Effect of hydrogen on ground-state structures of small silicon clusters

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We present results for ground-state structures of small Si_nH ($2 \leq n \leq 10$) clusters using the Car-Parrinello molecular dynamics. In particular, we focus on how the addition of a hydrogen atom affects the ground-state geometry, total energy, and the first excited electronic level gap of a Si_n cluster. We discuss the nature of bonding of hydrogen in these clusters. We find that hydrogen bonds with two silicon atoms only in Si_2H, Si_3H and Si_5H clusters, while in other clusters (i.e., Si_4H, Si_6H, Si_7H, Si_8H, Si_9H, and $Si_{10}H$) hydrogen is bonded to only one silicon atom. Also in the case of a compact and closed silicon cluster hydrogen bonds to the cluster from outside. We find that the first excited electronic level gap of Si_n and Si_nH fluctuates as a function of size and this may provide a first-principles basis for the short-range potential fluctuations in hydrogenated amorphous silicon. Our results show that the addition of a single hydrogen atom can cause large changes in the electronic structure of a silicon cluster, though the geometry is not much affected. Our calculation of the lowest-energy fragmentation products of Si_nH clusters shows that hydrogen is easily removed from Si_nH clusters.

I. INTRODUCTION

During the last decade clusters have attracted a lot of attention because of their interesting and novel properties.[1] Of particular interest are the binary clusters of hydrogen and silicon which are thought to be present in hydrogenated amorphous silicon (a-Si:H), porous silicon, and silicon surfaces. In addition to the fundamental interest, their study may throw some light on complex phenomena occurring in these systems. Hydrogen plays an important role in these systems in phenomena like photoluminescence of porous silicon, potential fluctuations, and the Staebler-Wronski effect in hydrogenated amorphous silicon (a-Si:H).[2–16] To understand these phenomena it is important to study how the addition of hydrogen affects the local electronic structure and geometry in these systems.[2,3] Since these systems are very difficult to handle computationally, some understanding in this regard can be gained by simpler calculations on small hydrogenated silicon clusters. With this motivation, we have carried out a detailed study of ground-state structures and electronic properties of small Si_nH clusters ($2 \leq n \leq 10$) using the Car-Parrinello molecular dynamics (CPMD), focusing particularly on the effects caused by hydrogen. In our study we have investigated the (1) ground-state geometries of Si_nH clusters, (2) effect of hydrogen on the geometry of a silicon cluster, (3) stability of a silicon cluster due to the addition of hydrogen, (4) first excited electronic level gaps of Si_nH and Si_n clusters, (5) bonding nature and position of hydrogen in silicon clusters, and (6) lowest-energy fragmentation products of Si_nH and Si_n clusters.

Several calculations have been done for many silicon hydrogen clusters by using various techniques. Using the Car-Parrinello method, Onida and Andreoni[17] studied the ground-state geometry and electronic structure of hydrogen passivated crystalline fragments of silicon such as Si_5H_{12}, Si_6H_{16}, Si_8H_8, $Si_{10}H_{16}$, and $Si_{14}H_{24}$. They found that Si-Si bond lengths were insensitive to size effects, but electronic properties were strongly affected. They also found that highest-occupied and lowest-unoccupied molecular orbital

(HOMO-LUMO) gaps were not simply related to the size of the clusters and the localization of electronic states near the gaps was not necessarily silicon like, even though the clusters are crystal fragments of silicon passivated by hydrogen. Quantum chemical calculations of Si_nH_m clusters were carried out by Meleshko et al.[18] for $n = 6–16$ and m ranging from 2 to 20. They found that each H atom was bonded with only one silicon atom and localized outside the silicon skeleton and that the packing density in the skeleton decreased as the hydrogen content of the cluster increased. Miyazaki et al.[19] performed density functional calculations for small hydrogenated silicon clusters of Si_6H_x ($0 \leq x \leq 14$) and showed that for the sequence $Si_6H_{x-2} + H_2 \rightarrow Si_6H_x$, the attachment of H occurred not at the site of silicon having dangling bonds but at the site where the LUMO of Si_6H_x has a large amplitude for $x = 2$ and 6. According to this calculation, the bonding interaction of $1s$ orbitals of hydrogen atoms with the LUMO of Si_6H_{x-2} should be the major cause of stabilization of the clusters. Their explanation makes it clear that hydrogen does not simply attach with silicon to saturate the dangling bonds, but it interacts at electronic level.

Swihart and Girshick[20] used *ab initio* molecular orbital calculations to investigate structure and energetics of selected hydrogenated silicon clusters containing six to ten silicon atoms. The clusters investigated were those that played the most important role in particle nucleation[21] in silane during chemical vapor deposition. Shvartsburg et al.[22] modeled the dissociation of neutral and positively charged Si_n clusters in the $n \leq 26$ range. They used dissociation energies to test the results of global optimization and fragmentation products of the clusters. Recently, nonorthogonal tight-binding molecular dynamics (NTBMD) with simulated annealing optimization method was used to calculate ground-state geometries of small Si_nH clusters[23] ($2 \leq n \leq 10$) and Si_2H_m ($n = 1, 2$ and $m = 2–6$) clusters.[24,25] Using the nonorthogonal tight-binding method, genetic algorithm optimizations were carried out for Si_nH_m clusters ($n = 1, 2$ and $m = 2–6$).[26,27] Experimental studies have been carried out for hydrogenated

silicon clusters using a quadrupole ion trap[28] where $Si_nH_x{}^+$ ($n=2-10$ and $x=0-20$) were grown from silane gas. From the mass spectra of these clusters, it was shown how the stability of a silicon cluster is affected by hydrogenation.

Our CPMD calculations show that hydrogen does not cause any drastic change in the geometry of the host silicon cluster although there is some distortion to the structure. To see clearly how the addition of a hydrogen atom affects the structure, stability, and electronic properties of the host silicon cluster, we have also done a number of calculations for host silicon clusters. We have discussed two kinds of stabilities: one is geometrical stability and the other is electronic. To examine the geometrical stability of a Si_n cluster,[29–32] we have calculated the difference between the total energy of modified Si_n geometry which is obtained by the removal of hydrogen from a Si_nH cluster and ground-state energy of a Si_n cluster. This energy difference gives information about the modification of the host silicon geometry due to the addition of hydrogen. To examine the electronic stability of Si_nH clusters we have calculated the first excited electronic level gap for Si_nH clusters. Comparison of the first excited electronic level gaps of Si_n clusters and Si_nH clusters shows that hydrogen, in general, brings electronic stability to silicon clusters. We have also calculated the lowest-energy fragmentation products of Si_n and Si_nH clusters.

The plan of the paper is as follows. In Sec. II we give computational details of the present work. In Sec. III the ground-state geometries are presented and discussed in detail. In Sec. IV we discuss the stability, cohesive energies, total energy differences between clusters, the first excited electronic level gaps, and the lowest-energy fragmentation products of Si_nH and Si_n clusters. Finally we summarize our results in Sec. V.

II. COMPUTATIONAL DETAILS

We have used the Car-Parrinello molecular dynamics[33,34] with simulated annealing optimization technique to find the ground-state structures of Si_n and Si_nH clusters. The CPMD method combines the density functional formalism with the molecular dynamics simulation. This scheme allows us to describe the dynamics of ions under the action of forces calculated by the Hellman-Feynman theorem. The pseudopotentials for silicon and hydrogen have been generated using the Bachelet-Hamann-Schlüter technique.[35] The local density approximation (LDA) of density functional theory has been used with the Ceperley-Alder[36] exchange-correlation energy functional parametrized by Perdew and Zunger.[37]

The wave functions were expanded in a plane-wave basis with 12 Ry energy cutoff and the **k**$=0$ point was used for Brillouin zone sampling. During the simulation, the volume of the system was kept constant and to avoid interaction between the clusters a big fcc supercell with side length of 35 a.u. was used. To perform simulated annealing, the system was taken to high temperatures (1200 K in steps of 300 K), equilibriated for a long time (about 16 000 steps), and then slowly cooled down (in the steps of 50 K) to 300 K. Below this temperature the steepest descent optimization was found to be more efficient to obtain the ground-state geometry. To

check the upper limit of temperature, some of the clusters were heated up to 1500 and 2000 K and it was found that the resulting ground-state structures were the same. The desired temperature was achieved by rescaling atomic velocities and the atoms were moved according to the velocity Verlet algorithm[38] with a time step of 5 a.u. The fictitious mass of the electron was taken to be 200 a.u. All calculations were performed with more than one initial condition. The initial structures for MD calculations were chosen without any pre-assumption about the ground-state geometry of the cluster. The starting atomic configurations were chosen arbitrarily with a constraint that atoms were neither very far away from each other nor too close.[30,39] As mentioned above these clusters were then heated to high temperatures and then equilibriated for a very long time. At this stage we find that the geometry of the hot cluster does not have any resemblance to the initial structure. At least two such CPMD calculations were performed for each cluster. For some clusters we have done a CPMD calculation with three (Si_9H) and four (Si_6H) starting atomic configurations and found that the final structures are the same. Furthermore, we performed the CPMD with steepest descent optimizations on the NTBMD structures and found that the resulting geometries either converge to our structures or get stuck in some local minima. The ground-state structures of Si_n ($2 \leq n \leq 10$) clusters obtained by us using the CPMD are similar to that obtained by previous calculations.[29,30] Also our result for the bond length of the SiH cluster (1.583 Å) is close to the earlier CPMD result[4] and other calculations.[40] This shows that our calculational procedure is able to give correct structures.

The first excited electronic level gap ($\epsilon_{i+1} - \epsilon_i$) of a cluster is calculated by transferring a small charge from its ground-state configuration to its first excited state and is given by[41]

$$\epsilon_{i+1} - \epsilon_i = \delta E / \delta q,$$

where δE is the difference between the total energy when δq amount of charge is transferred to the first excited state and total energy of the ground state.

III. GROUND-STATE STRUCTURES

In this section we discuss in detail the ground-state geometries of Si_nH clusters obtained by the CPMD (Ref. 33) with simulated annealing and steepest descent optimizations. By comparing our ground-state geometry of the Si_nH cluster with the Si_n cluster, we have investigated the effect of hydrogen on the geometry of the host silicon cluster. Furthermore, we have compared our ground-state geometries of Si_nH clusters with earlier calculated geometries of Si_nF (Ref. 42) and Si_nNa (Ref. 43) clusters. We have also made a detailed comparison of our work with earlier NTBMD (Ref. 23) work. It agrees with our geometries of Si_2H, Si_3H, Si_4H, and $Si_{10}H$ but the remaining geometries are different from our geometries, particularly the position and bonding of hydrogen. In the NTBMD (Ref. 23) results, hydrogen was found to be bonded with more than one silicon in most of the clusters but in the present case we find this only for Si_2H, Si_3H, and Si_5H clusters. We find that our structures have

lower energies than those of the NTBMD structures. The nature of bonding has been investigated by performing charge density calculations. In the following we discuss our results for each cluster.

A. Si_2H

The ground-state geometry of the Si_2H cluster is shown in Fig. 1(a). Two silicon atoms and hydrogen form a triangular structure. Note that the two silicon atoms are bonded to each other not only via Si-Si bond but also via Si-H-Si bridge type bond. The lowest-energy structure of Si_2F (Ref. 42) and Si_2Na (Ref. 43) are similar to the structure of Si_2H. In the Si_2H cluster, the Si-Si bond length is 2.131 Å and hydrogen is equidistant from both silicon atoms with bond length of 1.724 Å which is larger than its value of 1.583 Å in the Si-H dimer. The Si-Si bond length in the Si_2H cluster is smaller than the Si_2 dimer bond length of 2.184 Å. This implies that hydrogen pulls both silicon atoms closer and increases bonding between them. Thus, the additional bonding between silicon atoms is due to the Si-H-Si bridge bond which is attractive in nature. Such bridge type bonds are thought to be present in a:Si-H and play an important role in explaining the Staebler-Wronski effect.[2,3,12,44]

It is interesting to note that hydrogen is bonded with both silicon atoms although its valence is 1. This is seen clearly from the valence charge density plotted in Fig. 2, which shows the existence of bonds between hydrogen and the two silicon atoms. Such overcoordination of hydrogen has also been observed recently in the SiC system.[45] We also see from this figure that the electrons are more localized near the hydrogen atom. This is expected since hydrogen is more electronegative than silicon.[46] Thus there is a small charge transfer from silicon atoms to hydrogen.[47] As a result, the Si-H bond is neither purely covalent nor ionic but is polar covalent.[48]

B. Si_3H

The ground-state geometry of Si_3H is shown in Fig. 1(b). This is a planar structure with twofold symmetry and has some resemblance with the Si_4 cluster.[30] Hydrogen in this cluster is bonded with two silicon atoms (1 and 2) and is equidistant from both atoms with bond lengths of 1.715 Å. Silicon atom No. 3 is also equidistant from silicon atoms 1 and 2. The bond length between silicon atoms 1 and 2 is 2.377 Å which is more than the Si-Si bond length in Si_2H. This indicates that bonding between 1 and 2 silicon atoms is weaker than the Si-Si bond in Si_2H because of the presence of another silicon atom. Comparing this with Si_2H structure, we note that the additional silicon takes diagonal position opposite to hydrogen. We see that although hydrogen does not modify the Si_3 geometry much, it does modify the bond lengths. Particularly, the bond length between silicon atoms 1 and 2 in Si_3H is smaller than bond length of 2.613 Å in the Si_3 cluster. Thus, as in Si_2H, hydrogen pulls silicon atoms 1 and 2 closer, which can be attributed to the Si-H-Si bridge bond. We note that the lowest-energy structure of Si_3Na (Ref. 43) is similar to the present structure, but for the Si_3F cluster the ground-state geometry is different.[42]
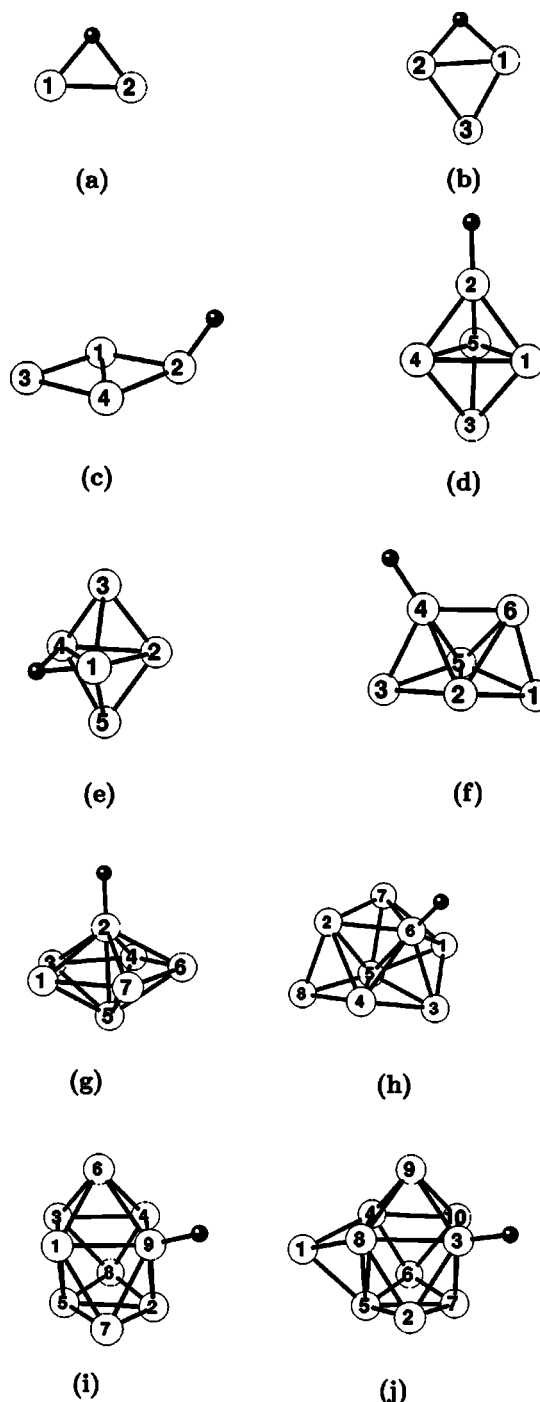

FIG. 1. Ground state geometry of (a) Si_2H, (b) Si_3H, (c) Si_4H. (d) Higher-energy geometry of Si_5H. Ground-state geometry of (e) Si_5H, (f) Si_6H, (g) Si_7H, (h) Si_8H, (i) Si_9H, and (j) $Si_{10}H$ clusters. Silicon atoms are numbered and the hydrogen atom is shown by a small dark circle. A thick line between two atoms indicates a bond between the atoms.

C. Si_4H

The ground-state geometry of the cluster is shown in Fig. 1(c). Four silicon atoms form a flat rhombus and the hydrogen atom is above the plane and bonded with one of the silicon atoms. The same structure was shown as the lowest-energy geometry of the Si_4F cluster.[42] The lowest-energy
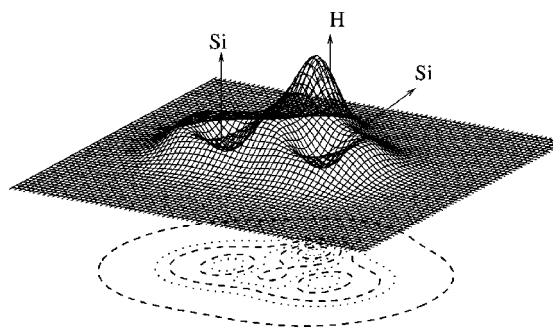
FIG. 2. Valence charge density of Si_2H cluster in arbitrary units plotted in the plane of the cluster. Constant charge density contours are also shown. Approximate positions of Si and H atoms are indicated by arrows.

structure of the Si_4Na (Ref. 43) cluster is similar to the present structure but differs in the coordination of the Na atom. Comparison of this structure with the Si_4 structure[30] shows that the addition of hydrogen does not bring much change to the Si_4 structure. Comparison with the Si_5 cluster[30] shows that this structure does not have any resemblance to the Si_5 cluster. Based on the idea of local softness and hardness, Galván *et al.*[49] predicted the sites preferred by hard and soft species in the Si_4 cluster. We find that hydrogen goes to the position according to their prediction.

D. Si_5H

The two lowest-energy structures of Si_5H are very close in energy and differ only by 0.06 eV. The geometry which is higher in energy is shown in Fig. 1(d). Three of the silicon atoms numbered 1, 4, and 5 form a triangular plane and silicon atom No. 2 is above and No. 3 is below the plane. Hydrogen takes the apex position in the structure and is bonded with only one silicon atom. The geometry of the silicon atoms is same as in Si_5 (Ref. 30) cluster. The lowest-energy structure of Si_5H cluster is shown in Fig. 1(e). The geometry of this cluster is similar to the Si_6 cluster[30] except that one of the silicon atoms is replaced by hydrogen. Note that hydrogen in this cluster is attached to two silicon atoms, which is also the case in Si_2H and Si_3H clusters. Geometrically hydrogen plays the role of silicon in these three clusters; i.e., the geometry of Si_2H is similar to Si_3, Si_3H is similar to Si_4, and Si_5H is similar to Si_6. We note that a two-coordinated silicon atom exists in Si_3, Si_4, and Si_6 clusters and hydrogen replaces this silicon atom to form Si_2H, Si_3H, and Si_5H, respectively. We speculate that this may be a general feature of Si_nH clusters; i.e., if a two-coordinated silicon atoms exists in a Si_{n+1} cluster, hydrogen will replace the two-coordinated silicon atom to form a Si_nH cluster, which will have the same geometry as the Si_{n+1} cluster. This seems to imply that hydrogen will form a Si-H-Si bridge type bond between two nearby silicon atoms which are doubly coordinated. In the context of a-Si:H this would imply that hydrogen will form a Si-H-Si bond between two nearby silicon atoms having two dangling bonds. Comparison with Si_5F geometry shows that one of the low-energy structures[42] is similar to Si_5H shown in Fig. 1(d). The low-energy geom-

etries for the Si_5Na (Ref. 43) cluster are similar to our low-energy geometries for Si_5H and the lowest-energy structure is also the same.

E. Si_6H

The ground-state geometry of Si_6H is shown in Fig. 1(f). In this structure, four silicon atoms numbered 1, 2, 3, and 5 form a distorted plane and the remaining two atoms numbered 4 and 6 are above the plane. The hydrogen atom is bonded to silicon No. 4 from outside the cluster. Comparing this with the ground-state geometry of the Si_6 (Ref. 30) cluster, we note that although the plane formed by four silicon atoms is same as in the Si_6 cluster, the other two silicon positions are different; i.e., in the Si_6 (Ref. 30) cluster one silicon atom is above and another is below the Si_4 plane, but in Si_6H two silicon atoms are above the plane. Comparing with the results of Si_6H_x clusters,[19] our geometry of Si_6H falls in the class of a tetrahedral bonding network. We find that this is the only cluster among the clusters considered here where the geometry of the silicon atoms differs from the ground-state geometry of the host silicon cluster.[30] This shows that hydrogen can cause a transition from one geometry to another geometry. One of the low-energy geometries of Si_6F (Ref. 42) cluster is same as the present structure. But in the case of Si_6Na (Ref. 43) one of the low-energy structures has similar geometry but it differs from our structure by coordination of the Na atom.

F. Si_7H

The ground-state geometry of the structure is shown in Fig. 1(g). Silicon atoms in this structure form a closed and compact unit and the cluster has pentagonal symmetry. Five silicon atoms numbered 1, 7, 6, 4, and 3 make a pentagonal plane and one silicon atom is above and another is below the plane. Silicon atoms which are not in the pentagonal plane are bonded to all the atoms in the pentagonal plane. Hydrogen takes the apex position in the structure and is bonded with one silicon which is out of the pentagonal plane. It is interesting to note that instead of bonding with four-coordinated silicon, hydrogen is bonded with five-coordinated silicon. In Si_7H, Si_8H, Si_9H, and $Si_{10}H$ we found the same trend of hydrogen preferring to bond with an overcoordinated silicon atom. This is surprising since one would have expected it to bond with less-coordinated silicon. This may be attributed to a slightly higher electronegativity of H compared to Si and, as a result, H prefers to bond with silicon atom having a greater number of electrons. This is consistent with the earlier calculation on structural evolution of Si_6H_x clusters,[19] where it was found that hydrogen is not necessarily bonded with a silicon site having dangling bonds, but with a site where the LUMO amplitude is larger. Comparison of Si_7H with the Si_7 (Refs. 29 and 30) cluster shows that hydrogen hardly changes the geometry of the Si_7 cluster, implying that the Si_7 cluster is a very stable cluster. The lowest-energy geometry of Si_7F (Ref. 42) and one of the low-energy structures of Si_7Na (Ref. 43) is similar to our ground-state geometry.

G. Si$_8$H

Figure 1(h) shows the ground-state geometry of Si$_8$H. This structure is also made of a compact, closed unit of silicon atoms with hydrogen sticking to the structure from outside. We see that Si$_8$H shows some similarity with the Si$_7$H cluster; i.e., the same pentagonal plane formed by silicon atoms numbered 4, 3, 1, 7, and 2 exists in Si$_7$H and one silicon is above and another is below the plane (6 and 5) as in Si$_7$H. Silicon atom 8 is attached to the triangular plane of the Si$_7$H structure in such a way that it is away from the hydrogen atom. As in Si$_7$H the hydrogen atom is attached to the silicon atom which is bonded with five silicon atoms. Figure 1(h) shows that Si$_8$H has two distorted Si$_4$ planes; silicon atoms numbered 8, 4, 3, and 5 form one distorted Si$_4$ plane and 2, 6, 1, and 7 form another. These planes are not parallel but rotated with respect to each other in such a way as to have more than one bond for each silicon atom with the atoms in the other plane. Comparing our ground-state geometry of Si$_8$H with Si$_8$ (Ref. 29) geometry, we see that silicon atoms have similar geometry except that the Si$_4$ planes are distorted in Si$_8$H.

H. Si$_9$H

The ground-state geometry of the cluster is shown in Fig. 1(i). This structure is also compact and closed by silicon atoms. The structure consists of two Si$_4$ planes formed by atoms 1, 3, 4, 9 and 5, 8, 2, 7 and silicon No. 6 forms a cap. Hydrogen is connected to silicon atom No. 9 which is coordinated with five silicon atoms. Comparison with the Si$_9$ (Ref. 29) cluster shows that the atoms forming Si$_4$ planes in Si$_9$H do not lie in a plane in Si$_9$.

I. Si$_{10}$H

The ground-state geometry of this cluster is shown in Fig. 1(j). The Si$_{10}$ structural unit in Si$_{10}$H is similar to the Si$_9$H cluster and the additional silicon (atom 1) makes a side cap to the Si$_9$H cluster [Fig. 1(i)]. Also there are two Si$_4$ planes rotated with respect to each other as in Si$_8$H and Si$_9$H. Silicon atoms 5, 2, 7, and 6 form one plane and 8, 3, 10, and 4 form another plane. In this cluster hydrogen is connected to the fivefold-coordinated silicon. Comparison with the Si$_{10}$ (Ref. 29) cluster shows that hydrogen hardly changes the geometry of the Si$_{10}$ cluster, implying that the Si$_{10}$ cluster is a very stable cluster. A general feature of clusters Si$_6$H, Si$_7$H, Si$_8$H, Si$_9$H, and Si$_{10}$H is that silicon atoms in the cluster form a closed compact unit with hydrogen outside this structural unit.

IV. STABILITY OF Si$_n$ AND Si$_n$H CLUSTERS

We find that the total energy of Si$_n$ as well as of Si$_n$H clusters increases approximately linearly with the cluster size n. The addition of hydrogen to an Si$_n$ cluster reduces the energy of the cluster by approximately 15 eV. The cohesive energy per particle versus number of silicon atoms is plotted in Fig. 3. As seen clearly from the figure the cohesive energy per particle increases rapidly up to the Si$_6$H cluster and then

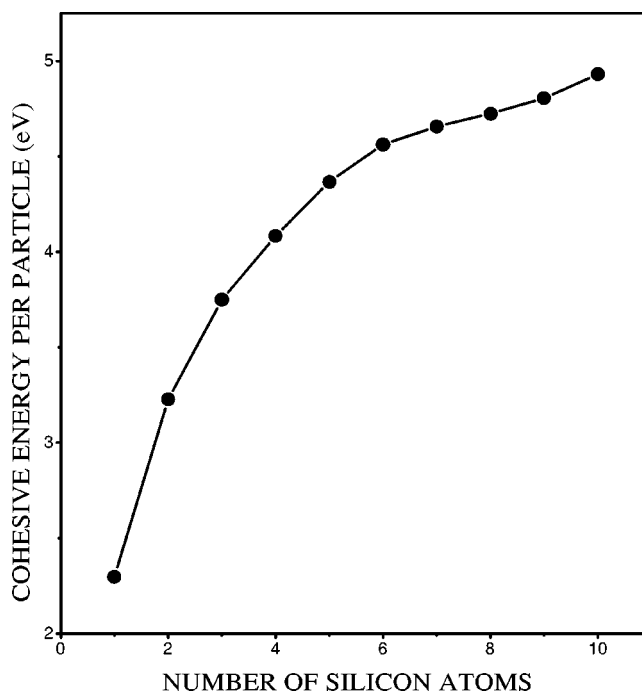FIG. 3. Cohesive energy per atom of Si$_n$H cluster vs number of silicon atoms.

increases slowly as a function of size. As noted earlier, from this size (Si$_6$H) onwards silicon atoms in the cluster form a closed compact unit and some of the silicon atoms have coordination number more than 4.

We take the first excited electronic level gap of a cluster as the difference between the first excited electronic level and the highest-occupied level. For closed-shell or subshell systems this gap will be the same as HOMO-LUMO gap which is related to the chemical hardness and electronic stability of a system.[50–52] Though the first excited electronic level gap is not equivalent to the HOMO-LUMO gap for Si$_n$H clusters, it can be related to electronic stability. A bigger value of the first excited electronic level gap for a system means that it is difficult to excite electrons from its ground state and thus the electronic system can sustain its ground state for larger perturbations. Thus the first excited electronic level gap can be taken as a measure of the electronic stability of a system. We have shown the first excited level gap as a function of cluster size in Fig. 4 for Si$_n$H and Si$_n$ clusters. Also shown in the figure are results of Lu *et al.*[30] for Si$_n$ clusters which are in good agreement with our results. We see that the general trend of variation of the first excited electronic level gap is quite similar for Si$_n$H and Si$_n$ clusters. The figure also shows that the addition of hydrogen can cause large changes in the electronic structure of the Si$_n$ cluster.

From Fig. 4 we see that the gap fluctuates with size, which indicates that the gap strongly depends on the size and geometry of a cluster. It might be interesting to draw parallels with short-range potential fluctuations in the a-Si:H system which occur at the length length scale of 3 Å .[16] It can be argued that an amorphous system can be considered as a loosely connected network of small clusters and thus our
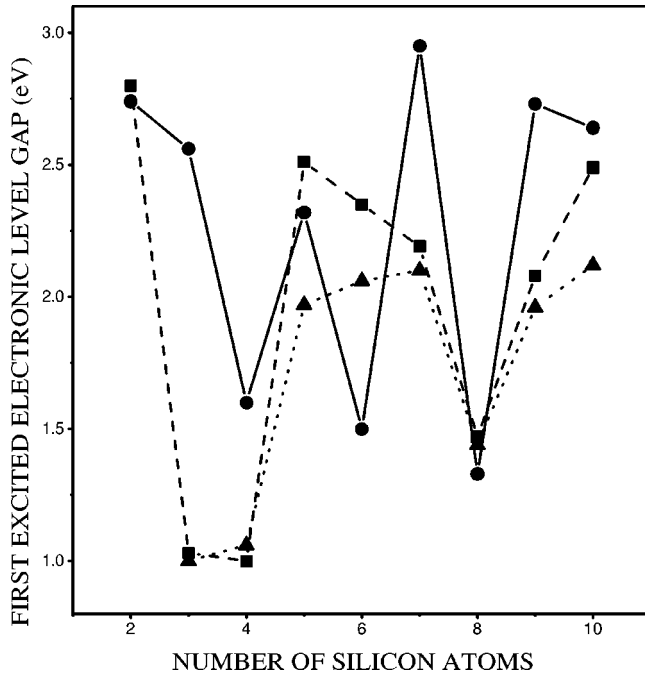
FIG. 4. First excited state electronic level gap of Si_nH and Si_n clusters vs number of silicon atoms in the cluster. The circles and squares correspond to Si_nH and Si_n clusters, respectively. The triangles represent the results of Lu *et al.* (Ref. 30) for the Si_n cluster.

FIG. 5. Difference dE, between the total energy of the modified geometry of Si_n and the ground-state energy of the Si_n cluster vs the number of silicon atoms in the clusters.

calculation provides a first-principle basis for the potential fluctuations.[13–16] Furthermore, we see that the first excited electronic level gap for Si_nH is, on an average, larger than that of Si_n cluster. This is consistent with the observation that the band gap of a:Si increases on hydrogenation.[53] Further, Fig. 4 shows that Si_2H, Si_3H, Si_5H, Si_7H, Si_9H, and $Si_{10}H$ clusters are electronically more stable compared to Si_4H, Si_6H, and Si_8H clusters. Also we see that Si_2, Si_5, Si_6, Si_7, and Si_{10} clusters are electronically more stable than other silicon clusters (Si_3, Si_4, Si_8, and Si_9 clusters), since they have larger gaps.

To examine the geometrical stability we have calculated the difference between the total energy of the modified Si_n cluster, which has the same positions of silicon atoms as in the Si_nH cluster, and the ground-state geometry of the Si_n cluster. This energy difference is a measure of how much a silicon cluster distorts from its ground-state geometry due to the addition of a hydrogen atom. The lower value of this difference for a Si_n cluster means that the cluster is geometrically stable. This total energy difference as a function of cluster size n is shown in Fig. 5. The figure shows that Si_2, Si_4, Si_7, and Si_{10} clusters are geometrically more stable than Si_3, Si_5, Si_6, Si_8, and Si_9 clusters. On the other hand Si_3, Si_5, Si_6, Si_8, and Si_9 clusters are stabilized by hydrogen and have a greater tendency to adsorb hydrogen. This is consistent with the conclusions drawn by comparing Si_nH and Si_n ground-state geometries in Sec. III, as Si_2, Si_4, Si_7, and Si_{10} clusters were least distorted by the addition of hydrogen. Thus the above discussion shows that Si_2, Si_7, and Si_{10} clusters are the most stable clusters from both viewpoints of electronic as well as geometrical stability.

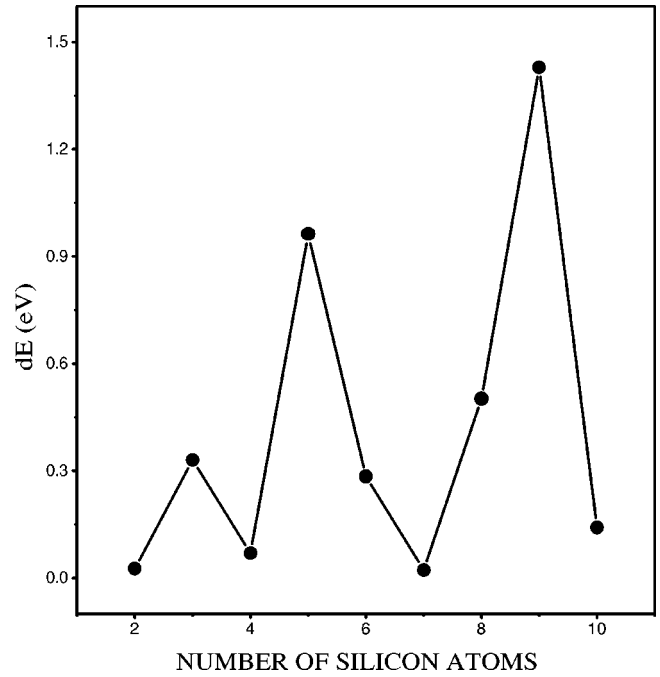As pointed out earlier in Sec. III, hydrogen is attached to silicon clusters from outside in several cases (Si_4H to $Si_{10}H$). To examine this further, we have performed the steepest descent optimization on Si_6H and Si_7H clusters with hydrogen surrounded by silicon atoms. We find that the hydrogen atom always comes out of the silicon cluster independent of the cluster size. This is mainly due to the higher electrostatic energy of the cluster when hydrogen is inside the cluster. Thus our result implies that hydrogen will tend to come out of crystalline silicon and would like to stay on the surface. This is consistent with the experimental observation in which hydrogen is used to produce a homogeneous silicon surface by terminating surface silicon dangling bonds to reduce the surface reconstruction.[12]

To investigate the fragmentation products of Si_n and Si_nH clusters, we have calculated the difference between the total energy of a cluster which undergoes fragmentation and that of its possible product clusters. The most probable pathway for the fragmentation of a particular cluster is the one which has the smallest total energy difference.[31] Since the clusters are small in size, we are assuming that the fragmentation results in only two product clusters. Our calculations are only for neutral fragmentation of Si_n and Si_nH clusters. Our lowest-energy fragmentation products of Si_n clusters agree very well with all primary fragmentation products calculated by Shvartsburg *et al.*[22] In Table I we have given the lowest-energy fragmentation products of Si_nH clusters with the corresponding dissociation energies. We see from the table that the lowest-energy fragmentation products have hydrogen atom as one of the products for all Si_nH clusters except for the Si_8H cluster. This shows that it is easy to remove hydrogen from Si_nH clusters.

TABLE I. Fragmentation pathways of a neutral Si_nH cluster into products Si_m and $Si_{n-m}H$ clusters.

Reactant clusters Si_nH	Product cluster Si_m	Product cluster $Si_{n-m}H$	Dissociation energy in eV
SiH	Si	H	4.60
Si_2H	Si_2	H	4.73
Si_3H	Si_3	H	3.97
Si_4H	Si_4	H	3.29
Si_5H	Si_5	H	3.38
Si_6H	Si_6	H	3.17
Si_7H	Si_7	H	2.57
Si_8H	Si_7	SiH	3.25
Si_9H	Si_9	H	3.04
$Si_{10}H$	Si_{10}	H	2.96

V. CONCLUSIONS

We have presented detailed results for the ground-state structures and electronic properties of Si_nH clusters using Car-Parrinello molecular dynamics simulations. We find that hydrogen can form a bridge like a Si-H-Si bond connecting two silicon atoms. Such bridgelike bonds are thought to be present in a-Si:H.[2,3,44] However, among the clusters considered here hydrogen forms a bridgelike bond only in Si_2H, Si_3H, and Si_5H clusters; in others, it is bonded with only one silicon atom and attached to the cluster from outside. Charge density calculations show that the Si-H bond in all clusters is polar covalent. In clusters from Si_7H to $Si_{10}H$, silicon atoms form a compact unit and hydrogen attaches to a silicon atom which is overcoordinated. Though hydrogen has a small effect on the geometry of the host silicon cluster, it changes bond lengths and tries to distort the silicon cluster. This is similar to the behavior of hydrogen in a-Si:H where it has been found that hydrogen creates local distortions as it moves.[2,3] We find that hydrogen has a tendency to come out of compact silicon clusters and prefers to stay out of the cluster. This is consistent with the behavior of hydrogen on silicon surfaces.[12]

The first excitation electronic level gap of the Si_nH clusters fluctuates as a function of size and this may provide a first-principles basis for the short-range potential fluctuations in a-Si:H.[13-16] Our calculations show that the addition of hydrogen can cause large changes in the electronic structure of the host Si_n cluster. Furthermore, it shows that Si_2H, Si_3H, Si_5H, Si_7H, Si_9H, and $Si_{10}H$ clusters are electronically more stable than Si_4H, Si_6H, and Si_8H clusters. We find that Si_2, Si_4, Si_7, and Si_{10} clusters are geometrically more stable than Si_3, Si_5, Si_6, Si_8, and Si_9 clusters, while Si_2, Si_5, Si_6, Si_7, and Si_{10} clusters are electronically more stable than Si_3, Si_4, Si_8 and Si_9 clusters. We have calculated the lowest-energy fragmentation products of Si_n and Si_nH clusters. Our results for the fragmentation products of Si_n clusters agree very well with the earlier predictions. The lowest-energy fragmentation products of Si_nH clusters show that it is easy to remove hydrogen from silicon clusters. Comparison of the Si_2H to the Si_7H cluster with the corresponding F- and Na-substituted clusters shows that almost all have similar low-energy geometries implying that the geometrical effects of H, F, and Na on Si_n clusters are similar.

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