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Simulation of bulk silicon crystals and Si(111) surfaces with application to a study of fluorine coverage of the surfaces

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Computational efficiency for the simulation of bulk crystals and surfaces is highly desirable. In an effort to study semiconductor crystals, we present a self-consistent treatment for the simulation of silicon crystals and surfaces based on the combination of a siligen model and a semiempirical Hamiltonian method. An artificial atom called siligen is introduced for the application of the semiempirical method to finite-size silicon clusters. The calculated average bond energies for the saturated silicon clusters are between 2.045 and 2.568 eV, compared to the measured value of 2.31 eV. A simulated bulk silicon surface using siligens is introduced in order to examine variation of the bond strength between fluorine atoms and the simulated silicon (111) surface. It is found that bond strength computed from the simulated surface, with siligens, rapidly converges to a saturated limit as the number of surface layers increases, while a pure silicon (111) surface without siligens yields no satisfactory convergence.

I. INTRODUCTION

Finite-size clusters have often been used to simulate bulk crystals and surfaces.[1-3] For molecular orbital calculations of silicon clusters, the unsaturated bonds (dangling bonds) at the surface of the finite-size clusters can cause difficulty in calculating bulk physical properties due to the failure of SCF (self-consistent field) convergence. Sometimes hydrogen atoms are used to saturate the dangling bonds.[4-8] This scheme, using hydrogen atoms, causes incorrect charge distributions, as the hydrogen atom is more electronegative than the silicon atom.[9] To remedy this problem Redondo and coworkers[9,10] introduced an artificial atom called siligen ($\overline{\mathrm{H}}$) to saturate the silicon dangling bonds. This allows the finite cluster to emulate the infinite system. In their *ab initio* treatment,[9] siligen was defined to retain the same physical properties as hydrogen except for the Slater 1*s* orbital ($e^{-\zeta_s r}$). They modified the value of the Slater exponent ζ_s to make the central silicon atom in the spherically shaped $\mathrm{Si}_5\overline{\mathrm{H}}_{12}$ cluster become electrically neutral. Later, they successfully used finite-sized silicon clusters with dangling bonds terminated by siligens to treat the oxidation and reconstruction of silicon surfaces.[9,10]

Here we apply a similar approach, i.e., dangling-bond termination by artificial siligen atoms, to AM1 (Austin Model 1) (Ref. 11) which is a further modified version of the MNDO (modified neglect of diatomic-differential overlap) method.[12] It is of note that the early version of MNDO, namely, the MINDO/3,[13] has been used by Badziag and Verwoerd[14] to study Si(111) reconstructions. In their application hydrogen atoms were used to terminate the silicon lattice at its periphery. The present treatment extends this technique with two improvements: (1) The latest version of MNDO, namely, AM1, is used, and (2) artificial siligen atoms are used for lattice termination. These refinements are needed for the application of this technique to silicon surface studies. In this approach, all of the hydrogen AM1 parameters are used for siligen, with values unchanged, except for the Slater exponent (ζ_s). The value of $\zeta_s(\overline{\mathrm{H}})$ is chosen to neutralize the central silicon in a spherically shaped silicon cluster covered by the siligens, namely, $\mathrm{Si}_5\overline{\mathrm{H}}_{12}$, shown in Fig. 1(d), where the interatomic distance is 2.35 A. The ζ_s value is found to be 0.726 94 a.u.

There exists a great deal of incentive for the research of chemisorption of fluorine on silicon. Fluorine is one of the primary active agents for etching crystalline silicon to selectively remove material in microdevice fabrication.[15] There has been active research in studying the process of etching silicon with fluorine, but much less theoretical work has been made for the interaction of fluorine with silicon surfaces to elucidate the etching mechanism. Much of this research, especially the experimental, has been carried out without distinguishing the surface orientation of silicon. On the other hand, we would like to point out that some *ab initio* calculations were also undertaken on a molecular basis to understand the general interaction mechanism of reactive ion etching and that a most systematic theoretical approach to this chemisorption study has been reported quite recently.[15] As a first attempt we focus our attention only to the interaction of fluorine with the Si(111) surface, with a particular emphasis on the surface coverage of fluorine.

Most recently, a good review article appeared to summarize some of the experimental findings in the past decade[16] regarding fluorine-silicon surface interactions. It is known that heavily doped n^+-type silicon etches faster than heavily doped p^+-type or undoped silicon in halogen-based reactive plasmas and that the influence of doping in n^+-type silicon increases with dopant concentration and decreases with ion bombardment. It was sug-

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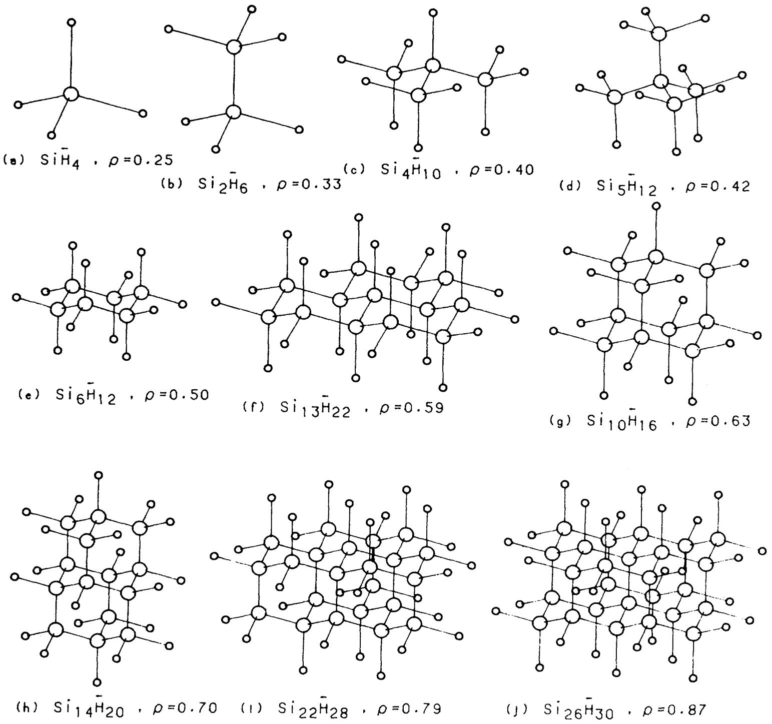


(a) $\mathrm{Si\bar{H}_4}$, $\rho=0.25$ (b) $\mathrm{Si_2\bar{H}_6}$, $\rho=0.33$ (c) $\mathrm{Si_4\bar{H}_{10}}$, $\rho=0.40$ (d) $\mathrm{Si_5\bar{H}_{12}}$, $\rho=0.42$

(e) $\mathrm{Si_6\bar{H}_{12}}$, $\rho=0.50$ (f) $\mathrm{Si_{13}\bar{H}_{22}}$, $\rho=0.59$ (g) $\mathrm{Si_{10}\bar{H}_{16}}$, $\rho=0.63$

(h) $\mathrm{Si_{14}\bar{H}_{20}}$, $\rho=0.70$ (i) $\mathrm{Si_{22}\bar{H}_{28}}$, $\rho=0.79$ (j) $\mathrm{Si_{26}\bar{H}_{30}}$, $\rho=0.87$

FIG. 1. Various finite-size clusters involving silicons (larger circles) and siligens (smaller circles) used for the examination of average bond energy. ρ is the number ratio of silicons to that of siligens.

gested that the doping effect was due to the number of free electrons on the surface, the position of the Fermi level, or the magnitude of the work function. For the reaction of a major gas reactant $\mathrm{XeF_4}$ with silicon, $\mathrm{SiF_4}$ is the major reaction product compared to radicals such as SiF and $\mathrm{SiF_2}$.[17] Further, the etch rate as a function of pressure[18,19] and light intensity[20] has been studied. The experimental bond dissociation energy[21] for the removal of a fluorine atom from $\mathrm{SiF_4}$ has been quoted in theoretical papers for indirect comparison with the computed bond energies between fluorine and silicon molecular clusters and between fluorine and silicon surfaces.

Several theoretical articles inspired by the etching of silicon by fluorine have been reported. These studies were focused on the comparison of the binding energy between a single fluorine atom and the Si(111) surface at various sites, bond energies of SiF_x with $x=1-3$, a reaction mechanism for fluorine etching of silicon with molecular models, the bonding energy between fluorine and the Si(111) surface and an etching mechanism in bulk silicon using a repeated-slab configuration. Theoretical calculation methods used were *ab initio* Hartree-Fock with LCAO (linear combination of atomic orbitals),[22] *ab initio* generalized valence bond-configuration interaction (GVB-CI),[23,24] and LDA (local-density approximation) theory[15] combined with *ab initio* pseudopotentials and large supercells. Through their LDA study, Van de Walle and co-workers[15] found that a fluorine atom could be inserted into Si-Si bonds when the steric constraints of the near-surface region were relaxed and calculated the F-Si bond strength to be 7.3 eV which is close to the experimental F-Si bond energy, 6.95 eV, of the $\mathrm{SiF_4}$ molecule.[15]

Our present study is twofold: (1) to examine the benefit of the use of siligen[9] atoms in the simulation of bulk silicon crystals with finite-size silicon clusters, and (2) to study the interaction between fluorine atoms and the simulated Si(111) surface. In this study we examine not only a single fluorine atom interaction but the interaction of multiple fluorine atoms with the silicon surface. This will reveal important information on the dependency of bond strength on fluorine surface coverage. To the best of our knowledge, such a study has not been reported thus far.

II. AVERAGE BOND ENERGY OF SILICON IN AN "ARTIFICIAL" BULK SILICON

The cohesive energy of a silicon atom in crystal silicon is known to be 4.63 eV.[25] Silicon atoms in bulk silicon are tetrahedrally bonded. The number of bonds in the bulk is then twice the number of atoms. Therefore the average bond energy, that is, average binding (cohesive) energy per bond, is half of the binding energy per atom, 2.31 eV. In this paper, we examine how well artificial bulk silicon as simulated by a finite-sized silicon cluster saturated (covered) by siligens correctly yields this bulk physical property. To thoroughly check the validity of using siligens for the simulation of the bulk silicon, we first present a study of average bond energy of siligen atoms to silicon clusters using the siligen parameter (ζ_s) value of 0.726 94 which is obtained by satisfying the charge neutrality of the central silicon atom in $\mathrm{Si_5\bar{H}_{12}}$. Later, we compute the average bond energy of silicon (binding energy of silicon per bond) against the number ratio of silicon to siligen in order to examine its convergence to the bulk value of 2.31 eV as this number ratio increases with cluster size.

We now calculate an average bond energy between siligen and silicon, $\overline{E}_{\overline{\mathrm{H}}\text{-Si}}$, for $\mathrm{Si}_n\overline{\mathrm{H}}_m$ clusters made of n silicon atoms and m siligen ($\overline{\mathrm{H}}$) atoms, by using

$$\overline{E}_{\overline{\mathrm{H}}\text{-Si}} = \frac{E_{\mathrm{Si}_n\overline{\mathrm{H}}_m} - (E_{\mathrm{Si}_n} + mE_{\overline{\mathrm{H}}})}{m} , \tag{1}$$

where $E_{\mathrm{Si}_n\overline{\mathrm{H}}_m}$, E_{Si_n}, and $E_{\overline{\mathrm{H}}}$ are the energy of formations of $\mathrm{Si}_n\overline{\mathrm{H}}_m$, Si_n, and $\overline{\mathrm{H}}$, respectively. We chose two different clusters. They are $\mathrm{Si}_5\overline{\mathrm{H}}_{12}$ and $\mathrm{Si}_{10}\overline{\mathrm{H}}_{16}$, which are the "open" and "closed" structures, respectively, as shown in Figs. 1(d) and 1(g). We have often experienced a difficulty in achieving convergence of self-consistent-field calculations for the larger unsaturated clusters. With the use of siligen, this difficulty has been relieved, at least for the systems that we have tested. Encouragingly, we obtained average bond energies $\overline{E}_{\overline{\mathrm{H}}\text{-Si}}$ of 2.17 eV for $\mathrm{Si}_5\overline{\mathrm{H}}_{12}$ and 2.28 eV for the larger cluster $\mathrm{Si}_{10}\overline{\mathrm{H}}_{16}$, in relatively close agreement with the experimental value of cohesive energy per bond, 2.31 eV, or cohesive energy per atom, 4.63 eV. This result is quite encouraging compared to our quantal calculation[26] without siligens which yielded 4.38 eV for a silicon cluster of size 62.

We now examine the average bond energy of various $\mathrm{Si}_n\overline{\mathrm{H}}_m$ clusters in the size range of $n=1-26$ for silicon, and from $m=4-30$ for siligen as shown in Figs. 1(a)–1(j). Thus, each cluster has a different number ratio of silicon to siligen. Larger ratios stand for larger clusters, and thus may simulate bulk properties better. If the average binding energy plotted against this ratio approaches a constant value at larger sizes, then the binding energy of silicon-siligen should be close to that of silicon-silicon in order to validate our present approach. To examine this we do the following. We calculate the average bond energy, that is, the average binding energy per bond as obtained by dividing the difference between the total energy of the cluster and the combined total energy of n isolated silicons and m isolated siligens by the number of bonds,

$$\overline{E}_{\mathrm{bond}} = \frac{E_{\mathrm{Si}_n\overline{\mathrm{H}}_m} - (nE_{\mathrm{Si}} + mE_{\overline{H}})}{N} , \tag{2}$$

where the number of bonds N for the geometries treated here is given by

$$N = \frac{4n+m}{2} . \tag{3}$$

The average bond energy $\overline{E}_{\mathrm{bond}}$ vs the number ratio ($\rho = n/m$) is represented by triangles as shown in Fig. 2. The average bond energies are predicted to be between 2.045 and 2.568 eV for the clusters shown in Fig. 1. See Table I for a quantitative analysis. The curve shows a tendency to converge to a constant value with increasing number ratio ρ. Encouragingly, we now find that the larger the cluster size, the closer the average bond energy of siligen is to the average bond energy of silicon. Average bond energy for the largest cluster is predicted to be 2.568 eV, compared to the measured value of 2.31 eV. For the sake of numerical comparison, we repeat this plot with different values of ζ_s for siligen. The parameter values chosen are 1.188 078 (ζ_s for hydrogen), 0.4, and 0.1, denoted by squares, + signs, and × signs, respectively. Hence the value $\zeta_s = 0.726\,94$ is chosen for use in the silicon cluster calculations since its use yields a bond energy in satisfactory agreement with the experimental value, as shown in Fig. 2.

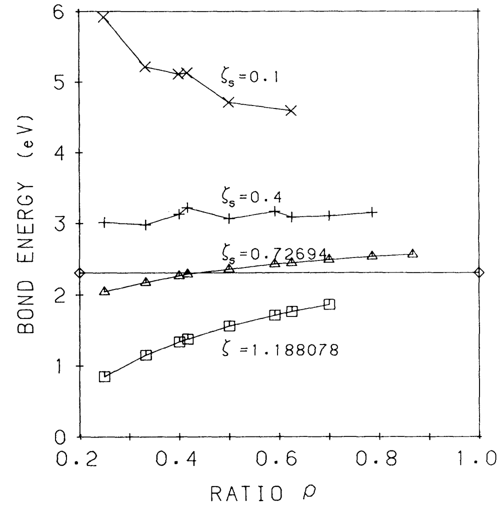


FIG. 2. Average bond energy (binding energy per bond) for various values of ζ_s as a function of the number ratio of silicons to siligens (ρ). The horizontal line indicated by diamonds shows bulk value for bond energy of 2.31 eV (Ref. 13).

III. INTERACTION OF FLUORINE WITH A SIMULATED BULK Si(111) SURFACE WITH SILIGENS

Now we extend the study to a surface problem. By using siligens we construct a simulated bulk Si(111) surface in order to study the interaction of fluorine with the surface. This is achieved by taking a cutout portion of the Si(111) surface, thus properly called a silicon surface cluster, and attaching siligens to the periphery of the cluster, except for the (111) face, in order to saturate the dangling bonds, thus simulating the bulk silicon surface.

Using the Si(111) surface clusters shown in Figs. 3(a)–3(c), we computed the bond strength of fluorine. The cluster geometry configurations represent two, four and six-layer silicon (111) surfaces with seven fluorine adatoms, and with siligens to saturate the peripheral dangling bonds. A top view of these clusters is given in Fig. 3(d) (all three clusters have the same top view). Figure 4 shows the average binding energy of an F adatom on silicon(111) surfaces as described in Figs. 3(a)–3(c). Here the average binding energy is defined to be

$$\Delta E = \frac{E_{\mathrm{system}} - E_{\mathrm{surface}} - nE_F}{n} , \tag{4}$$

where E_{system} is the heat of formation of the whole cluster (surface + adatoms), E_{surface} is that of the cluster without adatoms and E_F is that of the fluorine atom, and $n=7$. The binding energy is plotted against the number of silicon sublayers. The octagons represent the results for the surface with siligens, and the triangles represent the re-

TABLE I. Average bond energy (binding energy per bond) for various values of siligens Slater exponent (ζ_s) and various silicon-siligen clusters described in Fig. 1. The ratio (ρ) is the number ratio of silicons to siligens.

Cluster	Ratio (ρ)	Bond energy (eV)			
		$\zeta_s=0.1$	0.4	0.72694	1.188078
$Si\bar{H}_4$	0.250	5.918	3.015	2.045	0.848
$Si_2\bar{H}_6$	0.333	5.215	2.980	2.175	1.153
$Si_4\bar{H}_{10}$	0.400	5.113	3.131	2.269	1.340
$Si_5\bar{H}_{12}$	0.417	5.129	3.223	2.293	1.379
$Si_6\bar{H}_{12}$	0.500	4.711	3.066	2.360	1.562
$Si_{13}\bar{H}_{22}$	0.591		3.168	2.433	1.713
$Si_{10}\bar{H}_{16}$	0.625	4.590	3.088	2.450	1.766
$Si_{14}\bar{H}_{20}$	0.700		3.105	2.493	1.862
$Si_{22}\bar{H}_{28}$	0.786		3.152	2.537	
$Si_{26}\bar{H}_{30}$	0.867			2.568	

sults for the surface without siligen (i.e., the clusters in Fig. 3 minus the small circles). It is seen that poor convergence is achieved as a function of sublayer number. On the other hand, for the Si(111) surface with siligens, convergence of bond strength as a function of sublayer number is successfully achieved, as the variation of the binding energy ΔE with the number of sublayers is small. This implies that our bulk simulation of the silicon surface with siligens is satisfactory.

Now the average binding energy of F atoms to the surfaces is examined as a function of surface coverage (number of fluorine atoms on the surface). In Fig. 5(a), we show the cluster geometry configuration for a "wider" surface (involving ten silicons on the top layer) with only two sublayers of silicon. Figure 5(b) shows the top view for the geometry given in Fig. 5(a). Figure 6 shows the average binding energy of F on the surfaces against the number of fluorine adatoms (surface coverage). The fluorine atoms are numbered 1, 4, 7, and 10 in Figs. 3 and 5. Only fluorine numbered 1 is used to calculate the binding energy for the smallest coverage. Fluorine atoms numbered 1 and 4 are used for the next, and so on. Thus, to calculate the largest coverages, we used all fluorine atoms numbered 1, 4, 7, and 10. Binding energies were calculated for surfaces consisting of two layers, four layers, and a wider two-layer surface, as shown in Figs. 3(a), 3(b), and 5(a), respectively. Note that the average binding energies for six layers with fractional coverages (one and four fluorine adatoms) are not available due to SCF failure. As in Fig. 4, octagons are used to depict the clusters with siligen, and triangles are for clusters without siligen. Again we find that the clusters with siligens seem to give better convergence (octagons) compared to the clusters without siligens (triangles). The experimental value for the Si-F binding energy is 6.95 eV for the SiF_4 molecule.[15] Thus, the cluster with siligen certainly give closer binding energy to the experimental result compared to that for the cluster without siligen.

The use of siligen substantially increases the realism of the computed charge distributions. As indicated in Figs.

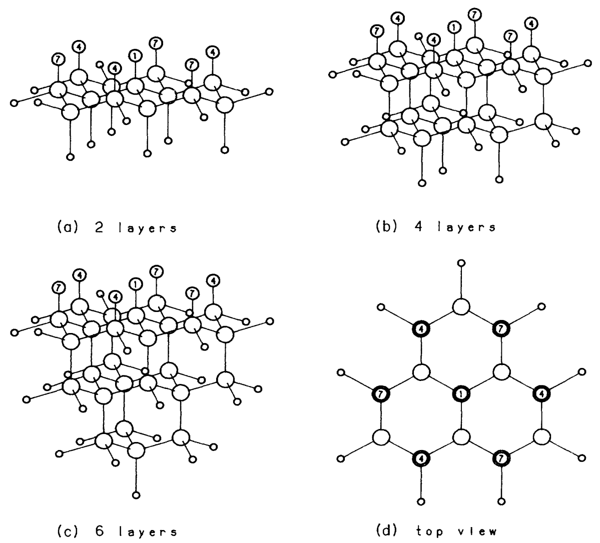


FIG. 3. Fluorine atoms on simulated Si(111) surfaces, which include (a) two surface layers, (b) four surface layers, and (c) six surface layers. (d) is the top view of these surfaces. The largest circles are the silicon atoms, the smallest circles are siligens, and the medium-sized circles are the fluorine atoms.

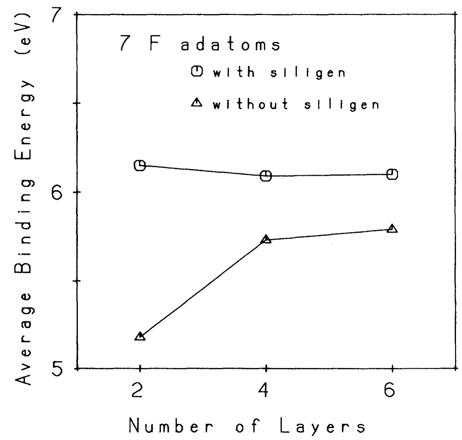
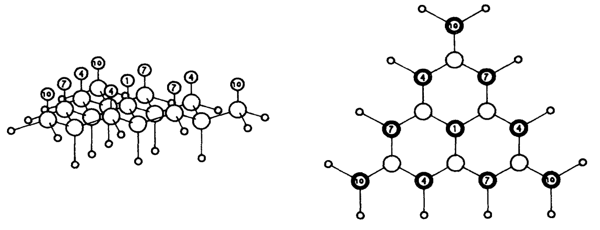


FIG. 4. Average binding energies of fluorine atoms on the simulated Si(111) surfaces as a function of number of surface layers. The surface is fully covered by the fluorine atoms (seven atoms).



(a) wider 2 layers (b) top view

FIG. 5. (a) A wider simulated Si(111) surface, which involves ten silicon atoms on the top surface; (b) top view of the surface.

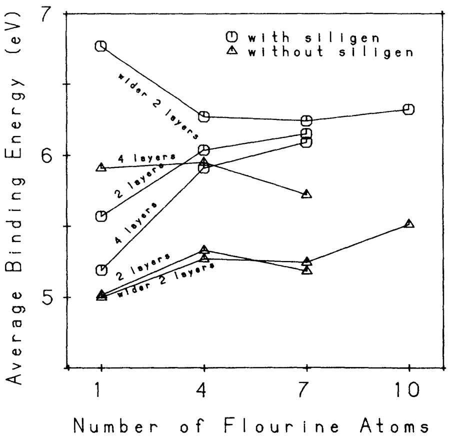


FIG. 6. Average binding energies of fluorine atoms on the surfaces as a function of surface coverage.

3 and 5, the surfaces exhibit $C3$ symmetry. The placement of the fluorine adatoms are selected to maintain that symmetry. Thus, the charge distributions are expected to follow that symmetry. However, we found that the charge distribution did not exhibit this symmetry for almost all clusters without siligen. The charge distribution was distributed symmetrically for all clusters with siligen, with the exception of the clusters which involved only a single fluorine adatom (lowest coverage). This is the reason for the lack of continuity in the binding energy curves shown in Fig. 6 for the single fluorine adatom cases (leftmost points). As expected, when only a single F is used, only one surface Si is saturated; the other six (nine for the wider surface) surface silicon atoms have unsaturated (dangling) bonds. Thus, the sp^3 orbital for each unsaturated silicon is not achieved, yielding unsymmetric charge distributions which break the charge symmetry for the whole cluster. In the most severe case, for the six-layer surface with a single fluorine, this symmetry breakdown was sufficient to inhibit convergence of the SCF computation. When four (especially seven) F adatoms are used, mot silicons are saturated. Thus, we find that a symmetric charge distribution can be achieved for the clusters with siligens.

IV. CONCLUSION

Computational efficiency for simulating bulk crystals is a subject of great interest. In the present paper the incorporation of a siligen model into the computationally efficient method of MNDO leads to a reasonably successful self-consistent treatment for the simulation of bulk silicon crystals, yielding a satisfactory bond energy or cohesive energy (twice the bond energy) for large clusters as compared to the bulk value. A comparison was made between the performance of hydrogen and siligen for terminating the silicon lattice, with siligen being found superior. The use of siligen is, therefore, recommended for the study of silicon surface interactions, since it enables the use of a finite-size silicon cluster to simulate a real surface. It is highly encouraging to find that the present siligen model study of small silicon clusters showed a tendency of rapid convergence close to the bulk limit value of cohesive energy per atom, 4.63 eV, compared to our earlier quantal calculation which yielded 4.38 eV even for the silicon cluster of size 62 without the use of siligens.

In the present paper, we examined the interaction of fluorine with a simulated bulk Si(111) surface. The simulated bulk silicon surface was constructed from a silicon cluster taken out of a "molecular" portion of bulk Si(111) surface to which pseudoatoms called siligens were attached. Compared to the pure Si(111) surface cluster without siligens that we examined, the Si(111) surface cluster with siligens yielded better agreement with the experimental value, and excellent convergence in bond strength as a function of silicon sublayer number, as well as a function of surface coverage. Furthermore, the use of siligen yields a charge distribution which reflects the symmetry of the cluster surfaces themselves.

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