

Magnetism in Transition-Metal-Doped Silicon Nanotubes

Abhishek Kumar Singh,¹ Tina M. Briere,¹ Vijay Kumar,^{1,2} and Yoshiyuki Kawazoe¹

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 19 February 2003; published 30 September 2003)

Using first-principles density functional calculations, we show that hexagonal metallic silicon nanotubes can be stabilized by doping with 3d transition metal atoms. Finite nanotubes doped with Fe and Mn have high local magnetic moments, whereas Co-doped nanotubes have low values and Ni-doped nanotubes are mostly nonmagnetic. The infinite Si₂₄Fe₄ nanotube is found to be ferromagnetic with nearly the same local magnetic moment on each Fe atom as in bulk iron. Mn-doped nanotubes are antiferromagnetic, but a ferrromagnetic state lies only 0.03 eV higher in energy with a gap in the majority spin bands near the Fermi energy. These materials are interesting for silicon-based spintronic devices and other nanoscale magnetic applications.

DOI: 10.1103/PhysRevLett.91.146802

PACS numbers: 73.22.-f, 31.15.Ar, 61.46.+w, 75.75.+a

Recent developments in metal-encapsulated silicon clusters [1–3] and nanotubes [4] have shown a novel way to produce new nanostructures of silicon that could hold promise for silicon-based nanoscale device components. From a technological viewpoint, such materials are interesting as there is a well-established infrastructure for Si device fabrication, whereas for other possible approaches, such as those based on carbon nanotubes or organic molecules, a new infrastructure would need to be developed. Metal encapsulation in silicon clusters leads to enhanced stability, strong size selectivity, and large highest occupied–lowest unoccupied molecular orbital (HOMO-LUMO) gaps as compared to elemental silicon clusters [1,2], which could facilitate their large scale production [5]. This is important for developing cluster-based technologies. Infinite silicon nanotubes stabilized by metal doping have very small diameters and are metallic [4,6]. The respective semiconducting and metallic properties of the clusters and nanotubes could lead to an entirely new range of silicon-based applications in optoelectronic and other devices. Metal-encapsulated nanotubes could be functionalized to develop individual device elements or used as interconnects between device components. Here we explore the possibility of magnetism in such silicon-based nanostructures and report the finding of strong ferromagnetic order in Fe-doped silicon nanotubes as well as nearly degenerate ferromagnetic and antiferromagnetic order in Mn-doped nanotubes. These nanotubes could be useful for spintronics and other magnetic device applications [7].

Finite hexagonal nanotubes of silicon were earlier stabilized with Be doping [4] and infinite nanotubes were also shown to be stable. The finite nanotubes were found to be semiconducting, whereas the infinite nanotubes were metallic. Transition metals (TMs) have been shown [1,2,8] to be particularly important for the stability of metal-encapsulated silicon cage clusters due to their large embedding energies in the silicon cage. It is therefore of

interest to explore the stability of silicon nanotubes with TMs. The atomic size of the TMs is an important factor in developing such nanostructures. From the relative sizes of Si and the TMs, 3d elements are more suitable for doping as the strain in the Si-Si bonds can be minimized. These TMs are also well suited for magnetism in such nanostructures. However, Cr has been shown to lead to significant distortions in the finite nanotubes [9]. Menon *et al.* [6] have studied nanotubes of Si with pentagonal rings stabilized with Ni doping. They obtained an icosahedral cluster with the stoichiometry Si₁₂Ni to be stable from first-principles calculations. Studies on larger clusters were performed using a tight-binding method and it was shown that the icosahedral packing can be continued in the form of nanotubes. A hexagonal nanotube was also stabilized with V doping [10]. This nanotube is both metallic and magnetic with a magnetic moment of $0.67\mu_B$ per V atom.

We have carried out a systematic study of the stability of finite and infinite nanotubes with the 3d magnetic elements Mn, Fe, Co, and Ni. We explored various structures with TM doping in the pursuit of finding the most stable units with a particular number of Si and dopant atoms that could be stacked to form nanotubes. The optimizations were performed using an *ab initio* ultrasoft pseudopotential plane wave method [11] and the conjugate gradient technique within the generalized gradient approximation (GGA) for the exchange-correlation energy [12]. The cutoff energy for the plane wave expansion depended on the TM atom, with a minimum of 227 eV for Mn and a maximum of 241 eV for Ni. The Γ point was used for the Brillouin zone integrations in the case of the finite nanotubes. However, for the infinite nanotubes, 15 *k*-point sampling along the nanotube axis was used for the optimizations. Forces were converged to 0.001 eV/Å. Different initial guesses were used for the local magnetic moments including ferromagnetic, anti-ferromagnetic (alternate up-down spins on TM atoms), and nonmagnetic spin configurations, which were then

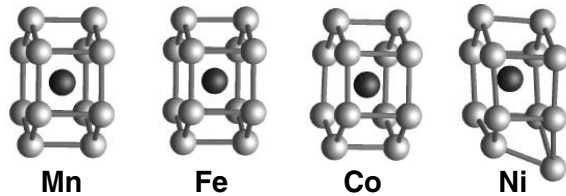


FIG. 1. Lowest energy structures of the finite nanotubes with stoichiometry $\text{Si}_{12}M$ ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni}$).

fully relaxed to obtain the final converged structures and spin alignments.

First we examined the stability of $\text{Si}_{12}M$ ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{and Ni}$) clusters by optimizing icosahedral, decahedral, hexagonal prism, and hexagonal antiprism structures. The hexagonal prism structure is the lowest in energy except in the case of Ni (Fig. 1) where one Si atom has elongated bond lengths. The icosahedral structure of Si_{12}Ni , obtained by Menon *et al.* [6] to be lowest in energy, is third lowest in energy from our calculations, while a chair structure lies second lowest in energy. We also examined the relative stabilities using the Gaussian method [13] with the B3PW91 hybrid functional [12,14] and confirmed the distorted hexagonal prism to be lower in energy than the icosahedron. Calculations on $\text{Si}_{17}\text{Ni}_2$ in the double icosahedron structure led to large distortions, suggesting that icosahedral packing is not favorable for Ni doping.

Stacking two units of the hexagonal prism cluster leads to structures that are slightly curved in a symmetric manner. Doping of these units with one more TM atom in between the prisms leads to an increase in the binding energy (BE) [15] of the nanotubes (Fig. 2) and an improved geometry with nearly planar Si hexagonal rings. The addition of more Si rings also generally leads to an

increase in the BE, but the ideal planar structures and highest BEs are most prevalent for the systems with one TM atom placed between each ring, as can be seen for the case of Fe (Fig. 3). This is unlike Be-doped nanotubes, where planar structures occur for lower doping levels [4]. The BEs of the TM-doped nanotubes (3.88–4.25 eV/atom) are higher than those doped with Be (3.62–3.86 eV/atom) [4], which is due to the participation of the TM d electrons in the bonding. For Mn, two units of Si_{12}Mn are quite far apart (about 0.7 Å greater than the Si-Si bond lengths in a Si_{12}Mn unit). This is due to the large HOMO-LUMO gap of 1.67 eV in Si_{12}Mn . The intercluster separation as well as the HOMO-LUMO gap decrease with increasing size or doping, leading to metallization of the nanotubes. For example, the HOMO-LUMO gap of $\text{Si}_{24}\text{Mn}_2$ is 0.96 eV, while the value for $\text{Si}_{24}\text{Mn}_3$ is only 0.32 eV. For Co doping significant distortions remain even in the case of the $\text{Si}_{48}\text{Co}_7$ nanotube, while the Ni-doped nanotubes are quite symmetric.

An important aspect of the doping of TMs is the magnetic behavior. We obtained a mixed behavior of magnetic ordering as the number of Si and TM atoms was changed. In the case of the finite Fe- and Mn-doped nanotubes, the local magnetic moments increase with an increase in the number of dopants for a given number of Si atoms (Fig. 2). For Fe doping there is a transition from antiferromagnetic to ferromagnetic coupling as the number of dopants is increased. $\text{Si}_{24}\text{Fe}_2$ and $\text{Si}_{36}\text{Fe}_3$, with no direct interaction between Fe atoms, have antiferromagnetic coupling, while other nanotubes are ferromagnetic. For $\text{Si}_{24}\text{Mn}_2$, $\text{Si}_{24}\text{Mn}_3$, and $\text{Si}_{48}\text{Mn}_4$, spins on neighboring Mn atoms are antiferromagnetically coupled, while in the other cases the coupling is ferromagnetic. The local moments of both Fe and Mn are highest towards the center of the nanotubes and lowest

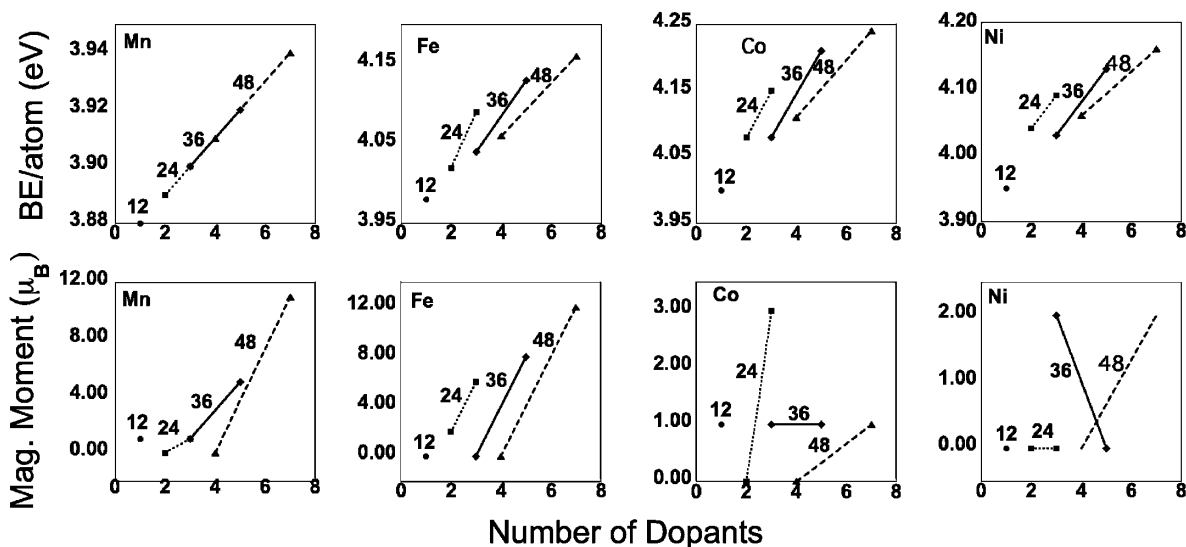


FIG. 2. Plots of BE/atom and magnetic moment versus the number of dopant atoms for finite TM-doped Si nanotubes. The number of Si atoms is indicated above each line.

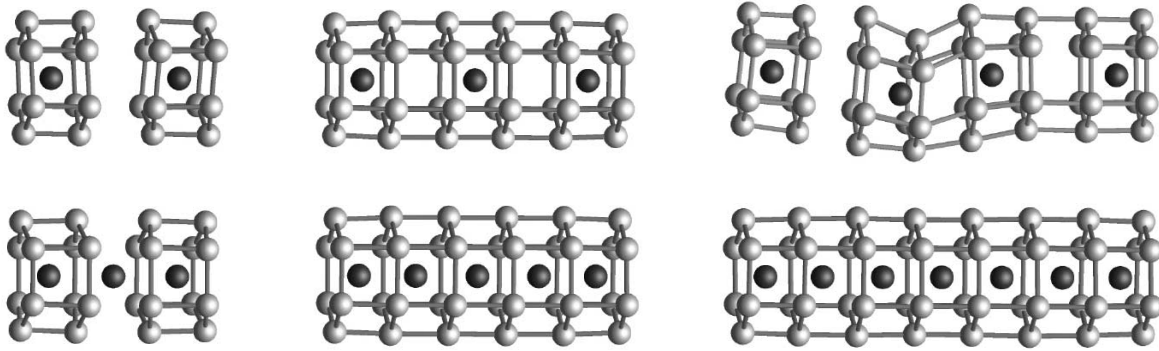


FIG. 3. Structures of Fe-doped finite silicon nanotubes with stoichiometries $\text{Si}_{24}\text{Fe}_2$, $\text{Si}_{36}\text{Fe}_3$, $\text{Si}_{48}\text{Fe}_4$, $\text{Si}_{24}\text{Fe}_3$, $\text{Si}_{36}\text{Fe}_5$, and $\text{Si}_{48}\text{Fe}_7$.

at the ends. The values of the local moments range from $1.0\text{--}2.6\mu_B$ for Fe and $0\text{--}3.6\mu_B$ for Mn. The magnetic moments of the Co-doped nanotubes are low (Fig. 2), while the magnetic moments of the Ni-doped nanotubes are in most cases completely quenched.

Typically in metal-encapsulated Si clusters the magnetic moments of the dopants are quenched due to the strong hybridization of the metal d states with the sp states of silicon. When clusters interact in the form of a nanotube, there is an increase in the Si-Si and TM-Si bond lengths that leads to a reduction in the hybridization. This is due to the participation of silicon orbitals in bonding between neighboring clusters. This can lead to the development of magnetic moments on the TM atoms particularly for elements with large atomic moments. A similar development of the magnetic moments in the Si_{12}Cr cluster was found when H was attached to the Si atoms [9]. This is further supported from our results of small or zero local moments towards the edges of the finite nanotubes and large moments towards the center of the nanotubes. The moments of the TM atoms also decrease systematically as we go from Mn to Ni. The TM atoms having larger atomic magnetic moments have higher local moments in the doped nanotubes, while in the case of Ni these generally remain quenched as its low atomic magnetic moments may be quenched by even a weaker hybridization. The high magnetic moments of $\text{Si}_{48}\text{Fe}_7$ ($1.7\mu_B$ per Fe atom) and $\text{Si}_{48}\text{Mn}_7$ ($1.6\mu_B$ per Mn atom) suggest that they could be useful for magnetic device applications.

The increased stability of the finite nanotubes with an increasing number of dopants led us to examine the stability of the infinite nanotubes with the stoichiometry $\text{Si}_{24}M_4$. This large unit cell was taken in order to allow for different spin configurations. However, for ferromagnetic and nonmagnetic solutions, the effective cell reduces to Si_6M . To further confirm the relative stability as a function of the number of dopants, we also performed a few calculations with the stoichiometry $\text{Si}_{24}M_2$ and again found an increase in the BE with an increase in the number of dopants. An interesting finding is the change in the position of the dopant atom (Fig. 4), which

drifts from 1.12 and 1.18 \AA away from the hexagons for antiferromagnetically coupled Mn leading to dimerization of the Mn atoms, to 0.98 , 0.79 , and 0.27 \AA for ferromagnetically coupled Mn, Fe, and Co, respectively. Ni lies at the center of the hexagons. The BEs of all the infinite nanotubes are higher than their finite counterparts. These values are also higher than those obtained for the Be-doped nanotubes [4]. The BE for the Mn-doped nanotube is almost 90% of the bulk Si GGA cohesive energy.

The infinite Fe-doped nanotube has ferromagnetic coupling [16] with a high total magnetic moment of $2.4\mu_B$ per dopant atom. This value is nearly the same as in bulk Fe. The antiferromagnetically coupled Fe-doped nanotube is 0.70 eV higher in energy, showing the stability of the ferromagnetic nanotube even at finite temperature. The one-dimensionality of this nanotube, along with its high moments, makes it attractive for use as a nanoscale magnet. Mn prefers an interesting spin arrangement in which pairs of ferromagnetically coupled Mn atoms are antiferromagnetically coupled with their neighboring pairs, resulting in a zero net moment. The ferromagnetically coupled pairs are 2.55 \AA apart as compared to 2.40 \AA for the antiferromagnetically coupled pairs. The local magnetic moments on the dopant atoms range from 2.4

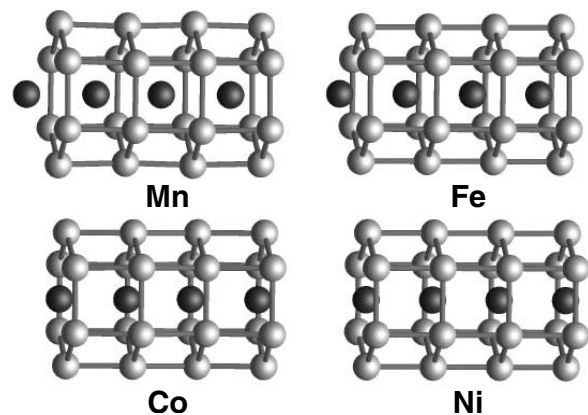


FIG. 4. Structures of infinite $\text{Si}_{24}M_4$ ($M = \text{Mn}, \text{Fe}, \text{Co},$ and Ni) nanotubes.

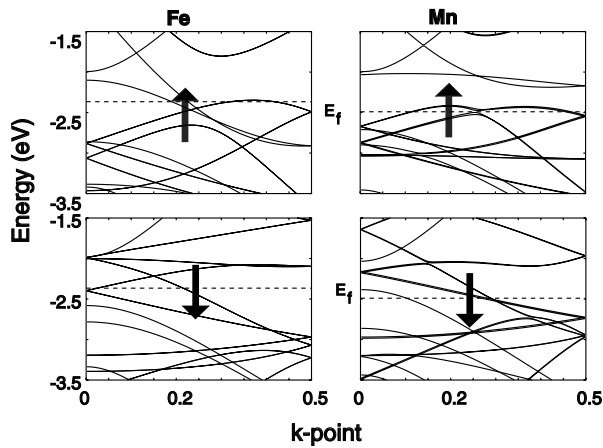


FIG. 5. Band structures of the infinite $\text{Si}_{24}\text{Fe}_4$ and $\text{Si}_{24}\text{Mn}_4$ ferromagnetic nanotubes along the nanotube axis. Both the spin-up and spin-down band structures are shown. The Fermi energies are represented by dashed lines.

to $2.7\mu_B$. This configuration, however, is only 0.03 eV lower in energy than the corresponding ferromagnetic nanotube [16]. This is another very important result as the transformation from antiferromagnetic to ferromagnetic coupling may be achieved by application of a weak magnetic field, suggesting that spin-polarized current flow could be controlled through application of a magnetic field. For the Co- and Ni-doped infinite nanotubes, ferromagnetic and antiferromagnetic starting configurations converge to nonmagnetic solutions.

The band structures of all the infinite nanotubes show band crossing at the Fermi level for both the spin-up and spin-down components, indicating metallic behavior. Therefore the magnetic ordering in these nanotubes also has itinerant behavior. For low doping the ordering is primarily mediated by the nanotube atoms and it can vary depending upon the position of the TM atoms. The Fe- and Mn-doped nanotube bands are shown in Fig. 5. Interestingly, the band structure of the Mn-doped ferromagnetic nanotube (Fig. 5) shows a gap just above the Fermi energy for the spin-up component and therefore it may become half-metallic by inducing a small shift in the Fermi energy. The partial and total densities of states also confirm the metallic behavior of these nanotubes. In general, most of the states arising at the Fermi level have the d character of the TMs and the p character of states derived from the Si atoms. The relative populations differ for the different metal-doped nanotubes, and thus we expect different conduction behavior. This may be an important aspect for the transport properties of these nanostructures.

In summary, we have shown that metallic nanotubes of Si can be stabilized by TM doping. There is a strong contribution to the binding energy from the TM d electrons. The Fe-doped nanotubes are ferromagnetic and have large magnetic moments per Fe atom that are nearly

the same as in bulk Fe. Mn-doped nanotubes are, however, antiferromagnetic with large local magnetic moments on the Mn atoms. The ferromagnetic state is nearly degenerate and can be achieved by application of a weak magnetic field. These results are interesting for spintronics as well as other nanoscale magnetic device applications.

The authors thank the staff of the Center for Computational Materials Science at the Institute for Materials Research for the use of the Hitachi SR8000/64 supercomputing facilities. A. K. S. is grateful for the support of Monbusho. V. K. acknowledges support from the Japan Society for the Promotion of Science and the hospitality at the Institute for Materials Research.

-
- [1] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **87**, 045503 (2001).
 - [2] V. Kumar and Y. Kawazoe, Phys. Rev. B **65**, 073404 (2002).
 - [3] H. Hiura, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **86**, 1733 (2001).
 - [4] A. K. Singh, V. Kumar, T. M. Briere, and Y. Kawazoe, Nano Lett. **2**, 1243 (2002).
 - [5] S. M. Beck, J. Chem. Phys. **90**, 6306 (1989).
 - [6] M. Menon, A. N. Andriotis, and G. E. Froudakis, Nano Lett. **2**, 301 (2002).
 - [7] B. E. Kane, Nature (London) **393**, 133 (1998).
 - [8] Doping of non-TM atoms leads to low values of embedding energies. See Q. Sun, Q. Wang, T. M. Briere, V. Kumar, and Y. Kawazoe, Phys. Rev. B **65**, 235417 (2002).
 - [9] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **90**, 055502 (2003).
 - [10] A. N. Andriotis, G. Mpourmpakis, G. E. Froudakis, and M. Menon, New J. Phys. **4**, 78 (2002).
 - [11] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); Comput. Mater. Sci. **6**, 15 (1996).
 - [12] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991).
 - [13] M. J. Frisch *et al.*, GAUSSIAN 98, Revision A.11.1, Gaussian, Inc., Pittsburgh PA, 2001.
 - [14] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
 - [15] The BEs are calculated with respect to the free atoms. It should be noted that density functional theory does not produce reliable energies for Fe, Co, and Ni atoms due to incorrect population of the $3d4s$ states. (The occupation for Mn is correct, however.) Therefore, we expect a small error in the absolute values of the BEs for systems that contain these three atoms.
 - [16] We have also performed LDA + U calculations using different values of the on-site Coulomb interaction parameter ranging from 2 to 6 eV. For Fe, the ferromagnetic state is lowest in energy in all cases. Also for Mn the nearly degenerate ferromagnetic and antiferromagnetic solutions now favor the ferromagnetic state to be lower in energy. The details will be published separately.