Ground state structures and properties of Si_3H_n ($n = 1$–6) clusters

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Abstract. The ground state structures and properties of Si_3H_n ($1 \leq n \leq 6$) clusters have been calculated using Car–Parrinello molecular dynamics with simulated annealing and steepest descent optimization methods. We have studied cohesive energy per particle and first excited electronic level gap of the clusters as a function of hydrogenation. Hydrogenation is done till all dangling bonds of silicon are saturated. Our results show that over coordination of hydrogen is favoured in Si_3H_n clusters and the geometry of Si_3 cluster does not change due to hydrogenation. Cohesive energy per particle and first excited electronic level gap study of the clusters show that Si_3H_6 cluster is most stable and Si_3H_3 cluster is most unstable among the clusters considered here.

Keywords. Car–Parrinello molecular dynamics; hydrogenated silicon clusters; electronic structure calculation.

1. Introduction

Hydrogen plays an important role in hydrogenated amorphous silicon (a : Si–H), porous silicon and silicon surfaces (Prasad and Shenoy 1996; Gupte *et al* 1997; Fedders 2000; Gallego *et al* 2000) and may be the cause of phenomena like photoluminescence of porous silicon, potential fluctuations and Staebler–Wronski effect in hydrogenated amorphous silicon (a : Si–H) (Prasad and Shenoy 1996; Agarwal 1996a, b). To understand these phenomena it is important to study structural evolutions and properties of silicon due to hydrogenation in these disordered systems. 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_3H_n clusters ($0 \leq n \leq 6$) using the Car–Parrinello molecular dynamics (CPMD). Our results show that Si_3 cluster does not change its geometry due to hydrogenation. We find that hydrogen can form two kinds of bonds with silicon, one is Si–H single bond and the other is Si–H–Si bridge type bond (Balamurugan and Prasad 2001). We find that Si_3H_6 cluster is most stable and Si_3H_3 cluster is most unstable among the clusters considered here. The plan of the paper is as follows. In §2 we give computational details of the present work. In §3, the ground state geometries are presented and discussed. In §4, we discuss stability, cohesive energy per particle and first excited electronic level gaps of the clusters. Finally we summarize our results in §5.

2. Computational details

We have used the Car–Parrinello molecular dynamics (CPMD) (Car and Parrinello 1985; Remler and Madden 1990; Parrinello 1997) with simulated annealing optimization technique to find the ground state structures of Si_3H_n clusters. The CPMD method, which combines the density functional theory formalism with the molecular dynamics simulation, allows us to describe dynamics of ions under action of forces calculated by the Hellman–Feynman theorem. The pseudopotentials for silicon and hydrogen have been generated using the Bachelet *et al* (1982) technique. The local density approximation (LDA) of the density functional theory has been used with the Ceperley–Alder (1980) exchange–correlation energy functional parametrized by Perdew and Zunger (1981).

The wave functions were expanded in a plane wave basis with 12 Rydberg energy cut-off and $k = 0$ point was used for Brillouin zone sampling. During simulation 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) and then slowly cooled down (in 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. The desired temperature was achieved by rescaling atomic velocities and the atoms were moved according to the velocity Verlet algorithm 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 first excited electronic level gap of a cluster was calculated by transferring a small charge from its ground state configuration to its first excited state (von Barth 1984).

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3. Ground state geometry

The ground state geometry of Si_3H cluster is shown in figure 1(a). This is a planar structure with two fold symmetry and has some resemblance with Si_4 cluster. Hydrogen in this cluster is bonded with two silicon atoms (1 and 2) and is equidistant from both silicon atoms. It is interesting to note that hydrogen is bonded with both silicon atoms although its valence is one. We have investigated this Si–H–Si bridge type bond in our previous work through charge density analysis (Balamurugan and Prasad 2001) and shown the existence of bond between hydrogen and silicon atoms. The nature of Si–H bond is polar covalent with a small charge transfer from silicon atoms to hydrogen. Such over coordination of hydrogen has also been observed recently in SiC system (Gali *et al* 2000). Also Si–H–Si bridge type bonds are thought to be present in a : Si–H and play an important role in explaining Staebler–Wronski effect (Fritzche 1971; Stutzmann *et al* 1985; Prasad and Shenoy 1996). The ground state geometry of Si_3H_2 cluster is a planar structure and is shown in figure 1(b). Comparing this structure with Si_3H cluster we can see that the additional hydrogen atom is attached with silicon atom 1 which is already bonded with another hydrogen through Si–H–Si bridge bond. The ground state geometry of Si_3H_3 cluster is shown in figure 1(c). We can see from figure that unlike Si_3H and Si_3H_2

clusters, position of hydrogen atoms are out of Si_3 plane in Si_3H_3 cluster. One of the hydrogen atom is connected to silicon atoms 1 and 3 and this unit (Si–H–Si) forms a plane almost perpendicular to Si_3 plane. The other two hydrogen atoms are connected to silicon atom 2 and forms a plane which is perpendicular to Si_3 plane and the plane formed by hydrogen atom and other two silicon atoms (1 and 3). The ground state geometry of Si_3H_4 cluster is shown in figure 1(d). This structure is a geometrical superposition of Si_3H_2 and Si_3H_3 clusters. There are two Si–H–Si bonds and SiH single bond present in this cluster. Silicon atom 1 is bonded with three hydrogen atoms. Figure 1(e) shows the ground state geometry of Si_3H_5 cluster. Three hydrogen atoms are above and two hydrogen atoms are below the Si_3 plane. We can see that Si–H–Si bond is absent in this cluster and thus it is different from the above mentioned clusters. The ground state geometry of Si_3H_6 cluster is shown in figure 1(f). Note that all the dangling bonds of silicon atoms in this cluster are completely saturated by hydrogen atoms. This structure has reflection symmetry about Si_3 plane. Like Si_3H_5 cluster all hydrogen atoms are out of Si_3 plane and forms only Si–H single bond with silicon atoms. Three hydrogen atoms are above and the other three hydrogen atoms are below the Si_3 plane.

4. Stability

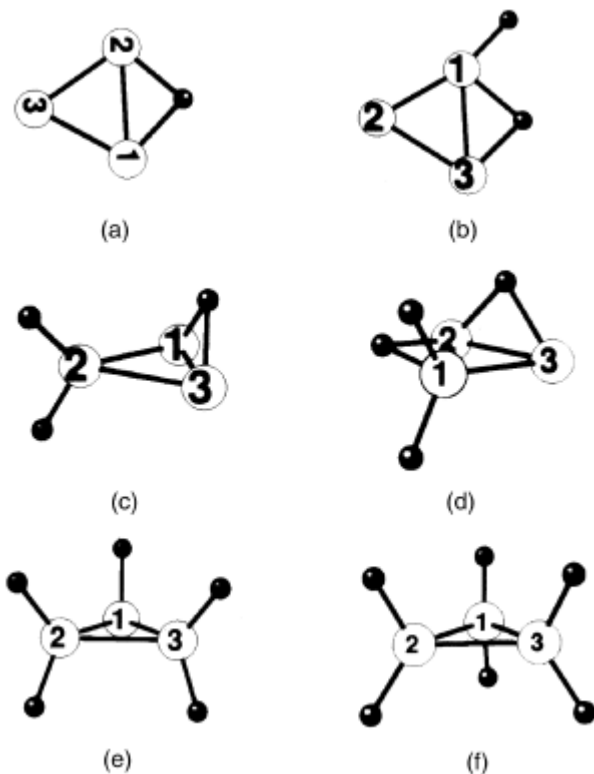The cohesive energy per particle for Si_3H_n clusters is shown in figure 2. From the figure we can see that the

Figure 1. Ground state geometry of (**a**) Si_3H, (b) Si_3H_2, (**c**) Si_3H_3, (**d**) Si_3H_4, (**e**) Si_3H_5 and (**f**) Si_3H_6 cluster.
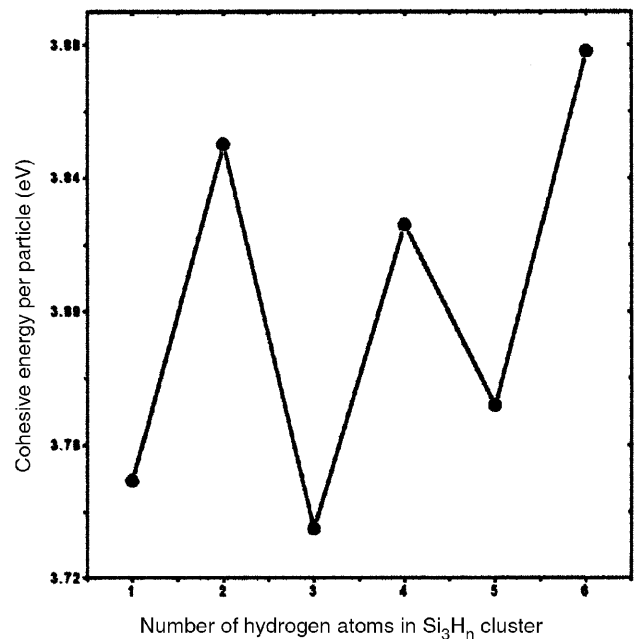

Figure 2. Cohesive energy per particle of Si_3H_n cluster vs number of hydrogen atoms.
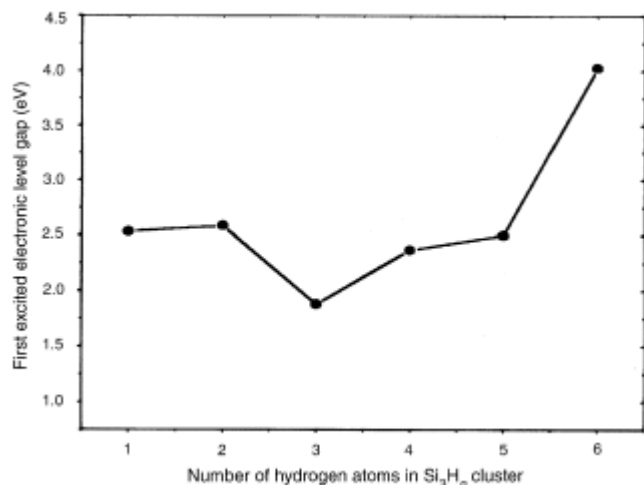
Figure 3. First excited state electronic level gap of Si_3H_n cluster vs number of hydrogen atoms in the cluster.

cohesive energy per particle fluctuates with number of hydrogen atoms in the cluster. Clusters with even number of hydrogen atoms have large value compared to clusters with odd number of hydrogen atoms. This shows that Si_3H_2, Si_3H_4 and Si_3H_6 are relatively stable than Si_3H, Si_3H_3 and Si_3H_5 clusters. Particularly Si_3H_6 cluster whose dangling bonds are completely saturated has largest cohesive energy per particle among the clusters considered here. The first excited electronic level gap of Si_3H_n clusters as a function of hydrogen atom is shown in figure 3. 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 (Balamurugan and Prasad 2001). We can see from the figure that Si_3H_3 cluster has lowest gap and Si_3H_6 cluster has highest gap among the clusters considered here. Hence Si_3H_3 cluster is electronically more unstable and Si_3H_6 cluster is electronically more stable and the electronic stability of other clusters fall in between these two clusters.

5. Conclusions

We have presented the ground state geometries and properties of small Si_3H_n $(1 \leq n \leq 6)$ clusters using Car–Parrinello molecular dynamics simulations. Our results show that the ground state geometry of Si_3 cluster does not change due to hydrogenation. We find that hydrogen forms Si–H–Si bridge type bond in Si_3H, Si_3H_2, Si_3H_3 and Si_3H_4 clusters and forms only SiH single bond in Si_3H_5 and Si_3H_6 clusters. Cohesive energy per particle of Si_3H_n clusters show that clusters with even number of hydrogen atoms i.e. Si_3H_2, Si_3H_4 and Si_3H_6 clusters are energetically more stable compared to clusters with odd number of hydrogen atoms i.e. Si_3H, Si_3H_3 and Si_3H_5 clusters. First excited electronic level gap of Si_3H_n clusters show that Si_3H_3 cluster is electronically more unstable and Si_3H_6 cluster is electronically more stable and the electronic stability of other clusters fall in between these two clusters. Si_3H_6 cluster is most stable and Si_3H_3 cluster is most unstable energetically and electronically among the clusters considered here. This is expected since all the dangling bonds of silicon atoms in Si_3H_6 cluster are completely saturated by hydrogen atoms.

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