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Structure and Properties of Covalently Bonded Si Clusters

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Abstract

We review theoretical work on structural models for Si clusters of intermediate size. The models, which are inspired by surface reconstruction induced geometries, attempt to explain the peculiar behavior of certain "magic number" sizes that have very low reactivity relative to their immediate neighbors in size. We use first-principles quantum mechanical calculations to compare the energy of these models to other clusters obtained by addition or removal of atoms from the parent clusters. The electronic states associated with these models allow for a qualitative discussion of their chemical properties. Analysis of electronic states provides insight to the possibility of assembling solid structures from the least reactive clusters.

1 Introduction

The physics and chemistry of small Si clusters have attracted considerable attention during the last decade. This stems from the intrinsic interest in these new forms of silicon, as well as the promise of creating structures with novel properties, using clusters as building blocks [1]. Significant advances have been made during this decade-long experimental and theoretical study of Si clusters. Yet, our underestanding of their structure is incomplete and much remains to be resolved in what concerns their physical and chemical properties.

The main physics issue has been the critical size at which the cluster structure changes from being compact and having high-coordination, to being open and covalently bonded which resembles the diamond lattice structure of bulk Si. The first arguments attempting to address this question came from theoretical considerations. Phillips [2] analyzed experimental fragmentation patterns and ionization channels [3, 4] and concluded that Si clusters should be described as "molecular" (i.e. having a unique, characteristic structure) for sizes smaller than 10, and as covalently bonded crystalline fragments for larger sizes. Indeed, detailed quantum mechanical calculations on the structure of very small Si clusters revealed that for sizes up to 10, they do not look like fragments of the bulk but instead have a high coordination [5, 6, 7]. Estimates for the critical size at which high coordination would revert to covalent bonding, ranged from a low of 50 [8] to a high of 4200 [9]. When these theoretical predictions were made, direct experimental evidence for this transition was not available. In fact, it was not even known for certain whether such a critical size existed or the transition was a gradual one over a very wide range of sizes. The simulations of Chelikowsky et al. [10], using a classical interatomic force field to model the interactions between Si atoms, predicted the possibility of a transition in the *shape* of Si clusters at a size of approximately 25: clusters of smaller size tended to be prolate, whereas larger clusters tended to be oblate.

In 1991, a set of experiments by Jarrold and collaborators showed that a transition does exist in the shape of Si clusters as a function of their size [11]. This transition was found to be quite sharp, at sizes between 24 and 27: clusters smaller than 24 atoms were found to be prolate whereas clusters larger than 27 atoms were found to be oblate, consistent with the theoretical predictions of Chelikowsky et al. [10]. The nature of this transition was also investigated by Kaxiras and Jackson [12], and was attributed to the existence of interior atoms and to optimized surface reconstruction in the larger clusters. The shape–vs.–size transition can be interpreted as evidence that some important change in the nature of bonding takes place within a very narrow range of sizes.

On the chemistry side, the main issue is the dependence of chemical properties, as measured by the chemical reactivity, on the cluster size. Evidently, the chemical properties would depend quite sensitively on the nature of bonding in the cluster, therefore the central physics and chemistry issues are closely related. Early on in the study of Si clusters, Smalley and collaborators established that there exists a strong dependence of the reactivity of Si clusters on their size [13]. In particular, some clusters exhibited reactivity that was several orders of magnitude lower than that of their immediate neighbors in size. These clusters, and especially the sizes 33, 39 and 45, were named "magic numbers" for their unusual behavior. The rest of the clusters in the range 26 – 50 exhibited reactivity almost 2 orders of magnitude larger than the magic number clusters. For clusters larger than 50, the reactivity did not depend sensitively on size. The reactivity of Si clusters of sizes in the range 26 – 50 appears to depend little on the reactive agent (NH_3, C_2H_4, O_2 and H_2O have been used [14, 15, 16, 17, 18]). Moreover, when the clusters are annealed, the pattern of difference in reactivity between the magic number clusters and the rest is accentuated [18]. These experiments strongly suggest that the unusually low reactivity of magic number clusters is an intrinsic property, which must be attributed to their atomic and electronic structure.

The fact that magic number Si clusters exist, at least as far as their reactivity is concerned, is very encouraging. This type of behavior is the prerequisite to isolating a population of monodisperse clusters in order to condense them into a cluster-assembled solid. Exploiting the unique behavior of magic number clusters relies on our understanding of their structure, from which chemical and physical properties derive. Very little is known directly from experiment about the structure of these clusters, making predictions of their properties rather difficult.

The present work is an attempt to rationalize the behavior of Si magic number clusters by constructing plausible structural models and by calculating from first-principles their electronic properties. We concentrate here on intermediate sizes, i.e. the range 26 – 50, where the clusters appear to be spherical [11], as one might expect from simple surface minimization arguments. We adopt the view proposed by Phillips [2], that in this size range the clusters have structures that are related to the preferred bonding in Si, that is, they are predominantly covalently bonded. The intriguing behavior of smaller clusters that tend to be elongated [11], must be examined from a different perspective. For example, Phillips has suggested that in the Si_{13} cluster electron correlations are rather strong dominating the behavior of the cluster [19].

In the next section we explain the logic behind the structural models for these intermediate size clusters [20]. Such hypothetical models are indispensable because, in contrast to the small Si clusters (sizes ≤ 10) for which extensive quantum mechanical calculations have determined the optimal structure [5, 6, 7], geometry optimization for larger clusters becomes untractable [21]. Section 3 discusses our first-principles results on the relative energies of the proposed models. Section 4 describes the electronic properties of the models in terms of the total charge distribution and the nature of individual electronic wavefunctions associated with these models. Section 5 compares our models to other work on the subject. Finally, section 6 draws some conclusions and discusses conjectures on how these clusters could be used as building blocks of new materials.

2 Structural models

It is well known that on the surface of a solid chemical reactivity is enhanced near defects, such as steps, small islands, missing atoms, impurities, etc. An atomically flat surface without any defects, in its equilibrium structure, should have the lowest possible reactivity for a given orientation of the surface plane. Of course, changes in surface orientation can produce significantly different reactivity. The equilibrium structures of solid surfaces are usually well defined, corresponding to unique atomic arrangements that minimize the surface energy. This is particularly true for semiconductor surfaces, where the bulk terminated plane has a very high surface energy due to the broken covalent bonds (usually referred to as dangling bonds). As a consequence, the surface reconstruction often involves rather elaborate rearrangements of the atoms in complicated patterns.

A case in point is the (111) surface of Si, which exhibits two stable structures: a metastable one obtained upon cleaving the surface at low temperature, and a stable one obtained after annealing. The metastable structure has a (2×1) periodicity relative to the bulk terminated plane. Its stability arises from the fact that the dangling bonds on the reconstructed geometry are at nearest-neighbor sites, as opposed to the unreconstructed surface where dangling bonds are at second neighbor sites [22]. The positioning of dangling bonds at first neighbor sites allows for strong π bonding, which lowers the surface energy relative to the unreconstructed geometry. The π bonding occurs along the short lattice constant of the surface unit cell, producing chains of π bonded atoms. This reconstruction is referred to as the π-bonded chain. In a simplified picture, the effect of the π bonding is to create one filled and one empty electronic state by pairing the two half-filled dangling bonds at nearest neighbor sites. This also reduces the surface reactivity, since there are no partially occupied states left on the surface.

The stable reconstruction on the Si(111) surface obtained upon annealing has a (7×7) periodicity and involves a rather complex geometry [23]. A new type of site is present, the so called adatom position, which is bonded to three surface atoms, thereby eliminating their dangling bonds. The adatom itself forms only three bonds to the surface atoms, thus it has a dangling bond. There exist also surface atoms which are not covered by adatoms and have an unsaturated dangling bond; these are called rest atoms. The relaxation of the adatoms and the rest atoms, and their relative positions are such that electronic charge is transferred from the rest atom dangling bonds to the adatom dangling bonds [24]. This partial charge transfer further reduces the surface energy and reactivity, by effectively pairing the dangling bond electrons, thereby rendering them less susceptible to chemical interactions. The (7×7) reconstruction involves certain other features, such as dimer bonds and a stacking fault in one half of the unit cell, which reduce the strain energy that the unusual adatom geometry introduces [25]. The (7×7) reconstruction is therefore called the dimer-adatom-stacking fault (DAS) structure.

Our models for the magic number Si clusters are based on the premise that they possess features analogous to a perfect surface. Since a perfect surface has a well defined geometry, which in a finite cluster has to be reproduced by a small number of atoms, only certain sizes will have the right number of atoms to resemble closely the geometry of the reconstructed bulk surface. If the number of atoms in the cluster is changed, the similarity to the surface reconstruction breaks down, effectively introducing "defects" on the cluster surface, which should raise the reactivity. If enough atoms are added or subtracted, one may obtain a cluster with a different surface reconstruction, or with the same reconstruction on a larger scale. An inherent assumption in the above idea is that the cluster also possesses a number of interior atoms, representing the "bulk", on which the surface reconstruction is anchored. We refer to this type of cluster model as surface reconstruction induced geometry (SRIG).

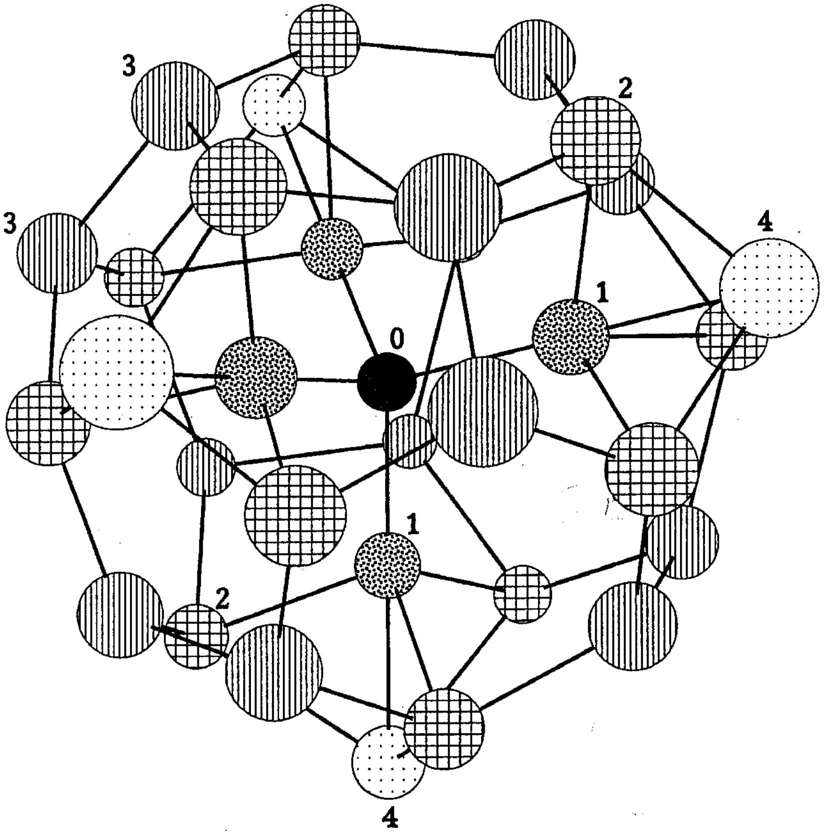

FIG. 1: Model for the 33-atom Si cluster, resembling the dimer-adatom-stacking fault reconstruction of the Si(111)7 × 7 surface. Atoms that are related by symmetry have the same type of shading. We refer to different shadings as "colors" for brevity. The convention is: black = very dark shading; grey = dense dot shading; blue = square pattern shading; green = parallel line shading; red = very sparse dot shading. The black and grey atoms constitute the interior five-atom core. The blue and green atoms are on the surface. The four red atoms are the adatoms at tetrahedral apex positions. The atoms labeled by numbers lie on a plane slicing through the cluster (see also Figure 4).

With this premise in mind we have constructed two classes of Si clusters, one with a surface resembling the (2×1) π-bonded chain reconstruction of Si(111) and the other with a surface resembling the (7×7) DAS reconstruction of the same surface. We have chosen to concentrate on this surface orientation because it corresponds to the lowest energy and therefore most stable Si surface. Both models have a core of atoms which are four-fold coordinated in tetrahedral arrangements, exactly as in bulk Si. For the π-bonded chain reconstruction we have constructed a model with a total of 45 Si atoms, a possible geometry for the Si_{45} magic number cluster.

For the DAS reconstruction we have constructed models with either 33 or 45 Si atoms, which are possible geometries for the Si_{33} and Si_{45} magic number clusters. We refer to the cluster models as the DAS or π-bonded models by analogy to the surface reconstruction they possess. For simplicity, here we will discuss in detail only one cluster of each type, the DAS model for Si_{33} and the π-bonded chain model for Si_{45}.

We begin with the DAS model for Si_{33}. The model for the cluster is shown in Fig. 1. Atoms that are in different bonding environments but are equivalent by symmetry are shown in the same color. Representative atoms of each type are labeled from 0 to 4. The cluster has overall tetrahedral symmetry (T_d). The central atom (black color, labeled 0) and its four neighbors (grey color, labeled 1) constitute the "bulk"-like core of the cluster. They are all four-fold, tetrahedrally coordinated as bulk Si atoms are. Twelve atoms attached to the core (blue color, labeled 2) form the third layer of surface atoms (counting, as usual, from the outermost layer) and have also four bonds, one to a grey atom, two to green atoms and one to a red atom. The green atoms are the second layer of surface atoms, and they resemble the dimer atoms of the DAS reconstruction. They each have three bonds, two to blue atoms and one to another green atom. There are twelve green atoms. An important feature is that the bond between two green atoms is stronger than the single covalent bonds, because of dimerization. This is a well established feature of the Si(100) surface, where surface atoms form pairs that exhibit the dimerization effect. Finally the red atoms form the first (outermost) layer of surface atoms. These atoms correspond to the adatoms of the DAS reconstruction. They sit directly above a bulk-like Si atom (the grey one) and are bonded to three third-layer atoms (the blue ones). Each adatom has three bonds. Because of the high symmetry of the cluster, the entire structure can be generated by applying the symmetry operations of the T_d point group to the positions of the representative atoms. The positions of these atoms are given in Table I.

Label	Si_{33}			Si_{45}^{DAS}			$Si_{45}^{\pi-bond}$		
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1	2.387	2.387	2.387	2.652	2.652	2.652	2.575	2.575	2.575
2	5.182	5.182	0.224	2.826	2.826	7.099	4.449	5.861	0.318
3	-1.540	-1.540	-6.987	-1.291	-4.385	-7.480	-5.029	-2.213	-7.915
4	4.943	4.943	4.943	5.833	5.833	5.833	-9.277	-0.881	-2.000
5							-6.027	-6.027	-6.027

TABLE I: Positions of representative atoms in a.u. for the Si_{33} DAS model and the Si_{45} DAS and π-bonded models.

By following similar procedures it is trivial to construct a DAS model for the Si_{45} cluster, having an identical core (5 atoms) and first layer surface atoms (12 atoms) and adatoms (4 atoms), as the Si_{33} model described above. The only difference in the Si_{45} DAS model is the replacement of the 12 dimer atoms by 24 atoms that form hexagons on four sides of a tetrahedron. This model also has T_d point group symmetry. In Table I we give the positions of representative atoms in the Si_{45} DAS model. Since this model introduces no new physics, we shall not discuss it in detail.

We describe next the model for the π-bonded chain Si_{45} cluster, shown in Fig. 2. This model also has a core of 5 atoms, one at the center and four next to it in a tetrahedral arrangement, all of them having four-fold coordination as Si bulk atoms do. The colors and labels for these atoms in Fig. 2 are the same as the core atoms in Si_{33} (compare to Fig. 1). The third layer surface atoms of the Si_{45} cluster are also very similar to the ones in the Si_{33} cluster and their color and label is also the same. The remaining features are quite different. There exist 24 atoms in the π-bonded chain Si_{45} model which form 6 short chains of 4 atoms each. These 24 atoms are in very similar environments to one another, although not all of them are related by symmetry operations. To suggest this similarity, they are all colored green in Fig. 2, and they are labeled 3 and 4, since they form two distinct dozens of symmetry-related atoms. Finally, there exists a set of four apex atoms, colored red and labeled 5, which connect the green chains. All the green and red atoms are three-fold coordinated, and are therefore true surface atoms. The green atoms form the second layer of surface atoms and the red atoms form the first layer of surface atoms, counting as usual from the outermost layer. Since together they make up a surface of three-fold coordinated nearest neighbors, their dangling bonds form π-bonded chains which reduces the energy. The short 4-atom sections of these chains composed of green atoms between successive red atoms are very similar in structure to the π-bonded chains on the Si(111) (2×1) reconstruction. For these atoms π-bonding among their dangling bonds should be quite effective. The four apex red atoms are at loci of higher curvature, where triplets of chains meet. Due to the distortion introduced by the curvature at these sites, π-bonding between their dangling bonds and those of their green neighbors will not be as effective as in the green chains.

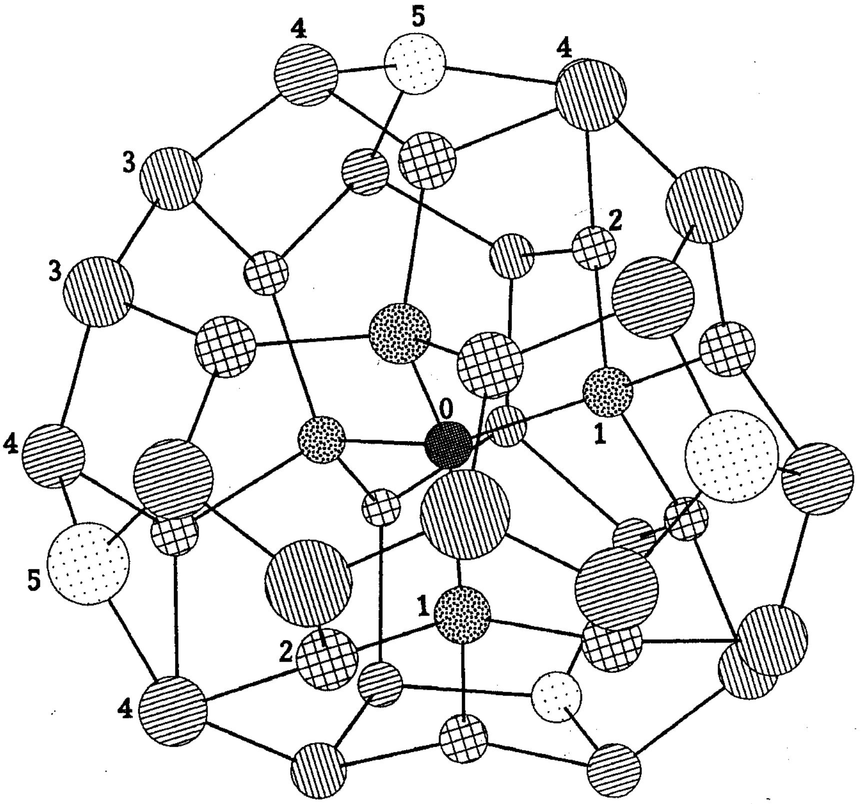

FIG. 2: Model for the 45-atom Si cluster, resembling the π-bonded chain reconstruction of the Si(111)2×1 surface. The "color" scheme is similar to that of Figure 1. The atoms labeled by numbers lie on or near a plane slicing through the cluster (see also Figure 7).

The Si_{45} model has lower symmetry than the Si_{33} model, because it is chiral: there exist two Si_{45} structures, a left-handed and a right-handed one, which are structurally equivalent in the sense that all the individual bonding features on a local scale are identical. Thus, the symmetry group of the Si_{45} π-bonded chain model does not contain any of the reflection symmetries of the T_d point group. Positions of representative atoms for the π-bonded chain Si_{45} cluster are included in Table I.

The models described above have the obvious property that by adding or subtracting atoms from them, one would ruin the perfect correspondence to the π-bonding and DAS surface reconstructions of bulk Si. Consequently, their immediate neighbors is size will not be able to acommodate the features of the surface reconstructions, introducing defects on the surface and thereby increasing both their relative energy and the chemical reactivity. These issues are discussed in more detail in the following two sections.

3 Energetics of the SRIG models

In order to provide more quantitative evaluation of the SRIG models, we have studied the energy of these structures relative to other structures derived by adding or removing atoms from the original models. In each case the atoms to be added or removed were chosen so as to produce the least disturbance of the cluster geometry, thus preserving the basic overall structure. These choices are justified in more detail below. We then performed first-principles total energy calculations, using the density functional formalism in the local density approximation (DFT-LDA) [26], and norm-conserving, non-local pseudopotentials [27] to represent the ion cores. We used a large supercell geometry and a plane wave basis consisting of plane waves with kinetic energy up to 8 Ry. These types of calculations are known to reproduce well various aspects of the structure of bulk and surface Si phases, and should therefore be equally reliable for the SRIG cluster models.

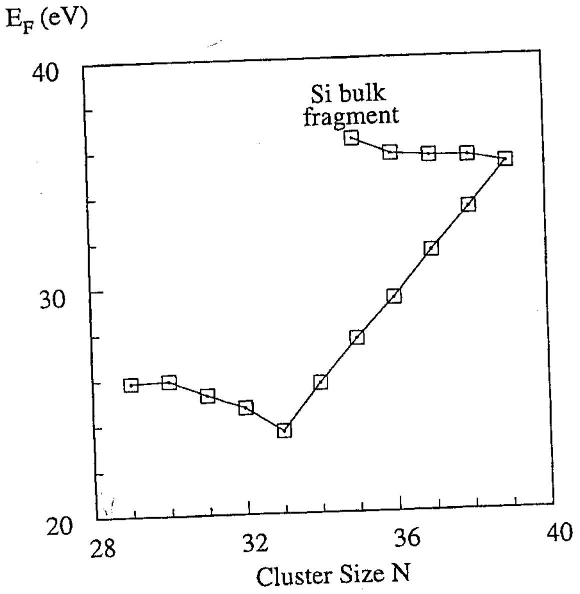

FIG. 3: Formation energy of the DAS model for the Si_{33} cluster and clusters derived from it by addition or removal of atoms.

Our calculations were more exhaustive for the Si_{33} model, and we concentrate on those results first. Similar results were found for the Si_{45} model. In Fig. 3, we show the formation energy of clusters derived from the Si_{33} model, by adding or removing atoms in various ways.

The formation energy is defined as the difference in energy between the cluster and equal number of bulk Si atoms. As expected from the arguments in the previous section, the Si_{33} cluster has the lowest formation energy, since it possesses a perfect surface reconstruction.

The clusters of size 29 – 32 were obtained by removing sequentially the red adatoms from the Si_{33} DAS model. The motivation for this choice is that the adatoms are the atoms with the overall weakest bonding to the rest of the cluster, having only three bonds to the blue surface atoms. The green dimer atoms also have three bonds only, but one of them is a strong dimer bond to another green atom as described in the previous section. If a green atom were to be removed, it would break two regular bonds and one dimer bond thus costing more energy than the removal of a red adatom. The expected relatively small energy cost for removing the adatoms is borne by the first-principles calculations: as seen from Fig. 3, the formation energy of the clusters so produced is not much higher than the formation energy of the Si_{33} parent cluster.

The atoms that were added to produce clusters larger than the Si_{33} model were placed in the middle of the dimer bonds, which were then opened and relaxed. Since there are six dimers (pairs of green atoms) in the Si_{33} cluster, a total of six atoms can be added to the parent cluster, bringing its size to 39. This choice of sites for adding atoms is probably not optimal from an energetic point of view since it disrupts the strong dimer bonds between green atoms. It is however, an interesting case to consider for two reasons: First, when all the extra atoms at dimer centers have been added, one obtains a model with the same overall symmetry and bonding topology as the Si_{33} parent, but of size 39, which happens to be another magic number cluster. The second reason is that, by removing the adatoms from the new cluster of 39 atoms, one obtains a cluster with 35 atoms which is a fragment of bulk Si. Comparison of this fragment to the models discussed here will be instructive.

From the arguments on the strength of the dimer bonds, one might expect the addition of the six atoms at dimer centers to increase the energy significantly. This is again borne out by the first-principles calculations, with the formation energy rising steeply for sizes 34 – 39. However, when the adatoms are removed from the 39-atom cluster to obtain the bulk fragment with 35 atoms, the formation energy rises very little. All these comparisons indicate that addition of the six atoms at dimer centers is unfavorable, and the resulting model is not a good candidate for the structure of the Si_{39} magic number cluster. The Si_{33} model is a very low energy structure, with much lower formation energy than a bulk fragment of slightly higher size. The bulk fragment is probably one of the most unfavorable structures, having many dangling bonds and lacking any kind of surface reconstruction. Thus, this comparison of relative energies is a vivid example of how surface reconstruction can lower the energy of the cluster.

We have obtained similar results for the Si_{45} π-bonded chain model, which also has a lower formation energy than models obtained by adding or subtracting surface atoms from it. Since all of the surface atoms in this model are bonded to each other by very similar arrangements, the energy cost should be approximately the same for subtraction of different kinds of surface atoms (type 3, 4 or 5 in Fig. 2). In this model, atoms were added as caps of the third-layer surface atoms (blue, labeled 2 in Fig. 1), at positions very similar to the adatoms in the Si_{33} cluster. There are four such positions, so that when they are all occupied the cluster size is 49. However, these adatoms are not surrounded by dimers as in the Si_{33} model. Thus, these adatoms are not as stable as the adatoms in the DAS model, and the formation energy of the ensuing clusters of sizes 46 – 49 are significantly higher than the formation energy of the 45-atom cluster.

The energetic comparisons described above cannot be taken as conclusive evidence of the absolute stability of these models. Instead, they simply confirm some of the ideas used to build the SRIG models. Much more extensive studies of relative energetics are needed to assess the models (see section 5).

4 Electronic structure of the SRIG models

We describe next the nature of electronic states in the SRIG models. Figures 4, 5 and 6 show the distribution of the total electronic density in the clusters of size 33, 29 and 39, that were described earlier. The sizes 29 and 39 are derivatives of the Si_{33} model, the first obtained by removal of the four adatoms, the second obtained by addition of six atoms in the middle of the dimer bonds in the parent model which corresponds to the (7 × 7) reconstruction of the Si(111) surface. The charge density in Fig. 4 is displayed on a plane slicing through the cluster, that contains the central atom (labeled 0 in Fig. 1), two of its nearest neighbors (labeled 1 in Fig. 1), one third layer surface atom (labeled 2 in Fig. 1) bonded to each of the "bulk"-like core atoms, one adatom (labeled 4 in Fig. 1) bonded to each of the third layer surface atoms, and finally a pair of atoms forming a dimer (labeled 3 in Fig. 1). Thus, this plane contains atoms of each distinct type appearing in the cluster. In Fig. 5 the adatoms have been removed, while in Fig. 6 an extra atom has been added near the middle of the dimer, which has opened and relaxed. It is evident from these figures that the clusters are covalently bonded, with high density of electronic charge between pairs of atoms, as illustrated by the bonds in Fig. 1.

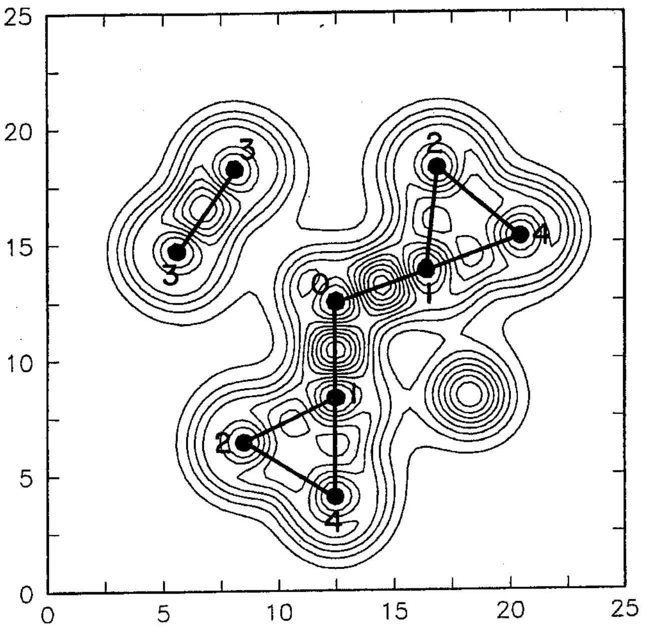

FIG. 4: Electronic charge density of the DAS model for the Si_{33} cluster. The labels of the atoms are the same as in Figure 1.

The specific features of the electronic charge density afford a comparison of the strength of the various covalent bonds. In particular, the strongest covalent bonds are between the central atom (0) and its immediate neighbors (1) in all three clusters. The dimer bonds (between pairs of atoms labeled 3) are also among the strongest covalent bonds in the cluster. The weakest covalent bonds are between the adatoms (labeled 4 in Fig. 4) and their immediate neighbors.

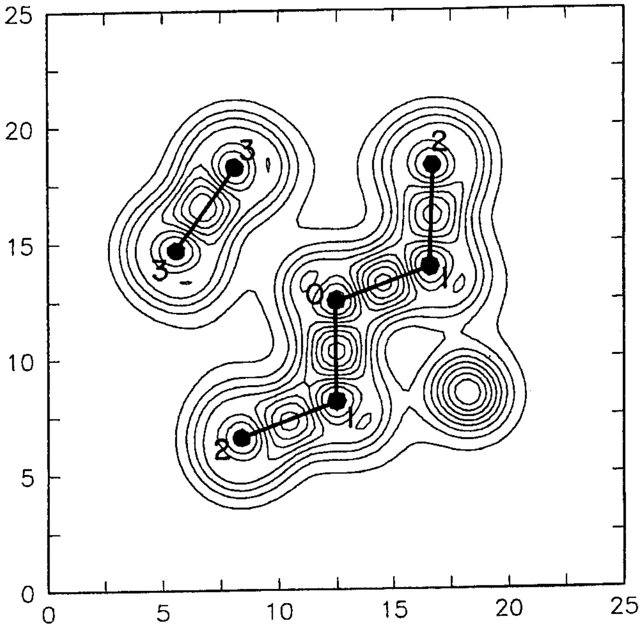

FIG. 5: Electronic charge density of the 29-atom model obtained by removing the four adatoms from the Si$_{33}$ DAS model.

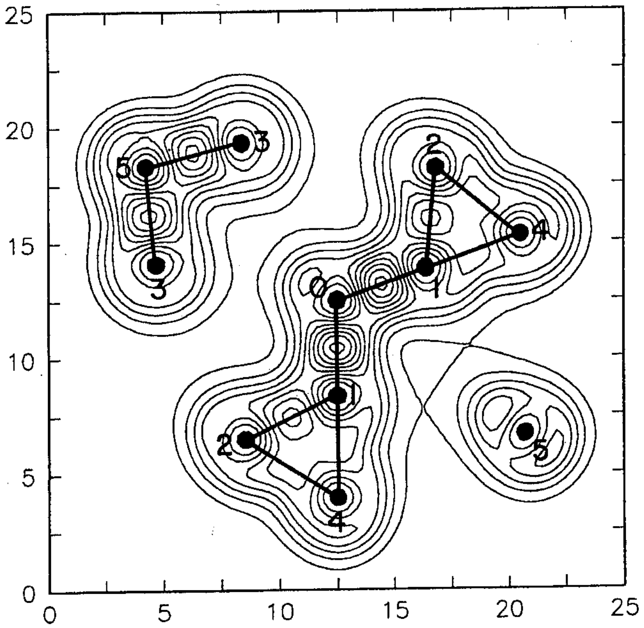

FIG. 6: Electronic charge density of the 39-atom model obtained by adding six atoms at the centers of dimers in the Si$_{33}$ DAS model.

In fact, the charge density reveals that there exists significant electronic charge concentration between the adatom and the "bulk"-like atom directly underneath them (labeled 1 in Fig. 1), which may be thought of as an extra weak bond between atoms 4 and 1 (as indicated in Fig. 1 and 4). Similar bonding effects between the surface adatoms and bulk atoms directly below them have been reported [24] for the case of the Si(111) (7×7) surface reconstruction containing adatoms. The bonding of adatoms is essentially the same in the Si_{39} model (compare Fig. 4 to Fig. 6).

Fig. 7 exhibits the total electronic charge density of the Si_{45} model corresponding to the (2×1) π-bonded chain reconstruction of Si(111). In this case the charge is again displayed on a plane that slices through the cluster and contains representative atoms of the "bulk"-like core (labeled 0 and 1 in Fig. 2), and the apex atoms (labeled 5 in Fig. 2), where the 4-atom π-bonded chains meet. Due to the lower symmetry of this cluster, the atoms that form the π-bonded chains do not lie on this plane. Thus, they are shown as smaller or larger shaded circles, lying in front of (the larger ones) or behind (the smaller ones) the plane of the figure. The total electronic charge distribution again displays the characteristics of covalent bonding among pairs of atoms, as illustrated by the bonds in Fig. 2.

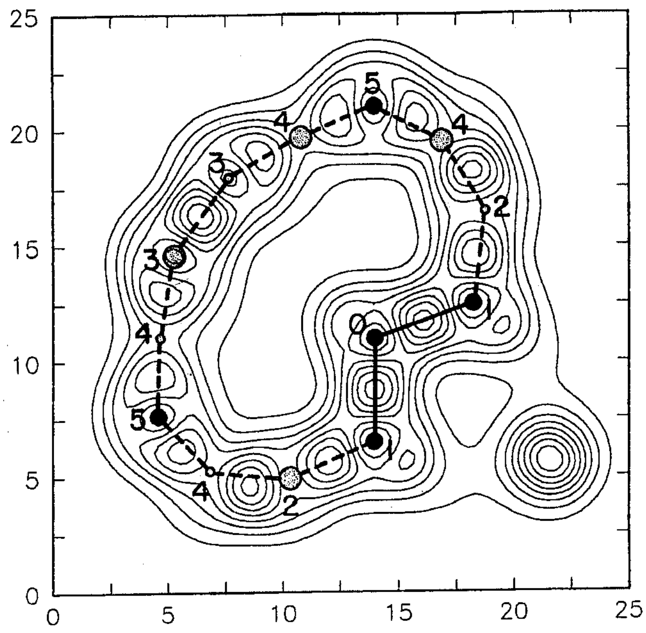

FIG. 7: Electronic charge density for the π-bonded chain Si_{45} cluster. The labels of the atoms are the same as in Figure 2. Atoms lying in front or behind the plane of the figure are shown as larger or smaller shaded circles.

Fig. 8 shows the electronic density of states (DOS) of the various cluster models discussed, and compares them to the DOS of bulk Si, calculated with the same computational parameters. The DOS of the clusters has the same overall distribution as the DOS of the bulk, extending over a band width of comparable magnitude. The DOS spectrum of the clusters is of course discrete, with the allowed multiplicities dictated by the sizes of the irreducible representations of the point groups that describe their overall symmetry (for example, T_d for the sizes 29, 33 and 39). The bulk energy spectrum is shifted so that the zero of energy is set at the valence band maximum. The cluster DOS spectra are shifted by exactly the same amount since the computational parameters are the same.

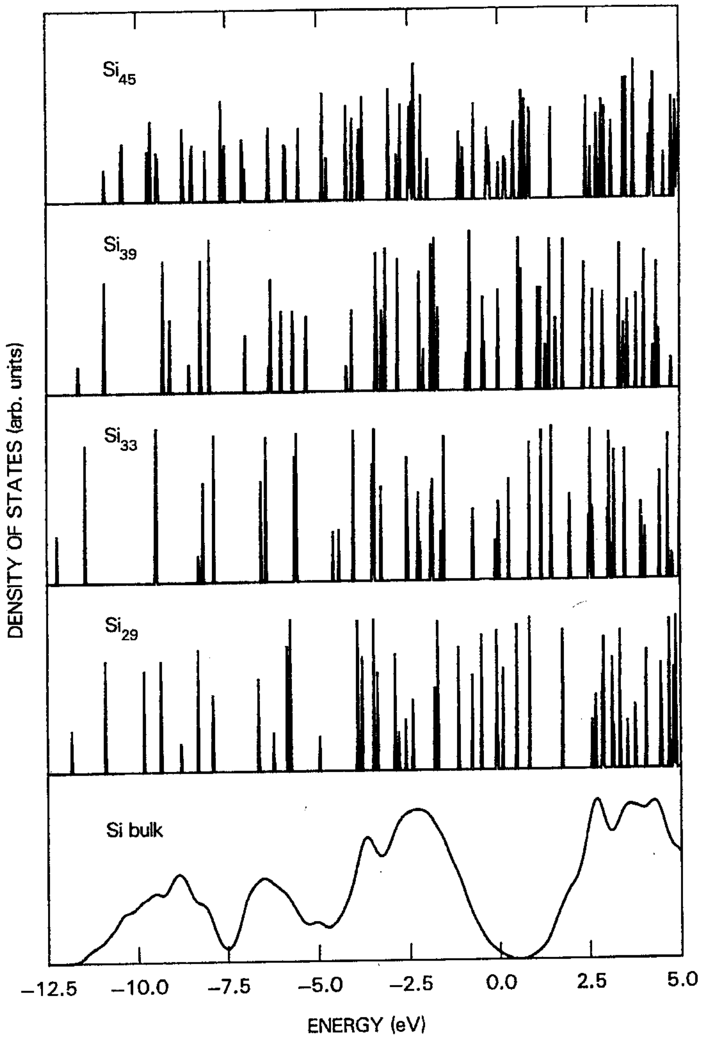

FIG. 8: Electronic density of states for the Si_{33} DAS model and its two derivatives with 29 and 39 atoms, the Si_{45} π-bonded chain model, and bulk Si.

Fig. 9 displays details of the cluster DOS in a small energy range around zero. From this figure, it is evident that the Si_{33} model has a gap in its electronic spectrum. The same is true for the Si_{29} cluster. The Si_{39} model has a very small gap separating occupied from unoccupied states. Finally the Si_{45} model has no gap, with the Fermi level falling in the middle of a set of degenerate states.

Equally interesting as the total charge density distribution is the wavefunction amplitude of states near the Fermi level. Of particular importance are the states just above the Fermi level. These would be natural candidates for reaction between the cluster and NH_3 molecules, which tend to form bonds by donating their lone-pair of electrons to unoccupied states.

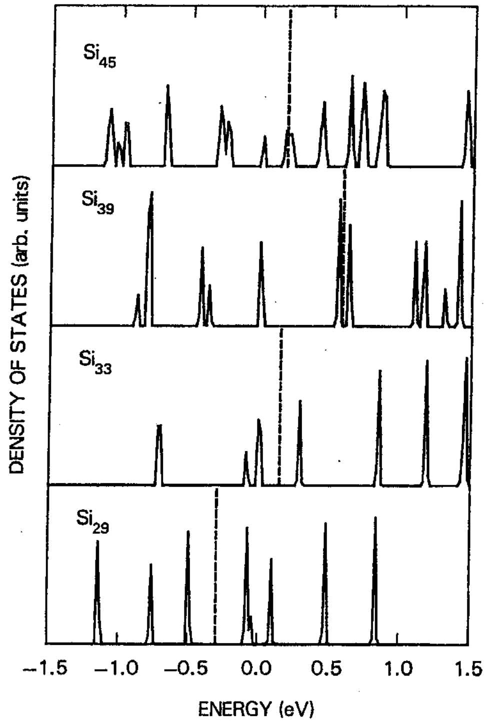

FIG. 9: Same as in Figure 8 for a narrow range near the Fermi level. The vertical dashed lines indicate the position of the Fermi level for each case.

In Fig. 10, we display the wavefunction amplitude of the first unoccupied state of the Si_{33} cluster. This state is rather delocalized, with significant amplitude at the dimer bond, as well as at regions in the interior of the cluster. In Fig. 11, we display the wavefunction amplitude of one of the degenerate states at the Fermi level of the Si_{45} model. This state is partially occupied. In contrast to the nature of the first unoccupied state of the Si_{33} model, this state is rather well localized, with most of its amplitude at the apex atom (labeled 5) and a much smaller amplitude on other surface atoms. It also appears to be a true surface state, with very little amplitude in the interior of the cluster.

The discussion of the nature of electronic states and the features of the DOS may help elucidate some aspects of the cluster reactivity properties. In particular, one would expect a cluster that has a gap in its electronic spectrum to be less reactive and more chemically stable. The models with 29 and 33 atoms, based on the Si(111) (7 × 7) DAS reconstruction, fulfill this criterion. Combining these facts with the relative formation energies (see Fig. 3) we conclude that the only model that is both energetically stable and chemically passive is the Si_{33} DAS model. The Si_{39} model obtained by adding atoms in the middle of dimers of the Si_{33} model has a very small gap and a very high formation energy, making it an unlikely candidate to explain the structure of the experimentally observed magic number cluster. Finally, the Si_{45} model based on the Si(111) (2 × 1) π-bonded reconstruction does not have a band gap, and the amplitude of states near its Fermi level is rather well localized on surface atoms, suggesting that this model would exhibit higher reactivity than the Si_{33} DAS model.

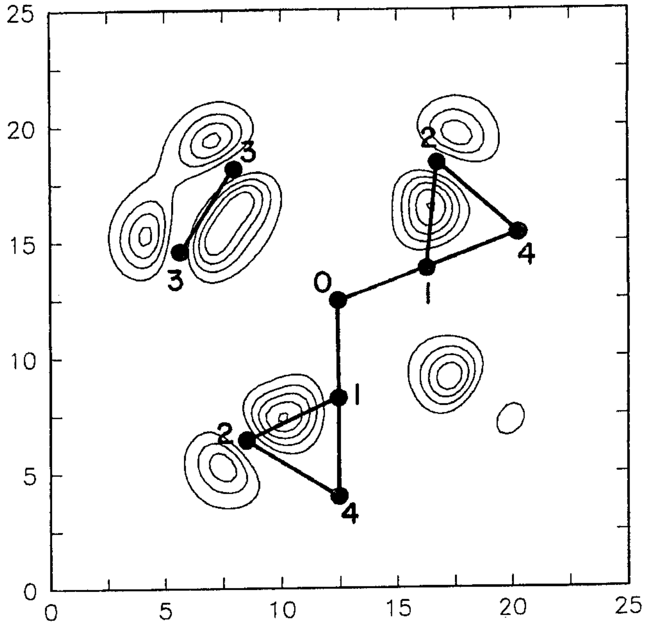

FIG. 10: Wavefunction amplitude of the first unoccupied state of the Si_{33} model.

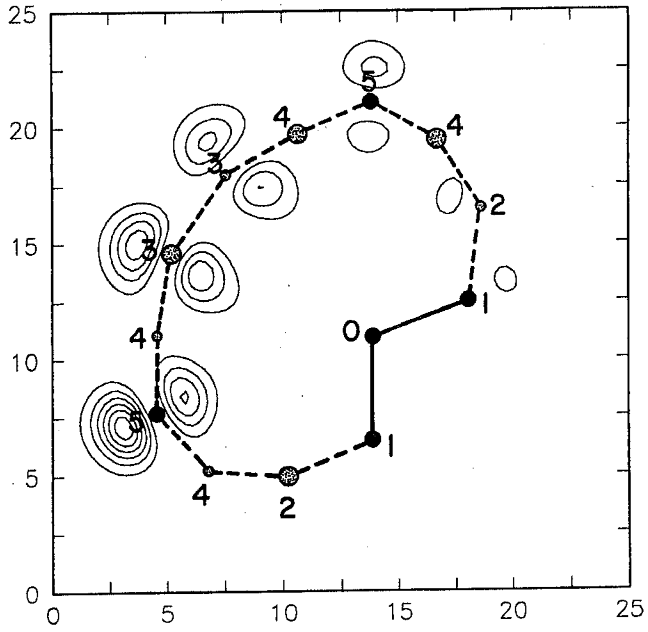

FIG. 11: Wavefunction amplitude of one of the degenerate states at the Fermi level of the Si_{45} model.

Therefore, the Si_{45} π-bonded model may not be the optimal candidate for the structure of the Si_{45} magic number cluster. Nevertheless, this model has certain other features that make it quite interesting as far as the possibility of a cluster-assembled solid is concerned, as will be discussed below (see section 6). The 45-atom model based on the DAS surface reconstruction discussed earlier (see section 2 and Table I) could be a better candidate for the low-reactivity magic number cluster of this size, since its electronic structure should be similar to that of the Si_{33} DAS model, with which it shares many structural features.

5 Comparison to other models

Following the original suggestion that magic number Si clusters may be induced by surface reconstruction [20], several authors have performed simulations to investigate the stability of these models. We discuss those studies in the order of sophistication of the calculations employed.

Jelski et al. [28] have performed molecular dynamics simulations using various classical interatomic force fields to describe the interaction between Si atoms [29]. Unlike the interatomic force field of Cehlikowsky and co-workers [10], which was specifically derived to capture the physics of Si clusters, the force fields employed by Jelski et al. had been fitted to reproduce the physics of bulk Si. No particular attention was paid to surface features. In fact, it is well known that one of the most widely used force fields for simulations of bulk Si, the one proposed by Stillinger and Weber [29], cannot reproduce one of the most important features of Si surfaces: specifically, it predicts that adatoms on the Si(111) surface are unstable, in direct contradiction with experiment. Thus, it is no surprise that the simulations of Jelski et al. found that the SRIG models, as described by the various interatomic force fields, were unstable and that other structures had lower energy. The limited ability of the interatomic force fields to describe surface features suggests that the lower energy structures found by Jelski et al. cannot be taken as likely candidates for explaining the structure of magic number Si clusters.

Pan and Ramakrishna [30] have considered models similar to the SRIG structures described above, and used various classical interatomic force fields and an empirical tight-binding hamiltonian to calculate optimal structures. Their model for the 33-atom Si cluster is identical to the DAS model proposed by Kaxiras [20] involving adatoms and dimers around a bulk-like core. Their model for the 45-atom cluster is the extension of the DAS structure to that size described in section 2, also based on the adatom, dimer and bulk-like interior pattern. Both models have T_d point group symmetry, and as discussed earlier should be good candidates for the structure of the Si_{33} and Si_{45} magic number clusters. A third model proposed by these authors for the 39-atom cluster, has the same overall pattern of adatoms around a bulk-like core, but has lower symmetry and is a contracted version of the 45-atom model. This contraction may induce considerable strain.

Pan and Ramakrishna rationalized their models in a manner different from the surface reconstruction arguments of Kaxiras. They proposed that the models resemble fullerene-like structures with a core. While the fullerene analogy is interesting from a visualization point of view, its relevance in explaining the structure of Si clusters is dubious. The reason why fullerene structures produce stable C clusters is the strong preference of C atoms to form three-fold coordinated graphitic structures. While graphite is the most stable form of bulk C, graphitic structures do not exist for Si. Even if it were fruitful to consider Si graphitic structures as hypothetical models, it is noteworthy that the interior atoms in these models are strongly bonded to the "fullerene" shell, which speaks against the relevance of the fullerene analogy. Once the "fullerene" shell becomes bonded to the interior atoms it looses its identity as a separate entity and becomes part of an integrated cluster structure. As argued in the previous sections, the integrated structure can be better understood as a miniature Si crystal with a bulk and a reconstructed surface.

A final argument against the fullerene analogy comes from the experimental observation that Si clusters of size larger than 45 do not show any magic number behavior. If the fullerene analogy were relevant, one might expect Si clusters of sizes 65 or larger to be rather stable and non-reactive, having a shell of 60 Si atoms, which is the most stable fullerene structure and an interior of 5 or more Si atoms. The fact that no magic number Si clusters appear in this size range suggests that the physics and chemistry of fullerenes is largely irrelevant to Si clusters.

Nagase and co-workers [31] also pursued the fullerene analogy for the structure of Si clusters, using the Hartree-Fock approximation for calculating relative energies. While this type of calculation involves a quantum mechanical description of electronic degrees of freedom, it emphasizes electronic exchange at the expense of electron correlation, which may limit its applicability to the study of Si clusters. It has been noted earlier that in some clusters, like Si_{13}, electron correlation effects may play a dominant role [19]. In the case of the clusters described here, the importance of electron correlations may be manifested in the surface reconstruction pattern, where dangling bonds rehybridize to form π-bonded chains or adatom-dimer units. Finally, as regards the rationalization of the obtained optimal fullerene geometries, the same arguments discussed above against the relevance of the fullerene analogy apply here also.

In the opposite extreme, Patterson and Mesmer [32] have used quantum mechanical calculations within the valence-bond picture which emphasizes electron correlations. They apply this approach to the study of both small (sizes less than 10) and intermediate Si clusters (sizes up to 50). In their study of small Si clusters they find covalent structures to be more stable than high coordination structures. This is in disagreement with the accepted notion on the structure of small Si clusters for which two very different approaches, the DFT-LDA calculations of Ballone et al. [6] and the quantum chemistry calculations of Raghavachari and Rohlfing [5] give identical results. Recent quantum Monte Carlo calculations, which describe electronic exchange and correlation very accurately, have confirmed the results of the DFT-LDA and quantum chemistry calculations for the small Si clusters [33]. These structures have been also verified recently by Raman spectroscopy studies [34]. This suggests that the valence-bond method does not provide reliable relative energies for small Si clusters. For the intermediate size clusters, Patterson and Mesmer proposed a Si_{33} cluster identical to the SRIG model described here. They have also proposed models for the other two magic number clusters, Si_{39} and Si_{45}. The Si_{39} model is identical to the one described above, obtained from the Si_{33} DAS model by inserting atoms in the middle of the dimer bonds. Patterson and Mesmer suggest that this model should have low energy, while our first principles calculations indicate that it has a very high formation energy (see section 3). Finally, these authors have proposed a Si_{45} cluster that has several highly strained four-membered rings, a structure that is not encountered in bulk forms or surface reconstructions of Si.

Röthlisberger, Andreoni and Parrinello (RAP in the following) [35] have performed first-principles calculations within the framework of DFT-LDA to determine the energy and the properties of Si clusters. These authors concentrated on the 45-atom Si cluster. They find that the SRIG models described above are not the lowest energy structures. Instead, their molecular dynamics simulations discovered new structures that consist of an outer shell of 38 or 39 atoms and an interior of 7 or 6 atoms, respectively. They also find that the interior atoms are highly coordinated, with an average coordination of 8. The average coordination of the entire cluster models is also quite high (approximately 7). They argue that the models obtained by their simulations have a lower number of dangling bonds than the SRIG models, which obviously have much lower coordination (3 for surface atoms and 4 for interior atoms).

While studies such as the RAP work are very important and useful in determining the properties of novel systems, these particular results need to be examined closer before they can be accepted as the final word on the subject. Several key points deserve close examination:

(1) As the detailed work of Jones and Gunnarson [21] has established, finding all the local energy minima for a cluster consisting of more than 20 atoms is an exceedingly difficult task, even when when one uses simple two-body interactions (such as the Lennard-Jones potential) to calculate the energy. This is an example of a non-deterministic polynomial-time (NP) complete problem, the difficulty of which increases exponentially with size. Thus, for a large cluster of 45 Si atoms, the problem is essentially unsolvable. The situation of course becomes even more complicated when the problem is treated quantum mechanically in the framework of DFT-LDA. Accordingly, studies of the type reported by RAP can only be viewed as extremely limited explorations of the possible configurational space. Moreover, it is quite likely that special structures, such as a Si magic number cluster, correspond to a deep and narrow well in the energy landscape, which would be impossible to locate in molecular dynamics simulation when the symmetry of the structure is not maintained.

(2) The models obtained by RAP as alternatives to the SRIG models apparently have a lower number of dangling bonds. However, as these authors repeatedly point out, their models have a rather high coordination, both for the interior and for the surface atoms. The concept of covalent bonds, and therefore the concept of dangling bonds, breaks down when the coordination exceeds the natural valence of Si atoms (4) by almost a factor of 2 (it is 7 on average and 8 for interior atoms in the RAP models). It is therefore unphysical to count the number of "dangling" bonds in a high-coordination Si structure, where the electrons are shared by many atoms in a metallic-like environment. For comparison, liquid Si has an average coordination of approximately 6, and is typically described as a metallic system. On the other hand, the SRIG models *appear* to have a large number of dangling bonds because the surface atoms are three-fold coordinated. But counting each three-fold coordinated surface Si atom as a dangling bond is unrealistic, because dangling bonds reconstruct (as in the π-bonded chain and the DAS surface reconstructions described in detail in section 2). The SRIG models have the optimal surface reconstruction and therefore the lowest possible number of surface dangling bonds. In fact the only relevant issue is the number of *partially occupied states* at the Fermi level. It is only such states that possess the properties of covalent dangling bonds. According to this definition, as discussed in section 3, the Si_{33} SRIG model has *no dangling bonds* since it has a band gap, whereas the Si_{45} SRIG model has *only four dangling bonds*, at the four apex (red) atoms. Thus both models, have fewer dangling bonds than the models found by RAP, when a physically meaningful definition for the concept of a dangling bond is used.

(3) Finally, the discussion that RAP provide in order to justify the stability of their models is in some respects a direct contradiction of experimental facts. They observe that when they augment by one atom the core of the 45-atom cluster consisting of a 38-atom outer shell and a 7-atom core, they obtain a cluster of 46 Si atoms which has the same cohesive energy and the same number of "dangling bonds" as the original 45-atom Si cluster. In other words, adding one atom to the 45-atom cluster gives a cluster of the same stability (same cohesive energy), the same surface structure (same outer shell) and similar electronic structure (same number of dangling bonds). This means that the reactivity of the 45 and 46 atom clusters obtained by RAP should be essentially identical. Thus, by using the models found in the simulations of RAP, it would very difficult to explain the experimentally observed difference in reactivity of more than 2 orders of magnitude between sizes 45 and 46.

Another molecular dynamics simulation has been reported recently by Menon and Subaswamy [36], using a tight-binding methodology that was fitted to reproduce the results of first-principles calculations for small Si clusters. These authors also concentrated on the 45-atom cluster. They considered both unconstrained optimizations of the cluster geometries, as well as constrained optimizations where the overall cluster symmetry is preserved during the simulation. They find results similar to those of RAP, characterized by high coordination of both the surface and the interior atoms. Since the tight-binding parameters were fitted to small Si clusters, which are predominantly highly-coordinated structures, it is not surprising that the molecular dynamics simulations produce clusters of the same type of bonding. The data base for fitting the tight-binding parameters included certain four-fold coordinated bulk phases of Si, but no surface structures. It is possible that surface reconstruction features are not captured accurately by this approach, restricting its applicability to problems where covalent surface structures dominate. Further exploration and tests of the approach are needed to establish its validity and applicability to the case of Si clusters in the range 26 – 50 atoms.

6 Prospects for cluster assembled materials

We conclude our discussion with some comments on the prospects for making cluster assembled materials based on the SRIG cluster models. As noted earlier, the existence of low-reactivity clusters is encouraging, since it provides a means for isolating monodisperse populations of clusters. Assembling these clusters into a solid will depend on how they react with one another and how their structure can be acommodated in a solid form.

We expect that clusters that have well defined structure would be able to maintain their identity when brought in contact with other similar clusters at low to moderate temperature. If the magic number clusters resemble the SRIG model structures, they should behave in this way. On this assumption, we explore the possible packings of such clusters that could lead to a stable solid form.

The Si_{33} DAS model for example, has tetrahedral symmetry with the four adatoms (red, labeled 4 in Fig. 1) at the corners of a tetrahedron. Since these atoms have the weakest bonds to the cluster, they may also form the four most reactive sites. A natural way to link these clusters into a three-dimensional crystalline network is to join them at the adatom sites in a diamond-like lattice. A similar possibility has been suggested recently for the C_{28} cluster [37], which also has four reactive sites at the vertices of a tetrahedron. The stability of this so called "hyperdiamond" structure will depend on the stability of the original Si_{33} cluster.

Another intriguing case is the Si_{45} π-bonded chain model. As discussed in section 4, this cluster has an open shell electronic structure. The states near the Fermi level constitute a set of four partially occupied levels which could accomodate up to eight electrons when spin degeneracy is taken into account. There are only four electrons available to occupy these levels. The wavefunctions of these states are heavily concentrated at the apex atoms (red, labeled 5 in Fig. 2), which form the corners of a tetrahedron. Thus, this cluster would behave as a tetravalent atom that prefers tetrahedral coordination. The natural choice for a crystal built out of these units would be a diamond lattice. As pointed out earlier, this particular cluster has chiral character. If the left and right handed isomers could be produced in equal numbers, then it might be possible to obtain a zincblende lattice where the two interpenetrating fcc sublattices are occupied by the left and right handed isomers respectively. The ensuing crystal should have very interesting electronic and optical properties, since polarized light should interact in a different manner with the two chiral isomers that compose it. Again, the stability of the original Si_{45} structure will determine the viability of the hypothetical crystal structure.

These possibilities should help sustain the interest in the study of Si clusters and the hope that formation of useful and exciting new solids will become possible, once the secrets of the cluster structure have been revealed.

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