Design of a very thin direct-band-gap semiconductor nanotube of germanium with metal encapsulation

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(Received 17 September 2004; published 16 February 2005)

Using *ab initio* total energy calculations we design a very thin semiconducting nanotube of germanium with a direct band gap by encapsulation of Mo or W. This finding is an outcome of studies of assemblies of $Ge_{18}Nb_2$ clusters into nanotubes. The infinite Nb-doped nanotube is metallic. However, the electronic structure has a significant gap above the Fermi level. When Nb is replaced by a $Z+1$ element such as Mo or W, it leads to the formation of a semiconducting nanotube. The atomic structure of these nanotubes is based on a novel alternate prism and antiprism stacking of hexagonal rings of germanium. Such an arrangement is optimal for $Ge_{18}M_2$ (M=Nb, Mo, and W) clusters that serve as the building blocks of nanotubes. These results demonstrate that by just changing the M atom in the growth process, we can form metallic, semiconducting, and n or p types of nanotubes, opening new possibilities for nanoscale devices.

DOI: 10.1103/PhysRevB.71.075312 PACS number(s): 73.22.−f, 61.46.+w, 31.15.Ar

I. INTRODUCTION

Silicon and germanium are the most important elements for the current microelectronics industry and much research is being carried out on their nanostructures to find suitable candidates for future miniature electronic devices through a bottom-up approach. Nanowires and nanoparticles of silicon and germanium could be possible building blocks.[1] These also have interesting photoluminescence properties[2,3] due to quantum confinement in contrast to bulk Si, which is a poor emitter of light. This is attractive for integration of optics with electronics, for sensors, tagging, and other biological applications. However, often there is a distribution of size, and as the properties are size dependent, this could be a problem for their usage. H-terminated Si nanowires of small diameters of 1.3–7 nm have been grown[4] with varying energy gap. However, subnanometer diameter nanowires of elemental Si are unstable[5] while the large-diameter nanowires may have reconstructed surfaces that are yet to be well understood. Nanowires of $ErSi_2$ with less than 1 nm height on a Si(100) surface have also been grown[6]. These experimental results demonstrate that it has become possible to develop nanostructures of Si in the size range of 1 nm.

A very interesting nanoform is the tubular structure that has intrigued researchers who tried nanotubes of silicon and other semiconducting elements similar to carbon.[7] Recently using the first-principles materials design approach very-small-diameter nanotubes of silicon were stabilized by Be encapsulation.[5] This finding has prompted experimental work and recently self-organized assemblies of $Si_{24}Be_2$ finite nanotubes have been obtained[8] on a large area of Si(111) surface. These results support the theoretical predictions and suggest a way to form large arrays of such very small systems using well-established methods. Subsequently magnetic nanotubes of Si (Refs. 9–11) and Ge (Refs. 11 and 12) have also been predicted by encapsulation of transition metal (M) atoms. The infinite nanotubes are metallic and have interesting magnetic properties.[9,12] However, for device development it is important to find nanotubes that are semiconducting. Here we demonstrate that a semiconducting nanotube of Ge can be stabilized by encapsulation of Mo or W.

In metal-encapsulated nanotubes of Si and Ge, either $Si_{12}M$ clusters[5,9] with hexagonal prism structure or $Ge_{12}M$ clusters[12] with hexagonal antiprism structure are assembled often with an M atom in between. Hexagonal prism structures of $Si_{12}M$ and $Si_{18}M_2$ clusters are found to be magic[13,14] for M=Cr and W. However, assembling a nanotube from these clusters is unfavorable due to distortions[14] and strong dimerization of M atoms. Here we consider germanium nanotubes as these can be more versatile with possibilities of doping of a larger variety of M atoms as compared to silicon because the Ge-Ge bond length is closer to the bond lengths found in several metals and explore the possibility of semiconducting nanotubes from the point of view of device development. Our results show that by choosing the M atom suitably, we can design metallic as well as semiconducting nanotubes.

II. METHOD

We use an ultrasoft pseudopotential plane-wave method[15–17] within the density functional theory and spin-polarized generalized gradient approximation[18] (GGA) for the exchange-correlation energy. Γ-point sampling is used for the Brillouin zone integrations in the case of clusters and finite nanotubes while 15 k-point sampling along the nanotube axis, for the optimization of the infinite nanotubes. Optimizations are performed without symmetry constraints until the forces are converged to 0.004 eV/Å. In most cases the convergence is even better than this. The band structures of the infinite nanotubes are calculated by considering 260 k points in the half Brillouin zone. In general clusters and finite nanotubes with an odd number of electrons have $1\mu_B$ magnetic moment with the spin polarization distributed over the

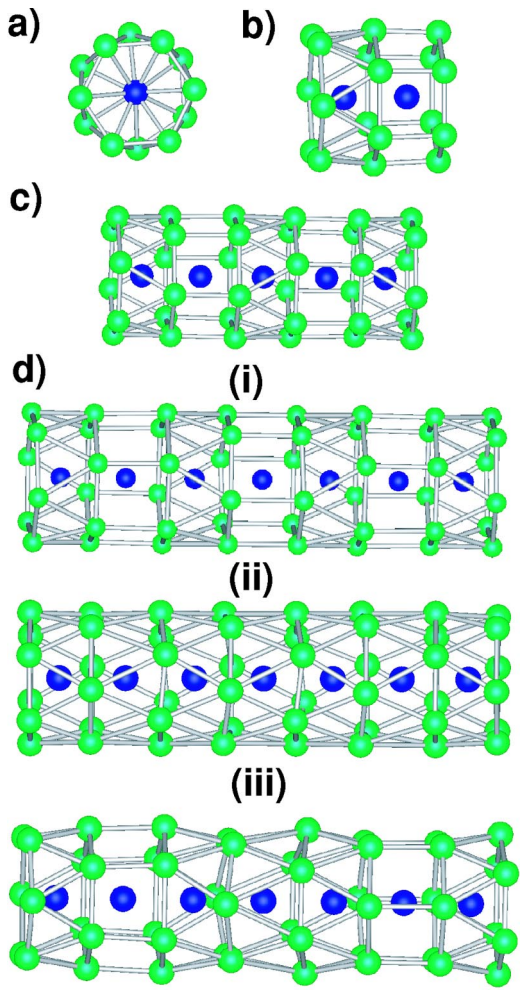

FIG. 1. (Color online) Optimized structures of clusters and finite nanotubes (a) $Ge_{12}Nb$, (b) $Ge_{18}Nb_2$, (c) $Ge_{36}Nb_5$, and (d) $Ge_{48}Nb_7$ with three isomers (i) antiprism-prism, (ii) antiprism-antiprism, and (iii) with terminal $Ge_{12}Nb$ clusters stacked in the prism while the rest stacked in antiprism structures.

whole structure. All other structures are nonmagnetic.

III. RESULTS AND DISCUSSIONS

Initially we considered $Ge_{12}Nb$ clusters[19] for assembling nanotubes and optimized icosahedron, decahedron, hexagonal prism, and antiprism structures. The lowest-energy isomer is a hexagonal antiprism (Fig. 1) with Ge-Ge bond lengths (BL's) of 2.60 (2.70)Å within a hexagon (interhexagon) and 2.85 Å for Ge-Nb. The highest-occupied–lowest-unoccupied molecular orbital (HOMO-LUMO) gap in this isomer is small (0.17 eV) and the binding energy (BE) is 3.54 eV/atom. For the growth of nanotubes we further studied the stability of $Ge_{18}M_2$ (M=Nb,Mo,W) clusters. As compared to a biprism structure[14] for $Si_{18}W_2$, we find that an antiprism-prism structure [Fig. 1(b)] is 0.44, 0.55, and 0.59 eV lower in energy for $Ge_{18}Nb_2$, $Ge_{18}Mo_2$, and $Ge_{18}W_2$, respectively. This difference arises due to the bigger size of Ge atoms. A prism-prism structure lies second in energy with a longer *M-M* bond while an antiprism-antiprism structure lies higher in energy (0.64, 0.71, and 0.72 eV for Nb, Mo, and W, respectively) with a shorter *M-M* bond. Both of these structures have distortions in Ge-Ge bond lengths. The prism-antiprism structure optimizes *M-M* as well as Ge-Ge and Ge-*M* interactions with the *M-M* bond length of 2.58 and 2.49 Å and the HOMO-LUMO gap of 0.33 and 1.03 eV for Nb and W, respectively. The latter is higher compared with a $Ge_{12}Nb$ cluster. Therefore we can consider these clusters as a unit for assembling nanotubes.

TABLE I. The binding energy (BE) in eV/atom and HOMO-LUMO gaps (eV) for the Nb- and W-doped finite and infinite nanotubes of Ge.

System	BE M=Nb	Gap M=Nb	BE M=W	Gap M=W
$Ge_{18}M_2$	3.70	0.33	3.76	1.03
$Ge_{36}M_5$	3.88	0.10	3.92	1.01
$Ge_{48}M_7$	3.91	0.16	3.96	0.85
$Ge_{24}M_4$(infinite)	4.00	0.00	4.04	0.50

When two clusters of $Ge_{18}Nb_2$ are assembled together with a Nb atom in between ($Ge_{36}Nb_5$), then as shown in Fig. 1(c), the antiprism-prism structure remains stable. It has sixfold symmetry, a HOMO-LUMO gap of 0.10 eV, and an increased BE (Table I). The Ge-Ge BL's within a hexagon remain the same but the value changes slightly (2.63, 2.62, 2.67, 2.67, 2.62, and 2.63 Å) in going from one outer hexagon to the other and the corresponding Nb-Nb BL's are 2.52, 2.72, 2.72, and 2.52 Å. The outer clusters have shorter bond lengths due to the lower coordination of atoms. We also checked an antiprism-antiprism stacking of hexagons.[12] However, it transforms to the antiprism-prism form, giving further confidence in this structure. It also shows that this preference does not change with an increase in the length of the nanotube. Further addition of a $Ge_{12}Nb$ cluster keeps this structure very symmetric [Fig. 1(d)(i)]. We also considered two more structures for this nanotube with the stoichiometry of $Ge_{48}Nb_7$. The one [Fig. 1(d)(ii)] with the antiprism-antiprism stacking[12] of $Ge_{12}Nb$ clusters and Nb atoms in between is now stable but has some distortions. It lies 0.66 eV higher in energy as compared to the one in Fig. 1(d)(i). A slightly different stacking [Fig. 1(d)(iii)] in which the central four hexagons are in the antiprism structure lies 0.05 eV higher in energy. Therefore, the rotation of a hexagon costs little energy as the length of the nanotube increases. However, for an infinite nanotube the antiprism-prism staking has the lowest energy. The BE of the nanotube increases with an increasing number of clusters.[20] This also implies that the nanotubes can be formed with a large aspect ratio. The HOMO-LUMO gap in finite nanotubes is small (Table I) and the infinite nanotubes become metallic.

The stability of a doped infinite nanotube is studied with a unit cell of $Ge_{24}Nb_4$ in antiprism-prism and antiprism-antiprism stackings. The nanotubes are optimized with respect to the cell size along the axis, allowing the atoms to relax freely. Like the finite nanotubes, in the infinite nanotube also, the antiprism-prism geometry is energetically the most favored [Fig. 2(a)] and the antiprism-antiprism structure lies 0.11 eV/cell higher in energy. The magnetic mo-

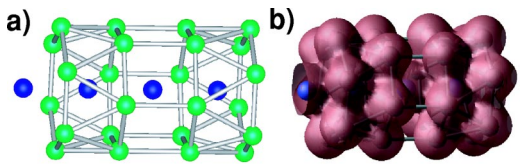

FIG. 2. (Color online) (a) Optimized unit cell of an infinite nanotube of $Ge_{24}Nb_4$. W-doped nanotube is similar. (b) An isosurface of the total charge density of the $Ge_{24}Nb_4$ nanotube.

ments in these nanotubes are completely quenched. All the different initial guesses for the magnetic moments get converged to the same nonmagnetic state. The Nb-Nb BL's are 2.72 Å and the intrahexagon Ge-Ge BL's (the same in all the hexagonal rings) are 2.62, 2.63, and 2.64 Å (two bonds in each case). This reduces the sixfold rotational symmetry to twofold. Interhexagon Ge-Ge BL's are 2.82 Å for the antiprism stacking and 2.96, 2.98, and 3.00 Å (two bonds in each case) for the prism stacking. This difference in the Ge-Ge bond lengths for the prism and antiprism units has important bearing on the bonding in the nanotube.

The band structure of this nanotube is shown in Fig. 3. The Fermi level lies in a band and therefore this nanotube is metallic similar to the previously reported[9,12] cases of *M*-doped nanotubes of Si and Ge. However, the reduced symmetry leads to the splitting of the degenerate bands. There is a gap just above the Fermi level, indicating the possibility of the formation of a semiconducting nanotube by filling of these states. For this we replaced all Nb atoms with Mo, which lies right next to Nb in the periodic table. The extra electron plays the role of filling up the empty states near the Fermi level and the nanotube becomes sixfold symmetric. Ge-Ge intrahexagon and interhexagon (antiprism and prism structures) and Mo-Mo BL's are 2.58 (2.77 and 2.98) and 2.70 Å, respectively, and semiconducting with a gap of 0.38 eV. Similar results are also obtained for W-doped nanotubes. The reduced Ge-Ge bond lengths with Mo or W doping are also good for the stability of the nanotubes. Therefore, unlike silicon, doping of Mo or W in germanium leads to the formation of a semiconducting nanotube with a direct band gap. The band gap is higher for W doping[23] with the GGA value of 0.5 eV. This is because the $Ge_{18}Mo_2$ and $Ge_{36}Mo_5$ finite nanotubes also have smaller HOMO-LUMO gaps of 0.96 and 0.75 eV as compared to 1.03 and 1.01 eV,

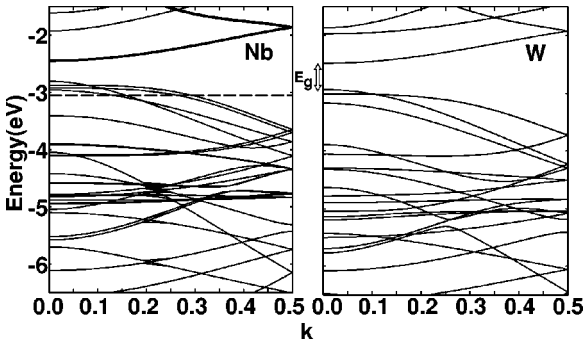

FIG. 3. Band structures of Nb- and W-doped infinite nanotubes. Dashed line shows the Fermi energy. E_g is the band gap for the W-doped semiconducting nanotube.

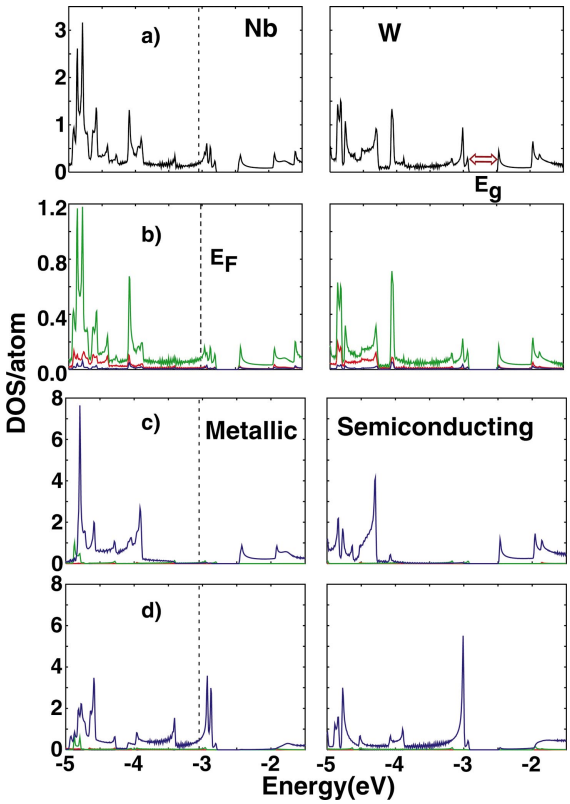

FIG. 4. (Color) Total and partial densities of states (DOS) of Nb- and W-doped infinite nanotubes obtained by using Gaussian broadening with width of 0.01 eV. (a) Total DOS, (b) partial DOS of Ge, (c) partial DOS for Nb atom in the antiprism environment, and (d) partial DOS for the Nb atom in the prism environment of Ge atoms. Red, green, and blue lines represent the contributions from *s*, *p*, and *d* orbitals. Dashed line shows the Fermi energy (E_F), while for the W-doped semiconducting nanotube the band gap is indicated by an arrow.

respectively for W doping. The true value of the gap in the infinite nanotube could be expected to be around 1 eV which is close to the value for bulk silicon. The BE for the W doped infinite nanotube is 4.04 eV/atom as compared to 3.81 eV/atom for Mo doping. So W doping is better from energetic point of view as well. This finding is important as it can open a way for applications in devices.

The partial densities of states of the $Ge_{24}M_4$ infinite nanotubes (Fig. 4) show that the two nonequivalent *M* atoms, one lying in the antiprism environment and the other, in the prism environment, have quite different local densities of states. The states near the Fermi energy arise mostly from the Ge 4*p* orbitals and the *d* orbitals of the *M* atom that lies in the prism environment [Fig. 4(d)]. The contribution to the states near the Fermi energy from the *d* orbitals of the *M* atom lying in the antiprism environment is negligibly small [Fig. 4(c)]. In the antiprism geometry Ge-*M* bond lengths are shorter and give rise to stronger hybridization of the *M d* and Ge 4*p* states which pushes the *d* states to higher binding energies. However, in the prism geometry Ge-Ge and Ge-M interactions are weaker. This is also supported from the charge density [Fig. 2(b)]. An isosurface of the total charge density shows [Fig. 2(b)] that the charge density is significantly

lower in the bonds connecting the two antiprism $Ge_{12}Nb$ clusters. Also there is high charge density around the chain of *M* atoms. This reflects the strong interaction between the Ge nanotube and the *M* atoms. We further analyzed it by subtracting the charge densities of Ge_{24} and M_4 (M=Nb or W) at their respective positions from that of $Ge_{24}M_4$. There is a depletion of charge between the *M* atoms and from the Ge nanotube while charge is accumulated between the *M* atoms and the nanotube. This is more significant in the antiprism cage environment of the *M* atom as it was also concluded from the density of states. The difference in the charge distribution for Nb or W doping is quite small. The empty states around the *M* atom with prismenvironment get filled when all Nb atoms are replaced with W, leading to the semiconducting behavior of the nanotube. The density of states also shows the van Hove singularities expected for such quasi-1D structures.

IV. SUMMARY

In summary, we have examined the stability of finite and infinite Ge nanotubes doped with Nb. The growth behavior of these nanotubes is found to be different from the earlier studies on silicon and germanium nanotubes but the infinite nanotubes are again metallic. However, these results have led to the most important finding for the first time that Mo or W doped nanotubes are semiconducting. These are the thinnest metal stabilized nanotubes possible, knowing that elemental structures of this dimension are unstable. Furthermore, the W-doped nanotubes have a 0.5 eV direct band gap within the GGA. This is comparable to bulk silicon and therefore it opens up new possibilities for device development at the smallest scale using conventional semiconducting elements. The electronic structure of these nanotubes shows a rigid-band-like behavior and one would be able to obtain *p*- or *n*-type behavior by substituting $(Z-1)$ or $(Z+1)$ *M* atoms, respectively. A significant advantage here would be that by changing the *M* atom in the growth process it can be possible to grow metallic or semiconducting or *p*- and *n*-doped nanotubes making novel possibilities for miniature devices. With the advances in techniques such as vapor deposition to grow one-dimentional structures of 1 nm dimensions, we hope that realization of such nanostructures would be possible and that our results will further stimulate research in this direction.

ACKNOWLEDGMENTS

We thankfully acknowledge the support of the staff of the Center for Computational Material Science, IMR, Tohoku University for the use of SR8000/H64 supercomputer facilities. A.K.S. is also thankful for the support of MEXT. V.K. gratefully acknowledges the hospitality at IMR and LAM of IMR Tohoku University.

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[19] V doped nanotubes of Ge have also been studied recently and similar results have been obtained. For details see A. K. Singh, V. Kumar, and Y. Kawazoe, Eur. Phys. J. D (to be published). Similar results could be expected for Ta doping.
[20] We have also studied the formation energies of small nanotubes. This is defined as the difference in energies of the metal doped finite nanotube A_nB_m and the sum of the energies of the ground states of the elemental clusters A_n and B_m. For $Ge_{18}Nb_2$ the doping energy is maximum (5.20 eV per Nb atom). However, it decreases with an increase in the length of the nanotubes ($\approx$5.09 for $Ge_{24}Nb_3$ and $\approx$4.30 eV per Nb atom for $Ge_{36}Nb_5$). This is very much expected as the ground state energies of Nb clusters (Ref. 21) increase much more rapidly compared with the energies of Ge clusters (Ref. 22) as well as the nanotubes with the increase in the number of atoms. Nanotubes are metastable structures and in the infinite nanotube limit the cohesive energy is expected to be lower than the corresponding bulk material as it is the case for carbon nanotube and the bulk graphite. However, the important point is the nucleation of these structures and appropriate conditions for their growth. In the case of metal doped nanotubes, the small nanotubes or appropriate clusters are

important as these could act as the nucleation centers for larger nanotubes.

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[22] The energy of Ge clusters in this size range changes slowly [see J. Wang, G. Wang, and J. Zhao, Phys. Rev. B **64**, 205411 (2001)]. We calculate the binding energy of Ge_{14} to be 3.28 eV/atom and take the representative values of 3.30 and 3.33 eV/atom for Ge_{14} and Ge_{36}.

[23] Calculations of finite nanotubes $Ge_{36}W_5$ and $Ge_{48}W_7$ show antiprism-prism stacking to be most preferred similar to the case of Nb. In these nanotubes the Ge-Ge BL's in each hexagonal ring are equal, leading to the sixfold-symmetric nanotubes. The HOMO-LUMO gaps are much larger as compared to Nb doping. This is due to the stronger hybridization of the W 5*d* states with the valence states of Ge. The states near the highest occupied level are significantly shifted downwards in W-doped nanotubes while for the other states this shift is small as compared to the case of Nb doping. This results in a higher BE of the W-doped nanotubes (Table I).