Eur. Phys. J. D **34**, 295–298 (2005)
DOI: 10.1140/epjd/e2005-00162-1

THE EUROPEAN PHYSICAL JOURNAL D

Metal encapsulated nanotubes of germanium with metal dependent electronic properties

A. Kumar Singh[1,a], V. Kumar[1,2], and Y. Kawazoe[1]

[1] Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577, Japan
[2] Dr. Vijay Kumar Foundation, 45 Bazaar Street, K. K. Nagar (West), Chennai 600 078, India

Received 6 September 2004
Published online 13 July 2005 –

Abstract. Using ab initio total energy calculations we demonstrate that the nanotubes of germanium with atomic structure based on an alternate prism and antiprism stacking of hexagonal rings, can be stabilized by metal encapsulation. The V or Nb doped infinite nanotube is metallic. However, Mo doping leads to the formation of a metal encapsulated direct band gap semiconducting nanotube of germanium. These nanotubes with metal dependent electronic properties could prove to be vital for the development of future nanotechnologies.

PACS. 73.22.-f Electronic structure of nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals – 31.15.Ar Ab initio calculations

1 Introduction

Currently carbon nanotubes are considered to be promising candidates for the future miniature electronic devices. However, there are problems in controlling the electronic properties of carbon nanotubes and most importantly it would require new developments for their usage in microelectronic industry. The current wide use of silicon and germanium in the device technologies, has led to extensive studies on their novel nanoforms in order to find components for future electronic devices through bottom-up approach. Nanowires and nanoparticles of silicon [1–5] and germanium [6–8] are projected to be possible building blocks [9–13] for the nanoscale devices. Recently using the first principles materials design approach, very small diameter nanotubes of silicon were stabilized by Be encapsulation [14]. This finding has prompted experimental work and recently self-organized assemblies of $Si_{24}Be_2$ finite nanotubes have been obtained [15] 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 [16–18] and Ge [19,18] have also been predicted by encapsulation of transition metal (M) atoms. The infinite nanotubes are metallic and have interesting magnetic properties [16,19]. 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.

[a] e-mail: abhishek@imr.edu

In metal encapsulated nanotubes of Si and Ge, either $Si_{12}M$ clusters [14,16] with hexagonal prism structure or $Ge_{12}M$ clusters [19] with a 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 were found to be magic [20] for M = Cr and W. However, assembling of a nanotube from these clusters was found to be unfavorable due to distortions [21] and strong dimerization of M atoms. Here, we consider germanium nanotubes as these can be more versatile with the possibility of doping a larger variety of M atoms as compared to silicon because Ge−Ge bond length is closer to the bond lengths found in several metals. We explore the possibility of semiconducting nanotubes from the point of view of device development and show that by a suitable choice of atoms we can design metallic and semiconducting nanotubes.

2 Method

We use an ultrasoft pseudopotential planewave method [22–24] within the density functional theory and spin-polarized generalized gradient approximation [25] (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 constraint until the force on each ion is converged to 0.001 eV/ Å. The band structures of the infinite nanotubes are calculated by considering 260 k-points in the half Brillouin zone.

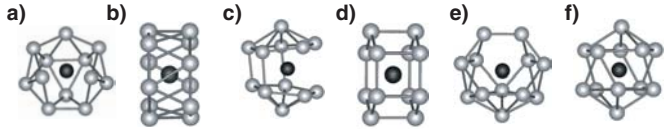

Fig. 1. Optimized low lying structures of $Ge_{12}V$ cluster: (a) lowest energy isomer with a capped pentagon and elongated hexagon, (b) perfect hexagonal antiprism (c) a structure obtained from a decahedron, (d) hexagonal prism, (e) cage-like structure, and (f) icosahedron. Dark(light) ball shows V(Ge) atom.

3 Results and discussions

First we consider doping with V as recently V doped nanotubes of silicon have been obtained by stacking of hexagonal rings in prism like geometry with M atom in between [17] using first principles calculations. These nanotubes are metallic and have small magnetic moments. In order to find a building block, we have considered $Ge_{12}V$ clusters and optimize an icosahedron, hexagonal prism, decahedron, hexagonal antiprism, and few other cage like structures. The magnetic moment on all these clusters is 1 μ_B due to the odd number of electrons except for the icosahedral cluster where it is 3 μ_B. The lowest energy isomer is a cage like structure (binding energy (BE = 3.46 eV/atom) consisting of a hexagon and a capped pentagon. The second lowest energy structure (BE = 3.44 eV/atom), hexagonal antiprism, lies 0.22 eV higher in energy (Fig. 1). The highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gap in this isomer is small (0.19 eV). Symmetric hexagonal prism-like structure lies slightly higher in energy.

With the icosahedral structure lying much higher in energy and the decahedral structure having a tendency for distortions, there is the option of assembling the hexagonal rings in the form of nanotubes. In order to check this, We further studied the stability of $Ge_{18}V_2$ clusters in three different geometrical arrangements of hexagons namely, antiprism-antiprism, biprism, and an antiprism-prism structure. As compared to a biprism structure [21] for $Si_{18}W_2$, we find that an antiprism-prism structure (Fig. 2a(i)) is 0.48 (0.92) eV lower in energy than an antiprism-antiprism (biprism) structure. This difference arises due to the bigger size of Ge atoms. A prism-prism structure has a longer V−V bond while an antiprism-antiprism structure has shorter V−V bond. All of these three structures have slight variation in Ge−Ge bond lengths. However, the Ge−Ge bond lengths in the same ring are equal. The prism-antiprism structure optimizes V−V as well as Ge−Ge and Ge−V interactions with the V−V bond length of 2.37 Å, and the HOMO-LUMO gap of 0.49 eV. Further the binding energy of this cluster increases in comparison to the $Ge_{12}V$ cluster (BE = 3.58). The magnetic moments on all the three forms of this cluster are 2.00 μ_B, but the distribution of local moments is very different. For the antiprism-prism isomer, the V atom with the prism-like environment has a local magnetic moment of 1.14 μ_B while the other one lying in the antiprism environment has 0.26 μ_B with opposite spin. Ge atoms at the terminal Ge ring in the antiprism environment, have induced magnetic moments of the order of 0.18 μ_B with opposite spin of the corresponding V atom. Ge atoms in the terminal Ge ring in prism environment, have negligibly small induced magnetic moment, whereas the middle ring has induced moments of intermediate values. For the antiprism-antiprism isomer interestingly, the magnetic moment on V atoms are almost completely quenched (0.05 μ_B/atom). However, there is a stronger induced magnetic moment on the Ge atoms in the terminal Ge-rings (0.15 μ_B/atom). The induced moments on Ge atoms in the middle Ge ring is quite small (0.01 μ_B/atom). For the biprism isomer, the local moments on V atoms are 0.86 μ_B and these are ferromagnetically coupled. Very small induced moments (0.02 μ_B/atom) are found on the Ge atoms in the terminal rings. The magnetic moments on the Ge atoms in the middle ring are 0.11 μ_B/atom and these are ferromagnetically coupled with the moments on V atoms. The local magnetic moments on V atoms follow very closely the V−V bond lengths, as well as Ge−V interaction. As the V−V bond length is the longest in the biprism isomer and smallest in antiprism-antiprism isomer, the local moments on V atom in the biprism environment is the largest and it is negligibly small for the antiprism-antiprism isomer. The antiprism-prism isomer shows an intermediate behavior of these two extremes.

When the two units of antiprism $Ge_{12}V$ clusters are stacked in (a) antiprism-prism and (b) antiprism-antiprism like arrangements with a V atom between the units, we can form a $Ge_{24}V_3$ nanotube. Upon optimization both the stackings converge to a) kind of stacking (BE = 3.66 eV/atom) form (Fig. 2b) indicating the strong preference for the growth behavior of these nanotubes in which antiprism-prism stacking of hexagonal rings are favored. The rings are slightly curved in a symmetric manner. The two of the Ge−Ge bond lengths in outer rings are

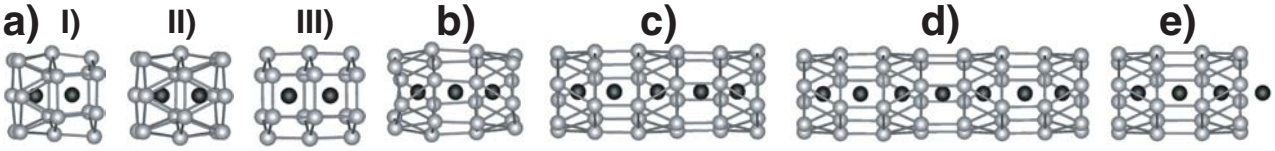

Fig. 2. Optimized structures of a finite nanotube: (a) $Ge_{18}V_2$ in three different possible ways of stacking (i) lowest energy antiprism-prism, (ii) antiprism-antiprism, and (iii) biprism structure. (b) , (c), (d), and (e) show the structures of finite nanotubes $Ge_{24}V_3$, $Ge_{36}V_5$, $Ge_{48}V_7$ and infinite nanotube of $Ge_{24}V_4$ in antiprism-prism stacking of hexagonal rings, respectively. Mo and W-doped nanotubes have similar structures.

2.49 Å and all other are 2.60 Å. The inner two rings are almost planar with two Ge−Ge bond lengths of 2.70 Å whereas all other bond lengths are 2.56 Å. V−V bond lengths are 2.37 Å. There is a mirror symmetry observed in this structure along the plane passing through the middle V atom. The magnetic moment on this nanotubes is 1.00 μ_B and it is distributed over all the atoms in the cluster.

When three units of $Ge_{12}V$ cluster are assembled with the stoichiometry $Ge_{36}V_5$ in the two ways as explained above, we find the antiprism-prism stacking to lie 0.60 eV lower in energy, giving an indication that the antiprism-prism growth mode is novel for such nanotubes. The structure becomes more symmetric with the Ge−Ge bond lengths within each ring remaining the same. The rings are now perfectly planar. The Ge−Ge bond lengths in the two outermost rings are 2.58 Å that are slightly shorter than in the middle ring (2.62 Å). The V−V bond lengths, going from left to right, are 2.29, 2.73, 2.73, and 2.29 Å. The *BE* has increased from the previous case significantly (3.73 eV/atom). There is again a mirror symmetry plane along the plane crossing through the middle V atom. The magnetic moment on this nanotube is 1 μ_B and is distributed over all the atoms in the nanotube.

Assembling four units of the cluster in the stoichiometry $Ge_{48}V_7$, in type (a) kind of stacking again leads to highly symmetric finite nanotube (*BE* = 3.75 eV/atom) (Fig. 2d) with the magnetic moment of 3.00 μ_B. Like in the case of $Ge_{18}V_2$ cluster, the local moments on the V atoms in prism-like environment is higher and in the opposite direction than the one in the antiprism environment. Further the magnetic moment increases in going from the terminal to the central V atom (−0.26, 0.70, −0.39, 1.55, −0.39, 0.70, −0.26 μ_B). The induced magnetic moments in Ge atoms are of the order of 0.03 μ_B. The V−V bond lengths are 2.41, 2.67, 2.63, 2.63, 2.67, and 2.41 Å. There is mirror symmetry along the plane passing through the middle V atom. Ge−Ge bond lengths in the terminal hexagonal rings remain nearly the same 2.56 Å as in the previous case. The Ge−Ge bond lengths in the second, third, and fourth ring from the end are 2.58 Å, 2.63 Å, 2.59 Å, respectively. The *BE* of the nanotubes has increased with increasing number of assembly units, showing the clear preference for the type (a) stacking leading to the geometry that is quite different from the previously reported nanotubes of metal encapsulated Si or Ge. Further it implies that these nanotubes could be formed in large aspect ratio. The HOMO-LUMO gap in finite nanotubes is small and the infinite nanotubes become metallic.

The stability of a doped infinite nanotube has been studied using a unit cell of $Ge_{24}V_4$. The larger unit cell was taken to consider different types of stacking as well as to allow the possibility of different magnetic orderings. The nanotubes were 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, antiprism-prism geometry is energetically most favored (Fig. 2e) and the antiprism-antiprism structure lies 0.16 eV/cell higher in energy. The magnetic moments on these nanotubes are

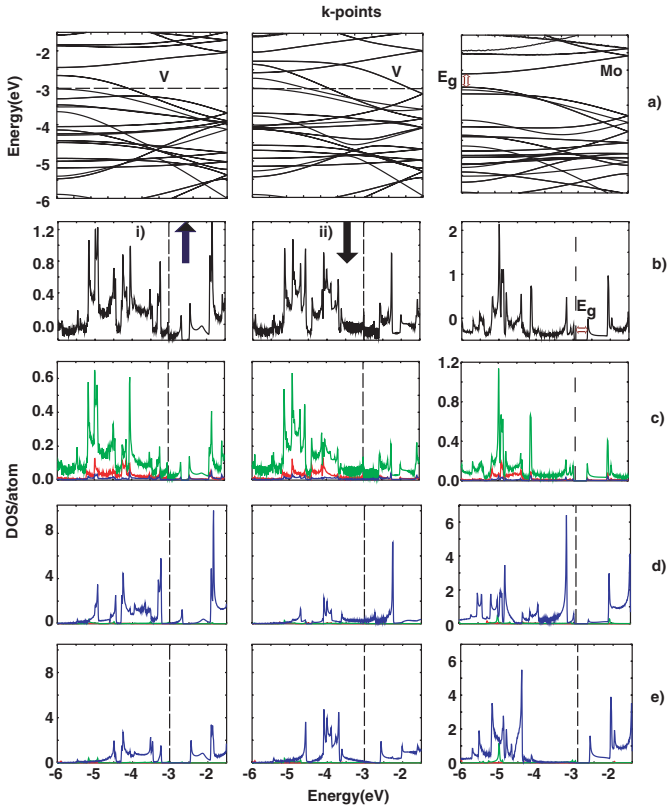

Fig. 3. (a) Band structures for spin-up, spin-down components of V-, and Mo-doped infinite nanotubes. Dashed line shows the Fermi energy. Total and partial densities of states (DOS) of V- and Mo-doped infinite nanotubes obtained by using Gaussian broadening with width of 0.01 eV. (b) Total DOS, (c) partial DOS of Ge, (d) partial DOS for metal atom in the antiprism environment, and (e) partial DOS for the metal atom in the prism environment of Ge atoms. Red, green, and blue lines represent the contributions from *s*, *p*, and *d* orbitals. Columns (i) and (ii) represent corresponding DOS for spin-up and spin-down component of V-doped nanotube E_g is the band gap. A colour version of the figure is available in electronic form at `http://www.eurphysj.org`.

2.13 μ_B. All the different initial guesses for the magnetic moments got converged to the same magnetic state. The V−V and intra-hexagon Ge−Ge bond lengths (same in all the hexagonal rings) are 2.63 Å and 2.60 Å, respectively. Inter-hexagon Ge−Ge bond lengths are 2.76 Å and 2.84 Å for the antiprism and prism stackings, respectively. This difference in the bond length has important bearing on the bonding in the nanotube.

The band structure of this nanotube is shown in (Fig. 3a). The Fermi level lies in a band for both the spin-up and spin-down components and therefore this nanotube is metallic similar to the previously reported cases of metal doped nanotubes of Si and Ge. Similar behavior has been obtained [26] for Nb doped nanotubes. In this case, however, the spin-up band structure has a gap just above the Fermi level indicating the possibility of the

formation of a semiconducting nanotube by filling of these states. Replacing V or Nb with Mo which lies right next to Nb in the periodic table, the extra electron fills up the empty states near the Fermi level (Fig. 3) and the nanotube becomes semiconducting. Doping with W also has the same effect [26]. 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 within the GGA and has the value of 0.5 eV. The true value could be expected to be around 1 eV. This finding is important as it can open a way for applications in devices.

The partial densities of states (PDOS) of the $Ge_{24}M_4$ (M = V and Mo) infinite nanotubes (Fig. 3 show that the two M atoms with non-equivalent environments namely antiprism and prism, have quite different local density of states. For the case of V-doped nanotube the V atoms in the antiprism environment have similar characteristic PDOS for both spin-up (Fig. 3d(i)) and spin-down (Fig. 3d(ii)) components. However, for the one in the prism environment they are significantly different (Figs. 3e(i) and 3e(ii)). This difference leads to higher local magnetic moment on the V atoms in the prism environment (1.54 μ_B) compared with the one in the antiprism environment (-0.54 μ_B). In general the states near the Fermi energy arise mostly from the Ge $4p$ states and the d states of the M atom that lies in the prism environment. In the antiprism geometry Ge–M bond lengths are shorter leading to stronger hybridization of the M d and Ge $4p$ states which push the d states to higher binding energies. This strong hybridization also results in stronger quenching of the magnetic moments on the V-atom in the antiprism environment, explaining why the local moments are very low on these atoms. However, in the prism geometry Ge−Ge and Ge−V interactions are weaker and lead to higher local moments on the V atom.

4 Conclusions

In summary, we have examined the stability of finite and infinite Ge nanotubes doped with V atoms. 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 very important finding of Mo doped semiconducting nanotubes. The band gap in Mo-doped nanotube is 0.4 eV and is direct, very much comparable to the gap in bulk silicon. It opens up new possibilities for device development at the smallest scale. A significant aspect of these results would be that by changing the metal atom in the growth process it can be possible to grow metallic or semiconducting nanotubes.

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. AKS is also thankful for the support of JSPS fellowship. VK gratefully acknowledges the hospitality at IMR,Tohoku University.

References

1. Y. Cui, C.M. Lieber, Science **291**, 851 (2001)
2. A.M. Morales, C.M. Lieber, Science **279**, 208 (1998)
3. J.D. Holmes et al., Science **287**, 1471 (2000)
4. D.D.D. Ma, C.S. Lee, F.C.K. Au, S.Y. Tong, S.T. Lee, Science **299**, 1874 (2003)
5. V. Kumar, Y. Kawazoe, Phys. Rev. Lett. **87**, 045503 (2001)
6. Y. Wu, P. Yang, Chem. Mater. **12**, 605 (2000); Y. Wu, P. Yang, J. Am. Chem. Soc. **123**, 3165 (2001)
7. G. Gu, M. Burghard, G.T. kim, G.S. Dusberg, P.W. Chiu, V. Krstic, S. Roth, J. Appl. Phys. **90**, 5747 (2001)
8. T.I. Kamins, X. Li, R.S. Williams, X. Liu, Nano Lett. **4**, 503 (2004)
9. Y. Huang, X. Duan,Y. Cui, K.K. Lauhon, C.M. Lieber, Science **294**, 1313 (2001)
10. Y. Huang, X. Duan, Q. Wei, C.M. Lieber, Science **291**, 630 (2001)
11. T. Tsutsumi, K. Tomizawa, J. Vac. Sci. Technol. B. **18**, 2640 (2000)
12. S. Chung, J. Yu, R. Heath, Appl. Phys. Lett. **76**, 2068 (2000)
13. Y. Cui, Q. Wei, H. Park, C.M. Lieber, Science **293**, 1289 (2001)
14. A.K. Singh, V. Kumar, T.M. Briere, Y. Kawazoe, Nano Lett. **2**, 1243 (2002)
15. A.A. Saranin, A.V. Zotov, V.G. Kotlyar, T.V. Kasyanova, O.A. Utas, H. Okado, M. Katayama, K. Oura, Nanolett. **4**, 1469 (2005)
16. A.K. Singh, T.M. Briere, V. Kumar, Y. Kawazoe, Phys. Rev. Lett. **91**, 146802 (2003)
17. A.N. Andriotis, G. Mpourmpakis, G.E. Froudakis, M. Menon, New J. Phys. **4**, 78 (2002)
18. A.K. Singh, V. Kumar, Y. Kawazoe, J. Mater. Chem. **14**, 555 (2004)
19. A.K. Singh, V. Kumar, Y. Kawazoe, Phys. Rev. B **69**, 233406 (2004)
20. H. Hiura, T. Miyazaki, T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001)
21. V. Kumar, Y. Kawazoe, Phys. Rev. Lett. **90**, 055502 (2003)
22. G. Kresse, J. Hafner, J. Phys. Condens. Matter **4**, 8245 (1994)
23. G. Kresse, J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); Comput. Mater. Sci. **6**, 15 (1996)
24. D. Vanderbilt, Phy. Rev. B **41**, 7892 (1990)
25. J.P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche, H. Eschrig (Akademie Verlag, Berlin, 1991)
26. A.K. Singh, V. Kumar, Y. Kawazoe, Phys. Rev. B **71**, 075312 (2005)