been rearranged, or disturbed. The disturbance value for each case is listed in Table I and appears to be a reasonable indication of the extent of rearrangement in the surfaces. A positive sign of D indicates that after reaction with acetylene the average distance between silicon atoms increased. The most positive D values correspond to the initial placement of the acetylene at position 1, which un-

TABLE II. Results of the analysis of Si—C bonding and the change in the Si—Si bonding in the optimized acetylene added surfaces.

C_2H_2 position	Nearest-neighbor silicons[a,b] (1_N Si)	Second-nearest-neighbor silicons[c] (2_N Si)				
X_0	Si(05) (0.81)	Si(15) (0.89,0.70)	Si(16) (0.80,0.32)	Si(19) (0.78,0.54)		
	Si(09) (0.81)	Si(16) (0.80,0.32)	Si(17) (0.80,0.70)	Si(20) (0.78,0.54)		
	Si(16) (0.28)	Si(05) (0.80,0.32)	Si(06) (0.80,0.32)	Si(09) (0.74,0.14)	Si(28) (0.69,0.25)	
	Si(28) (0.39)	Si(02) (0.30,0.13)	Si(16) (0.69,0.25)	Si(39) (0.86,0.67)	Si(40) (0.86,0.67)	Si(43) (0.66,0.57)
Y_0	Si(02) (0.51)	Si(13) (0.51,0.56)	Si(14) (0.51,0.62)	Si(25) (0.56,0.42)	Si(26) (0.56,0.44)	Si(28) (0.30,0.19)
	Si(05) (0.90)	Si(15) (0.89,0.22)	Si(16) (0.80,0.02)	Si(19) (0.74,0.07)		
	Si(06) (0.44)	Si(16) (0.80,0.51)	Si(17) (0.89,0.74)	Si(20) (0.78,0.34)		
	Si(16) (0.77,0.35)	Si(05) (0.80,0.02)	Si(06) (0.80,0.51)	Si(09) (0.74,0.09)	Si(28) (0.69,0.31)	
	Si(28) (0.35)	Si(02) (0.30,0.19)	Si(16) (0.69,0.31)	Si(39) (0.86,0.79)	Si(40) (0.86,0.71)	Si(43) (0.66,0.56)
Z_0	Si(02) (0.53)	Si(13) (0.51,0.20)	Si(14) (0.51,0.27)	Si(25) (0.56,0.46)	Si(26) (0.56,0.60)	Si(28) (0.30,0.21)
	Si(05) (0.77)	Si(15) (0.89,0.43)	Si(16) (0.80,0.01)	Si(19) (0.78,0.02)		
	Si(06) (0.52,0.37)	Si(16) (0.80,0.44)	Si(17) (0.89,0.72)	Si(20) (0.78,0.09)		
	Si(16) (0.47)	Si(05) (0.80,0.01)	Si(06) (0.80,0.44)	Si(09) (0.74,0.07)	Si(28) (0.69,0.33)	
	Si(28) (0.67)	Si(02) (0.30,0.21)	Si(16) (0.69,0.33)	Si(39) (0.86,0.66)	Si(40) (0.86,0.63)	Si(43) (0.66,0.62)
X_1	Si(08) (0.26,0.29)	Si(16) (0.74,0.01)	Si(31) (0.54,0.01)	Si(32) (0.32,0.10)	Si(43) (0.40,0.03)	
	Si(11) (0.27,0.30)	Si(22) (1.15,0.85)	Si(23) (0.97,0.72)			
	Si(12) (0.83)	Si(23) (0.97,0.61)	Si(24) (1.15,0.59)			
	Si(23) (0.38,0.21)	Si(11) (0.97,0.72)	Si(12) (0.97,0.61)	Si(35) (0.73,0.26)	Si(49) (0.12,0.75)	
	Si(35) (0.63)	Si(23) (0.73,0.26)	Si(46) (0.77,0.78)	Si(47) (0.77,0.65)	Si(49) (1.22,0.89)	
Y_1	Si(08) (0.52)	Si(18) (0.85,0.14)	Si(18) (0.71,0.06)	Si(22) (0.79,0.52)		
	Si(09) (0.42,0.47)	Si(16) (0.74,0.03)	Si(31) (0.54,0.35)	Si(32) (0.32,0.03)	Si(43) (0.40,0.02)	
	Si(11) (0.47,0.52)	Si(22) (1.15,0.75)	Si(23) (0.97,0.51)			
	Si(22) (0.50)	Si(08) (0.79,0.52)	Si(11) (1.15,0.75)	Si(34) (0.93,0.70)		
	Si(23) (0.63)	Si(11) (0.97,0.51)	Si(12) (0.97,0.77)	Si(35) (0.73,0.35)	Si(49) (0.12,0.79)	
	Si(35) (0.42)	Si(23) (0.73,0.35)	Si(46) (0.77,0.61)	Si(47) (0.77,0.77)	Si(49) (1.22,0.96)	
Z_1	Si(09) (0.55)	Si(16) (0.74,0.00)	Si(31) (0.54,0.01)	Si(32) (0.32,0.04)	Si(43) (0.40,0.00)	
	Si(11) (0.75,0.45)	Si(22) (1.15,0.54)	Si(23) (0.97,0.02)			
	Si(12) (0.33,0.42)	Si(23) (0.97,0.54)	Si(24) (1.15,0.53)			
	Si(23) (0.85)	Si(11) (0.97,0.02)	Si(12) (0.97,0.54)	Si(35) (0.73,0.38)	Si(49) (0.12,1.22)	
X_2	Si(06) (0.34,0.57)	Si(16) (0.80,0.16)	Si(17) (0.89,0.66)	Si(20) (0.78,0.48)		
	Si(07) (0.77)	Si(17) (0.94,0.51)	Si(21) (0.97,0.77)			
	Si(10) (1.01)	Si(20) (0.72,0.44)	Si(21) (0.85,0.61)	Si(24) (0.80,0.49)		
	Si(17) (0.54)	Si(03) (0.92,0.86)	Si(06) (0.89,0.66)	Si(07) (0.94,0.51)	Si(29) (0.69,0.24)	
Y_2	Si(06) (0.90)	Si(16) (0.80,0.18)	Si(17) (0.89,0.54)	Si(20) (0.78,0.31)		
	Si(09) (0.81)	Si(16) (0.74,0.08)	Si(31) (0.54,0.15)	Si(32) (0.36,0.22)	Si(43) (0.40,0.02)	
	Si(10) (0.86)	Si(20) (0.72,0.46)	Si(21) (0.85,0.08)	Si(24) (0.80,0.69)		
	Si(16) (0.79)	Si(09) (0.80,0.83)	Si(10) (0.74,0.08)	Si(11) (0.80,0.18)		
Z_2	Si(06) (0.74)	Si(16) (0.80,0.06)	Si(17) (0.89,0.19)	Si(20) (0.78,0.01)		
	Si(07) (0.75)	Si(17) (0.94,0.68)	Si(21) (0.97,0.65)			
	Si(10) (0.58,0.60)	Si(20) (0.72,0.72)	Si(21) (0.85,0.34)	Si(24) (0.80,0.11)		
	Si(17) (0.28,0.51)	Si(03) (0.92,0.87)	Si(06) (0.89,0.19)	Si(07) (0.94,0.68)	Si(29) (0.69,0.39)	
	Si(21) (0.47)	Si(07) (0.97,0.65)	Si(10) (0.85,0.34)	Si(20) (0.40,0.19)		

[a] 1_N Si denotes silicon atoms that are nearest neighbors to carbon atoms. Si—C bond orders are given in parentheses. Two values given for the bond order indicate the silicon bonded to both carbon atoms.
[b] Silicon atoms are numbered in accordance with Fig. 1.
[c] 2_N Si are silicon atoms that were nearest neighbors to 1_N Si in the initial surface, prior to placement of acetylene. The 2_N Si in a given row are bound to 1_N Si of the same row. The initial and final bond orders are given in parentheses (initial, final).

derwent the greatest changes during optimization (see Fig. 3). In those cases where D was found to be negative, the average interatomic distance decreased, indicating the net effect of the reaction with acetylene was to bring the silicon atoms closer together.

The final energies ΔE_r appear to be related to the degree of rearrangement in the final structures. Figure 4 depicts the relationship between final energy and disturbance value D. A negative correlation is observed, with the lowest-energy states corresponding to the most dramatically rearranged surfaces. This result can be understood in terms of the strain induced by formation of Si—C bonds. The breaking of Si—Si bonds serves to dissipate strain and is energetically favorable to the distribution of strain over the entire structure. It is evident, from Fig. 4, that the structures that best support the etching mechanism are the most stable. Consideration of the effect of temperature would further strengthen this result. As noted above, the energy states of the final structures cover a range of more than 15 eV. Each structure corresponds to a local energy minimum of the global potential energy surface. At zero temperature, individual structures are "trapped" in these minima. Additional energy supplied by thermal activation would enable trapped structures to surmount potential barriers separating them from lower-energy states. Therefore, because of their lower energy, the most disturbed surfaces are expected to be the most probable structures at high temperatures.

While the above results are consistent with the etching mechanism, they do not preclude the possibility that a solid-state diffusion process contributes to the formation of SiC particles. Diffusion is a temperature-dependent process in which the chemical bonds of diffusing atoms must be broken to allow for atomic mobility. However, the bond order analysis revealed that 1_N Si—2_N Si bonds were broken and weakened to such an extent that something more than diffusion is suggested. This, along with the greater stability of the more rearranged surfaces and the additional effect of temperature, indicates that the etching mechanism is not only possible, but indeed, is more probable than diffusion as an explanation of the conversion of silicon particles to silicon carbide. These results may also shed some light on the difficulties involved in the epitaxial growth of single-crystal β-SiC on silicon substrates. The requirement of low temperatures for formation of a buffer layer may be explained by the fact that the rearrangement and etching mechanisms are expected to be temperature dependent. At lower temperatures, a silicon surface interacting with hydrocarbon molecules from the gas phase would be less disordered and less dynamic, allowing the formation of a buffer layer with a fewer number of defects. Similar considerations may need to be taken into account to achieve growth of large-area, high-quality, single-crystal diamond films, although this process is further complicated by a greater lattice mismatch between diamond and silicon and the fact that diamond is metastable at low pressures.

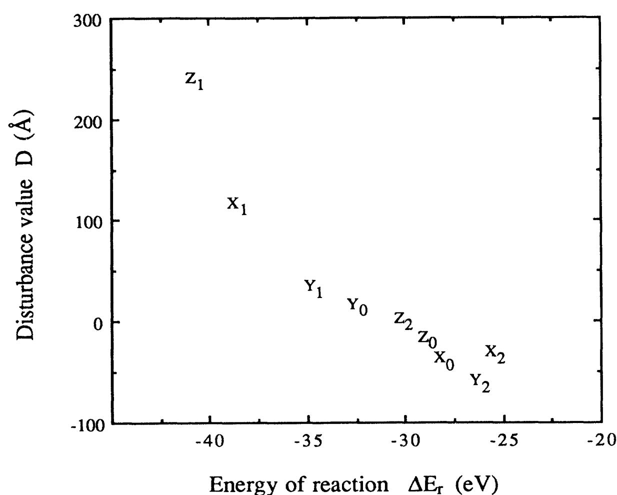

FIG. 4. Correlation between the final energy of the surfaces and the disturbance value D. The disturbance value is an indication of the degree of restructuring of the surfaces and is defined by Eq. (1).

IV. CONCLUSION

The results of this quantum chemical study indicate that during the reaction of acetylene with a Si(111) surface the triple bond of the C_2H_2 molecule is transformed to nearly a single bond while the C—H bonds were only slightly weakened. Carbon atoms from acetylene were found to penetrate, rather than merely adsorb to, the silicon surface. A significant restructuring of the silicon surface took place, and the final geometry was found to be dependent on the initial position and orientation of the acetylene molecule. A bond order analysis revealed that Si—Si bonds neighboring the carbon atoms were often weakened and in many cases entirely broken. The energy of the final structures was found to correlate with the amount of surface rearrangement, the most distorted surfaces being the most energetically stable. When the effect of temperature is considered, these results support a proposed mechanism for the formation of SiC powders via the etching of silicon surfaces by products of hydrocarbon pyrolysis at high temperatures.

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