Formation of Metal-Encapsulating Si Cage Clusters

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We report the formation of a series of metal-containing hydrogenated silicon clusters using an ion trap. Mass analyses reveal that many types of transition metal ions M^+ (M = Hf, Ta, W, Re, Ir, etc.) react with silane (SiH_4) to form dehydrogenated MSi_n^+ cluster ions (n = 14, 13, 12, 11, 9, respectively) as an end product, indicating that the metal atom is endohedral and stabilizes the Si polyhedral cage. This finding is confirmed by our *ab initio* calculation that WSi_{12} is a W-encapsulating Si_{12} cage cluster, and is very stable owing to both the electronic and the geometrical shell closures.

There is currently great interest in utilizing small atomic clusters as constituent elements to build up well-controlled nanostructures. Because silicon is a semiconducting element of great importance in microelectronics industry, Si clusters have been extensively investigated both experimentally [1] and theoretically [2,3]. Despite many attempts at obtaining Si clusters well suited for building blocks, the fabrication of Si cage clusters with self-complete bonding is still a challenge although carbon forms stable clusters (fullerenes). Unlike fullerene cages, a hollow Si cage is unstable because sp^2 hybridization is highly unfavorable in silicon [4]. A possible approach to stabilize the Si cage is to locate a guest atom in the center of the cluster as suggested by theoretical calculations [5]. Beck had already succeeded in preparing mixed metal-silicon cluster ions, MSi_n^+ (M = Cr, Mo, and W), by the laser vaporization supersonic expansion technique [6], and found MSi_{15}^+ and MSi_{16}^+ to be dominant and stable to dissociation. However, it has not so far confirmed whether, in MSi_n clusters, Si atoms encage a metal atom or not. Here we report the formation of a series of hydrogenated Si clusters with a single metal atom, MSi_nH_x (M = transition metal) using an ion trap. In particular, the clusters are dehydrogenated for specific compositions, implying that they are so stable they can be used as a tunable building block for cluster-assembled materials.

In this paper we used a newly developed ion trap (EQSIT: external quadrupole static attraction ion trap) for producing $MSi_nH_x^+$ cluster ions. A detailed description of EQSIT is given elsewhere [7]. In brief, the EQSIT comprises a linear quadrupole and a surrounding cylindrical cage electrode. Applying both ac and dc voltages between them gives rise to a trapping potential, at the bottom of which ions are trapped. As a silicon source, SiH_4 gas of 5×10^{-7} Torr was introduced into a vacuum chamber equipped with the EQSIT. At the same time, metal vapor was generated by resistive heating of a metal wire (purity $\geq 99.9\%$), and then ionized by electron irradiation of ≈ 80 eV. The chamber was left at ambient temperature.

The resulting metal ions were immediately confined in the EQSIT and allowed to react with SiH_4 molecules. The produced cluster ions were taken out of the EQSIT, followed by mass analysis using quadrupole mass spectrometers.

In addition to the experiments, we performed *ab initio* calculations to identify the concrete structure model of the WSi_{12} cluster. Starting from various initial structures, we optimized the atomic positions of the cluster. The total energy of a cluster was obtained from electronic-structure calculation based on density functional theory [8]. Most calculations were done with the Gaussian basis sets (LCAO) [9] using the Becke'88 [10] and Perdew-Wang'91 [11] functionals for the exchange and correlation energies, respectively. The effective-core potentials [12] for Si and W were used. In order to check basis-set effects on the obtained results, independent calculations with plane wave (PW) basis sets were performed for some cluster models [13]. For the latter, we used the Perdew-Burke-Ernzerhof'96 [14] functional for the exchange and correlation energies. The electron-ion Coulomb interactions for Si and W were modeled with the Troullier-Martins' [15] and the Vanderbilt's [16] pseudopotentials, respectively. A cluster was located in a cubic supercell with the edge being ~ 10.6 Å. The wave functions were expanded in plane waves up to 23 Ry. The optimized geometries and electronic states of some chosen WSi_{12} clusters agreed very well between the LCAO and PW calculations.

Figure 1 shows the time-resolved quadrupole mass spectra of $WSi_nH_x^+$ cluster ions, which were extracted electrically from the EQSIT to a mass spectrometer after a given reaction time (denoted as holding time) from a 10-ms electron beam pulse. A sequential growth starting from W^+ up to $WSi_{12}H_x^+$ is clearly seen. The growth can be thus be identified as a typical ion-molecule reaction of W^+ or $WSi_nH_x^+$ ions with neutral SiH_4 molecules. The growth rate of $WSi_nH_x^+$ decreased as n increased; in particular, when $n \geq 10$, $WSi_nH_x^+$ grew very slowly. In addition,
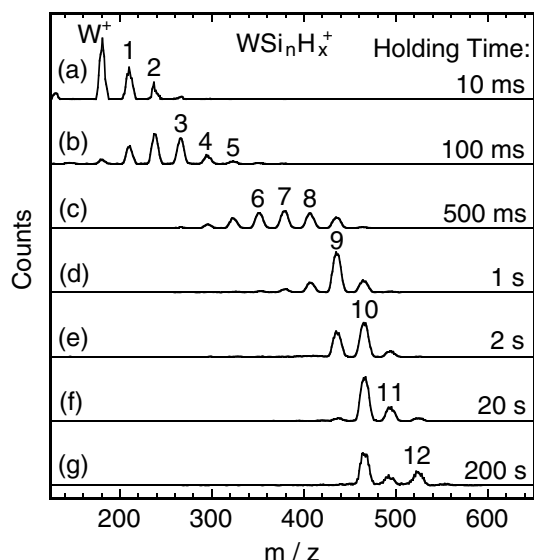
FIG. 1. Time-resolved mass spectra of $WSi_nH_x^+$ cluster ions produced in the EQSIT ion trap. Each spectrum was observed after a given holding time: (a) 10 ms, (b) 100 ms, (c) 500 ms, (d) 1 s, (e) 2 s, (f) 20 s, and (g) 200 s. The numbers shown above the peaks represent the number of Si atoms, n, in $WSi_nH_x^+$.

FIG. 2. Comparison of mass spectra of $MSi_nH_x^+$ showing the presence of end products at $n = 9-14$ depending on metal species: (a) $M = $ Hf, (b) $M = $ Ta, (c) $M = $ W, (d) $M = $ Re, and (e) $M = $ Ir. The insets represent magnified spectra as indicated. The inset in (c) shows a mass spectrum of $W_2Si_nH_x^+$, emerging only when W_2^+ ions were formed. The numbers shown above the peaks indicate n in $M_ySi_nH_x^+$ ($y = 1$ or 2).

$WSi_nH_x^+$ with $n > 12$ were rarely found even at the longest holding time. In other words, the clusters lost a reactivity to SiH_4 molecules when n reached 12. It was observed that the same group metal elements had an equal termination number; e.g., the growth for $M = $ Mo, as well as for $M = $ W, terminated at $n = 12$. As shown in an inset of Fig. 2(c), when diatomic W_2^+ ions were generated, they reacted with SiH_4 molecules to give $W_2Si_nH_x^+$ ($n = 17$ and 18) as end products. It is worth noting that 12 atoms are necessary to surround a single atom with close packing, whereas 17 or 18 atoms are needed for a diatomic molecule. The observations thus imply that the metal atom acted as a reaction site until it was completely covered with Si atoms.

Many transition metal ions M^+ ($M = $ Hf, Ta, Re, Ir, Nb, Mo, Co, Ni, etc.) underwent a similar clustering reaction with SiH_4. Figure 2 shows mass spectra of $MSi_nH_x^+$ cluster ions for $M = $ Hf, Ta, W, Re, and Ir under steady state conditions. In this case, M^+ ions were continuously generated by a dc electron exposure, and the produced $MSi_nH_x^+$ cluster ions were automatically transported from the EQSIT to another mass spectrometer through the inside of the quadrupole of the EQSIT. This procedure made it possible to provide all of the $MSi_nH_x^+$ cluster ions from $n = 1$ to m simultaneously. Note that any reaction almost stopped when n approached a specific number, m. The relative peak intensities varied with several factors, such as SiH_4 pressure and trapping parameters, but the end products were always observed at the same size for each metal species. The value of m depended on the metal element; i.e., $m = 14$ for Hf, 13 for Ta, 12 for W, 11 for Re, and 9 for Ir. As described later, when $n = m$, the clusters tended to lose all of their H atoms, i.e., dehydrogenated clusters,
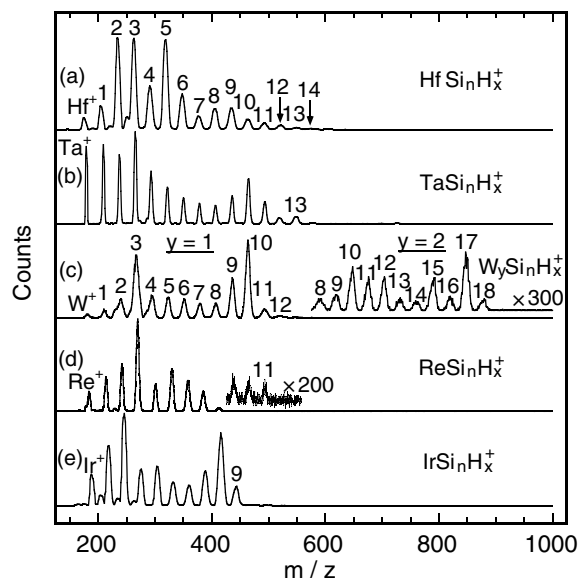
MSi_m^+ were highly abundant. Rare-earth metal ions (La^+, Ce^+, Gd^+, etc.) and noble metal ions (Cu^+, Pd^+, Ag^+, Au^+, etc.) reacted with SiH_4 molecules, but yielded cluster ions different from those for $M = $ Hf, etc. Most of the cluster ions were represented by a molecular formula of $MSi_nH_{2n}^+$ ($n = 1-4$), and therefore assigned to metal-silylene ($:SiH_2$) coordination complex ions. Main group metal ions (Al^+, Sn^+, Pb^+, Bi^+, etc.) and an alkaline-earth ion, Ba^+, exhibited no reactivity to SiH_4. To summarize, metal ions with a partially filled d shell (d electrons ≥ 2, in the ground state) can serve as an "ultimate template" for assembling Si atoms from SiH_4 molecules.

Figure 3(a) shows a high-resolution mass spectrum of $WSi_nH_x^+$ for $n = 1-12$. The spectra were measured with a resolution of about 0.5 amu, which is enough to evaluate the hydrogen contents, x, by a standard mass analysis method [17]; e.g., the observed $WSi_3H_x^+$ cluster ions were thereby estimated to comprise 52.8% of WSi_3^+, 41.4% of $WSi_3H_2^+$, and 5.8% of $WSi_3H_4^+$. This estimation reproduces the observed $WSi_3H_x^+$ spectrum very well, as shown in Fig. 3(b). Similarly, the hydrogen contents of $WSi_nH_x^+$ for $n = 1-12$ were obtained, as summarized as histograms in Fig. 3(c), exhibiting a few notable features, which were commonly observed for $M = $ Hf, Ta, Re, and Ir. First, even larger cluster ions possessed only a small number of hydrogens ($x \leq 4$ for all n). This observation suggests that the cluster ions are not chainlike, but consist of highly coordinated Si atoms or condensed Si rings. Hydrogens are well known to terminate and stabilize dangling bonds of Si atoms. Taking this into account, the metal atom will play a similar role with hydrogens and should therefore be
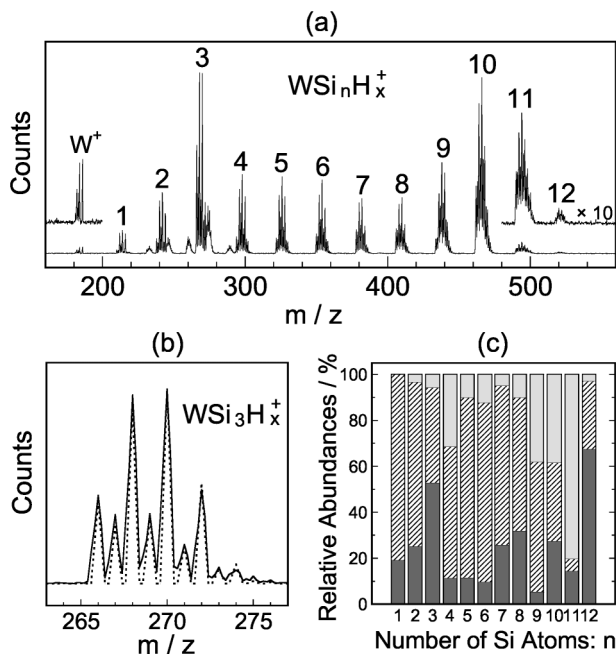
FIG. 3. (a) High resolution mass spectrum of $WSi_nH_x^+$ for $n = 1-12$. The numbers shown above the peaks indicate n in $MSi_nH_x^+$. (b) Magnified high resolution mass spectrum of $WSi_3H_x^+$. The solid and dotted lines, respectively, represent the observed and calculated spectra. (c) Distribution of the hydrogen contents of $WSi_nH_x^+$ for $n = 1-12$. The dark gray, shaded, and pale gray parts indicate the relative abundance of WSi_n^+, $WSi_nH_2^+$, and $WSi_nH_4^+$, respectively.

FIG. 4. Comparison of the relative abundance of MSi_n^+ among $MSi_nH_x^+$ for various n. The circles, squares, triangles, and crosses correspond to $TaSi_n^+$, WSi_n^+, $ReSi_n^+$, and $IrSi_n^+$, respectively. For $M = Ta$, $TaSi_{13}^+$ (as well as $TaSi_{12}^+$) is dominant. For $M = Re$, a low signal-to-noise ratio of the peaks of $ReSi_{11}H_x^+$ prevented us from accurately estimating the relative abundance of $ReSi_{11}^+$, but it is abundant.

located in the center of the clusters in order to interact with all of the Si atoms equivalently. Second, a completely dehydrogenated MSi_n^+ ($x = 0$) dominated when n reached the specific number, m (e.g., $m = 12$ when $M = W$). This observation means that there should be enough stabilization at $n = m$ to compensate for the entire lack of hydrogen termination.

Figure 4 plots the relative abundance of MSi_n^+ among $MSi_nH_x^+$ versus the number of Si atoms, n, for $M = Ta$, W, Re, and Ir. As seen, the sum of the specific number, m, and the atomic number of the metal element tends to keep a constant value of 86, which corresponds to the atomic number of the rare gas, Rn. This reminds us of the so-called octet [18] (18 electrons [18] or effective atomic number [19]) rule; e.g., in WSi_{12}, assuming that each Si atom in the cluster donates a single electron to the central metal atom, the W atom possesses 18 electrons in total (12 electrons from the Si_{12} cage and 6 valence electrons by itself), resulting in closed electronic shells, such as Rn. At the same time, 3 valence electrons are left for each Si atom, making it possible to form a Si polyhedron without forming appreciable dangling bonds. WSi_{12} is therefore expected to be stable, and the same argument can be applied for MSi_m clusters when $M = Hf$, Ta, Re, and Ir. The above argument requires metal atoms to be neutral. Although starting metal atoms were ionized positively, they would nevertheless be almost neutral after encapsulated by Si cages because the positive charges would be widespread on
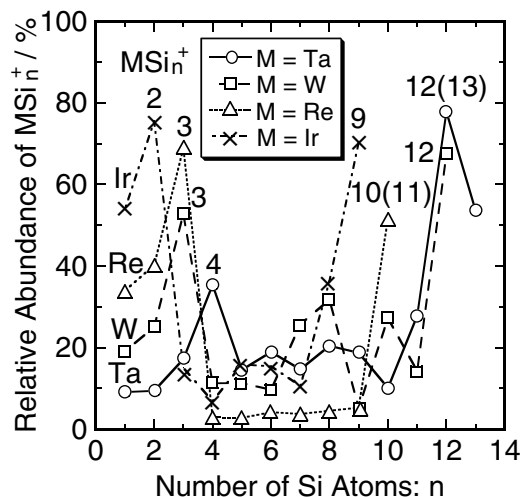
the whole clusters. Actually, e.g., for WSi_{12}, our *ab initio* calculations indicate its HOMO is extended over the Si cage, but not on the W atom.

As mentioned earlier, Beck found that MSi_{15}^+ and MSi_{16}^+ ($M = Mo$ and W) were abundant [6], whereas we rarely observed MSi_n^+ with $n > 12$ for both metals. The explanation for this discrepancy may lie in the difference in Si sources for the MSi_n^+ formation. In Beck's laser vaporization experiments, bare Si atoms and clusters, including neutral and charged species, seem to have served as Si sources. However, only neutral SiH_4 molecules were used as a Si source in our study. Because bare Si atoms and clusters are much more reactive than SiH_4 molecules, the former could make MSi_n^+ grow to $n = 15$ and 16, but the latter no longer reacted with the stable MSi_{12}, making it a final product.

Our *ab initio* structure optimization supports the view that the metal atom is endohedral in MSi_n. By optimizing a number of feasible structures for WSi_{12}, we found that a W-encapsulating basketlike structure [C_{2v} symmetry, inset (a) of Fig. 5] has the lowest total energy. A metal-centered icosahedral WSi_{12} (I_h symmetry) is energetically unfavorable because the fivefold degenerate HOMO is occupied by only four electrons including spins. The basketlike WSi_{12} has closed electronic shells with an energy gap of 1.18 eV, the large value of which is suggestive of its high chemical stability. Note that the basketlike Si_{12} cage shows a topological resemblance to a partial structure of the reconstructed Si(001)-(2 × 1) surface. This accounts for the energetic favoring of the basketlike Si_{12} cage. Moreover, the C_{2v} symmetry of this cage is preferable for a substantial overlap between the dangling bonds of the cage and the d orbitals of the W atom. Thus, the formation of the
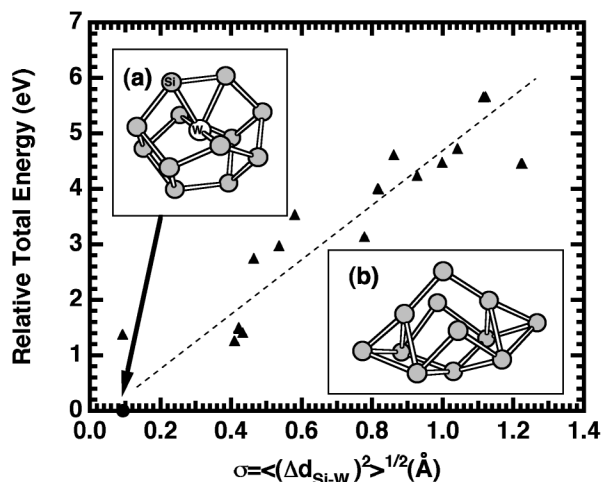
FIG. 5. The total energies of WSi_{12} clusters plotted against σ, the standard deviation of the W-Si distance in a cluster. Insets (a) and (b) represent, respectively, the lowest-energy structures of WSi_{12} and Si_{12} [3]. A bond connecting two atoms is drawn if the distance is less than 2.7 Å. The closed circle corresponds to the total energy of structure (a), and the triangles to those of the WSi_{12} structures optimized from structure (b) with a W atom. The dotted line is a guide to the eyes.

encapsulating basketlike Si cage is very desirable for maximizing total energy gain due to both the Si-Si and Si-W interactions.

To confirm this conclusion systematically, we optimized a number of WSi_{12} structures generated by placing a W atom at various positions, such as vertices, edges, and faces, in the lowest-energy S_{12} structure [3] [Inset (b) of Fig. 5]. For all the optimized WSi_{12} clusters, we then calculated the standard deviation of the interatomic distance between the W and Si atoms, σ, and found an approximately linear relationship between the relative total energy and σ, as illustrated in Fig. 5. The energies are shown relative to that of the basketlike WSi_{12} structure, which has not only the lowest total energy but also the smallest σ value of 0.094 Å among the anisotropic cages studied. Because the σ value is a measure of how equivalently the 12 Si atoms are located around the W atom, the relationship shows that the W atom prefers to be encapsulated in a Si cage as spherical as possible.

We expect a metal-encapsulating Si cluster to act as a tunable building block of new phases of materials. For instance, it will have a HOMO-LUMO gap that can be controlled by choosing the endohedral metal atom. This is because the gap is governed by the number of Si atoms and the structure of the Si cage, both of which are determined by the metal element. When assembled, the resulting crystal will form a new phase in the silicon-metal binary system between pure silicon and metal silicides.

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Note added.—A new WSi_{12} structure was recently found to be lower in total energy by ~1 eV than the basket-like one described in this Letter. It has a regular hexagonal prism Si_{12} cage with a W atom at the center. These results further confirm our claim that a metal is endohedral and stabilized in the Si polyhedral cage [20].

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[17] The method of determining x in $MSi_nH_x^+$ was as follows: first, isotope polynomial distributions of MSi_nH_x were calculated for x ranging from 0 to a certain value according to the natural abundance of M, Si, and H (e.g., natural Si consists of 92.23% of ^{28}Si, 4.67% of ^{29}Si, and 3.10% of ^{30}Si). Then, the observed spectrum was fitted to overlapping of the calculated distributions with weights as adjustable parameters, giving hydrogen content distribution. In addition, we analyzed mass spectra of $M\,^{28}Si_nH_x^+$ formed from $^{28}SiH_4$ (^{28}Si enrichment: 99.94%) and confirmed the validity of the method described.

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