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Magic numbers of silicon clusters

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A structural model for intermediate-size silicon clusters is proposed that is able to generate unique structures without any dangling bonds. This structural model consists of a bulklike core of five atoms surrounded by a fullerenelike surface. Reconstruction of the ideal fullerene geometry results in the formation of crown atoms surrounded by π-bonded dimers. This model yields unique structures for Si_{33}, Si_{39}, and Si_{45} clusters without any dangling bonds and hence explains why these clusters are the least reactive towards chemisorption of ammonia. Finally, reagent-specific chemisorption reactivities observed experimentally are explained based on the electronic structures of the reagents.

Smalley and co-workers carried out extensive studies on chemisorption of various reagents on intermediate-size silicon clusters.[1] These studies revealed that the reactivity rates for ammonia (NH_3) chemisorption vary by over three orders of magnitude as a function of cluster size, with 21-, 25-, 33-, 39-, and 45-atom clusters being particularly unreactive. Clusters containing more than 47 atoms are highly reactive and they do not display strong oscillations in reactivities as a function of the cluster size. Similar results were obtained with methanol (CH_3OH), ethylene (C_2H_4), and water (H_2O). On the other hand, nitric oxide (NO) and oxygen (O_2) were found to react readily with all clusters in this size range.

Several structural models have been proposed to explain these experimental data.[2-7] However, these models do not yield unique and consistent structures for different cluster sizes and each cluster structure has to be obtained independently. Furthermore, these models do not satisfy the essential criterion that the structures of the unreactive clusters should not have any dangling bonds.

In this paper we propose a consistent model that generates the structures of the intermediate-size unreactive silicon clusters in a systematic way. The structures thus generated are unique for Si_{33}, Si_{39}, and Si_{45} clusters. Furthermore, these clusters do not have any dangling bonds, explaining why these clusters are unreactive for chemisorption. Finally, our model is consistent with the experimental finding of Jarrold and Constant that silicon clusters undergo a shape transition from prolate to spherical shapes at Si_{27}.[8]

Our structural model for silicon clusters[9] consists of a bulklike core of five atoms surrounded by a fullerenelike surface. The core atoms bind to the 12 surface atoms, thus rendering them bulklike with fourfold coordination. The surface then relaxes from its ideal fullerene geometry to give rise to crown atoms and dimers. The crown atoms are called adatoms in surface science literature.[10] These crown atoms are formally threefold coordinated and possess one dangling bond each. The dimers are also formally threefold coordinated, but they eliminate their dangling bonds through local π bonding. This model yields structures with 17 fourfold-coordinated atoms, four crown atoms, and the rest dimers. The essential feature of this construction is that the bulklike core and fullerenelike surface make these structures stable. This model is applicable to clusters containing more than 20 atoms.

Unlike carbon, silicon does not form strong delocalized π bonds. Consequently, fullerene cage structures,[11,12] which require strong delocalized π bonds, are energetically unfavorable for silicon. For this reason, silicon clusters prefer as few surface atoms as possible. Nonetheless, the fullerene geometry for the surface, consisting of interlocking pentagons and hexagons, gives special stability to the surface atoms. Furthermore, since delocalized π bonding is not favorable in silicon, we expect the surface atoms to relax from their ideal fullerene geometry to allow for dimer formation through strong local π bonding. Our model accounts for all these facts.

The five-atom core in our model has the exact structure of bulk silicon with one atom in the center bonded to four atoms arranged in a perfect tetrahedral symmetry. There are numerous ways to orient the five-atom core inside the fullerene cage and bind it to the surface atoms. Furthermore, structural isomers may exist for fullerenes of any size.[12,13] Thus it is possible to use this model to generate all possible structural isomers for any odd-numbered intermediate-size cluster. However, a particular orientation of the five-atom core inside the fullerene cage will yield structures with the maximum number of dimers and the least number of dangling bonds. Such isomers are likely to be most stable.

The 28- and 40-atom fullerenes are the only ones belonging to the symmetry group T_d in the 20–60-atom size range.[12] We generate the Si_{33} and Si_{45} structures by inserting the five-atom core inside the 28- and 40-atom fullerene, respectively. We orient the five-atom pyramid in such a way that the central atom (A), the apex atom (B) of the pyramid, and the crown atom (C) on the surface lie on a line. The C atom is the central atom shared by three fused pentagons. This atom is surrounded by three other surface atoms (D), which relax inwards to bind to the four core atoms B. This relaxation motion is identical to that necessary to form the 2×1 reconstruction on the bulk Si(111) surface.[14,15] With an activation barrier of only ≈ 0.01 eV (Refs. 14 and 16) and a gain of

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2.3 eV/bond due to σ bond formation between B and D,[15,17] such a relaxation of the fullerene surface is feasible even at 100 K. Finally, the remaining surface atoms (E) readjust to form as many dimers as possible. This relaxation is similar to that on Si(100) surface yielding dimers.[15,18] The dimers are σ-bonded pair of atoms whose dangling bonds are saturated through strong local π bonds. Because of the tetrahedral symmetry of the core as well as of the reconstructed fullerene cage, the final Si_{33} and Si_{45} structures also have tetrahedral symmetry. The Si_{39} structure is also generated in this way, starting from the 34-atom fullerene cage and stuffing five atoms inside it. However, the structure thus generated has only C_{3v} symmetry, because of the lower symmetry of the fullerene cage.

The Si_{33}, Si_{39}, and Si_{45} cluster structures thus generated are displayed in Fig. 1. These structures have 17 fourfold-coordinated atoms, four crown atoms, and a variable number of dimers. The Si_{33} structure has six dimers, whereas Si_{45} has 12 dimers forming four hexagons. On the other hand, the surface of the Si_{39} cluster consists of nine dimers, three of which form a hexagon.

We constructed Si_{35} and Si_{43} clusters also using the proposed model, but found that these structures do not possess the characteristic crown-atom-dimer pattern found in unreactive clusters. Consequently, these structures possessed a large number of dangling bonds. This explains the highly reactive nature of these clusters.

In principle, the proposed model can be used to con-

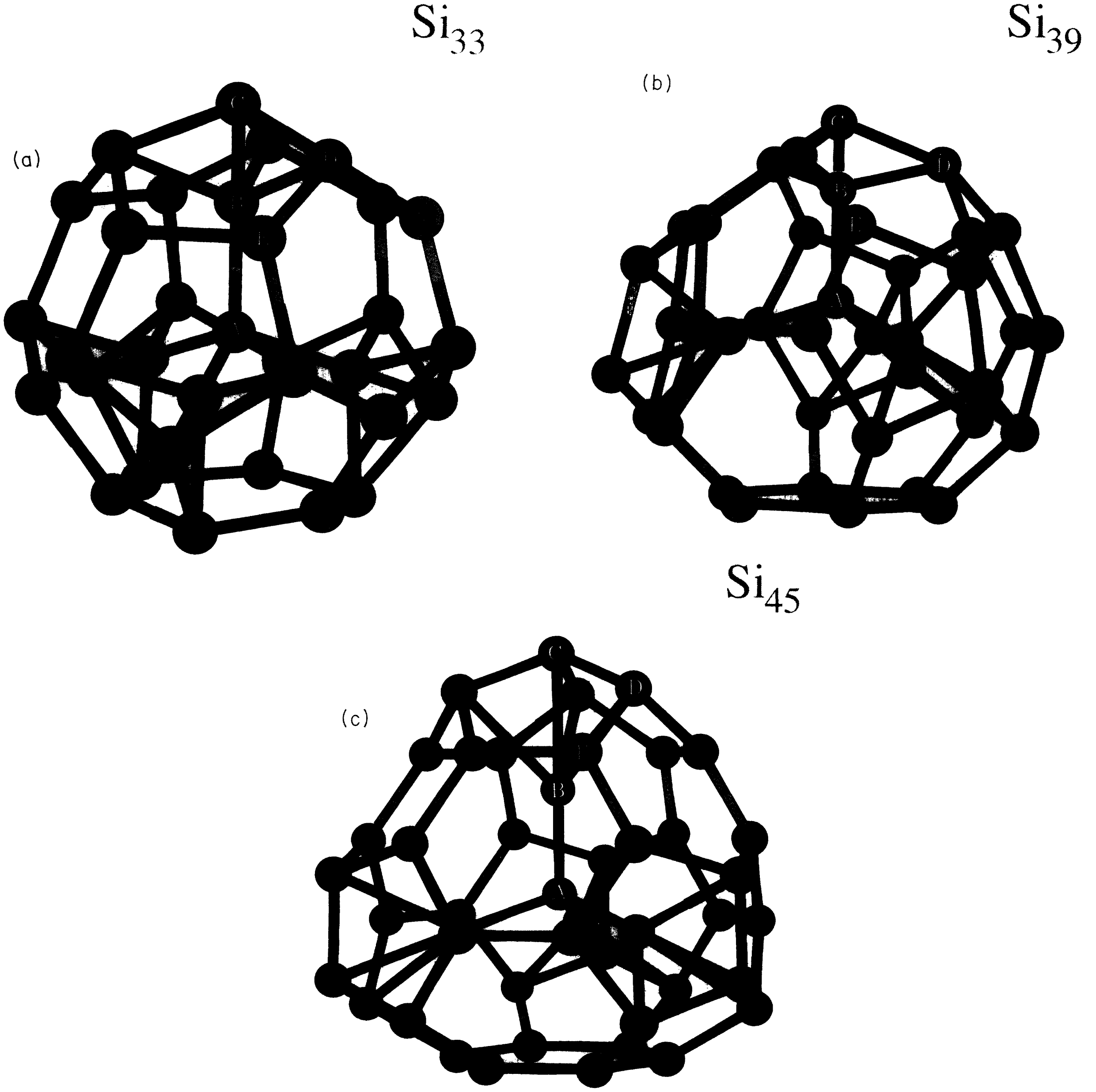

FIG. 1. Structures of Si_{33}, Si_{39}, and Si_{45} clusters obtained using the proposed stuffed fullerene model. The atoms in different chemical environments are labeled from A to E. These clusters do not possess any dangling bonds and hence are least reactive towards the closed-shell reagents ammonia, methanol, ethylene, and water.

struct a Si_{25} structure also. However, the Si_{20} cage is too small to accommodate five atoms inside it without undue strain. Consequently, Si_{25} will prefer a different geometry. Indeed, there is experimental evidence that clusters smaller than Si_{27} do not possess spherical shapes characteristic of larger clusters; instead they seem to prefer prolate shapes.[8] Our inability to generate a compact structure for Si_{25} explains this experimental observation also.

We verified our model by constructing structures of all the clusters discussed here using the molecular modeling kits.[19] These structures unambiguously demonstrated that only 33-, 39-, and 45-atom clusters possess the crown-atom-dimer pattern on their surfaces. We then calculated the atomic coordinates of these clusters from the tetrahedral geometry of the five-atom core and the known geometries of the fullerene structures,[12] assuming that all bond lengths are approximately equal to the bulk value of 2.35 Å. The structures thus generated are displayed in Fig. 1. We then relaxed these structures by carrying out molecular dynamics using the Kaxiras-Pandey potential[20] and the tight-binding Hamiltonian.[21] The final structures obtained from these simulations are nearly identical to the initial ones. This indicates that the proposed structures are locally stable.

The computer-generated structures displayed in Fig. 1 revealed that the crown atoms are able to form a fourth bond to the core atoms *B*, thus rendering the *B* atoms formally fivefold coordinated. The *B*-*C* bond arises from the back donation of the electrons from *C* to *B* and it weakens the neighboring bonds through electronic repulsion. The dangling bond on the crown atom is thus eliminated and these magic number clusters become unreactive.

The classical and tight-binding potentials available at present[20–22] are most appropriate for structures to which they are fit. Such potentials may not be suitable for describing unusual bonding patterns, such as the fivefold-coordinated silicon atoms found in these clusters. Consequently, we cannot use the available classical potentials to prove that the proposed structures correspond to the lowest-energy structures. Structural determination based on the first-principles electronic structure calculations are extremely demanding computationally at present for such large clusters, especially if adequate basis sets and grid sizes are employed and the calculations are converged to better than 0.01-eV accuracy. Furthermore, such complicated calculations do not provide the conceptual framework for understanding cluster chemical properties. On the other hand, our simple physically motivated stuffed fullerene model yields insights into the nature of bonding in silicon clusters and explains the experimental trends in reactivities.

These exist several competing structural models[2–7] of silicon clusters that attempt to explain the experimental reactivity data of Smalley and co-workers.[1] For example, Kaxiras has proposed structures of Si_{33} and Si_{45} clusters based on the reconstructed 7×7 and 2×1 surfaces of bulk Si(111), respectively.[4] However, this model does not explain the reactivity data since bulk surfaces are highly reactive. Furthermore, it is inconsistent that the surface of Si_{45} should be the metastable 2×1 surface rather than the more stable 7×7 surface.[15] Finally, the Si_{45} structure of Kaxiras has 40 dangling bonds, which make it highly reactive, contrary to the experiments. To overcome this discrepancy between experiment and theory, Kaxiras has proposed that the dangling bonds on Si_{45} form π-bonded chains, analogous to the 2×1 reconstruction of the bulk Si(111) surface.[23] However, silicon favors strong local π bonds over delocalized π-bonded chains. This is the reason why the 2×1 reconstruction, involving π-bonded chains,[23] is metastable with respect to the locally π-bonded 7×7 reconstruction on the bulk Si(111) surface.[15] For the same reason, the Si_{45} structure proposed by Kaxiras is a metastable and highly reactive structure. Indeed, Jelski and co-workers disputed the Kaxiras model of Si_{45} by constructing alternative structures for Si_{45} that are lower in energy, but do not possess any of the features of the reconstructed bulk surfaces.[6] More recent first-principles molecular-dynamics calculations of Andreoni and co-workers also gave a different structure for Si_{45}.[7] However, these very complicated calculations do not explain the reactivity trends observed experimentally.

The bonding characteristics of silicon differ in subtle ways from that of carbon. In carbon, delocalized π bonds are favored over local π bonds, whereas the opposite is true in silicon. For this reason, graphite is the most stable form of carbon at room temperature and atmospheric pressure, but not the graphite form of silicon. Likewise, the bulk (111) surface of the diamond form of carbon exhibits the 2×1 reconstruction, but not the 7×7 reconstruction.[24,25] These examples illustrate how subtle differences in bonding characteristics determine possible crystal structures and surface reconstructions. The same is true of clusters and the models of cluster structures should account for these characteristics. Our model of silicon clusters accounts for these facts by focusing on structures that are able to form maximum number of σ bonds and eliminate their surface dangling bonds through local π bonding.

Our structure for Si_{33} is identical to that proposed by Kaxiras[4] and Patterson and Messmer.[5] This structure has been shown to be locally stable.[26] But our Si_{45} structure is different from that of Kaxiras[4] and Röthlisberger, Andreoni, and Parrinello.[7] However, we can generate the Si_{45} structure of Kaxiras by stuffing one atom inside a 44-atom fullerene cage and allowing for the reconstruction of the fullerene surface.[27] Thus our model is very general, subsuming the Kaxiras model within it.

The reactivity patterns of NO and O_2 are different from those found for NH_3, CH_3OH, C_2H_4, and H_2O.[1] This may be explained based on the ground-state electronic structures of these reagents. NH_3, CH_3OH, C_2H_4, and H_2O in their ground states have closed-shell electronic structure with all electrons paired. On the other hand, NO and O_2 in their ground states are $^2\Pi_g$ and $^3\Sigma_g^-$, possessing one and two unpaired electrons, respectively.[28] Consequently, NH_3, CH_3OH, C_2H_4, and H_2O can chemisorb only at those sites where excess electron density is present due to dangling bonds. Such a selectivity gives rise to highly oscillatory pattern in the reactivities, because the number of dangling bonds varies as a function of cluster size. The magic number clusters are unreactive because they do not possess any dangling bonds. On the other hand, NO ($^2\Pi_g$) and O_2 ($^3\Sigma_g^-$) can chemisorb anywhere, because these reagents carry the necessary dangling bonds for instigating the reaction anywhere on the cluster surface. Hence, NO and O_2 readily react with all clusters and do not display the oscillatory pattern in their chemical reactivities. This explains the reagent specific chemisorption reactivities observed experimentally.[1]

The magic number clusters are not completely inert towards the closed-shell reagents.[1] These clusters are more reactive towards NH_3, CH_3OH, and H_2O than towards C_2H_4. This is because NH_3, CH_3OH, and H_2O have lone pairs on either nitrogen or oxygen and these lone pairs have a small probability of instigating reaction on the cluster surface. A lone pair is a pair of electrons that is not part of a bond. C_2H_4 does not have any lone pairs and hence the magic number clusters are quite unreactive towards this molecule. The electronic structure of reagents thus explains even subtle variations in the reactivities of magic number clusters towards a group of related reagents.

In summary, we propose a structural model for the unreactive silicon clusters containing more than 20 atoms. This model consists of a bulklike core of five atoms surrounded by a reconstructed fullerene surface. The resulting structures for Si_{33}, Si_{39}, and Si_{45} have a maximum number of fourfold-coordinated atoms, a minimum number of surface atoms, and zero dangling bonds. Such structures cannot be built for other intermediate-sized clusters and hence they will have a larger number of dangling bonds. This explains why Si_{33}, Si_{39}, and Si_{45} clusters are least reactive towards the closed-shell reagents ammonia, methanol, ethylene, and water.[1] Our model also indicates that the Si_{25} cluster cannot be formed in a spherical shape. This result is consistent with the experimental finding that silicon clusters undergo a shape transition from prolate to spherical shapes at Si_{27}.[8] Finally, two distinct patterns of chemisorption reactivities observed experimentally are explained based on the electronic structures of the reagents. The reactivities of closed-shell reagents depend on the available number of dangling-bond sites, whereas the reactivities of free radical reagents are not so dependent. Consequently, only the closed-shell reagents are sensitive to the cluster structure and hence exhibit the highly oscillatory pattern in reactivities as a function of the cluster size.

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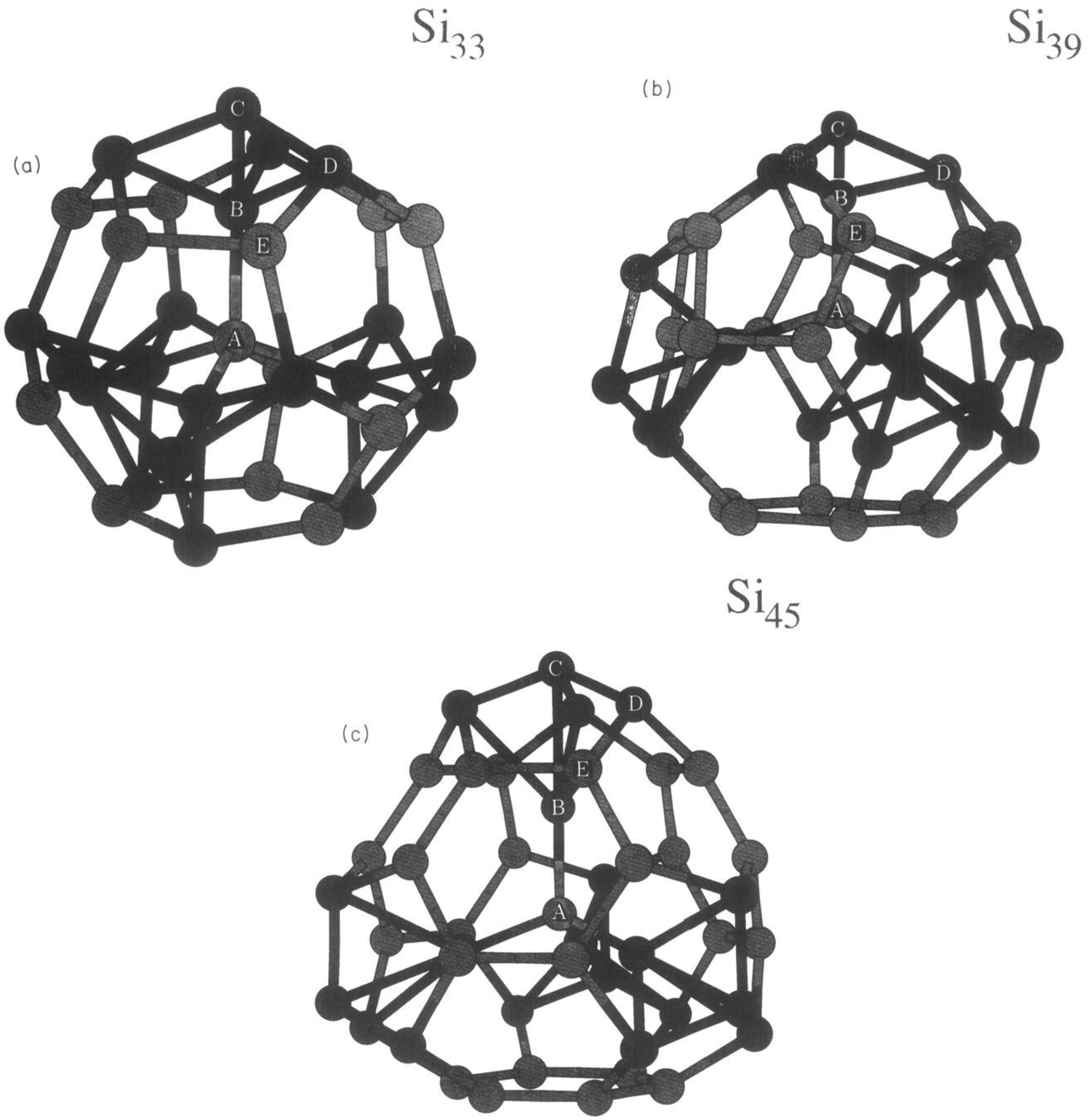

FIG. 1. Structures of Si_{33}, Si_{39}, and Si_{45} clusters obtained using the proposed stuffed fullerene model. The atoms in different chemical environments are labeled from *A* to *E*. These clusters do not possess any dangling bonds and hence are least reactive towards the closed-shell reagents ammonia, methanol, ethylene, and water.