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Stability and electronic properties of nanoscale silicon clusters

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The Si_{28} and M@Si_{28} (M=tetravalent atoms) clusters have been studied by the density-functional theory. We find that both Si_{28} and C_{28} clusters have similar electronic structures, and the dangling bonds of the Si_{28} cluster can be stabilized by some superatoms. The covalent interaction between the Si_5 superatom and Si_{28} cluster opens a gap at the Fermi level, which makes the Si_5@Si_{28} cluster kinetically stable. In good agreement with experiments, a strong similarity in the density of states between silicon clusters and bulk phase has been observed.

Currently nanoscale clusters have become the subject of intensive study, since they may possess properties much different from those of the bulk materials and also can be good candidates for the building blocks of new materials. Many efforts have been devoted to the study of carbon and silicon clusters. The fullerenes C_{60} and C_{70}, and even larger fullerenes, were found a few years ago and recently the smaller fullerene C_{28} and the doped M@C_{28} (M are tetravalent atoms) were observed.[1] The fullerenelike C_{28} cluster has tetravalent chemical bonding with four electrons in a p-like state as the highest occupied molecular orbital (HOMO), and an s-like state as the lowest unoccupied molecular orbital (LUMO) which is only 0.3 eV above the HOMO. But with proper doping, e.g., with Zr, the HOMO becomes completely filled and a gap between the HOMO and the LUMO appears.[2] The atomic structure of the C_{28} cluster can be approximately considered as four benzene rings on the four faces of a tetrahedron with four additional atoms situated between the center of the tetrahedron and its vertices, and hence it has tetrahedral symmetry. The relative positions of the atoms are determined by three independent bond lengths R_h (the hexagon bond), R_a (the apex pentagon bond), and R_p (a basal pentagon bond) as defined in Ref. 3. A few people have optimized the bond lengths and found that the cage of the C_{28} cluster expands a little upon doping.[2,3] The change of bond lengths is smaller than 5% with group-IVA and group-IVB endohedral atoms in the C_{28} cluster. But the interaction between the endohedrals and the C_{28} cage depends on the endohedral atoms, and the results of Jackson *et al.*[3] indicate that the bonding of the group-IVA endohedral atoms in the C_{28} fullerene is essentially ionic in character, and the bonding of the group-IVB atom Zr with high angular momentum valence states greatly enhances the energetic stability of the Zr@C_{28} complex.

Compared with the carbon atom, a silicon atom has also four valence electrons. The bonding characteristics of silicon differ in subtle but important ways from those of carbon. Both carbon and silicon atoms have strong ability to form sp^3 hybridization. But the carbon atom, which has a smaller atomic size with valence levels far from the empty d levels, can also form sp and sp^2 hybridizations. Because of the subtle difference in bonding, there are many differences in the properties of bulk phases and surfaces. For instance, graphite is the stablest phase of carbon, but the graphite phase of silicon has never been experimentally observed. Especially in the case of atomic clusters, carbon clusters form a stable chain, ring, or cage structure;[4] however, silicon clusters prefer a multiply coordinated network structure, with a maximum coordination of 6.[5] In the mass spectrum of clusters, some magic numbers for the carbon clusters have been observed at C_{60}, C_{70}, etc. But for the larger silicon clusters with $N \geq 10$, no magic numbers have been observed in experiments.[6] However, the experiments have shown that the shape of clusters changes from prolate-like to more spherical-like in a narrow range at around $N = 27$,[7] and the dissociation energy, which is strongly size dependent in the smaller clusters, becomes a smooth function of N. It is found that the reactivity of several clusters (N=33, 39, 45) is lower by 2–3 orders in magnitude than that of the most stable Si surface.[8] In order to understand why these clusters have lower reactivity, recently many theoretical works have been focused on constructing a structural model of Si_{33} and Si_{45} clusters. Kaxiras proposed two models of Si_{33} and Si_{45} clusters based on the reconstructed 7×7 and 2×1 Si(111) surfaces, respectively;[9] Patterson and Messmer[10] have also proposed a similar structure for the Si_{33} cluster. More recently Rothlisberger, Andreoni, and Parrinello[11] have determined the structure of the Si_{45} cluster by using the Car-Parrinello method[12] through simulated annealing; they obtained a few low-lying isomers of the Si_{45} cluster. The structure of Si_{45} can be divided clearly into two shells of atoms, the outer one being fullerenelike and the inner one consisting of a few atoms saturating the dangling bonds. All these papers have focused on the study of the structure of clusters, while the electronic structure and the lower reactivity are not discussed in detail. In this paper, by using the density-functional theory, we have tried to study the electronic structures of the Si_{28} cluster, the dopant-Si_{28} cluster with a few tetravalent elements, and the *superatom* consisting of a few atoms. We have also calculated the electronic structures of a few Si_{33} models proposed previously,[9,10,13] and tried to understand why the Si_{33} cluster has very low reactivity according to the electronic structure.

All the calculations presented in this paper are based on the density-functional theory with the local density approximation.[14] A linear combination of atomic orbitals is used as the basis to expand wave functions of the cluster. We have also applied the discrete-variational method[15] to calculate the matrix elements in the Kohn-Sham equation. The binding energy of the cluster is calculated by $E_b = E_{\mathrm{ref}} - E_{\mathrm{tot}}$, where E_{tot} is the total energy of the cluster and E_{ref} is the sum of the total energies of individual atoms.

First of all, we have studied the equilibrium structure of the Si_{28} cluster by calculating the binding energies at different values of the parameters R_a, R_h, and R_p as defined in Refs. 2 and 3. The equilibrium bond lengths obtained are R_a=2.43 Å, R_h=2.40 Å, and R_p=2.54 Å; the largest binding energy of the Si_{28} cluster is 3.98 eV/atom. The equilibrium bond lengths of the Si_{28} cluster are expanded a few percent compared with those in the bulk silicon phase. In the C_{28} cluster, we have obtained R_a=1.46 Å, R_h=1.44 Å, and R_p=1.52 Å, which are very close to the values obtained by Jackson *et al.*[3] However, in the C_{28} cluster the bond lengths are reduced a few percent compared with the bond length in the diamond phase. A similar trend of bond length change from bulk to cluster has also been observed in the Si_{60} and C_{60} (Ref. 16) clusters. These different trends in the change of bond lengths between silicon and carbon clusters may come from the subtle difference in their bonding characteristics. From analysis of the Mulliken population, one can see qualitatively the difference of bonding characteristics between the Si_{28} and C_{28} clusters. In the C_{28} cluster, the average number of $2s$ electrons is 1.22, the average number of $2p$ electrons is 2.78, and the atom in the apex position has slightly more s electrons ($\sim$ 1.26). However, in the Si_{28} cluster, the average number of $3s$ electrons is 1.72 which is about 0.5 electrons more than in the C_{28} cluster, and the average number of $2p$ electron is 2.28. So silicon is more atomiclike and carbon has a stronger s-p hybridization.

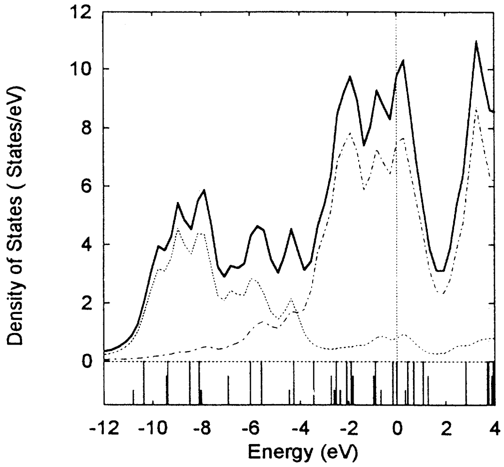

FIG. 1. The density of states and the eigenvalue distribution for the Si_{28} cluster. The dotted line denotes the partial density of states for $3s$ and the dashed line denotes the partial density of stats for $3p$.

In Fig. 1, we show the electronic density of states (DOS) in the Si_{28} cluster obtained from the Lorentz expansion of eigenvalues; the eigenvalues are also shown in the lower panel. From Fig. 1, we can see that the s part of the DOS is mainly at about -9 eV, and the p part is just below the Fermi level and is not completely filled. The resemblance of the DOS of the Si_{28} cluster to the bulk DOS can be observed. The electronic structures near the Fermi level for Si_{28} and C_{28} clusters are similar. Both clusters have a threefold HOMO contributed by p electrons; the distribution of the levels near the Fermi level in the Si_{28} cluster is denser than that in the C_{28} cluster, because of weaker bonding.

Similarly to what has been done in C_{28},[3] and in other clusters,[17] we have tried to dope some tetravalent atoms (C, Si, Ge, Ti, Zr) into the center of the Si_{28} cage to stabilize the dangling bonds in the Si_{28} cluster. In all these doped clusters we have examined the electronic structures with various cluster sizes. We find that the bonding between the fullerene cage and the endohedral atom is ioniclike and there is a small amount of electronic charge transferred from the endohedral atom to the cage. It is known that in the M@C_{28} cluster the HOMO can be completely filled by trapping an endohedral atom with four valence electrons, but in the Si_{28} cluster the HOMO is not yet completely filled. These results mean that those atoms cannot stabilize the dangling bonds in the Si_{28} cluster. This might be due to the size of the fullerene cage of Si_{28} being too big, which makes it impossible for one atom at the center to have strong enough bonding to stabilize the dangling bonds in the fullerene cage.

From the electronic structure calculations, we have found that in the Si_5 cluster, which has full T_d symmetry, there are ten dangling bonds, but those unfilled dangling bonds stay about 0.6 eV above the Fermi level; the HOMO of the Si_5 cluster is a completely filled twofold level and it is contributed by four outer atoms. The level just below the HOMO is threefold and is about 1.8 eV lower than the HOMO, so the Si_5 cluster can be approximately considered as a *superatom* with four valence electrons in a twofold degenerate HOMO and with a large size. Hence we have tried to put the Si_5 cluster into the center of the Si_{28} cage. There are many ways to arrange this Si_5 cluster in the fullerene cage of the Si_{28} cluster. In this paper we choose a particular orientation of the Si_5 cluster to the cage, which leads to the highest T_d symmetry, i.e., the apex atom of the Si_5 cluster is on the line from the adatoms on the cage to the central atom. We expect such a structure to have the largest binding energy. The structure of Si_5@Si_{28} is optimized by keeping T_d symmetry. Finally we find that the adatoms on the cage have a tendency to move outwards, the core Si_5 is compressed about 8%, and the other 24 atoms on the fullerene cage moved a little inward. The total binding energy gain is as large as $\sim$9 eV. As expected, we have found that the electronic shell of the Si_5@Si_{28} cluster is closed. The HOMO is a onefold (aside from the spin) state and is completely filled with two electrons. The eigenvalue distribution, shown in the lower panel of Fig. 2, is similar to that of the C_{28} cluster with endohedral group-IVB atoms.[3] The HOMO is an *s*-*p* hybridized state formed by 3*s* electrons from the endohedral Si_4 (aside from the central atom) and 3*s*3*p* electrons on the fullerene cage. Just 0.1 eV below the HOMO is a threefold level, which has *p*-π bonding character formed mainly by the atoms on the six benzene rings. The LUMO is another *p*-π bonding level, contributed by all the atoms on the fullerene cage.

Now it is known that the interaction between the small endohedral atom and the large fullerene is ioniclike, since the overlap between the endohedral orbits and fullerene orbitals will be small. In fact the size of the endohedral atoms is an important factor in the strength of the interaction between the endohedral atoms and the fullerene. The Zr atom with atomic radius of 1.59 Å is adequate in size to fill the hollow C_{28} cage; hence it can have a large overlap between Zr orbitals and the fullerene orbitals, and at the same time provide four electrons to stabilize the dangling bonds of the cage. But C, Si, and Ge atoms with much smaller atomic radius, as shown by Ref 3, can hardly be able to stabilize the dangling bonds in the fullerene cage of the C_{28} cluster, although all of them have four valence electrons. Of course the size effect is only one of the effects which determine the bonding character between the endohedral atom and the fullerene; the angular momentum of endohedral orbitals[18] and the position of endohedral orbitals relative to the Fermi level of the fullerene are also important in the interaction between the endohedral atom and fullerene cage. In the Si_{28} cluster, the radius is about 1.7 times larger than the radius of the C_{28} cluster; this is too big for one atom to fill the space in the cage and provide four electrons to stabilize the dangling bonds in the cage. Fortunately the Si_5 superatom, which has approximately a radius of 3.44 Å and has four *valence* electrons in the twofold HOMO, can do this. From the Mulliken population analysis, we find that there is no evidence of charge transfer between the fullerene cage and the endohedral Si_5 superatom. This is very similar to what is observed in Ref. 3, where Jackson, Kaxiras, and Pederson have found that the interactions between the fullerene C_{28} cage and the endohedral Zr or Ti atom are strong covalentlike. The covalent interaction between the orbitals of the Si_5 superatom and the Si_{28} cluster opens a relatively large gap between the HOMO and LUMO. In contrast to the case of the Zr@C_{28} cluster, in which Zr orbitals hybridize with the fullerene orbitals about 3 eV below the Fermi level, the orbitals of the Si_5 hybridize strongly with the Si_{28} orbits at the Fermi level. Our calculations show that the Si_4C cluster has an electronic structure similar to that of Si_5 with a slightly smaller size, and it can also stabilize the dangling bonds in the Si_{28} cluster with a large binding energy. In a similar way, Si_{60} can be stabilized by the fullerene C_{60}.[16]

In Fig. 3, we have presented the total charge density for the Si_5@Si_{28} cluster. Covalent bonding can be observed near the core atom and the global features are similar to those in Kaxiras's results.[9] We have also tried to study the compressibility of the clusters. The volume of a cluster is approximately defined by $V = \frac{4\pi}{3}R_0^3$, and the conventional formula for the bulk modulus $B = V\frac{d^2E}{dV^2}$ is used, where E is the total binding energy of the cluster. From this formalism, we obtained the modulus about 6.5×10^{11} N/m^2 and 0.95×10^{11} N/m^2 for the C_{28} and the Si_{28} clusters, respectively. The smaller modulus in the Si_{28} cluster can be attributed to much weaker bonding in Si_{28} than in the C_{28} cluster. The modulus of the Si_5@Si_{28} cluster is about 3.07×10^{11} N/m^2; the significant increase of modulus from Si_{28} to Si_5@Si_{28} suggests that the latter would be much more stable.

Several alternative structure models for Si_{33} cluster have been proposed in recent years. In fact the Si_5@Si_{28} cluster can also be considered as a model for the Si_{33}

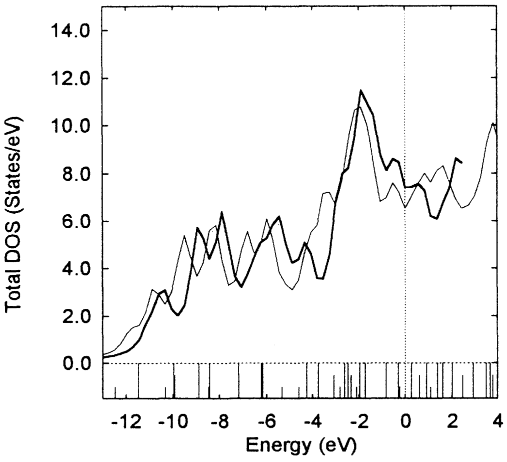

FIG. 2. The density of states for Si_5@Si_{28} (thin line) and Kaxrais's model of Si_{33} cluster (thick line).

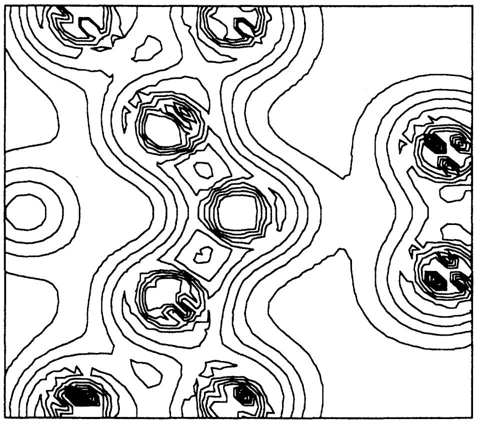

FIG. 3. The charge density of states for the Si_5Si_{28} cluster.

cluster. To study the difference between the present model and the models proposed previously, we have also performed electronic structure and binding energy calculations for the models proposed by Kaxiras,[9] and Pan and Ramakrishna.[13] We found that Pan and Ramakrishna's model has very small binding energy, probably because some atom's neighbors are too close. For Kaxiras's model, we relaxed the structure by maximizing the binding energy with various cluster sizes. We have found a small gap (~ 0.5 eV) between the HOMO and LUMO, and obtained the average equilibrium bond length of 4.657 a.u., which is close to 4.477 a.u. in the pseudopotential calculations.[9] The obtained binding energy of 4.12 eV/atom is in very good agreement with the pseudopotential result 4.16 eV/atom.[19] These results on the bond length and binding energy for Kaxiras's model indicate that the present calculations are consistent with the pseudopotential results. But for the $Si_5@Si_{28}$ cluster the binding energy, which is 4.17 eV/atom, is a little larger than that obtained for Kaxiras's model. The larger binding energy suggests that the present structure of the $Si_5@Si_{28}$ cluster will be energetically more stable. In the $Si_5@Si_{28}$ cluster we have found the average bond length of 4.67 a.u.; the largest bond length is 5.34 a.u., which is related to the adatom, and the smallest bond length 4.14 a.u., which is related to the core atom. In Fig. 2, we have presented the total DOS for the Si_{33} cluster. The thick line shows the results of the $Si_5@Si_{28}$ cluster and the thin line the results for Kaxiras's model; both results are calculated at their equilibrium bond lengths with the largest binding energy. We can see that the global features of the DOS for $Si_5@Si_{28}$ and Kaxiras's model are similar, but they have some differences near the Fermi level, although the Fermi levels are at a small valley. Upon a detailed analysis of the structural properties for the $Si_5@Si_{28}$ cluster and Kaxiras's model of the Si_{33} cluster, we have found both models are essentially the same, except for some differences in bond lengths and bond angles.

As we stated above, there is a HOMO-LUMO gap (~0.6 eV) in the $Si_5@Si_{28}$ cluster. The electronic structure has a closed shell, which makes the $Si_5@Si_{28}$ cluster inert in some chemical reactions. To confirm the existence of a gap unique to the Si_{33} cluster, we have calculated the Si_{32} cluster by moving away the central atom in the $Si_5@Si_{28}$ cluster, and found that the binding energy is almost the same as the binding energy of the $Si_5@Si_{28}$ cluster, but no HOMO-LUMO gap is found at all. These results imply that the $Si_5@Si_{28}$ cluster is not energetically more stable than its neighboring clusters. Since there is a HOMO-LUMO gap, the $Si_5@Si_{28}$ cluster will be more inert in some chemical reactions, which is in agreement with experimental results of Smalley and co-workers.[8]

To see the interaction between the core Si_5 and the fullerene cage Si_{28} in the $Si_5@Si_{28}$ cluster, we have plotted the sum of the DOS's of isolated Si_5 and Si_{28} clusters at their equilibrium bond lengths in Fig. 4; the DOS of the $Si_5@Si_{28}$ cluster is also shown for comparison. We find that the interaction between Si_5 and the Si_{28} cage only changes the DOS significantly near the Fermi level; the value at the Fermi level is decreased. These results strongly suggest that the hybridization between the Si_5 and Si_{28} is only at the Fermi level; the dangling bonds in the Si_{28} cage are saturated by covalent bonding between the core Si_5 and the fullerene cage.

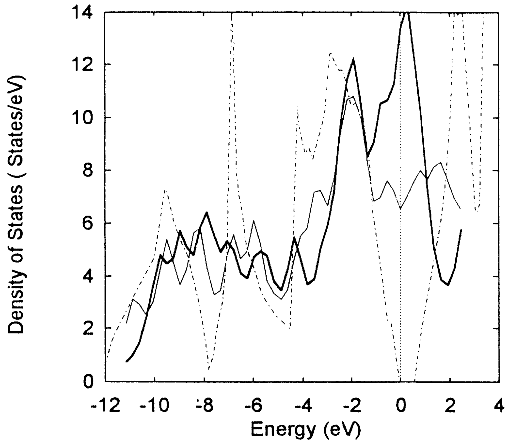

FIG. 4. The sum of DOS's of the superatom Si_5 and Si_{28} clusters (the thick line) and the bulk DOS (Ref. 19) (dotted line); the thin line denotes the DOS of the $Si_5@Si_{28}$ cluster.

There is another important point which is worth noting. Recently optical experiments have shown strong similarities between the optical signals of minute clusters and silicon bulk forms.[20] From the present calculations, we can see that the DOS's for Si_{28} and $Si_5@Si_{28}$ clusters are quite similar, the only difference being near the Fermi level. If we compare the DOS's of Si_{28} and $Si_5@Si_{28}$ with the bulk DOS,[21] which is also shown in Fig. 4 by the dotted line, a strong similarity can be clearly seen. This means that the bulk states about 2 eV below the Fermi level have been almost developed in these clusters. This may be attributed to the fact that in Si_{28} and Si_{33} clusters the atoms have similar hybridization in the bulk, and the dangling bonds on the cluster surface only change the DOS significantly near the Fermi level. So the present calculations have confirmed the strong similarity of the optical spectra in the cluster and the bulk.

In summary, we have studied the electronic structures of the fullerenelike Si_{28} cluster and Si_{28} doped with tetravalent atoms (superatoms). We have found that the electronic structure of the Si_{28} cluster near the Fermi level is similar to the counterpart C_{28} cluster. Because of the large size of the Si_{28} cage, the dangling bonds can be well stabilized by a superatom with four valence electrons. Through electronic structure calculations we have found that the Si_5 cluster with T_d symmetry is adequate to fill the hollow Si_{28} clusters and at the same time provides four electrons to saturate the dangling bonds on the Si_{28} cage. The obtained $Si_5@Si_{28}$ cluster is similar to the model proposed by Kaxiras,[9] but the slightly larger binding energy and lower DOS at the Fermi level suggest that the former is more stable. The covalent bonding between Si_5 and the fullerene cage opens a gap between the HOMO and LUMO. The existence of a HOMO-

LUMO gap unique to the $Si_5@Si_{28}$ cluster is confirmed, which makes it more inert in agreement with experimental data.[8] We have also found that Si_4C is a good candidate to stabilize the Si_{28} cluster and the $Si_4C@Si_{28}$ cluster has a very large binding energy. It is also interesting to find that there is a strong similarity between the DOS's of nanoscale silicon clusters (Si_{28}, $Si_5@Si_{28}$) and the DOS of the bulk. This similarity can be used to explain the experimental observation,[20] which found similar optical spectra in clusters and the bulk diamond phase of silicon.

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