Theoretical Design of Metal Encapsulated Clusters and Cluster Assembled Nanotubes of Si and Ge(Si Ge)

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論 文 内 容 要 旨

Theoretical Design of Metal Encapsulated Clusters and Cluster Assembled
Nanotubes of Si and Ge
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Chapter 1: Introduction

Quasi-one-dimensional nanostructures such as nanotubes and nanowires are currently of great interest due to the possibilities of their applications in miniature devices. Therefore, much effort is being devoted to develop fundamental understanding of the electrical, optical, magnetic, and mechanical properties of such materials and their dependence on size as well as interaction with other species. Extensive research on carbon nanotubes over the past decade has shown a wide range of possible applications. While these developments are exciting, there is the problem of separating semiconducting and metallic nanotubes. However, conventional silicon based technology is so well established that only overwhelmingly compelling new technology will be able to replace it. Therefore, continuous efforts for the miniaturisation of silicon devices are worthy as these could prove more convenient and economical for commercialization than any other process. Applications of Si nanowires (SiNWs) have also been explored. A recent significant development in nanostructures of silicon is the possibility to produce novel forms such as silicon fullerenes and clusters using metal encapsulation. These are more stable than nanostructures formed from elemental silicon, have high symmetries and potential for mass production with size selection. Such metal encapsulated silicon clusters could be assembled to form new varieties of silicon.

Chapter2: Computational Method

The results on nanotubes and clusters as presented here are obtained mainly by using a spin-polarized first-principles pseudopotential plane wave approach based on the density functional theory and ultrasoft pseudopotentials. The clusters are placed in a cubic box with periodic boundary conditions. The optimizations are performed using the conjugate gradient technique. The cut-off energy for the plane wave expansion depends on the metal atom. Γ-point sampling is used for the Brilliouin zone integrations in the case of clusters and finite nanotubes. For infinite nanotubes a tetragonal cell is used and a few units of the clusters are considered in the cell in order to explore changes in the structure as well as magnetic ordering.

Further 15 k-point sampling along the nanotube axis is used for the optimizations of the infinite nanotubes. Forces are converged to 0.001 eV/Å. Different initial guesses are used for the local magnetic moments, including ferromagnetic, antiferromagnetic, and non-magnetic spin configurations in order to find the lowest energy spin and atomic configurations of the nanotubes. A few calculations in which lanthanides and actinides have been considered, we used projected augmented wave method.

Chapter3: Metal Encapsulated Clusters

In this thesis we have pursued assembling metal encapsulated clusters and discovered the nanotubes of silicon and germanium. To achieve this, stabilities of various metal encapsulated silicon and germanium clusters were also studied. Two important results on metal encapsulated clusters have been obtained. The first one is the finding of smallest cage-like clusters of group 14 elements with the doping of group 10 elements. Recently anion binary clusters of Co/Ge, Co/Sn, and Co/Pb have been produced by laser ablation with high abundance of $X_{10}M^-$ (X = Si, Ge, Sn, and Pb; M = Co) clusters followed by a minimum for $X_{11}M^-$. There is an extraordinary peak in the mass distribution for $Ge_{10}Co^-$. The ground state of these clusters is predicted to be a bicapped tetragonal antiprism. The unusual stability of these charged clusters has been explained and several binary combinations to predict new magic clusters of Si, Ge, Sn, and Pb with ten atoms doped with Ni, Pd, or Pt have been explored.
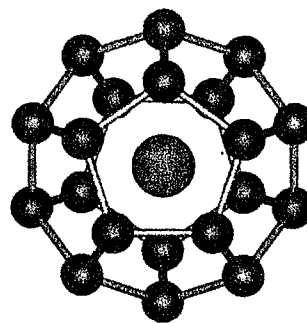

Further it has been also shown that encapsulation of one Th atom stabilizes Si_{20} in the fullerene structure with perfect icosahedral (I_h) symmetry(Fig.1). This is the largest cage of silicon that can be stabilized with a metal atom and thorium

Fig. 1 I_h-Th@Si_{20} fullerene the largest fullerene of silicon stabilized by one metal atom.

is predicted to be the only element that would do it with perfect symmetry. In contrast to carbon fullerenes for which pentagons create strain in the bonding, for silicon, pentagonal faces are most preferred and hexagons are the places for strain. Therefore this is predicted to be the ideal cage structure of silicon
similar to C_{60} and it should be strongly abundant.

Chapter 4: The Discovery of Silicon Nanotube

The preference for the sp^3 bonding in silicon and germanium leads to distortions in their quasi-one-dimensional tubular nanoforms so that they tend to become rather three-dimensional structures than to form nanotubes. The strategy adopted to stabilize these finite nanotubes in this study was quite simple. The stability of various structures of $Si_{12}M$ with M a divalent metal atom was explored. For M = Be the cluster was found to have a chair shaped structure with Be at the center. However, in this study when two such $Si_{12}Be$ units were stacked, surprisingly a transformation occurred from the chair-shaped units to the hexagonal shape. Studies on further doping and different arrangements of Be atoms showed that the doped portion of the nanotube was symmetric and nearly hexagonal in shape, while the undoped portion was distorted back to chair shaped

Fig. 2 Stable unit of $Si_{24}Be_2$ that could be repeated to form nanotube of any desired length.

structure, giving a clear indication of the stabilization of sp^2 bonding due to metal atom doping. It was noted that the packing of two units of $Si_{24}Be_2$ leads to a symmetric $(Si_{12}Be)_4$ nanotube with very small sp^3 character. Thus, we found that $Si_{24}Be_2$ represents a stable unit

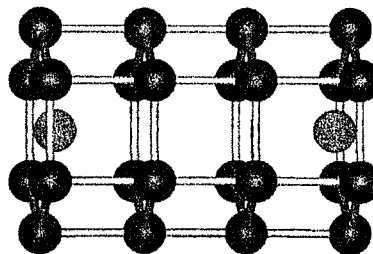that (Fig. 2) can be repeated to obtain a nanotube of desired length. The band structures of these nanotubes show metallic characteristic. Recently these predictions have found experimental support.

Magnetism in silicon nanotubes

The presence of metal atoms in silicon nanotubes opens up also the possibility of magnetism in these silicon-based structures. Following the case of Be doping, stability of a basic unit of $Si_{12}M$ was first explored that could be assembled to form nanotubes. The hexagonal prism structure of $Si_{12}M$ was found to be lowest in energy for M = Mn, Fe, and Co as compared to the chair shape structure of $Si_{12}Be$ while in the case of Ni, the structure is slightly distorted. Stacking two units of the hexagonal prism cluster leads to weak interaction between the units due to large HOMO-LUMO gap of $Si_{12}M$ cluster. However, continuation of assembling and doping of these units with one more TM atom in between the prisms leads to an increase in the BE of the nanotubes, an improved geometry with nearly planar Si hexagonal rings and generally an enhancement in the magnetic moments. In 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. The infinite nanotubes with the stoichiometry $Si_{24}M_4$ and $Si_{24}M_2$ also show enhanced
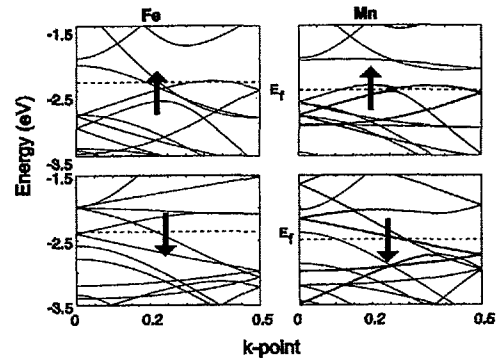

Fig. 3 The band structures of Fe and Mn doped nanotubes. There is a gap just above the Fermi level in the spin-down component of band structure of Mn giving indication formation of half-metallic nanotube.

stability as the number of M atoms is increased. The infinite Fe-doped nanotube has ferromagnetic coupling with a high magnetic moment of 2.4 μ_B per Fe atom. This value is nearly the same as in bulk Fe. Mn prefers an interesting spin arrangement in which pairs of ferromagnetically coupled Mn atoms are antiferromagnetically coupled with their neighbouring pairs resulting in zero net moment. This configuration, however, is only 0.03 eV lower in energy than the corresponding ferromagnetically coupled nanotube. This is another very important result as the transformation from antiferromagnetic to ferromagnetic coupling may be achieved by application of a weak magnetic field. The band structure (Fig. 3) of the Mn-doped ferromagnetic nanotube shows a gap just above the Fermi energy for the spin-up component and therefore there could be interesting possibilities of making half-metallic nanotubes by inducing a small shift in the Fermi energy. For the Co- and Ni- doped infinite nanotubes, ferromagnetic and antiferromagnetic starting configurations converge to non-magnetic solutions.

Chapter 5: Metal Encapsulated Nanotubes of Germanium

We have also shown in this study that nanotubes of Ge could be formed by doping with metal atoms. However, in this case instead of hexagonal prism units, the lowest energy structure of $Ge_{12}M$ clusters is hexagonal antiprism or an icosahedral structure. Both are nearly degenerate in the case of $Ge_{12}Mn$ clusters. The pentagonal and
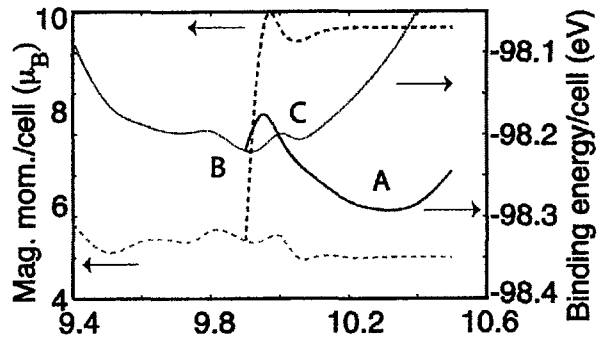

Fig 4. Magnetic phase diagram for the infinite pentagonal nanotube. A corresponds to the ferromagnetic state while B and C, to ferrimagnetic states.

hexagonal units can be repeated to form finite or infinite pentagonal or hexagonal antiprism structures to develop nanotubes of Ge doped with Mn atoms. Both the pentagonal and hexagonal infinite nanotubes have the ferromagnetic state to be of the lowest energy. However, for the pentagonal antiprism nanotubes there is a transition to a ferrimagnetic state upon compression (Fig. 4) in which long-range ferromagnetic and short-range antiferromagnetic coupling become more favourable giving rise to nano-piezomagnetic behaviour in this tube. Hexagonal antiprism nanotube has the highest average magnetic moment of 3.06 μ_B per Mn atom found so far in metal doped nanotubes of semiconductors. These nanotubes are, therefore, interesting as nanomagnets, nanosensors and for other magnetic applications at the nanoscale.

Further 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 0.5 eV direct band gap within 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. 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/n-doped nanotubes making novel possibilities for miniature devices.

Chapter 6: Effects of O on Fe Doped Silicon Nanotubes: Finding of Half Metallic Nanotubes

An understanding of the effects of adsorption of H or O is important for the study of the stability of these nanotubes. In this pursuit systematic studies on the effect of O on the Fe-doped silicon nanotubes were carried out. It was found that by the change of O concentration we could very well change the electronic properties of nanotubes. $Si_{24}Fe_4O$ is found to be metallic, whie $Si_{24}Fe_4O_3$ is nearly half-metallic, and $Si_{24}Fe_4O_6$ exists in two phases as pure half-metallic and nearly half-metallic (Fig. 5). $Si_{24}Fe_4O_{12}$ possess two different kinds of carriers for the two spin components.
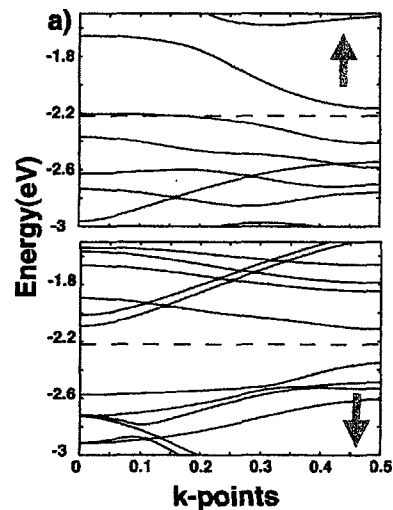
Fig. 5 Band structure of half-metallic $Si_{24}Fe_4O_6$ nanotube.

Chapter 7: Semiconducting and Insulating Nanotube of SiO_x (x = 1,2)

Oxide layers are needed as the most fundamental component for the currently used MOSFET devices. The most important limiting factor for the present approach of device size miniaturisation is the thickness of the oxide layer. We have studied finite and infinite nanotubes of Si by stacking square, pentagonal and hexagonal rings which are stabilized with the help of O atoms. In the finite nanotubes the number of O atoms mostly controls the band gap and therefore this can be controlled to design the appropriate nanotubes with desired properties. The finite nanotubes are in general semi-conducting. The band structure of infinite nanotubes shows that nanotubes with SiO_x (x < 2) are semiconducting. However, SiO_2 nanotubes are insulating. Bonding in these nanotubes are mostly covalent-like.

Chapter 8: Conclusions

An over all conclusion and suggestions for future work have been made in this chapter.

論文審査結果の要旨

　　従来の微細化技術であるシリコンテクノロジーが終焉を迎えつつあり、原子・分子を基盤としたナノテクノロジーが期待されている。それに従い、材料研究においても、従来のバルクを基本とした研究対象が大幅に変わり、クラスターやその組合せに急激に移行しつつある。そこでは、従来のバルクでは全く考えられなかった高機能性新物質を実現することが可能であり、極めて魅力ある研究領域が形成されつつある。本論文は、理論的に各種ナノチューブを提案し、量子力学に基づく第一原理シミュレーション計算を適用して、それらの原子構造と電子状態を決定した結果をまとめたものである。具体的には、従来なされていた規模をはるかに超えた大規模シミュレーション計算を行うことにより、種々の新ナノチューブの構造と物性の詳細を明らかにしたもので、全編8章よりなる。

　　第1章は序論であり、本論文の対象である擬一次元系に対する理論研究の重要性に言及している。

　　第2章では、本論文で用いる研究手法である第一原理シミュレーション計算法について、その概要を述べている。特に、本研究で採用した局所密度近似における擬ポテンシャル法と原子構造最適化、さらにクラスターやその集合体としてのナノチューブに対する理論の適用に於ける留意点に関する詳細を述べている。

　　第3章では、本研究の基盤となる金属内包クラスターの第一原理設計を行った。特に、$Th@Si_{20}$ が極めて対象性の良い構造を持ち、シリコン・フラーレンを構成することを示している。

　　第4章では、本論文において世界に先駆けて発見した金属内包シリコン・クラスターを擬一次元系として結合して構成するシリコン・ナノチューブの構造と電子状態の詳細を述べている。さらに、シリコン・ナノチューブの磁性に関するシミュレーション計算も系統的に行い、そのバルクと異なる特異な磁性を明らかにした。実験的には、極めて最近、本研究で予言した構造体が、シリコン基板上に整列した形で操作トンネル顕微鏡によって観測されている。

　　第5章では、ゲルマニューム・クラスターを結合して構成するゲルマニューム・ナノチューブの原子構造と電子状態の詳細を述べている。

　　第6章では、鉄原子を内包したシリコン・ナノチューブへ酸素を導入することにより half-metal 状態が実現できることを発見し、ナノスケールでのスピントロニクスの可能性を示した。

　　第7章では、SiO_x（x=1,2）の作るナノチューブの構造と電子状態を算定し、現在の集積回路の極微細化過程において必要となるナノスケールでの絶縁体設計を行った。

　　第8章は結論である。

　　以上要するに、本論文は、スーパーコンピューターを活用した超大規模第一原理シミュレーション計算により、金属内包シリコン及びゲルマニューム・ナノチューブの原子構造と電子状態を明らかにしたもので、材料物性学の発展に寄与するところが少なくない。

　　よって，本論文は博士(工学)の学位論文として合格と認める。