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HYDROGENATED SILICON CLUSTERS

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Ground state structures and electronic properties of small hydrogenated silicon clusters are reviewed. It is found that although addition of a single hydrogen atom does not change the geometry of a silicon cluster, further hydrogenation can distort it completely. In some hydrogenated silicon clusters it is found that single hydrogen atom is bonded to two silicon atoms. Charging a cluster results in a large change in its geometry as in SiH_4 cluster. The implications of these results for Staebler-Wronski effect and potential fluctuations in hydrogenated amorphous silicon are discussed.

Key Words: Silicon clusters; Hydrogenated; Ground state; Electronic properties; Car-Parrinello; Potential fluctuations; Charge-induced

1 Introduction

During the last few years small hydrogenated silicon clusters have been attracting considerable interest[1-15]. Although understanding electronic and structural properties of these clusters is important in their own right, a lot of interest has arisen due to the fact that hydrogen plays an important role in porous silicon and hydrogenated amorphous silicon(*a*-Si:H). These materials are important, not only for technology but also from scientific point of view, as they exhibit interesting phenomena like Staebler-Wronski effect[16-17] and photo-luminescence[18] which are not well understood. These materials are difficult to model as these are highly disordered. However, if one is looking at some generic features, some understanding can be gained by studying small clusters of silicon and hydrogen, which are much easier to model. It is hoped that an understanding of these clusters will help explain various complex phenomena occurring in these systems.

Since structure of a cluster may not be directly amenable to experiments, theoretical models and computation play an important role in the study of clusters. Several methods ranging from semi-empirical tight-binding method to *ab initio* Car-Parrinello method have been used to obtain geometry and structure of hydrogenated silicon clusters[1-15]. Gupte and Prasad[4] used non-orthogonal tight-binding molecular dynamics with simulated annealing to calculate ground state structures of small Si_nH clusters (n=2-10) and Si_2H_m clusters (m=2-6). Genetic algorithm optimizations were also carried out for these clusters[5]. Some of the important findings of these calculations were that H can bond with more than one silicon and the existence of Si-H-Si bond. Subsequently, Balamurugan and Prasad[1] used the Car-Parrinello method[19] to calculate the ground state structures of these clusters and the conclusions of earlier calculations were verified. Also these calculations indicated towards the origin of potential fluctuations in hydrogenated amorphous silicon. Charge induced effects were studied in these clusters[2-3], which showed that a very dramatic change can occur in the geometry of a cluster by charging it. Also it was found that Si-H-Si bond can get weaker upon charging and this has some important implication for Staebler -Wronski effect.

Using the Car-Parrinello method[19] Onida and Andreoni[6] studied the ground state geometry and electronic structure of hydrogen passivated crystalline fragments of silicon such as Si_5H_{16}. They found that Si-Si bond lengths were insensitive to size effects but the electronic properties were strongly affected. Quantum chemical calculations of Si_nH_m clusters were carried out by Meleshko *et al.*[7] for n=6-16 and m running from 2 to 20. Miyazaki *et al.*[8] performed density functional calculations for small hydrogenated clusters of Si_6H_x (x=0-14). Swihart and Girshick[9] used *ab initio* molecular orbital calculations to investigate structure and energetics of selected hydrogenated silicon clusters containing 6 to 10 silicon atoms. Kumar and Kawazoe[10] studied hydrogenated silicon fullerenes using *ab initio* density functional calculations and

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discussed the effect of hydrogen on the stability of metal-encapsulated silicon clusters. More recently, Lehtonen and Sundholm[11] have calculated molecular structures of $Si_{29}H_{24}$, $Si_{29}H_{36}$ and $Si_{35}H_{36}$ in the ground state as well as in the lowest singlet and triplet excited states using the density functional theory and the first order linear response theory.

There has been considerable interest in the optical properties of hydrogenated silicon clusters both experimentally and theoretically. One of the motivations for such studies has been stimulated by the discovery of photoluminescence in porous silicon[18]. Vasiliev *et al.*[12] have calculated photoabsorption spectra of hydrogenated silicon clusters using a linear response theory within the time-dependent local density approximations. Rohling and Loui[13] calculated excitonic effects and photoabsorption spectra by solving the Bethe-Salpeter equation for the two-particle Green's function using an *ab intitio* approach.. More recently, Dagoli *et al.*[14] have calculated optical and electronic properties of hydrogenated silicon clusters as a function of dimension using *ab initio* technique.

The plan of the paper is as follows. In section 2, the ground state structures of hydrogenated silicon clusters are presented. In section 3, the charge induced effects on various hydrogenated clusters and bonds are described. In section 4, the implication of these results for Staebler-Wronski effect is discussed. In section 5, the first excited state level gaps for Si_nH clusters are presented and its implication for potential fluctuations in *a*-Si:H are discussed. Finally, we conclude with section 6.

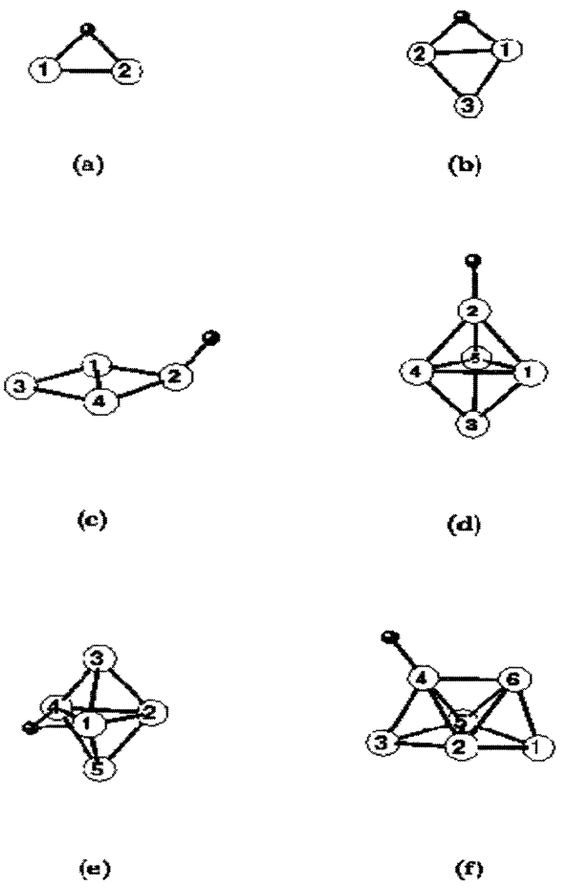

Fig. 1 Ground state geometry of (a) Si_2H, (b) Si_3H, (c) Si_4H, (d) Higher energy geometry of Si_5H, (e) Ground state geometry of Si_5H cluster, (f) Ground state geometry of Si_6H cluster. Silicon atoms are numbered and hydrogen atom is shown by a small dark circle

2 Ground State Structures

Using the Car-Parrinello method[19] and the simulated annealing, the structure and geometry of a large number of clusters have been studied. We first discuss the results for Si_nH clusters.

The ground state geometries of Si_nH clusters from n = 2 to n = 6 are shown in Fig. 1[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 hydrogenated amorphous silicon and play an important role in explaining Staebler-Wronski effect[16-17]. 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 Fig. 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. It is interesting to copmpare these geometries with those obtained by the tight-binding molecular dynamics (TBMD)[4]. It is seen that although the TBMD gives similar geometries for Si_2H, Si_3H, Si_4H and Si_5H , it gives different geometry for Si_6H. The TBMD results also show the presence of the bridge type bonds in some clusters and that H can bond with more than one silicon atom.

The ground state structures of Si_nH clusters from n = 7 to n = 10 are shown in Fig.2[1]. 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. However, in the TBMD results[4] it is found that H is bonded with more than one silicon atom in Si_7H, Si_8H and

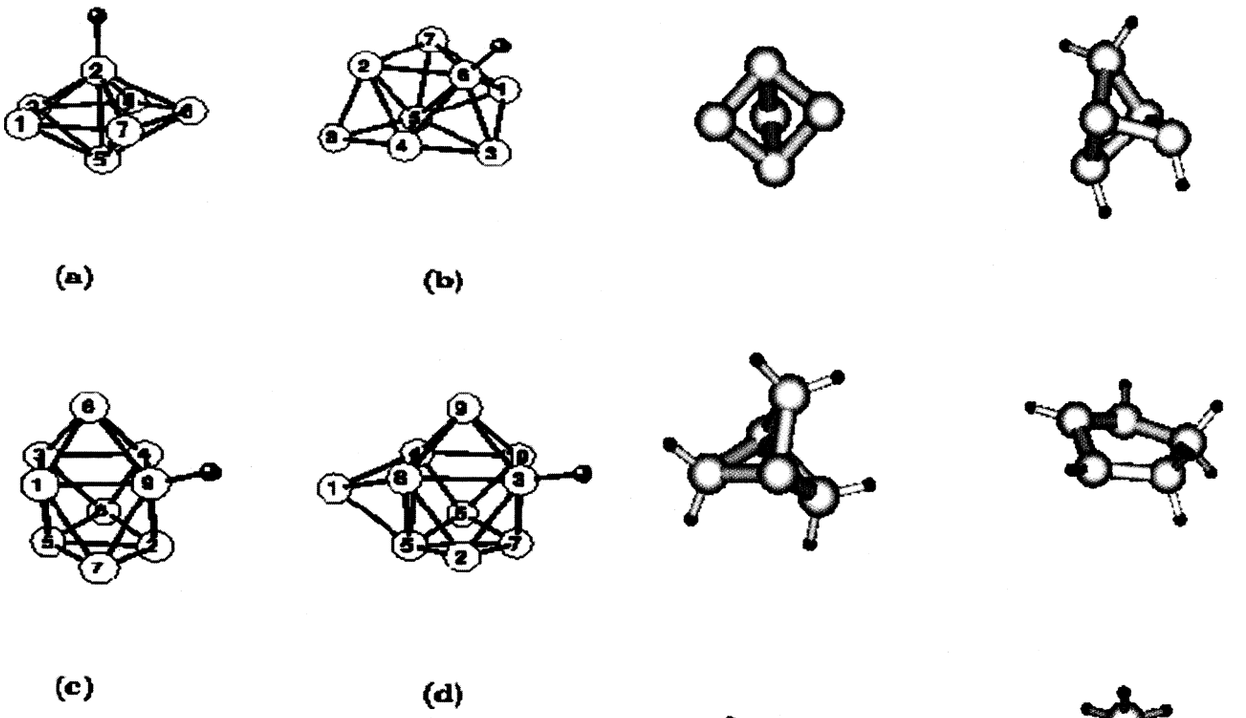

Fig. 2 Ground state geometry of (a) Si_7H, (b) Si_8H (c) Si_9H and (d) $Si_{10}H$ cluster.

Si_9H, but is bonded to only one sicon atom in $Si_{10}H$. From charge density calculations, it was found that Si-H and Si-H-Si bonds are polar covalent[1]. We note that all these structures are closed and compact structures with hydrogen attached to a silicon atom from outside. These results show 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 electrons. Also, it is found that hydrogen prefers to stay outside the compact structure. To examine this, further simulations were done with hydrogen surrounded by silicon atoms. It was 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.

Although the addition of a single hydrogen to a silicon cluster does not change its geometry very much, further hydrogenation can change it completely. This is shown in Fig. 3, where it is seen how the ground state structure of Si_5 cluster changes with the addition of hydrogen[15]. As the cluster grows it undergoes significant rearrangements and reconstructions. Si_5 cluster has a symmetric cage like closed structure which is trigonal bipyramid.

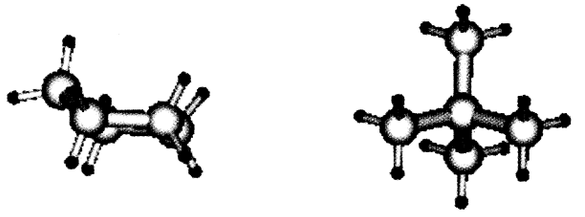

Fig. 3 Evolution of Si_5 cluster with hydrogenation. The bigger circles are Si and dark dots are H

When hydrogen is added, the structure of Si_5 does not change up to the addition of 3 hydrogen atoms. But with the addition of 4 hydrogen atoms, Si_5 cage begins to distort. With 6 hydrogen atoms, Si_5H_6 structure is fully saturated as each Si has 4 saturated bonds. We also note that Si_5H_6 has a highly symmetric structure. With 7 hydrogen atoms, the structure of Si_5 is completely changed and takes the shape of a pentagonal ring. With 10 hydrogen atoms this pentagonal structure gets fully saturated. With 12 hydrogen atoms the Si_5 structure goes into a more open structure and results in a symmetric tetrahedral structure. Thus we see that addition of hydrogen atoms can cause drastic changes in the geometry and structure of Si clusters. This change in structure can change the electronic structure which in turn can produce large changes in the chemical properties.

3 Charge Induced Effects

We have also investigated what happens to a cluster when it is charged[2-3]. The geometry and structure

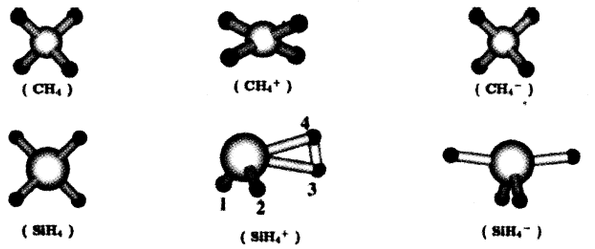

Fig. 4 Effect of charging on the geometry of SiH_4 and CH_4 clusters

of some clusters can change considerably by charging them. For example, neutral SiH_4 has a very symmetric tetrahedral structure as shown in Fig. 4. When it is charged, it shows a very large change in its geometry and has no longer the tetrahedral symmetry. This is often referred to as symmetry breaking. Interestingly, SiH_4 has different structures when charged positively and negatively. This symmetry breaking is due to the fact that in the distorted structure the system lowers its energy by lifting the degeneracy of electronic levels in the symmetric structure. This is called the Jahn-Teller effect. Surprisingly, CH_4^+ cluster distorts differently from SiH_4^+ but CH_4^- has the same geometry as CH_4^+. These surprising results can be understood very simply in terms of electronegativities of the constituent atoms and charge transfer between them[2].

Charging the clusters not only changes Si-H bond orientations but also Si-H, Si-H-Si and Si-Si bond lengths. It is found that Si-H bond length of a positively charged cluster is shorter than that of the corresponding neutral cluster while it is longer for the negatively charged cluster[3]. On the other hand, Si-H-Si and Si-Si bond lengths of both positive as well as negative charged cluster are longer than that of the neutral cluster. However, $Si_2H_3^+$ is an exception where Si-Si and Si-H-Si bond lengths are shorter than those of the neutral cluster. This has been attributed to the formation of π bonds.

It is found that charging the cluster shifts the stretching frequency of Si-H, Si-Si and H-Si-H bonds. These frequency shifts are consistent with their bond length variations. The Si-H stretch frequency of SiH dimer is 2013 cm^{-1} which increases to 2137 cm^{-1} for SiH^+ and decreases to 1827 cm^{-1} for SiH^-. Note that the bond length is shorter for SiH^+ while it is longer for SiH^- from that of the neutral SiH dimer. This shows that the trend of frequency variation induced by charging SiH dimer is just opposite to the trend of Si-H bond length variation. The trend is followed by Si-H stretch modes of all the clusters when charged. It is found that such a relationship between the bond length variation and frequency variation holds true for Si-Si and Si-H-Si bonds of the clusters[3]. In general, longer bond length reduces the frequency and vice versa. This relationship is reasonable since expansion of the bond means that the bond gets weaker and hence the corre sponding stretch mode has lower frequency. On the other hand shortening of the bond length means that the bond gets stronger and hence the stretch mode has larger frequency. The calculation of force constant for Si-H-Si bond shows that it gets reduced when the cluster is charged[3]. Thus Si-H-Si bond gets weaker when the cluster is charged.

4 Staebler-Wronski Effect

It is interesting to note a connection between these results and the Staebler-Wronski effect in *a*-Si:H. It was discovered by Staebler and Wronski[16] in 1977 that when light is shone on *a*-Si:H, the photo-conductivity and dark conductivity decay with time and that the original conductivities can be recovered by annealing near 170 ^{0}C. This effect is known as the Staebler-Wronski effect. It was found that the light exposure creates metastable dangling bond defects which degrade the optoelectronic properties of *a*-Si:H. Although this effect is not yet well understood, it is generally agreed that weakly bonded hydrogen atoms diffuse upon light illumination creating dangling bond defects. In some models[17] these H atoms are associated with Si-H-Si bonds which have been found in some clusters. As discussed in Section 3, upon ionization Si-H-Si bond expands and its force constant is reduced which means that Si-H-Si bond is weakened. This indicates that the light exposure can weaken Si-H-Si bonds as a result of photoexcitation.These weakened Si-H-Si bonds can easily be broken by phonons produced by non-radiative recombinations thus creating more dangling bond defects[17]. We note that our results pertain to clusters, they nonetheless indicate that as a result of photoexcitation Si-H-Si bonds can get weakened in *a*-Si:H

5 Potential Fluctuations

The first excited level gap as a function of cluster size is shown in Fig. 5 for Si_nH and Si_n clusters[1]. Also shown in the figure are results of Lu *et al.*[20]

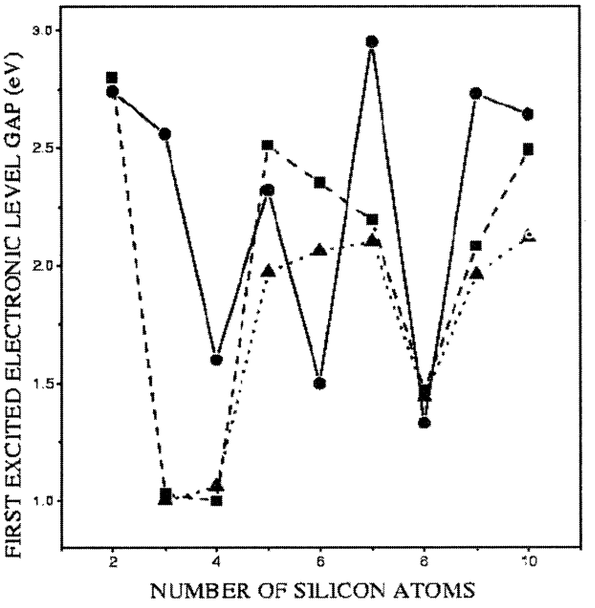

Fig. 5 First excited state electronic level gap of Si_nH and Si_n cluster versus number of silicon atoms in the cluster for the most stable geometry. The circles and squares correspond to Si_nH and Si_n clusters respectively. The triangles represent the results of ref. [20] for Si_n cluster

for Si_n clusters which are in good agreement with the results of Balamurugan and Prasad[1]. 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 Fig. 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*-Si:H system which occur at the length scale of 3Å[21-22]. It can be 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[21-23]. 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 amorphous silicon increases on hydrogenation. Further, Fig. 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.

6 Conclusions

The ground state structures and electronic properties of hydrogenated clusters using *ab initio* calculations have been reviewed. 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*-Si:H[17]. 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 single hydrogen has small effect on the geometry of the host silicon cluster, further hydrogenation can change the geometry of the silicon cluster in a significant way. We find that hydrogen has a tendency to come out of compact silicon clusters and prefers to stay out of the cluster. Charging a cluster induces structural changes in a cluster. Charging SiH_4 breaks the symmetry of the cluster and this has been attributed to the Jahn-Teller effect. The vibrational analysis shows that frequencies of Si-H, Si-Si, Si-H-Si stretch modes show significant changes when the clusters are charged. These frequency shifts are consistent with their bond length variations. The calculated force constants suggest that Si-H-Si bond weakens upon ionization. This is consistent with some experimental results regarding Staebler-Wronski effect in *a*-Si:H[22]. 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[21-24].

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References

1 D Balamurugan and R Prasad *Phys Rev* **B 64** (2001) 205406

2 D Balamurugan, M K Harbola and R Prasad *Phys Rev* **A 69** (2004) 033201

3 D Balamurugan and R Prasad *Phys Rev B* **73** (2006) 235415

4 G R Gupte and R Prasad *Int J Mod Phys* **B 12** (1998) 1607, *ibid* **B 12**, (1998) 1737

5 N Chakraborti, P S De and R Prasad *Z Metallkd* **90** (1999) 508

6 G Onida and W Andreoni *Chem Phys Lett* **243** (1995) 183

7 V Meleshko, Yu Morokov and V Schweigert *Chem Phys Lett* **300** (1999) 118

8 M Miyazaki, T Uda, I Stich and K Terakura *Chem Phys Lett* **261** (1996) 346

9 M T Swihart and S L Girshick *J Phys Lett* **307** (1999) 64

10 V Kumar and Y Kawazoe *Phys Rev Lett* **90** (2003) 055502

11 O Lehtonen and D Sundholm *Phys Rev* **B 72** (2005) 085424

12 I Vasiliev, S Ogut and J R Chelikowsky *Phys Rev Lett* 86 (2001) 1813

13 M Rohlfing and S G Louie *Phys Rev Lett* **80** (1998) 3320

14 E Degoli, G Cantele, E Luppi, R Magri, D Ninno, O Bisi and S Ossicini *Phys Rev* **B 69** (2004) 155411

15 D Balamurugan Ph D Thesis I I T Kanpur (2004)

16 D L Staebler and C R Wronski *Appl Phys Lett* **31** (1977) 292

17 R Prasad and S R Shenoy *Phys Lett* **A 218** (1996) 85

18 L T Canham *Appl Phys Lett* **57** (1990) 1046

19 R Car and M Parrinello *Phys Rev Lett* **55** (1985) 2471

20 Z Lu, C Wang and K Ho *Phys Rev* **B 61** (2000) 23

21 A K Sinha and S C Agarwal *J Vac Sci Technol* **B 18** (2000)1805

22 H Fritzche *J Non-Cryst Solids* **6** (1971) 49

23 S C Agarwal, *Indian Journal of Pure & Applied Physics* **34** (1996) 597

24 S C Agarwal *Bull Mater Sci* **19** (1996) 39