NANO LETTERS

xxxx
Vol. 0, No. 0
A−D

Structure and Stability of Ni-Encapsulated Si Nanotube

Madhu Menon,*,†,‡ Antonis N. Andriotisc,§ and George Froudakis||

Department of Physics and Astronomy, University of Kentucky, Lexington, Kentucky 40506-0055, Center for Computational Sciences, University of Kentucky, Lexington, Kentucky 40506-0045, Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, P.O. Box 1527, 71110 Heraklio, Crete, Greece, and Department of Chemistry, University of Crete, P.O. Box 1470, Heraklio, Crete, Greece 71409

Received December 10, 2001; Revised Manuscript Received January 15, 2002

ABSTRACT

Using tight-binding molecular dynamics and ab initio methods, we predict the existence of a novel quasi-one-dimensional Ni−Si form in which a Si nanotube is stabilized by an encapsulation of the Ni chain. The resulting structure is found to be metallic with finite DOS at the Fermi level. Our work follows the recent experimental work showing that endohedral encapsulation of transition metal atoms stabilizes the Si polyhedral cage.

Silicon-based materials have been the focus of extensive research due to their technological importance. However, new forms of carbon in the form of fullerenes and nanotubes are providing increasing challenges to Si in the field of nanotechnology. New forms of stable silicon are, therefore, needed to sustain the current Si-based technology. It should be noted that even though both Si and C are isovalent, their behavior in forming chemical bonds is quite different. For example, in the most stable bulk phase Si prefers sp^3 bonding while C prefers sp^2 bonding. The remarkable stability of closed carbon cages can be attributed to the sp^2 affinity for carbon. By contrast, Si cages are highly unstable.[1,2] Very recently, experimentalists have succeeded in synthesizing polyhedral Si cages stabilized by endohedral encapsulation of transition metal atoms.[3] In the experiment reported by Hiura et al.,[3] the metal ion was found to serve as a reaction site, nucleating a cluster of Si atoms until it was completely covered. Although the starting metal atoms were ionized positively, they became neutral after encapsulation by Si. Furthermore, the number of Si atoms that formed the cage cluster depended on the chemical identity of the metal atom. The transition metal atoms observed to undergo complete covering by Si atoms included Cr, Mo, W, Hf, Ta, Re, Ir, Nb, Mo, Co, and Ni. The complete encapsulation of the metal atoms by Si causes an efficient isolation of the metal atoms from the surrounding environment, providing an exciting possibility of their use in tunable building blocks for new nanostructures. Also, by varying the type of endohedral atom, one can control the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap, enabling band-gap engineering.

Hiura et al., also provided theoretical support for their findings by performing ab initio optimizations for a WSi_{12} cluster. They found a W-encapsulating regular hexagonal Si_{12} prism to be the most stable geometry for this binary system. Additionally, they also found a basket-like structure (C_{2v} symmetry) to be a local minimum, although 1 eV higher in energy. More recently, Kumar and Kawazoe[4] have performed theoretical analysis of several stable structures in which a metal atom is endohedrally encapsulated by different sized Si cages and discussed the possibility of altering band gaps.

In this Letter we report results of our theoretical investigations using ab initio and tight-binding molecular dynamics (TBMD) methods of various cage-like structures of Si stabilized by encapsulation of Ni. Nickel silicides are of major research interest since they offer high-temperature materials for Si metalization as well as rectifying junctions with a variety of Schottky barrier heights.[5−7] Also, transition metal silicides such as $NiSi_2$ constitute prototype systems in surface science studies for understanding the effect of the transition metal atoms in surface reconstruction and heterodiffusion.[8] Our results show that complete encapsulation of the Ni atom by Si atoms does indeed stabilize the Si cage, supporting the experimental findings of Hiura et al. We also find that larger Si cages can be made stable by the

† Department of Physics and Astronomy, University of Kentucky. E-mail: super250@pop.uky.edu.
‡ Center for Computational Sciences, University of Kentucky.
§ Foundation for Research and Technology-Hellas. E-mail: andriot@iesl.forth.gr.
|| University of Crete.

10.1021/nl015695w CCC: $22.00
Published on Web 00/00/0000

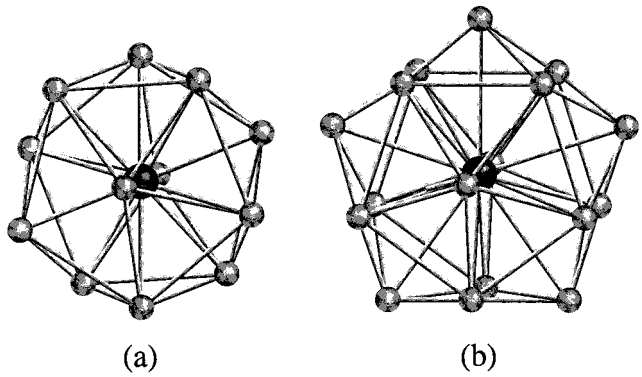

Figure 1. Optimized geometries obtained by both ab initio and TBMD methods for (a) $NiSi_{12}$ (C_{5v} symmetry) and (b) $NiSi_{17}$ (D_{5h} symmetry) clusters.

encapsulation of clusters containing two or more Ni atoms. More interestingly, our results show that quasi-one-dimensional forms of Si such as nanotubes can be made stable by an encapsulation of a linear chain of Ni atoms lying along the axis of the Si nanotube.

The structural optimizations were carried out using both ab initio and TBMD methods. The ab initio calculations were performed using the GAUSSIAN 98 program package and includes density functional theory (DFT) calculations with the three-parameter hybrid functional of Becke using the Lee−Yang−Parr correlation functional.[9] The atomic basis set used is of double-ζ quality and includes relativistic effects for heavy atoms. The TBMD calculations use the tight-binding parametrization, transferable from small binary Ni_mSi_n clusters up to bulk $NiSi_2$. The details of our TBMD method for the Ni−Si system is given in ref 10. The method has been used to study the dynamics of the Ni atoms in a Si environment and vice versa,[10] giving results in good agreement with experiments. While TBMD simulations were used to perform fully symmetry unconstrained optimizations in all cases, the computational complexity of the ab initio method allowed optimizations for Ni_mSi_nclusters with $m + n \leq 20$ only. The ab initio method was used for the calculation of total energies and for determining the HOMO−LUMO energy differences in all cases, however.

We start with the study of cage-like structures of Si stabilized by the encapsulation of Ni. The smallest Si cage consists of 12 Si atoms in the form of an icosahedron. This is the well-known McKay's 13 atom icosahedron,[11] but without the central atom. This 12 atom structure has been predicted to be a local minimum for Si.[12] We place a Ni atom in the center of the cage and optimize the resulting structure without any symmetry constraints using both ab initio and TBMD methods. The optimized geometries obtained by both methods had the same C_{5v} symmetry (Figure 1a) but differed slightly in bond lengths. The ab initio optimized $NiSi_{12}$ cluster had an average Ni−Si bond length of 2.63 Å and Si−Si bond length of 2.55 Å. The corresponding bond lengths for the TBMD relaxed $NiSi_{12}$ cluster were 2.50 and 2.56 Å, respectively. The cluster has spherical geometry and the central Ni has 12 Si neighbors, while each Si has 6 neighbors. Note that in the bulk fcc phase (most stable), Ni has 12 nearest neighbors. The heat of formation for this $NiSi_{12}$ cluster (relative to a relaxed Si_{12} cluster and free Ni atom) obtained using our ab initio method is −5.39 eV, indicating a high degree of stability. The ab initio calculations give the value of the HOMO−LUMO gap to be 1.22 eV. The degeneracy of the HOMO level is 4. These 4 levels host the 8 d-electrons of the Ni. There is only one LUMO level containing 2 empty d orbitals of Ni.

We next examined another $NiSi_{12}$ cluster in which a Ni atom is located in the middle of two Si hexagons facing each other in a "staggered" (not eclipsed) configuration. Both ab initio and TBMD methods give a distorted structure with only a C_{2v} symmetry on optimization. Our ab initio calculations find this structure to be 2.6 eV less stable than the C_{5v} cluster shown in Figure 1a.

We also considered two other structures for the $NiSi_{12}$ cluster in which the Ni atom is completely enclosed by Si cages. The first structure consisted of a Ni atom in the middle of a pentagonal prism of Si atoms capped at both ends with two Si atoms. The symmetry-unrestricted optimization of this cluster using both ab initio and TBMD methods resulted in a highly distorted structure with no particular symmetry. The second structure consisted of a Ni atom in the middle of a regular hexagonal prism consisting of Si atoms. Optimization of this cluster using both ab initio and TBMD methods resulted in a much lower symmetry structure (C_{2v}).

A single Ni atom can also be completely surrounded by a Si cage consisting of 17 atoms. Although this structure deviates from spherical shape, the fully relaxed structure obtained using both ab initio and TBMD methods (shown in Figure 1b) has a D_{5h} symmetry. The ab initio optimized $NiSi_{17}$ cluster had an average Ni−Si bond length of 2.94 Å and Si−Si bond length of 2.55 Å. The corresponding bond lengths for the TBMD-relaxed $NiSi_{17}$ cluster were 2.84 and 2.50 Å, respectively.

It is apparent that a single Ni encapsulation in a larger Si cage will result in greater distortion from the spherical shape and larger strain. To maintain optimal coordinations for both Ni and Si, larger Si cages should enclose more than one Ni atom. We begin with a Ni dimer and note that a 17 atom Si cluster can completely enclose the dimer in a symmetric fashion. The computational complexity of the ab initio method makes a full symmetry unconstrained optimization prohibitively expensive. We, therefore, carry out the structural optimization using the TBMD method only since the method has been shown to give results in agreement with ab initio results from small Ni_mSi_n clusters. We do, however, use the ab initio method for calculating the total energies as well as the HOMO−LUMO gaps for all relaxed structures. The TBMD-relaxed Ni_2Si_{17} cluster is shown in Figure 2a. This structure also has a D_{5h} symmetry. As seen in the figure each Ni has 12 neighbors, 11 Si and one Ni.

We have also optimized larger Ni clusters in appropriately larger Si cages in the form of Si-fullerenes. In particular, Si_{24}, Si_{30}, and Si_{36} fullerenes were used to encapsulate Ni_2, Ni_3 (triangle), and Ni_5 (trigonal bipyramid), respectively. The molecular dynamics relaxation of these structures resulted in considerable distortions with initial spherical structures

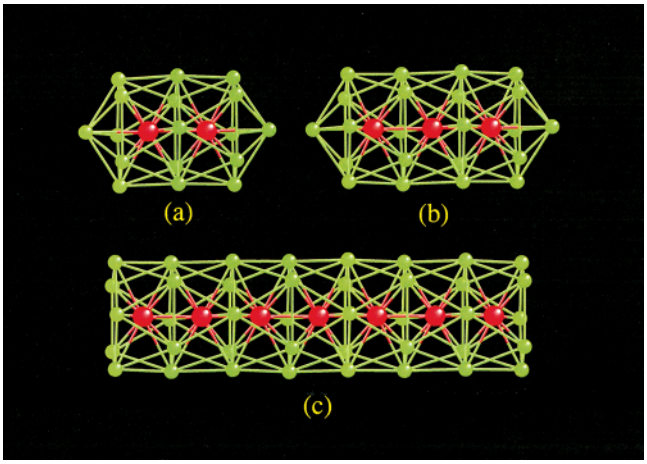

Figure 2. TBMD-relaxed Ni encapsulated Si "capsules": (a) Ni_2Si_{17} and (b) Ni_3Si_{22}. (c) Infinite Ni−Si nanotube complex.

transforming into elongated structures with more separation between Ni atoms. The maximum symmetry obtained for any of these structures is only C_{2v}. Interestingly, these distortions result in larger coordination for both Ni and Si atoms. This is consistent with the tendency of the Ni atom to have a large coordination even in cluster forms. This shows that encapsulation of larger Ni clusters in Si cannot proceed via the Si-cage route and a different avenue has to be explored.

An examination of structures in Figures 1a and 2a seems to reveal the emergence of a pattern for stable quasi-one-dimensional mixed Ni−Si geometry in which extended Ni clusters may be encapsulated by nanotubes of Si. We investigate this by checking the stability of a 22 atom Si "capsule" containing a 3 atom linear Ni chain along the symmetry axis. The fully relaxed Ni_3Si_{22} cluster is shown in Figure 2b. This structure also has a C_{5v} symmetry. The stability of such quasi-one-dimensional mixed Ni−Si systems extends to much larger clusters, as illustrated by the stability of a relaxed structure containing a 42 Si atom "capsule" stably encapsulating a 7 atom linear Ni chain. The Ni_7Si_{42} cluster thus obtained also has C_{5v} symmetry. The same symmetry is also obtained for the $Ni_{15}Si_{82}$ cluster on relaxation. In the extended structures each Ni has 12 neighbors: 10 Si atoms and 2 Ni atoms. Each Si atom, on the other hand, has 8 neighbors: 6 Si atoms and 2 Ni atoms.

We next examine the stability of the infinite Ni−Si nanotube structure derived from these cluster sequences by constructing a unit cell consisting of 4 Ni and 20 Si atoms. We perform TBMD relaxation using a constant pressure ensemble that allows for simultaneous relaxation of lattice and basis degrees of freedom. A set of uniformly spaced 32 *k*-points was sufficient to obtain convergence. The relaxed Ni−Si nanotube complex is shown in Figure 2c.

The implications of these findings are intriguing. It is now generally accepted that cage or nanotube configurations of Si cannot be stable in general. Furthermore, linear chains of Ni are also unstable.[13] The positioning of the Ni atoms along the symmetry axis of the Si nanotube, however, permits a substantial overlap between the dangling bonds of the Si

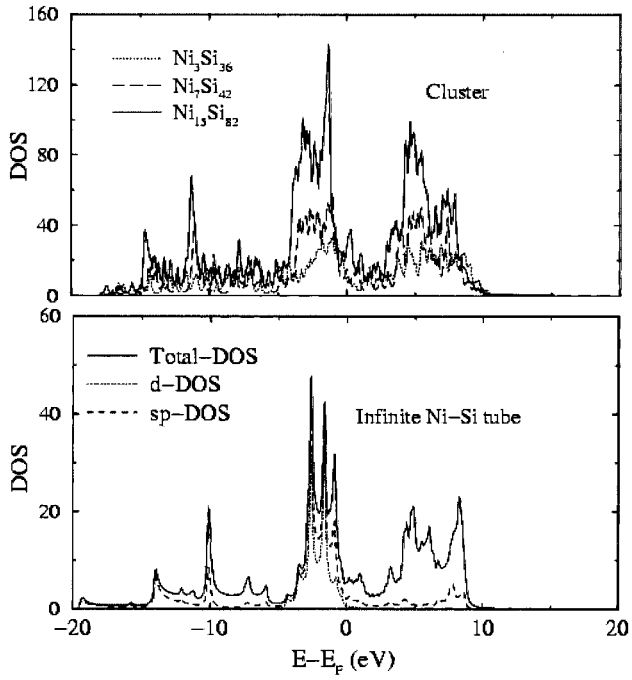

Figure 3. Top panel: electron DOS (in arbitrary units) for Ni_3Si_{22}, Ni_7Si_{42}, and $Ni_{15}Si_{82}$ clusters. Bottom panel: electron DOS for the infinite Ni−Si nanotube complex.

nanotube and the d orbitals of the Ni chain, stabilizing the compound structure. Such stabilization cannot be achieved by the encapsulation of Si atoms.

It is worth noting that our calculations are spin unrestricted and our results indicate that the magnetic moment of each encapsulated Ni atom is passivated, in agreement with recent calculations that indicate similar trends for Ni atoms interacting with carbon nanotubes.[14]

As reported in ref 3, the recent advances in experimental techniques have made it possible to synthesize stable cage forms of Si containing isolated transition metal atoms inside even though pristine Si cages are known to be unstable. The smallest such cage identified through mass spectra contained 12 Si atoms.[3] Our ab initio and TBMD results support these experimental findings and obtain two distinct stable Si cage structures encapsulating isolated Ni atoms. Our calculations suggest that the structure shown in Figure 1a may represent a likely candidate for the ground state of the $NiSi_{12}$ cluster. Furthermore, the same calculations also predict the existence of a quasi-one-dimensional Ni−Si form in which a Si nanotube is stabilized by the encapsulation of a Ni chain. Since nanotubes are the next stage in the evolutionary step for cage structures, experimental synthesis of the quasi-one-dimensional Ni−Si nanotube structure proposed in the present work should be very plausible.

More insights can be gained by an examination of the densities of states (DOS) of various Ni−Si clusters as well as the infinite quasi-one-dimensional Ni−Si complex obtained from this cluster sequence. In the top panel of Figure 3 we show the DOS for Ni_3Si_{22}, Ni_7Si_{42}, and $Ni_{15}Si_{82}$ clusters. As seen in the figure, all three clusters show metallic behavior in their DOS. Furthermore, there is an increase in DOS at the Fermi level with the increase in the cluster size

resulting from the incorporation of more Ni atoms. The bottom panel of Figure 3 contains the DOS for the infinite Ni−Si nanotube complex shown in Figure 2c. The finite DOS seen at the Fermi energy indicates that a truly metallic quasi-one-dimensional structure is possible with the Ni−Si system in the form of a Ni chain encapsulating a Si nanotube. Examination of the partial DOS in the same panel indicates that d-states lie below E_F and, therefore, do not contribute to conductivity and conduction takes place via the s and p electrons.

While the Ni-induced metalization of the Si nanotube is perhaps not surprising, the Ni-to-Si ratio of 1:5 makes it an extremely efficient way for the metallic wire formation. This structure also constitutes one of the smallest stable molecularly conducting wires. The diameter value of 4.53 Å is less than that of most nanotubes made from pure carbon. Also, since the Si enclosure effectively isolates the Ni cluster, potential applications of such systems may include quantum computers, where a Ni−Si nanotube compound could store a single bit of information in the spin state of the enclosed chain of transition metal atoms. Furthermore, this spin can also break up into linear domains. Investigations of these properties might be worthwhile.

Interestingly, successful synthesis of Si nanowires using a new method of laser ablation has been reported very recently.[15,16] Their surfaces were observed to be coated with oxygen. The higher coordination of Si atoms in the Ni encapsulating Si nanotube structure predicted in the present work is expected to make them less reactive and, consequently, less prone to attacks by oxygen. The stability resulting from this makes them more suitable for useful device applications.

Acknowledgment. The present work is supported through grants by NSF (98-62485, NER-0165121, MRSEC Program under award number DMR-9809686), DOE Grant (00-63857), NASA grant (00-463937), EU-GROWTH research project (G5RD-CT-2001-00478), and the University of Kentucky Center for Computational Sciences.

References

(1) Khan, F. S.; Broughton, J. Q. *Phys. Rev. B* **1991**, *43*, 11754.
(2) Menon, M.; Subbaswamy, K. R. *Chem. Phys. Lett.* **1994**, *219*, 219.
(3) Hiura, H.; Miyazaki, T.; Kanayama, T. *Phys. Rev. Lett.* **2001**, *86*, 1733.
(4) Kumar, V.; Kawazoe, Y. *Phys. Rev. Lett.* **2001**, *87*, 045503.
(5) Tung, R. T.; Gibson, J. M.; Poate, J. M. *Phys. Rev. Lett.* **1983**, *50*, 429.
(6) Hamann, D. R.; Mattheiss, L. F. *Phys. Rev. Lett.* **1985**, *54*, 2517.
(7) van den Hoek, P. J.; Ravenek, W.; Baerends, E. J. *Phys. Rev. Lett.* **1988**, *60*, 1743.
(8) Yongnian, X.; Kaiming, Z.; Xide, X. *Phys. Rev. B* **1986**, *33*, 8602.
(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.6; Gaussian, Inc.: Pittsburgh, PA, 1998.
(10) Andriotis, A. N.; Menon, M.; Froudakis, G. E.; Fthenakis, Z.; Lowther, J. E. *Chem. Phys. Lett.* **1998**, *292*, 487.
(11) MacKay, A. L. *Acta Crystallogr.* **1962**, *15*, 916. 12.
(12) Bahel, A.; Ramakrishna, M. V. *Phys. Rev. B* **1995**, *51*, 13849.
(13) Andriotis, A. N.; Menon, M. *Phys. Rev B* **1998**, *57*, 10069.
(14) Andriotis, A. N.; Menon, M.; Froudakis, G. E. *Phys. Rev. Lett.* **2000**, *85*, 3193.
(15) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
(16) Zhang; et. al. *Appl. Phys. Lett.* **1998**, *72*, 1835.

NL015695W