Design of a heterostructure peapod using magic silicon clusters

Q. Sun,1,2 Q. Wang,1,2 Y. Kawazoe,1 and P. Jena2

1Institute for Materials Research, Tohoku University, Sendai 980-77, Japan
2Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284

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We show that the fabrication of one-dimensional Si nanostructures with tailored electronic structure and optical properties can be achieved by encapsulating magic metal-doped Si clusters in carbon nanotubes. This cannot only effectively change the properties of the so-called peapod, but also can keep the intrinsic structure of Si clusters growing in one dimension due to its confinement by the nanotube. Using density functional calculations, the minimum tube size is found to be (9,9) for encapsulating magic WSi12 clusters. Due to its nonspherical shape, the interaction of the magic cluster with the tube is orientation dependent. The larger atomic size of Si also forces the cluster-tube and cluster-cluster distances to be larger than those of a C60@C tube, resulting in a weaker interaction with the tube. The experimental optical absorption spectra are well reproduced for empty carbon nanotubes, which can be greatly changed with WSi12 encapsulation, thus enabling the nanoheteropeapod to have important applications in nanodevices.

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I. INTRODUCTION

Small atomic clusters containing about a dozen atoms constitute subnanoscale systems that exhibit unique size and composition specific properties. It has been suggested1 that assembling these clusters into bulk form, while maintaining their structural integrity, can lead to a novel route for the synthesis of cluster assembled materials with tailored properties. Since the atomic clusters are in general metastable, they tend to coalesce when brought into each other’s vicinity. To minimize or prevent the possibility of this coalescence it is necessary either to start with clusters that are unusually stable (so-called magic clusters) and/or isolate them in matrices. Recent discoveries of carbon fullerenes2 and nanotubes3 have provided a way in which clusters can be assembled. The C60 carbon fullerenes are so stable that they can be assembled withoutpassivation to form a bulk crystal. These fullerenes containing endo- or exodohedral metal atoms can also be assembled to form bulk structure. Individual single-wall carbon nanotubes (SWNT’s), on the other hand, enclose a cylindrical empty space which can be filled with atoms or clusters. One such system consists of C60 clusters embedded inside a nanotube and resembles the structure of a peapod. We call this as homopeapod as both fullerenes and nanotubes consist of carbon atoms. The first homopeapod C60@SWNT’s was observed in material prepared by laser ablation using high-resolution transmission electron microscopy (TEM).4 Thus studies of peapods link the cluster science and nanotube science. The excitement in the research of nanopeapods arises from the fact that one can vary the size and composition of the embedded clusters as well as the size of the nanotube, thus providing flexibility in their synthesis.5–11 Recent measurements of the electronic and structural properties for the homonanopeapods have been performed using electron-energy-loss spectroscopy in transmission mode.12 It has been found that C60 peapods with a SWNT diameter distribution of 1.29–1.45 nm have an average fullerene filling of 60%. However, as for the electronic and optical properties, the overall shape of the response of the SWNT and the peapods is very similar: the difference exists only in the fine structure. This indicates that there are no big changes in the properties of the homopeapod of a C60@C tube compared to the empty C tube. This experiment proposed a new challenge for the studies of the peapods. Can one find a suitable cluster that, when inserted into the nanotube, will change the properties of the nanotube?

In this paper, we investigate the design of a heteropeapod in which non-carbon-based clusters are inserted into a carbon nanotube. In order to form such a peapod, the encapsulating clusters should be stable by themselves to reduce the possibility of their coalescence. We have chosen the WSi12 cluster as dopant due to the following reasons: Silicon plays an integral part in electronic devices. Although Si is tetravalent like C, Si clusters do not form cagelike structures. In a recent experiment, WSi12 has been found to be a magic cluster.13 Theoretical studies show that it is composed of two hexagonal rings with a W atom in its center. This new magic cluster has attracted wide publicity and interest because of the possible applications of silicon cage clusters in nanoscience and nanoelectronic devices.14–17 One very basic question is how to assemble this much promising magic cluster? It is natural to imagine the possibility of constructing a one-dimensional chain of these caged clusters. However, detailed studies18 of their dimer indicate that in free space the two clusters interact and consequently their structures are seriously destroyed. Thus it is difficult to construct a one-dimensional Si nanostructure in free space using this WSi12 tube-shaped unit. We discuss an alternate possibility where the magic WSi12 cluster is inserted into a C nanotube. There are several questions that need to be addressed. (1) What is the minimum tube size to encapsulate this magic cluster? (2) What is the favorable orientation of this nonspherical cluster in the carbon tube? (3) How strong are the interactions between the cluster and tube? (4) How far apart should the two Si clusters be in the tube? (5) Are the properties of this heteropeapod different from that of the empty tube and/or the homopeapod of the C60@C tube? In the following we describe our theoretical procedure and results.
II. COMPUTATIONAL PROCEDURE

We have performed ab initio calculations using an iterative solution of the Kohn-Sham equations, based on the minimization of the norm of the residual vector to each eigenstate and an efficient charge density mixing.\textsuperscript{19,20} For the exchange-correlation functional, gradient-corrected functionals in the form of the generalized gradient approximation\textsuperscript{21} (GGA) have been chosen. In order to optimize geometry effectively, a plane-wave basis set is adopted with the projector-augmented-wave (PAW) method originally developed by Blöchl\textsuperscript{22} and recently adapted by Kresse and Joubert.\textsuperscript{23} The particular advantage of the PAW method over the ultrasoft pseudopotentials is that the pseudization of the augmentation charge can be avoided. The structure optimization is symmetry unrestricted and carried out using conjugate-gradient algorithm. Since experimentally it is not yet possible to synthesize a perfect nanotube of “infinite” length, we have considered a tube with finite length. The dangling bonds are terminated with H atoms, which does not produce any localized states near the tube edges.\textsuperscript{24} We used supercells with 12-Å vacuum spaces along $x$, $y$, and $z$ directions for all the calculated peapods. The Gamma point is used to represent the Brillouin zone due to the large supercell. The cutoff energy is 300 eV, and the convergence criteria for energy and force are $10^{-4}$ eV and 0.002 eV/Å, respectively.

In the present calculations, we used armchair tubes as they are energetically more stable.\textsuperscript{25} To reduce the computa-
tional costs, the supercells are chosen with different sizes for different purposes. To determine the minimum tube size for encapsulating this magic cluster, (6, 6), (7, 7), (8, 8), and (9, 9) tubes with 9.22 Å length are used, which are composed of (84C, 24H), (98C, 28H), (112C, 32H), and (126C, 36H) atoms, respectively. The WSi_{12} cluster is put in the central part of the tubes. Due to the nonspherical shape of WSi_{12}, the interactions are orientation dependent, which makes the calculations more costly as compared with the C_{60} case. We have chosen three typical orientations as shown in Fig. 1: (1) sixfold axis of the cluster aligned parallel to the tube axis (configuration A), (2) twofold axis (through the two opposite squares) of the cluster aligned parallel to the tube axis (configuration B), and (3) twofold axis (through the two opposite edges) of the cluster aligned parallel to the tube axis (configuration C).

The encapsulating energies are defined as the energy cost in inserting a WSi_{12} cluster into the nanotube: namely,

\[ DE = E[\text{WSi}_{12} @ \text{tube}] - E[\text{tube}] - E[\text{WSi}_{12}] \]  \hspace{1cm} (1)

### III. RESULTS AND DISCUSSION

The encapsulating energies in Eq. (1) are shown in Fig. 2 for the four tube sizes. Due to the small size of (6, 6), (7, 7), and (8, 8), the WSi_{12} cluster is seriously distorted and unfavorable energetically. The (9, 9) tube is the smallest one for encapsulating this magic cluster. The encapsulating energies for the (9, 9) tube are \(-0.071, -0.133\), and \(-0.176\) eV for the configurations of A, B, and C, respectively. Therefore, the favorable orientation is configuration C. The shortest distance \(D\) between the cluster and the tube wall is 4.138 Å. This can be understood using the following simple augment: It has been found that the smallest tube to encapsulate C_{60} is (9,9), and the shortest distance \(D_0\) between C_{60} and the tube wall is 3.31 Å.\(^6\) This distance can be approximated by using the sum of atomic radii \(R\) with some scale factor \(K\). In the C_{60} @ C tube case, \(D_0 = K(R_C + R_C)\), while in the Si case, \(D = K(R_{Si} + R_C)\). (Because Si and C have the same valence configurations, the scaling factor \(K\) can be taken to be the same value in the first order approximation.) We know that the Si atom is 1.5 times larger in radius than the C atom, so \(D = 2.5 \times K \times R_C\). This yields \(D/D_0 = 1.25\), which is exactly the ratio of cluster-tube distances between WSi_{12} and C_{60}-doped systems (4.138 to 3.31). The larger distance in the WSi_{12} case results in weaker interactions with the tube as compared with the C_{60} case, where the encapsulating energy is \(-0.51\) eV.\(^6\) Therefore, we can see that size is a main factor to determine whether a cluster can be encapsulated or not.

We have next examined the case where two WSi_{12} clusters are inserted into the nanotube. For this purpose, we used the (9, 9) tube with length of 21.6 Å, which contains 306 C atoms and 36 H atoms. Two clusters are put symmetrically in the tube with orientation C (Fig. 1), and the initial distance is set to be 2.3 Å (the bond length in bulk Si). The structure of the dimer after full optimization is shown in Fig. 3. The equilibrium distance between the two clusters became 3.458 Å, which is larger than 2.5 Å in the C_{60} case.\(^5\) Note that with this distance between the clusters, each WSi_{12} is 4.27 Å from the edge of the tube. This is significantly larger than the dimer bond length, and thus we do not expect properties of the embedded dimer to be affected by edge effects. The structure of the embedded WSi_{12} cluster remains essentially unaltered from that of its gas phase structure. This can be clearly seen from Fig. 4, where we have compared these two structures in free space and in the carbon nanotube. The bond length changes very little bit, and the \(D_{6h}\) symmetry also remains unchanged. This results from a weak interaction between the clusters and between the clusters and tube. This can be demonstrated by examining the charge density profile plotted in Fig. 5. In Fig. 5(a) we have shown the charge density contours corresponding to densities in the range of 0.1–1.0 \(e/Å^3\) along the dimer axis, while that in Fig. 5(b), it corresponds to charge distributions in the plane perpendicular to the dimer axis. We can see that there is very little overlap in density between the clusters or between the cluster and tube wall.

It is very interesting to note that due to the confinement of the tube wall, the two clusters can only move along the tube axis, and the intrinsic structure of the cluster itself can be kept. In this way one-dimensional Si nanostructures can be fabricated, which is totally different from the situations in free space.\(^18\) This can be understood as follows: The larger number of core electrons in Si makes it much more difficult for two Si atoms to form double or triple bonds. Conse-

![FIG. 4. Geometrical structure of WSi_{12} with \(D_{6h}\) symmetry in free space (a) and in the nanotube (b).](image)

![FIG. 5. Charge density contour plots on the planes through the tube axis (a) and perpendicular to the tube axis (b) in the range of 0.1–1.0 \(e/Å^3\) with contour spacing 0.05 \(e/Å^3\).](image)
numerical atomic basis sets augmented with polarization functions (DNP) are used. The exchange correlation is treated using the generalized gradient approximation prescribed by Perdew and Wang and Becke (BPW91). The calculation for optical absorption spectrum is based on two basic approximations:27 (1) The absorption is approximated by the dipole transition, and (2) the excited state is described by the Kohn-Sham orbitals of the ground state, which ignores both relaxation effects and more fundamental problems describing excited states within density functional theory (DFT).

For the empty tube, it has been found recently12 that there are three main absorption peaks at 0.7, 1.3, and 1.8 eV, and the intensity order follows as first peak > third peak > second peak, as shown in Fig. 7(c). These features are well reproduced in our calculations as shown in Fig. 7(a), where the Gaussian expansion with width of 0.1 eV is used. Three peaks are calculated to be at 0.7, 1.2, and 1.7 eV, and the intensity order is also in agreement with experiment.13 This is particularly gratifying since density functional theory even with the GGA does not yield the band gap in quantitative agreement with experiment. One possible reason is that the approximated method used in the DMOL package for the optical absorption may compensate in some way for the deficiency in DFT. We also note that the small differences between the calculated spectra and the experiment could be attributed to the tube size: we used a (9,9) tube with 12.2 Å diameter, while in experiment the tube size ranges from 12.9 to 14.5 Å.12 It is very encouraging to see that when WSi12 is encapsulated, the optical absorptions are changed a lot, the peaks are shifted towards the higher energies (1.0, 1.6, and 2.1 eV), and the intensities are also changed, as indicated in Fig. 7(b). This is due to the different geometry and different bonding features in WSi12 and C60. Therefore, the heteropeapod WSi12@C tube shows quite different electronic and optical properties as compared to those of the homopeapod C60@C tube.

IV. SUMMARY

In this paper, we have studied the structure, stability, electronic, and optical properties of WSi12 clusters encapsulated in carbon nanotubes. Both Si clusters and carbon nanotubes individually are important subjects in chemistry, physics, and nanomaterial science. We have combined these two technologically important systems into one by designing a heteropeapod. This combination provides more variables for nanomaterials design and control, especially since the tube size as well as the composition of encapsulated cluster can be tuned. Such flexibility could allow one to search for some new nanostructure with exotic properties. Following is a summary of our results: (1) The (9, 9) SWNT is the smallest tube for encapsulating the WSi12 cluster. (2) Of the three configurations of the cluster with respect to the tube considered, the energetically favorable structure is configuration C in Fig. 1, in which the twofold axis through the two opposite edges of the WSi12 cluster is parallel to the axis of the carbon nanotube. (3) The equilibrium distance between WSi12 clusters in configuration C of the (9, 9) tube is 3.46 Å, and the
cluster-cluster and cluster-tube interactions are weak. (4) The
electronic density of states at the Fermi energy of this het-

eropeapod is much higher than the empty carbon tube, sug-

gesting that this heteropeapod behaves more metallic. (5) 
The three main absorption peaks in the optical spectrum for 
the empty carbon nanotube are well reproduced in our cal-


culations, while these absorption peaks are shifted to higher 
energies and the intensities are changed when WSi$_{12}$ clusters 
are encapsulated. Since the synthesis of WSi$_{12}$ cluster,$^{13}$ 
many other metal-stabilized Si cage clusters have been found 
recently, such as $M@\text{Si}_{16}$ ($M = \text{Hf and Zr}$),$^{28}$ $M@\text{Si}_{20}$ ($M = \text{Ba, Sr, Ca, Zr, and Pb}$),$^{29}$ and $\text{Cr}@\text{Si}_{12}$. $^{30}$ It will be inter-
esting to see if these clusters can be assembled inside a car-
bon nanotube without compromising the structural integrity 
of the cluster and/or the tube.

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$^5$ S. Berber, Y. K. Kwon, and D. Tomanek, Phys. Rev. Lett. 88, 
185502 (2002).
$^7$ B. Burteaux, A. Claye, B. W. Smith, M. Monthioux, D. E. Luzzi, 
$^9$ J. Sloan, R. E. Dunin-Borkowskib, J. L. Hutchisonb, K. S.
Colemana, V. C. Williansma, J. B. Claridgea, A. P. E. Yorka, C. Xua, 
S. R. Baileya, G. Browna, S. Friedrichtsa, and M. L. H. Green, 
$^{10}$ K. Hirahara, K. Suenaga, S. Bandow, H. Kato, T. Okazaki, H.
17 Slashdot web site: Silicon Buckyballs=Quantum Bits? http://slashdot.org

Molecular Simulations Ins., computer code DMOL3, version 4.2.