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Oscillatory Band Gap Behavior in Small Diameter Si-Clathrate Nanowires

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ABSTRACT

Electronic structure analysis of small cagelike silicon nanowires is carried out and reveals many surprising features. The band gap values for all the nanowires are found to be smaller than their bulk counterparts. The most intriguing aspect appears to be the alternating sequence of direct and indirect band gaps as the diameter changes. This is attributed to the type of surface geometry. We illustrate this with two well-known clathrate forms as well as a new hexagonal clathrate structure with a direct band gap in the optical region.

Silicon nanowires (Si-NWs) have established themselves as one of the most promising candidates in nanotechnology applications. In particular, their useful device applications have been demonstrated in recent works.[1−5]

The device properties, however, could depend sensitively on the precise structural configurations of these nanowires. The structural predictions for small diameters Si-NWs were first made by Menon and Richter[6] and Marsen and Sattler.[7] Subsequently, theoretical structural determinations of the Si-NWs were made by other groups revealing a wide variety of possible structures containing single-crystalline, clathrate-like and polycrystalline forms.[8−16] The single crystalline Si-NWs can be carved out from the stable bulk crystalline forms of Si, the latter including tetrahedral as well as clathrate or cagelike forms.[10] The clathrate forms, while possessing the same coordination as tetrahedral forms, show deviations in bond angles from the ideal tetrahedral case.[17,18]

Although there are many bulk clathrate forms of Si possible, two are known to be the most stable with cohesive energies very close to the bulk tetrahedral Si. These are (i) Si clathrate structure consisting of a face-centered cubic lattice with a 34 atom basis (Si_{34}-Clath) and (ii) a simple cubic lattice with a 46 atom basis (Si_{46}-Clath).[17,18] The bulk Si_{34}-Clath structure can be visualized as three-dimensional (3D) periodic arrangement of Si_{20} and Si_{28} cages with shared faces. Similarly, the bulk Si_{46}-Clath structure can be visualized as 3D periodic arrangement of Si_{24} cages with shared faces interpenetrated by Si_{20} cages. The interstitial spaces are occupied by Si_2 dimers.

Experiments have unequivocally demonstrated the 4-fold coordination of the crystalline bulk in nanowires. The rich morphology of nanowires observed in experiments include even polycrystalline types.[19] In the case of single crystalline Si-NWs, however, the experiments have not conclusively determined their crystalline bulk to be tetrahedral to the exclusion of cagelike. This is because cagelike Si-NWs also contain a 4-fold coordinated core as in tetrahedral cases. In fact, the only distinguishing feature between the two types is the bond angle. Given the fact that the bulk clathrate forms are very close in energy to the tetrahedral form of Si, one could expect that in Si-NWs the corresponding energy difference could be even smaller due to the natural surface reconstruction afforded in cagelike forms.

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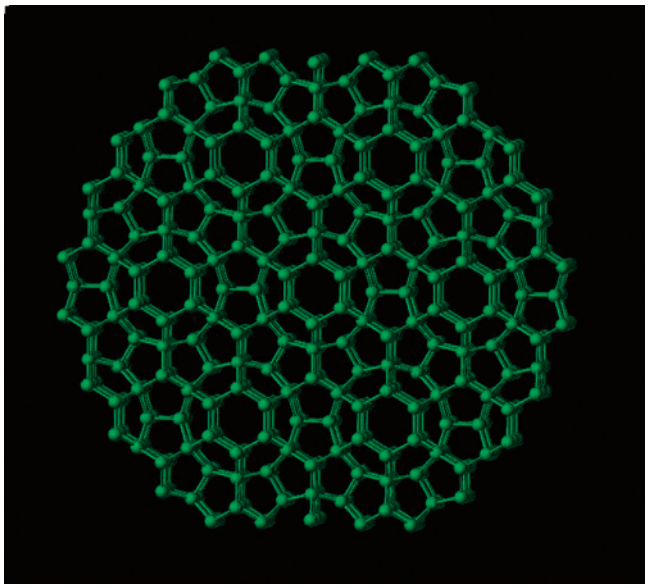

Figure 1. Bulk Si_{40}-Clath structure consisting of 36 atom Si-cages with interstitial regions occupied by Si dimers. The structure was fully optimized without any symmetry constraints using the GTBMD scheme.

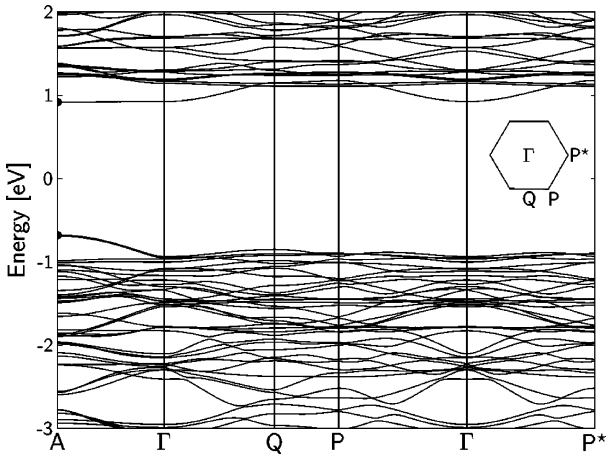

Figure 2. Electronic band structure for the bulk Si_{40}-Clath structure shown in Figure 1. The inset shows the zone scheme used in the plot. The "A"-point is above the plane along the symmetry axis. The gap is direct with a value of 1.56 eV.

The small diameter nanowires having clathrate cores have been determined to be energetically only slightly less stable than the tetrahedral Si-NWs.[13] The cage closure in clathrate Si-NWs provides surface formation with minimal strain in a natural way. This closure, however, depends sensitively on the diameters of the nanowires and could, in turn, affect the electronic properties in an interesting way. While the electronic properties of tetrahedral Si-NWs are rather well studied and understood,[11−15,20] there is very little such study on cagelike nanowires. Very recently, electronic band gap of the smallest diameter clathrate nanowire has been calculated.[21] A detailed electronic structure characterization of low dimensional clathrate forms of Si is, therefore, necessary and timely. In particular, the quantum confinement effects, crucial for their device applications, may also exhibit intriguing features.

In this letter, we investigate the electronic structure effects of cagelike Si-NWs for novel electronic phenomena using theoretical methods. The clathrate structures from which the Si-NWs are carved out consisted of Si_{34}-Clath and Si_{46}-Clath as well as a new stable clathrate form of bulk Si to be described below. All the structures considered in this work were fully relaxed without any symmetry constraints using the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy.[22] This scheme has been successfully used in obtaining geometries and vibrational properties of various bulk phases of Si as well as Si clusters of arbitrary sizes.[22]

The new clathrate form of bulk Si proposed as the underlying crystalline core for stable nanowires is shown in Figure 1. It contains 40 atoms in the unit cell and consists of 36 atom Si-cages with interstitial regions occupied by Si dimers. All the Si atoms are 4-fold coordinated (all sp^3) and the structure has hexagonal (D_{6h}) symmetry. We denote it as Si_{40}-Clath. This new clathrate form has been found to be stable with GTBMD as well as the ab initio method. The ab initio calculations were carried out using the density functional theory (DFT) method as implemented in Quantum-ESPRESSO package.[23] In these calculations, we used the exchange-correlation functional introduced by Perdew, Burke, and Ernzerhof[24] and ultrasoft pseudopotentials. The relative cohesive energies (relative to bulk tetrahedral) for bulk forms of Si_{34}-Clath, Si_{46}-Clath, and Si_{40}-Clath obtained using the GTBMD scheme are, respectively, 0.02, 0.03, and 0.28 eV. The corresponding ab initio values are 0.05, 0.06, and 0.25 eV, respectively. The electronic band structure for the bulk Si_{40}-Clath is shown in Figure 2. The zone scheme is shown in the inset with the "A"-point along the symmetry axis above the plane. The band structure was obtained using a five orbital sp^3s^* tight-binding Hamiltonian,[25] which ensures an accurate conduction band edge. This model accurately reproduces the band gaps in bulk Si.[25] The exciton energies for Si nanocrystals obtained using this model is in quantitative agreement with photoluminescence data.[26] Furthermore, the model also shows agreement with the correlation between visible and infrared photoluminescence for porous Si.[27] The bulk Si_{34}-Clath structure is found to be a direct band gap material with a gap value of 2.47 eV, while the Si_{46}-Clath structure is found to be an indirect band gap material with a gap value of 2.43 eV. These bulk clathrate forms have also been studied using the DFT within the local density approximation (LDA).[28] The bulk Si_{34}-Clath structure is found to be a direct band gap material, while the band gap for the bulk Si_{46}-Clath is found to be indirect using LDA, in complete agreement with the scheme of Vogl et al.[25] The corresponding LDA gap values are, respectively, 1.20 and 1.11 eV. It should be noted, however, that the LDA gap value for bulk diamond Si is $\approx$2 times smaller than the experimental value. The band gap values obtained using the scheme of Vogl et al. is therefore in very good quantitative agreement as well with the LDA values when a correction factor of 2 is applied to the LDA values. The gap value obtained for the bulk Si_{40}-Clath using the scheme of Vogl et al. is 1.56

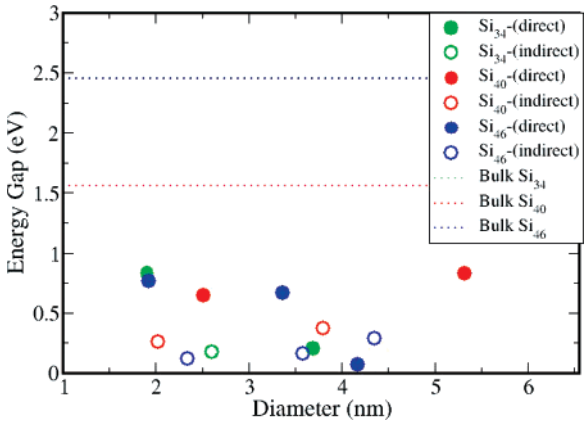

Figure 3. Plot showing the dependence of the electronic gap values on the diameter for cagelike Si-NWs. The filled circles indicate direct band gaps, while the unfilled circles indicate indirect gaps. The horizontal lines denote the bulk band gap values. Note that bulk gap values for Si_{34}-Clath and Si_{46}-Clath are almost identical and therefore overlap on the plot.

eV, which is just inside the visible spectrum (1.5−2.5 eV) and direct.

The nanowires considered in this work contain 4-fold coordinated (sp^3) inner crystalline cores consisting of Si_{34}-Clath, Si_{46}-Clath, and Si_{40}-Clath forms. The surface Si atoms all have 3-fold coordination (sp^2). All the Si-NWs were taken to be of infinite length and modeled by large supercells containing ≈900 atoms. The diameters of these Si-NWs were in the range 1−5 nm. The structural relaxations were performed using the GTBMD scheme incorporating a constant pressure ("movable wall") ensemble.[29] This allows for a simultaneous relaxation of lattice and basis degrees of freedom. A uniform grid consisting of 126 *k*-points were used in the calculation of forces. All nanowires had crystalline cores consisting of 4-fold coordinated atoms and 3-fold coordinated surface atoms. Surface reconstructions for all structures were obtained carefully.

As stated before, due to the small diameters the surface reconstruction of the Si-NWs will be affected not only by the surface effects but also by the curvature effects.[30] The electronic structure in turn will sensitively depend on both these two factors. We performed the detailed electronic band structure analysis of all these fully relaxed Si-NWs using the scheme in ref 25. The gap values as a function of nanowire diameter are plotted in Figure 3.[31] The same figure also contains the gap values for their bulk counterparts. The gap behavior seen in Figure 3 reveals many interesting points. A striking feature is that for all cagelike or clathrate Si-NWs, the gap values lie below their respective bulk gap values. Furthermore, the gap values of clathrate Si-NWs exhibit large fluctuations with even semimetallic behavior for some diameters. The most intriguing aspect, however, appears to be the oscillation between direct and indirect band gaps as the diameter changes.

It should be noted that, while all the Si-NWs considered in this work have 3-fold coordinated surface atoms surrounding 4-fold coordinated core atoms, a unique feature of the cagelike nanowires is that the surface geometry itself is

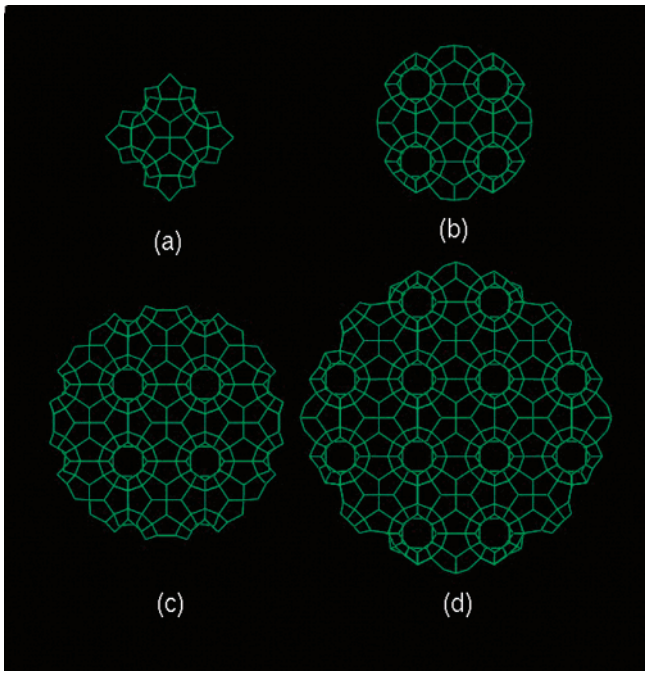

Figure 4. Cross sections of some of the Si_{46}-Clath nanowires considered in the present work. All the nanowires are fully relaxed. The surface atoms are 3-fold coordinated, while the interior atoms are 4-fold coordinated. Cross sections in (a) and (c) show incomplete cage closure for the outer atoms, while those in (b) and (d) show complete cage closure. The incomplete and complete cage closure is shown to lead to direct and indirect band gaps, respectively.

diameter dependent. It is herein that we must look for the origin of the oscillations in the nature of the electronic band gap.

In Figure 4, we show the cross sections of some of the Si_{46}-Clath nanowires considered in the present work. Recall that the bulk form of this clathrate consists of Si_{24} cages with shared faces interpenetrated by Si_{20} cages. The cross section of a small diameter nanowire cut from the bulk is shown in Figure 4a after full relaxation. As can be seen in this figure, the Si_{24} cages in the central region are interpenetrated and surrounded by "incomplete" Si_{20} cages. The relaxation results in 3-fold coordination for all surface atoms. The surface is highly strained not only due to the large curvature but also due to the lack of cage completion on the surface. The band gap for this nanowire is direct. For a slightly larger diameter, we obtain the cross section in Figure 4b where the Si_{20} cages are now "complete" on the outside reducing the surface strain. The structure shown is fully relaxed, and all the surface atoms are 3-fold coordinated. The band gap for this nanowire is indirect. Another cross section for larger diameter is shown in Figure 4c where the outer atoms form incomplete cage structures and possess a direct band gap. Completion of outermost cages gives rise to the cross section seen in Figure 4d, which has an indirect band gap.

Similar results are obtained for Si_{34}-Clath nanowires as illustrated in the cross sections shown in Figure 5. The smaller diameter nanowire shown in Figure 5a contains incomplete cage formation for outermost Si atoms. Once again, the surface atoms are all 3-fold coordinated. The band

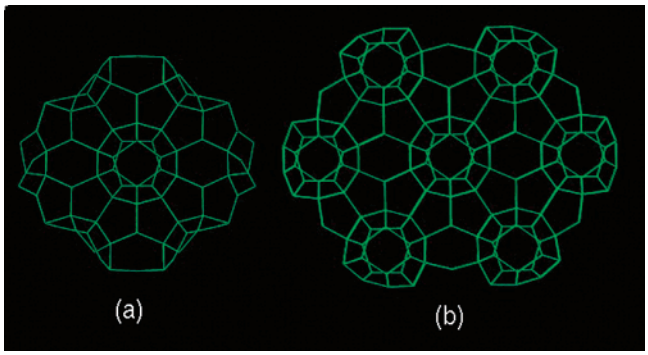

Figure 5. Cross sections for the Si_{34}-Clath nanowires showing (a) incomplete and (b) complete cage closure. The former has direct band gap while the latter has indirect band gap.

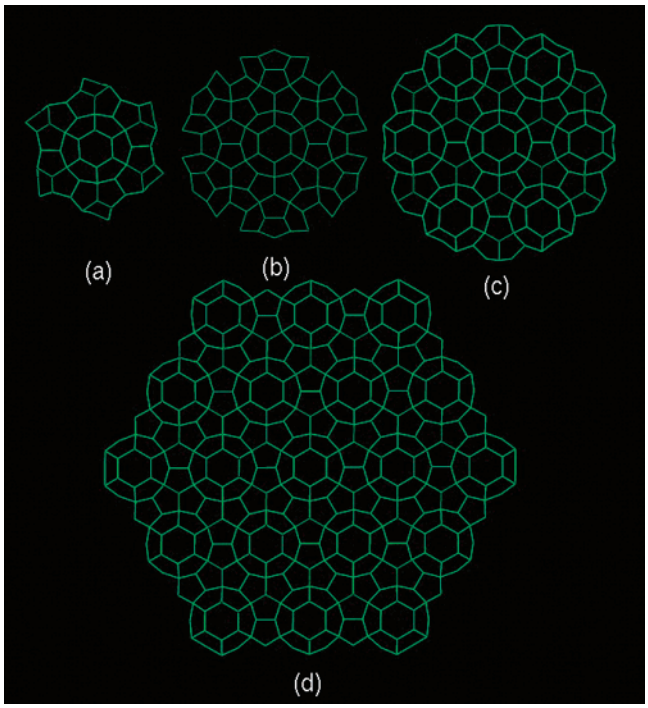

Figure 6. Cross sections for the Si_{40}-Clath nanowires showing (a) complete, (b) incomplete, (c) complete, and (d) complete cage closure. Band gaps are direct for (b) and (d) and indirect for (a) and (c).

gap for this nanowire is direct. Completion of the cage formation on the outer boundaries results in the larger diameter cross section shown in Figure 5b with an indirect band gap.

Cross sections for Si_{40}-Clath nanowires are shown in Figure 6 The smallest diameter nanowire shown in Figure 6a has completed cages on the periphery and has an indirect band gap. Increasing the diameter results in the cross section with incomplete outer cages shown in Figure 6b with a direct band gap. This is followed by the indirect band gap nanowire structure shown in Figure 6c containing completed cages on the outside. The largest diameter Si_{40}-Clath nanowire considered in the present work (Figure 6d), even though containing completed cages on the outside, possesses a direct band gap. This seems to contradict the trend observed so far showing the relationship between the nature of the band gap and the cage closure. It should be noted, however, that the bulk form of this clathrate contains direct band gap. The diameter of this nanowire is sufficiently large enough (5.3 nm) to reach bulk behavior in this case.

Our results, thus, indicate a direct correlation between the nature of the band gap and the details of the surface geometry for small diameter cagelike or clathrate nanowires. When the nanowire diameters are such that the surface atoms can form full cages, the electronic band gaps are found to be indirect. In other cases, they are direct. This remarkable property could have important technological implications. That is, by simply changing the diameter of the nanowire one could change the electronic properties. This is especially useful in optoelectronic applications when controlled emission is desired.

The semimetallic behavior of the small diameter cagelike Si-NWs may have useful applications in molecular electronic circuitry. The electronic properties of these nanowires can be altered by inserting metal atoms into the hollow cage interiors. This allows for band gap engineering, crucial for optoelectronic applications. We would like to note, however, that the successful use of the Si−NW geometry in molecular electronic applications relies on the ability to fine tune their diameter and shape, which is obviously a technological challenge.

In summary, we have presented results for electronic properties of cagelike Si nanowires. The unusual electronic properties exhibited by them could prove useful in nanotechnology applications. Furthermore, we have also proposed a new hexagonal clathrate bulk structure with direct band gap in the optical region.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) A recent work using ab initio density functional theory has reported a band gap value in the range 0.4−0.44 eV for the smallest diameter clathrate nanowires (see arXiv:cond-mat/0611128 v1 5 Nov 2006). Because DFT is well known to underestimate the band gap for Si by ≈2 times, the true value is expected to be −0.8−0.9 eV, in very good agreement with the present calculations.

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