

Ground state structures and properties of small hydrogenated silicon clusters

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Abstract. We present results for ground state structures and properties of small hydrogenated silicon clusters using the Car–Parrinello molecular dynamics with simulated annealing. We discuss the nature of bonding of hydrogen in these clusters. We find that hydrogen can form a bridge like Si–H–Si bond connecting two silicon atoms. We find that in the case of a compact and closed silicon cluster hydrogen bonds to the silicon cluster from outside. To understand the structural evolutions and properties of silicon cluster due to hydrogenation, we have studied the cohesive energy and first excited electronic level gap of clusters as a function of hydrogenation. We find that first excited electronic level gap of Si_n and Si_nH fluctuates as function of size and this may provide a first principle basis for the short-range potential fluctuations in hydrogenated amorphous silicon. The stability of hydrogenated silicon clusters is also discussed.

Keywords. Ground state; hydrogenated silicon; Car–Parrinello; simulated annealing.

1. Introduction

During the last decade there has been a very rapid development in the study of small clusters. This has been partly due to the growing importance of these systems in applications like catalysis and due to possibilities of developing nano-electronic devices. Also some clusters are found to be very stable and referred to as magic clusters. There have been attempts to design novel materials using these clusters as basic building blocks. These materials may have very different properties compared to the naturally occurring solids.

Small hydrogenated silicon clusters are of particular interest because of the importance of the materials like hydrogenated amorphous silicon ($a\text{-Si:H}$) and porous silicon. These materials are important, not only from technological point of view, they also exhibit interesting phenomena like Staebler–Wronski effect ($a\text{-Si:H}$) and photoluminescence (porous silicon) which are not well understood. These systems are difficult to model theoretically as these are highly disordered. However, if one is looking at some generic features such as changes in structure or electronic structure due to addition of hydrogen, some understanding can be gained by studying small clusters of silicon and hydrogen, which are much easier to model. This has been the prime motivation behind this study.

We have carried out our study using the Car–Parrinello molecular dynamics. This is an *ab initio* method which involves no adjustable or empirical parameter. In §2, we briefly discuss the Car–Parrinello method. In §3, we dis-

cuss the ground state structures of small hydrogenated clusters and in §4, we discuss how the stability of silicon cluster is affected by hydrogenation. Finally in §5 we give our main conclusions and their implications for $a\text{-Si:H}$.

2. Car–Parrinello method

Car and Parrinello (1985) proposed a Lagrangian in which the single particle electronic orbitals, $\mathbf{y}(\vec{r}, t)$, are also dynamical variables along with nuclear coordinates, $\vec{R}(t)$. The dynamics of nuclei is real while the dynamics of the orbitals is fictitious. This was a great idea which led to considerable saving in computational cost and made the first-principle molecular dynamics possible. They proposed the following Lagrangian

$$L = \frac{1}{2} \sum_{\ell} M \left| \dot{\vec{R}}_{\ell} \right|^2 + \sum_{i, \text{occ}} \int |\mathbf{y}_i(\vec{r}, t)|^2 d^3 r - E[\{\mathbf{y}_i\} \{\vec{R}_{\ell}\}] + \sum_{ij} \Lambda_{ij} \left(\int \mathbf{y}_i^*(\vec{r}, t) \mathbf{y}_j(\vec{r}, t) d^3 r - \mathbf{d}_{ij} \right) \quad (1)$$

where

$$E[\{\mathbf{y}_i\} \{\vec{R}_{\ell}\}] = E_E(\vec{R}) + V_{\text{II}}(\vec{R}) \\ = \sum_{i=1}^N \int \mathbf{y}_i^*(\vec{r}, t) \left(-\frac{\hbar^2}{2m} \nabla^2 \right) \mathbf{y}_i(\vec{r}, t) d^3 r \\ + \int v(\vec{r}) n(\vec{r}) d^3 r + \frac{1}{2} \iint \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r d^3 r'$$

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$$+ E_{xc}[n] + V_{II}(\vec{R}). \quad (2)$$

In (2) $V_{II}(R)$ is the potential energy corresponding to ion–ion repulsion, $E_{xc}[n]$ the exchange correlation energy and $n(\vec{r})$ the electron density given by

$$n(\vec{r}) = \sum_{i \text{ occ}} |\mathbf{y}_i(\vec{r}, t)|^2. \quad (3)$$

The first term in (1) is the total kinetic energy of the atoms and the last term arises because of the constraint that the orbitals be orthonormal. In this term Λ_{ij} are the Lagrange multipliers. Since the Lagrangian is real, the matrix Λ is Hermitian, i.e. $\Lambda_{ij} = \Lambda_{ji}^*$. The second term was introduced by Car and Parrinello as a computational device and as such has no physical meaning. It represents a fictitious kinetic energy associated with the orbitals which are frequently referred to as electronic degrees of freedom. m is fictitious mass such that in the limit $m \rightarrow 0$, we get the true Lagrangian of the system.

Using the Lagrangian (1), equations of motions for the dynamical variables $\{\vec{R}_\ell\}$ and $\{\mathbf{y}_i\}$ can be written as

$$M\ddot{\vec{R}}_\ell = -\frac{\partial E[\{\mathbf{y}_i\}, \{\vec{R}_\ell\}]}{\partial \vec{R}_\ell}, \quad (4)$$

and

$$m\ddot{\mathbf{y}}_i(\vec{r}, t) = -\frac{\mathbf{d}E[\{\mathbf{y}_i\}, \{\vec{R}_\ell\}]}{\mathbf{d}\mathbf{y}_i^*(\vec{r}, t)} + \sum_j \Lambda_{ij} \mathbf{y}_j(\vec{r}, t) \quad (5)$$

$$= -H_{KS} \mathbf{y}_i(\vec{r}, t) + \sum_j \Lambda_{ij} \mathbf{y}_j(\vec{r}, t), \quad (6)$$

where H_{KS} is the Kohn–Sham Hamiltonian given by

$$H_{KS} = -\frac{\hbar^2}{2m} \nabla^2 + v(\vec{r}) + v_{xc}(\vec{r}) + \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r'. \quad (7)$$

Equations (4) and (6) are the desired equations of motion for $\{\vec{R}_\ell\}$ and $\{\mathbf{y}_i(\vec{r}, t)\}$. If one starts from an initial condition, when all the electrons are in the ground state (i.e. the system is on B–O surface), from (4) and (5) one can find $\{\vec{R}_\ell(t)\}$ and $\{\mathbf{y}_i(\vec{r}, t)\}$ by using say Verlet algorithm. Note that at subsequent time steps one need not solve the electronic structure problem but one simply updates the orbitals using (5). Thus the Car–Parrinello strategy results in tremendous saving in computational cost.

3. Ground state structures

The ground state structures were obtained by using the Car–Parrinello method and simulated annealing optimization. Wherever necessary we have also used steepest descent method. The details of the calculation are given elsewhere (Balamurugan and Prasad 2001).

The ground state geometries of Si_nH clusters from $n=2$ to $n=6$ are shown in figure 1. It is interesting to note that hydrogen is bonded with two silicon atoms in Si_2H , Si_3H and Si_5H although its valence is one. Such Si–H–Si bridge type bonds are thought to be present in amorphous hydrogenated silicon and play an important role in explaining Staebler–Wronski effect. Two lowest energy structures of Si_5H are very close in energy and differ only by 0.037 eV. We have shown both of these in figure 1. We find that although the addition of H does not affect the geometry of a silicon cluster much, it changes bond lengths and tries to distort the cluster.

In figure 2, we show the ground state structures of Si_nH clusters from $n=7$ to $n=10$. In these structures, hydrogen is bonded to only one silicon atom in contrast to Si_2H , Si_3H and Si_5H clusters where it was bonded to two silicon atoms. From charge density calculations, we find that Si–H and Si–H–Si bonds are polar covalent. We note that all these structures are closed and compact structures with hydrogen attached to a silicon atom from outside. From our results we find that hydrogen prefers to attach to an over-coordinated silicon atom. This is because hydrogen is slightly more electronegative than silicon and thus prefers a site where it finds more elec-

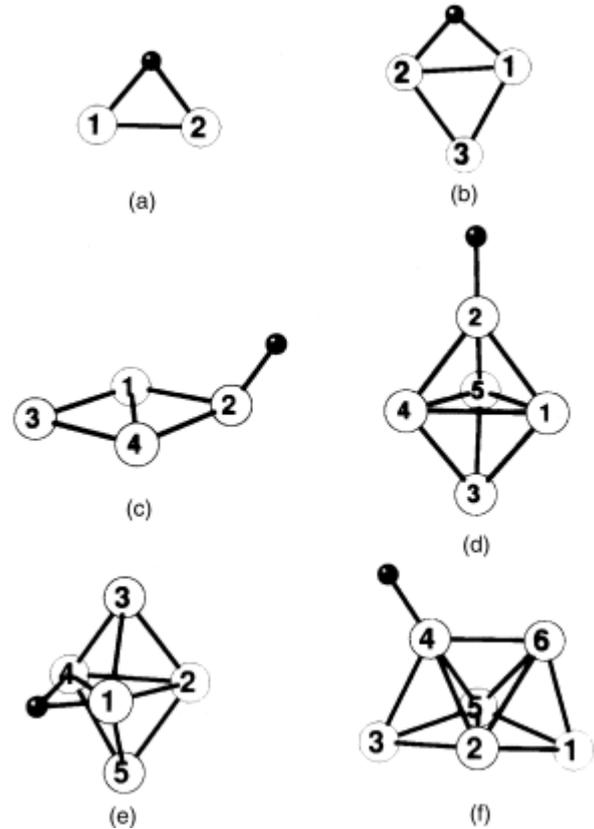


Figure 1. Ground state geometry of (a) Si_2H , (b) Si_3H , (c) Si_4H , (d) higher energy geometry of Si_5H , (e) ground state geometry of Si_5H cluster and (f) ground state geometry of Si_6H cluster. Silicon atoms are numbered and hydrogen atom is shown by a small dark circle.

trons. Also, we find that hydrogen prefers to stay outside the compact structure. To examine this further, we performed simulations with hydrogen surrounded by silicon atoms. We found that hydrogen always comes out of the silicon cluster. This is because when hydrogen is inside a compact structure, the electrostatic energy is more compared to when it is outside.

The effect of adding more than one hydrogen on the geometry of Si_2 cluster is shown in figure 3. The ground

state geometry of Si_2H_2 cluster is a non-planar rhombus, in which we see two Si–H–Si type bonds. This type of bond is also seen in Si_2H_3 whose ground state geometry is shown in figure 3(c). There is no Si–H–Si type bond in Si_2H_4 , Si_2H_5 and Si_2H_6 clusters. The variation of Si–Si bond length in Si_2H_n cluster as a function of n is shown in figure 4. We see that hydrogenation can change the Si–Si bond length approximately by 10%.

4. Stability

The first excited electronic level gap can be taken as a measure of the electronic stability of a system (Balamurugan and Prasad 2001). We have shown the first excited level gap as a function of cluster size in figure 5 for Si_nH and Si_n clusters. Also shown in the figure are results of Lu *et al* (2000) 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_nH clusters. The figure also shows that the addition of hydrogen can cause large changes in the electronic structure of Si_n cluster.

From figure 5 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 $a\text{-Si}:\text{H}$ system which occur at the length scale of 3 Å (Fritzsche 1971; Sinha and Agarwal 2000). It can be

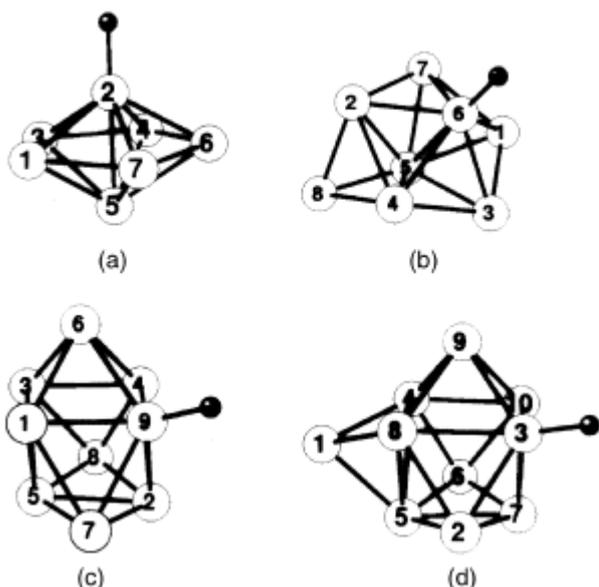


Figure 2. Ground state geometry of (a) Si_7H , (b) Si_8H_m , (c) Si_9H cluster and (d) Si_{10}H cluster.

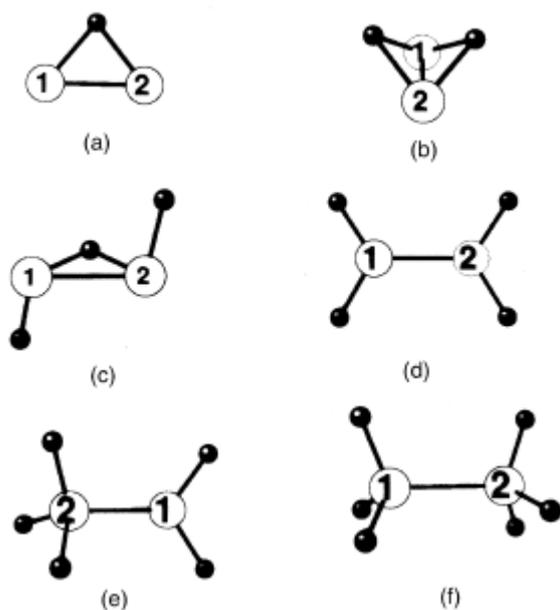


Figure 3. Ground state geometry of (a) Si_2H , (b) Si_2H_2 , (c) Si_2H_3 , (d) Si_2H_4 , (e) Si_2H_5 and (f) Si_2H_6 cluster. Silicon atoms are numbered.

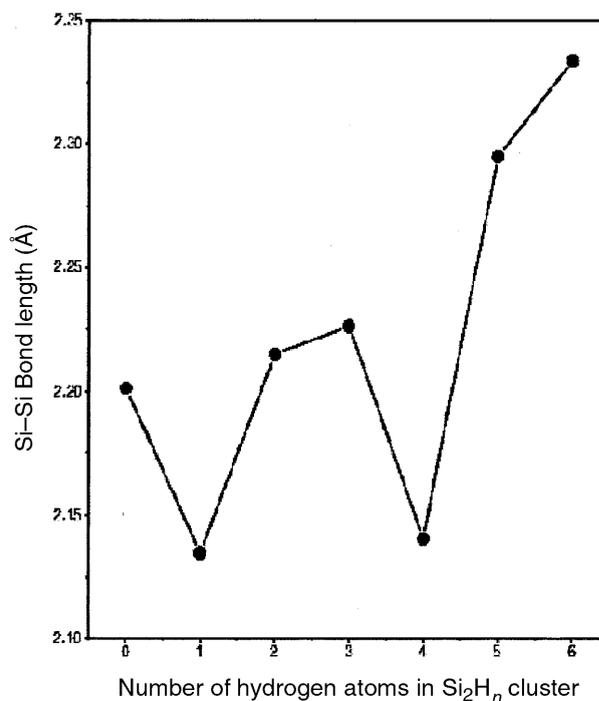


Figure 4. The Si–Si bond of Si_2H_n cluster vs number of hydrogen atoms in the cluster.

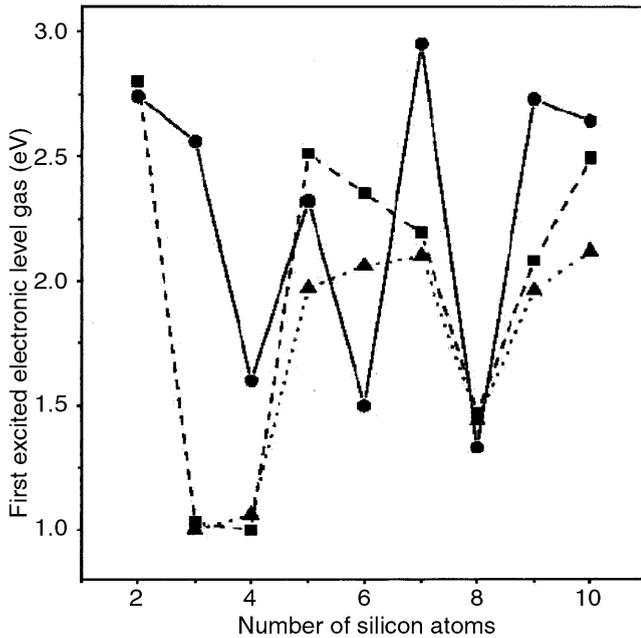


Figure 5. First excited state electronic level gap of Si_nH and Si_n clusters vs number of silicon atoms in the cluster. The circles and squares correspond to Si_nH and Si_n clusters, respectively. The triangles represent the results of Lu *et al* (2000) for Si_n cluster.

argued that an amorphous system can be considered as a loosely connected network of small clusters and thus our calculation provides a first-principle basis for the potential fluctuations (Fritzche 1971; Agarwal 1996a, b; Sinha and Agarwal 2000). Furthermore, we see that the first excited electronic level gap for Si_nH is, on average, more than that of Si_n cluster. This is consistent with the observation that the band gap of $a\text{:Si}$ increases on hydrogenation. Further, figure 5 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 geometrical stability we have also 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 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 hydrogen atom. 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 figure 6. 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 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

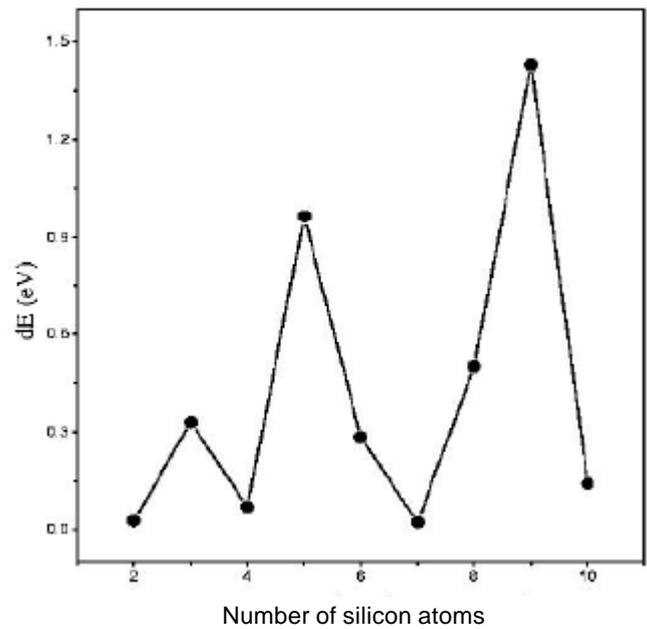


Figure 6. Difference, dE , between total energy of the modified geometry of Si_nH , and the ground state energy of Si_n cluster vs number of silicon atoms in the clusters.

drawn by comparing Si_nH and Si_n ground state geometries in §3, 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.

5. Conclusions

Results for the ground state structure and electronic properties of Si_nH clusters have been presented using the Car-Parrinello molecular dynamics simulations. We find that hydrogen can form a bridge like Si-H-Si bond connecting two silicon atoms. Such bridge like bonds are thought to be present in $a\text{-Si:H}$ (Stutzmann *et al* 1985; Prasad and Shenoy 1996). 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 over-coordinated. Though hydrogen has 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 behaviour of hydrogen in $a\text{-Si:H}$ where it has been found that hydrogen creates local distortions as it moves (Prasad and Shenoy 1996). We find that hydrogen has a tendency to come out of compact silicon clusters and prefers to stay out of the cluster.

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 $a\text{-Si:H}$ (Fritzche 1971; Agarwal 1996a, b;

Sinha and Agarwal 2000). Our calculations show that the addition of hydrogen can cause large changes in the electronic structure of 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.

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