Topology and energetics of metal-encapsulating Si fullerenelike cage clusters

Takehide Miyazaki,[1,2] Hidefumi Hiura,[1,3] and Toshihiko Kanayama[1,2]

[1]*Millennium Research for Advanced Information Technology (MIRAI),*

[2]*Advanced Semiconductor Research Center (ASRC), National Institute of Advanced Industrial Science and Technology (AIST),*

AIST Tsukuba Central 4, 1-1-1 Higashi, Tsukuba 305-8562, Japan

[3]*Association of Super-Advanced Electronics Technologies (ASET), c/o ASRC-AIST, AIST Tsukuba Central 4, 1-1-1 Higashi,*

Tsukuba 305-8562, Japan

On the basis of a topological discussion as well as an *ab initio* calculation, we show that it is possible to construct a fullerenelike Si cage by doping a transition metal atom in the cage center. The cage is a simple 3-polytope which maximizes the number of its inner diagonals close to the metal atom. Our topological argument also reveals how closely the structure of the fullerenelike Si cages studied is related to that of fullerenes themselves.

Synthesis of fullerene-cage-like clusters composed of elements other than carbon (C) is a subject of great interest.[1] It is especially intriguing to study whether silicon (Si) analogues of the fullerenes can exist in energetically favorable forms. Production of Si cage clusters is also important from a technological point of view. They may be used as building blocks for fabrication of various structures in electronic devices in ten nanometer scales.

A main question which we would like to answer in this study is how one can obtain a smooth fullerenelike cage composed of Si atoms. Due to their sp^3 nature, the Si atoms tend to bind themselves *against* generation of fullerene cages. As a matter of fact, Si_n clusters (n up to ~ 50) usually favor compact forms which are completely different from fullerene cages.[2,3] The structure of a Si_{60} cluster in a fullerene cage is highly distorted.[4]

As is well known, the structure of a typical fullerene cage (C_n) is composed of only 5- and 6-membered rings. The number of the 5-membered rings is twelve irrespective of n. Each atom is connected with three neighbors. Stability of fullerenes may be attributed to two factors: σ bonding among $sp_\parallel^2$ hybrids, where $p_\parallel$ stands for the intra-cage component of the C p orbital, and π conjugation among p-orbital components normal to the cage surface ($p_\perp$).

A fundamental difficulty to maintaining a smooth Si fullerene cage stems from the fact that the π conjugation among the $p_\perp$ orbitals does not occur. Thus the caging mechanism is only the σ bonding of the $sp_\parallel^2$ hybrids. The distortion of the fullerene cage of Si_{60} is due to admixture of substantial $p_\perp$ components with $sp_\parallel^2$.

A promising solution to the augmentation of Si cage structures is to put one or more additional atoms in the cages. If electron orbitals of these "doped" atoms have a substantial overlap with the $p_\perp$ orbitals, then the additional cohesion forces would be supplied to the cage. This idea originally sprouted from the construction of Si_n clusters with n larger than ~ 20 (Ref. 5) to account for the exceptional chemical inertness of Si_{39} and Si_{45} (Ref. 6) and also for "prolate-oblate" structural change in Si_n around $n \sim 27$.[7] A common aspect of the Si_n configurations studied in Ref. 5 is that they

are configured to mimic as much of the bulk Si structure as possible, while the outermost cages resemble the counterparts of fullerenes.

As explained above, there are at least two mechanisms to stabilize a doped Si fullerene-cage cluster: (a) σ bonding within the $sp_\parallel^2$ hybrid network of the cage (Si-Si binding) and (b) bonding among the $p_\perp$ orbitals of the cage and the orbitals of doped atoms (Si-dopant binding). A key issue to be solved for production of stable fullerenelike Si cage clusters is how these two factors should be tuned in order to maximize the total binding among the constituent atoms in the clusters.

The goal of this study is to give an explicit answer to this question from a theoretical point of view. In the previous publication,[8] we obtained a rough answer: if the Si-dopant binding [mechanism (b)] is stronger than the Si-Si binding [mechanism (a)], then the Si atoms may surround the dopant atom. We have systematically observed for metal-doped Si clusters $M @ Si_n$ (M = Hf, Ta, W, Re, Ir, etc. and $n \leqslant \sim 14$) that there is a "magic number" for n which decreases with the increasing metal atomic number (N_M). The "effective atomic number (EAN)," defined as $n + N_M$, equals the atomic number of the rare-gas atom of the same row in the periodic table as that of M. Our preliminary *ab initio* calculation of low-energy structures of a $W @ Si_{12}$ cluster reveals that the W atom strongly favors being surrounded by twelve Si atoms rather than attached to the Si_{12} cluster. On the basis of these results, we have arrived at the above chemical insight into the origin of Si cage formation.

Premising this knowledge, we shall study more precise aspects of the Si cage formation mechanism. For this purpose, we again target $W @ Si_n$. The important problem which remains unanswered in the previous paper[8] is why the contribution from the Si valence electrons to the EAN is n. We shall investigate this in two ways.

First, we perform a topological discussion as to what atomic configuration is suitable for a cage of $M @ Si_n$ ($n \leqslant 20$). A very important clue to the solution has been recently given by mathematicians, Bremner and Klee.[9] They studied inner diagonals (see below or Ref. 9 for definition) of convex polytopes. The quantity of our interest here is the
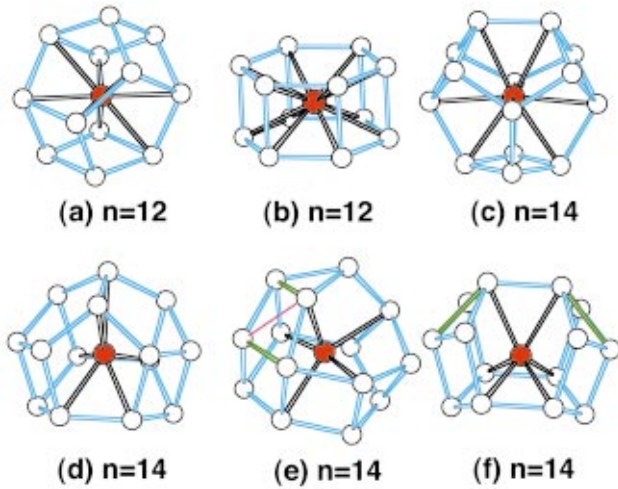
FIG. 1. (Color) Calculated structures of $W@Si_n$ in fullerenelike cages. Double line segments are drawn when the inter-atom distance is less than 2.7 Å. The double line segments corresponding to the edges of simple 3-polytopes are colored with blue. In panels (e) and (f), red single lines should be supplemented and also green double lines should be removed to retrieve connectivity in the corresponding simple 3-polytopes. See also a note.[13]
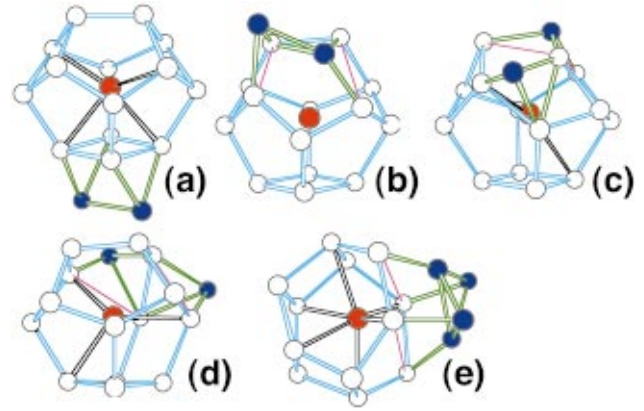

FIG. 2. (Color) Calculated structures of $W@Si_{16}$. Si atoms colored with dark blue are regarded as "attached" to either the (6,0,2)-cage $W@Si_{12}$ [panel (e)] or (3,6,0)-cage $W@Si_{14}$ clusters [panels (a), (b), (c), and (d)]. Other conventions are the same as in Fig. 1.

number of inner diagonals, δ_3. We will propose that a simple 3-polytope,[10] in which the number of inner diagonals close to the dopant (δ_3^{eff}) is maximized, should be a candidate of a stable fullerenelike Si cage of $M@Si_n$. Our hypothesis explains why the EAN of $M@Si_n$ should be $n + N_M$. Although some theoretical[11] as well as experimental[12] studies have been performed for metal-doped Si clusters, roles of cage topologies in stabilization of $M@Si_n$ clusters have been little argued.

Next, we perform a first-principles energetics of the $W@Si_n$ clusters with $8 \leq n \leq 16$. Independent of the initial configurations, the clusters in fullerenelike cages predicted by the above topological picture are indeed obtained for $n = 12$ [Fig. 1(b)] and $n = 14$ [Fig. 1(c)]. For $n = 8$ and 10, however, the caging with corresponding simple 3-polytopes (cube and pentagonal prism, respectively) may not occur, because their total energies are significantly higher than those of the respective isolated atoms. For $n = 16$, a single cage is unstable (Fig. 2). The cage is relaxed into a skeleton similar to either $n = 12$ [Fig. 1(b)] or $n = 14$ [Fig. 1(c)]. Thus we conclude that it is possible to construct energetically favorable fullerenelike Si cage clusters doped with a transition metal atom, whose cage sizes depend on the dopant.

Now we describe our results. First a topological discussion of Si cages is given. We denote the number of p-membered rings of a Si cage as N_p. Throughout this study, we limit the range of p to $4 \leq p \leq 6$. To define the structure of a simple 3-polytope, we use a vector notation $\vec{N} = (N_4, N_5, N_6)$ for brevity. For example, simple 3-polytopes with $n = 8$ and 10 vertices are a cube $[\vec{N} = (6,0,0)]$[13] and a pentagonal prism $[\vec{N} = (5,2,0)]$, respectively. For each $n \geq 12$, simple 3-polytopes with different $\vec{N}$'s exist as shown in Fig. 1 and Table I.[14]

An inner diagonal (or a 3-diagonal) of a convex

3-polytope P is defined as a segment that joins two vertices of P and that lies, except for its ends, in P's relative interior.[9] There are two other kinds of diagonals of P, 1- and 2-diagonals. The former are the edges and the latter are the diagonals of a facet. As for the latter, there are two, five and nine 2-diagonals in a 4-, 5-, and 6-membered ring, respectively. If we denote the number of i-diagonals by δ_i, then $\delta_1 + \delta_2 + \delta_3 = n(n-1)/2$, where n is the number of vertices. For example, $\delta_3 = 4$ for $\vec{N} = (6,0,0)$ and $\delta_3 = 10$ for $\vec{N} = (5,2,0)$. In this study, we further define δ_3^{eff} as $\delta_3^{eff} = \sum_{i>j} \theta(d_{cut} - d_{ij})$, where i and j are indices of Si atoms, d_{cut} is the cutoff radius and d_{ij} is the distance between a metal atom and a diagonal joining the i-th and j-th Si atoms. $\theta(x)$ is a step function; $\theta(x) = 1$ for $x \geq 0$ and $\theta(x) = 0$ otherwise. Obviously, δ_3^{eff} approaches $n(n-1)/2$ for $d_{cut} \to \infty$. In order to count the number of only inner diagonals, d_{cut} must be small. In practice, we vary d_{cut} from 1.0 Å down to 0.25 Å to check the d_{cut}-dependence of δ_3^{eff}. The overlap between the $p_\perp$ orbitals of a Si cage and the counterparts of the dopant metal atom may be roughly proportional to the number of the $p_\perp$ orbitals pointing toward the metal atom, which should also be approximately proportional to δ_3^{eff} at a small value of d_{cut} by its definition. Thus analyzing δ_3^{eff} is a good measure for the strength of the bonding between the doped atom and the Si cage. Our first-principles calculation shows that δ_3^{eff} at $d_{cut} = 0.25$ Å is maximized for the lowest-energy $W@Si_n$ cluster for $n = 12$ and 14.

Turning to the topology of a *carbon* fullerene cage, its peculiarity can be characterized in the light of δ_3. Let Q be a simple 3-polytope with n vertices. For each of $n \geq 24$, Q with $F(= n/2 + 2)$ facets composed of only twelve pentagons and $F - 12$ hexagons maximizes δ_3 which is $n(n-13)/2 + 30$. For $n = 20$, Q with the largest δ_3 ($= 100$) is a dodecahedron which has only twelve pentagons. In the case of $n = 22$, however, Q with $N_5 = 12$ cannot be realized.[9] The maximum possible value of δ_3 is 128 when $\vec{N} = (1,10,2)$. Thus a typical fullerene C_n cage ($n \geq 20$) can be identified to be a simple 3-polytope with a maximum value of δ_3 except for $n = 22$. The Si_n cages we consider for $8 \leq n \leq 16$ include Q's with

TABLE I. Topological properties and energetics of $W@Si_n$ clusters. For definitions of n, $\vec{N}$, δ_3, δ_3^{eff}, and d_{cut}, see text. d_1 and d_2 are the Si-W and Si-Si distances in Å, averaged over the respective pairs whose separations are less than 2.7 Å. ΔE is the total energy (eV) relative to that of the lowest-energy cluster, $\vec{N} = (6,0,2)$ for $n = 12$ and $\vec{N} = (3,6,0)$ for $n = 14$.

n	$\vec{N}$	δ_3	$d_{cut}(\text{Å}) =$	$\delta_3^{eff}(d_{cut})$				d_1	d_2	structure	ΔE
				1.0	0.6	0.3	0.25				
12	(4,4,0)	20		8	4	0	0	2.59	2.42	Fig. 1(a)	2.16
12	(6,0,2)	18		6	6	6	6	2.67	2.39	Fig. 1(b)	0.00
14	(3,6,0)	34		4	4	4	4	2.69	2.34	Fig. 1(c)	0.00
14	(4,4,1)	33		11	5	1	0	2.66	2.35	Fig. 1(d)	0.95
14	(5,2,2)	32		13	4	2	2	2.64	2.39	Fig. 1(e)	0.63
14	(6,0,3)	31		9	7	4	0	2.63	2.39	Fig. 1(f)	0.89

maximum δ_3's. Although $\delta_3 = 18$ of the (6,0,2)-cage [Fig. 1(d)] is not a maximum, it is the second largest value. This is why we can say that our Si cages are fullerenelike.

In order to substantiate the above topological argument, we perform a first-principles energetics of the $W@Si_n$ clusters. Here we adopt a recently proposed single-parent evolution algorithm (SPEA)[15] to update the atomic coordinates. For SPEA simulation, we calculate the total energies of clusters with a linear combination of atomic orbitals (LCAO) using the Gaussian 98 package.[16] Then we use the calculated coordinates of the clusters as the inputs of plane-wave[17] (PW) total energy calculations[18] where quenched molecular dynamics is performed for final convergence. Electronic structures of clusters are calculated with density-functional theory[19] within generalized gradient approximation to the exchange-correlation energy functionals (Becke '88 (Ref. 20) and Perdew-Wang '91 (Ref. 21) for LCAO and Perdew-Wang-Ernzerhof '96 (Ref. 22) for PW).[23]

The SPEA-based geometry optimization of $W@Si_n$ clusters is extremely time-consuming due to the lack of the established tight-binding (TB) parameters to describe accurate W-Si interactions. We have to perform SPEA updates and subsequent relaxations of the clusters *entirely* at the generalized gradient approximation (GGA) level of theory. This severely limits the number of the potential energy surface (PES) points which we can sample within an available computer time. Concretely, only ~ 50 SPEA updates are performed per cluster per optimization run, by using the Gaussian 98 package.[16] Thus we do not insist that the fullerenelike Si cage structure of a $W@Si_n$ cluster found in this study is of the global-energy-minimum (GEM).

An SPEA structure optimization is initiated from a stable Si_n cluster with already published atomic positions[3] to which a W atom is attached. Independent of the initial structures, we find that lowest-energy structures of $W@Si_{12}$ and $W@Si_{14}$ clusters are simple 3-polytopes with $\vec{N} = (6,0,2)$ [Fig. 1(b)] and (3,6,0) [Fig. 1(c)], respectively. Varying d_{cut} from 1.0 Å down to 0.25 Å, we find that δ_3^{eff}'s of both are constants (6 and 4; see Table I for the summary of the result). On the other hand, δ_3^{eff}'s of the other $W@Si_{12}$ and $W@Si_{14}$ clusters decrease to 0–2 as d_{cut} becomes smaller, whose total

energies are all higher than those of the (6,0,2) and (3,6,0) cages, respectively. These results support the topological argument made above.

It should be noted that the $W@Si_n$ ($n \sim 10$) clusters may be viewed as metastable phases of Si-rich tungsten silicides, which do not appear in the equilibrium W-Si phase diagram.[24] It is suggested in the previous experiment[8] that the $W@Si_n$ clusters are obtained via a sequential growth by attaching additional m Si atoms to a smaller $W@Si_{n-m}$ cluster. Although the sequential growth is a dynamical process, let us speculate its essence on the basis of our energetics. We calculate differential binding energy, defined as $\Delta E(n) = E_{bind}(n+2) - 2E_{bind}(n) + E_{bind}(n-2)$, where $E_{bind}(n) = E_{total}^{atom}(W) + nE_{total}^{atom}(Si) - E_{total}^{cluster}(WSi_n)$. A negative value of $\Delta E(n)$ means that generation of a $W@Si_n$ cluster as an end product is favorable. We find that $\Delta E(10) = 1.6$ eV, $\Delta E(12) = -2.8$ eV and $\Delta E(14) = -0.3$ eV. For $n = 10$, stable caging of a W atom in simple 3-polytopes is unlikely to occur. The cluster should be chemically very reactive, because there are too few Si atoms to react with W. If additional Si atoms can arrive at the cluster prior to its collapse, then subsequent growths to $W@Si_{12}$ and possibly to $W@Si_{14}$ should occur with high probabilities.

We also find that there exists a threshold cage size for $W@Si_n$ beyond which the cages become unstable. In Fig. 2, some of calculated structures of $W@Si_{16}$ clusters are shown. The initial configurations of the cages are taken as simple 3-polytopes with 16 vertices. Upon relaxation, all cages we considered are completely distorted and become similar to either the (6,0,2) cage plus two Si atoms or the (3,6,0) cage plus four Si atoms. It appears that $n = 14$ is the threshold size in the case of W doping. For a cage beyond a critical size, there are too many Si atoms to react with W.

In conclusion, we show that it is possible to construct Si clusters in fullerenelike cages with transition-metal atom doping. A topological discussion suggests that simple 3-polytopes with maximum numbers of inner diagonals close to the dopant may be good candidates of fullerenelike Si cages. First-principles calculation shows that, in the case of W doping, $W@Si_{12}$ and $W@Si_{14}$ are energetically most favorable and also have the cages predicted by the above topological picture.

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[13] It is cautioned that the Si cage structures are not necessarily convex simple 3-polytopes, especially in high-energy structures. Some of them are not even convex. In spite of this, one can *model* well low-energy structures with convex simple 3-polytopes.

[14] Suppose that P has E edges and F facets, then $E = (4N_4 + 5N_5 + 6N_6)/2$ and $F = N_4 + N_5 + N_6$. Since P is simple, $E = 3n/2$, meaning that n must be even. Combining these with the Euler's formula $n + F = E + 2$, we get $2N_4 + N_5 = 12$ and $N_5 + 2N_6 = n - 8$. Note that P's with $\vec{N} = (6,0,1)$ and $(5,2,1)$ do not exist.

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[17] Each cluster is located in a simple cubic supercell with the edge length of 30 a.u. in PW calculation. The self-consistent field iterations are continued until the total energy converges to $\sim 3 \times 10^{-6}$ eV/atom. Only a Γ point is sampled for Brillouin-zone integration. The atomic positions of all atoms in supercell are relaxed until the residual forces are less than ~ 0.06 eV/Å.

[18] *STATE (Simulation Tool for Atom TEchnology)*, Version 3.50, Joint Research Center for Atom Technology (JRCAT), May 2000.

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