Magnetic Properties of Transition Metal Atoms Doped in Silicon Nanotubes With Hexagonal Prism Structure

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Magnetic properties of magnetic transition metals doped in the infinite Si nanotubes (SiNTs) with hexagonal prism structure (Si₁₂₅₃₉ᵣ, M = Fe, Co, Ni, n = 1, 2) have been investigated for two different numbers of dopants per hexagonal prism by using the localized basis calculational method. The decrease (increase) of spin-down (spin-up) electrons for the n = 2 case results in the increase of magnetic moments compared with the n = 1 case. The calculated magnetic moment per dopant Fe atom (2.39 μₐ) is larger than both of the bulk value (2.22 μₐ) and previous result for finite nanotube (1.7 μₐ). For Co and Ni atoms doped in the tube, the magnetic moments are smaller than those of bulk metals. The Si–Si bond lengths for the hexagonal prisms decrease compared with that of the nanotube without transition metals, but there is no dependency on different dopants. The distances between the transition metals and Si atoms decrease as the atomic number of transition metals increases, which is the same trend for the atomic radii of transition metal atoms. The doping of transition metal atoms leads to the increase of the binding energy (BE).

Index Terms—Binding energy, hexagonal prism structure, magnetic moment, silicon nanotube, transition metal encapsulation.

I. INTRODUCTION

RECENTLY, silicon nanowires (SiNWs) have attracted a lot of attention because of their potential applicability for nanoscale devices. Theoretical results using the generalized tight-binding molecular dynamics showed that quasi-one-dimensional structures of Si can be stabilized by stacking superatom clusters [1]. The distribution of SiNWs with different growth directions and cross-sectional shapes are discussed in relation to various growth methods [2]. The study on elastomechanical stability of SiNWs using molecular dynamics simulations showed that the cage-like SiNWs are a good candidate for structural strength, chemical sensor, and electronics applications under strain conditions [3]. The fabrication of small-diameter SiNWs and spectroscopy experiments provided an evidence for quantum confinement effect and indicated that the bandgap increases with decreasing diameter, but it is insensitive to nanowire orientation [4].

The metal-doped clusters [5] and nanotubes [6] have also attracted much attention due to the possibility of applications for magnetic devices. It has been reported that very long Si nanotubes (SiNTs) stabilized by metal doping have metallic character [6], [7] while the finite nanotubes are semiconducting. From the consideration of relative atomic sizes of Si and transition atoms, it can be seen that the 3d transition metals are suitable for doping elements in SiNTs. There have been investigations about the stabilization or distortion in SiNTs with transition metal doping such as Ni [7], V [8], and Cr [9]. Recently, theoretical calculations were carried out [10] on the stability of finite and infinite SiNTs with the 3d transition metals (Mn, Fe, Co, Ni) using the ultrasoft pseudopotential plane wave method.

In the present work, using the localized basis calculational method, magnetic properties of doped magnetic transition metals in the infinite SiNTs with hexagonal prism structure

![Fig. 1. Schematic structures of transition metal doped infinite Si nanotubes (Si₁₂₅₃₉ᵣ, M = Fe, Co, Ni, n = 1, 2) have been investigated for two different numbers of dopants per hexagonal prism.](image-url)

II. METHOD

We considered two different cases of transition metal doping in SiNTs with hexagonal prism structure as shown in Fig. 1. The stable geometries for each doping case are determined by minimizing the total energies of doped nanotubes.

We have performed first-principles spin-polarized total energy calculations within the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof 1996 (PBE96) [11] for the exchange-correlation energy. We solved the self-consistent Kohn–Sham equations using the SIESTA code [12] by direct diagonalization of the Hamiltonian in atomic orbitals basis set consisting of finite-range numerical pseudoatomic orbitals with the Sankey and Niklewski form [13]. The standard norm
conserving Troullier–Martins pseudopotentials [14] factorized in the Kleinman–Bylander form were used to consider core electrons. We used 14 $k$-points for the Brillouin zone integration along the tube axis. The geometry is optimized until the atomic force is less than 0.04 eV/Å using the conjugate gradient method.

### III. RESULTS AND DISCUSSION

Firstly, we determined the equilibrium stacking distance for infinite hexagonal SiNTs without doping by calculating the total energy as a function of distance. We then inserted the transition metals at the middle of two hexagonal prisms as shown in Fig. 1 and optimized the equilibrium positions of Si and transition metals.

The calculated binding energy (BE) per atom for Si$_{12}M_n$ and equilibrium bond lengths of Si–Si and Si–M are presented in Table I.

The Si–Si bond lengths within the hexagonal prisms decrease compared with that of the nanotube without transition metals, but they are nearly the same with different dopants. The distances between the transition metals and Si atoms decrease as the atomic number increases, which is the same trend for the atomic radii of transition metal atoms.

We found that the transition metals attract neighboring hexagonal prisms for the $n = 1$ doping system, which gives alternate short and long distances between prisms. Contrary to the previous calculation for infinite Si$_{23}$M$_4$ nanotubes [10], we cannot find any change in the position of the dopant atom from the midpoint of two prisms for $n = 2$ infinite nanotubes.

We can see that present calculations of BEs for alternately ($n = 1$) doped infinite nanotubes give nearly the same values as those for finite Si$_{18}$M$_7$ in the previous calculation [10]. Furthermore, the BEs of all the $n = 2$ infinite nanotubes are higher than those obtained for the $n = 1$ ones, which is consistent with the trend in finite nanotubes [10].

The calculated number of electrons for each spin, sum of electrons, amount of charge transfer, and magnetic moments (in $\mu_B$) for the doped transition metal in the infinite hexagonal SiNTs with two different doping systems are summarized in Table II.

The calculated magnetic moment per dopant Fe atom (2.39 $\mu_B$) for $n = 2$ infinite nanotubes, slightly larger than the bulk value (2.22 $\mu_B$), is nearly the same as the previous calculation [10] for doped infinite (2.4 $\mu_B$) nanotubes but larger than the previous result for finite nanotube (1.7 $\mu_B$), which means that Fe is more magnetic in nanotubes than in a pure metallic form. The magnetic moment of Fe for $n = 1$ infinite nanotube (1.22 $\mu_B$) gives small but still larger value than the average magnetic moment in the calculation for finite (Si$_{36}$M$_3$ and Si$_{48}$M$_4$) nanotubes [10].

For Co and Ni for both doping cases, the magnetic moments are smaller than those of bulk metals (1.72 $\mu_B$ and 0.61 $\mu_B$, respectively) due to an internal pressure effect. The above results for the magnetic moments imply that direct interaction between magnetic ions is essential for maintaining strong magnetism.

The fact that the sum of electrons at the transition metal and the amount of charge transfer from the transition metal to Si are irrelevant to the number of dopants suggests that the decrease (increase) of spin-down (spin-up) electrons for $n = 2$ results in the increase of magnetic moments compared with the $n = 1$ case. In the case of Ni, the calculated magnetic moments are calculated to be very small for both cases, which is consistent with the argument that low magnetic moments may be quenched by even a weaker hybridization in the previous calculation [10] for doped finite and infinite SiNTs.

The calculated density of states (DOS) of Si$_{12}Fe$ and Si$_{12}Fe_2$ are shown in Fig. 2. The exchange splitting of Fe gives nearly full occupancy of majority spin but the peak of minority spin lies at the Fermi energy, which leads to a small magnetic moment for $n = 1$. For $n = 2$, a stronger exchange interaction gives more splitting, which results in a larger magnetic moment.

The study on the electron density at the Fermi energy shows that the Co-doped SiNTs has the largest spin polarization defined as the ratio of difference and sum of electrons at the Fermi energy, which implies a potential application to magnetic transport devices.

### IV. CONCLUSION

Magnetic properties of doped magnetic transition metals in the infinite Si nanotubes (SiNTs) with hexagonal prism structure (Si$_{12}M_n$, $M = Fe$, Co, Ni, $n = 1$, 2) have been investigated for two different numbers of dopants per hexagonal prism by using the localized basis calculational method. The decrease (increase) of spin-down (spin-up) electrons for the $n = 2$ case results in the increase of magnetic moments compared with the $n = 1$ case. The calculated magnetic moment per dopant Fe atom (2.39 $\mu_B$) is larger than both the bulk value (2.22 $\mu_B$) and the previous result for finite nanotube (1.7 $\mu_B$). For Co and Ni doped in the SiNT, the magnetic moments are smaller than those of bulk metals. In the case of Ni, the calculated magnetic moments are calculated to be very small for both cases, which is consistent with the argument that the low magnetic moments are quenched by even a weaker hybridization. These results imply

<table>
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<th>Si–M (Å)</th>
<th>E$_B$ (eV/atom)</th>
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<th>$M$</th>
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<td>4.81</td>
<td>9.63</td>
<td>-0.37</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>
that direct interaction between magnetic ions is essential for maintaining strong magnetism.

The Si–Si bond lengths for the hexagonal prisms decrease compared with that of the nanotube without transition metals, but they are nearly the same with different dopants. The distances between the transition metals and Si atoms decrease as the atomic number increases, which is the same trend for the atomic radii of transition metal atoms. The doping of transition metal atoms leads to increase of the binding energy (BE). The exchange splitting of Fe gives nearly full occupancy of majority spin, but the peak of minority spin lies at the Fermi energy, which leads to a small magnetic moment for \( n = 1 \). For \( n = 2 \), a stronger exchange interaction gives more splitting, which results in a larger magnetic moment.

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REFERENCES


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