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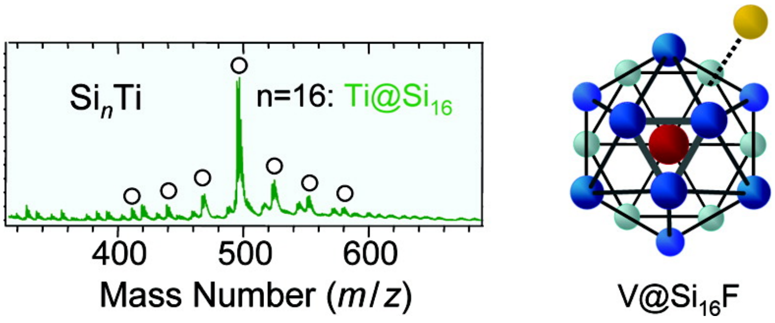

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Selective Formation of MSi_{16} ($M = Sc$, Ti, and V)

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Nanostructured materials assembled from finite-sized stable clusters have been extensively sought after since the discovery of C_{60}.[1] Fabrication of cluster-assembled materials is dependent upon finding a suitable building block for a cluster that is chemically stable and interacts weakly with other clusters of the same material. To ensure the chemical stability of a cluster, it is crucial to satisfy a closed electron configuration with a large energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Indeed, the large HOMO−LUMO gap of C_{60} is responsible for its chemical inertness and its ability to assemble into molecular crystals, as well as its high symmetry.[2]

Silicon is undoubtedly an important material in electronic devices, and silicon clusters have also attracted great attention as building blocks for silicon-based nanomaterials. However, pure silicon clusters are unsuitable as building blocks because they are chemically reactive due to the existence of dangling bonds.[3−8] With metal atom doping, closed-shell electronic structures might lead to species that are remarkably stable as a new class of metal atom-encapsulated silicon clusters. Depending on the kind of metal atom, even a single metal atom may significantly affect the structure of a silicon cluster, exhibiting magic number behavior in the mass spectrometry of MSi_n. Both experimental and theoretical studies have been performed extensively on these compounds in recent decades.[9−17] A "magic" cluster in which metal is encapsulated in a Si cage can be viewed as a superatom,[18] and it is therefore of much interest to verify this "superatom" behavior in metal atom-encapsulated silicon clusters experimentally. The existence of superatoms suggests that it should be possible to develop silicon-based devices for various optoelectronic applications by assembling them properly.[14]

We have intensively studied the electronic and geometrical structures of mixed-metal silicon clusters using mass spectrometry and anion photoelectron spectroscopy (PES). An improved ability to produce cold mixed clusters enabled us to selectively form MSi_{16} clusters together and obtain more detailed electronic structure information. In this paper, we report that $TiSi_{16}$ clusters exhibit a HOMO−LUMO gap of around 1.9 eV together with definitive PES peak assignments by halogen atom doping. The change in total valence electrons involving the substitution of Sc or V for Ti altered the magic number behavior and instead produced charged mixed clusters of $ScSi_{16}^-$ or VSi_{16}^+ as magic numbers, and suggests the possibility of producing an ionically bound superatom complex of $VSi_{16}^+F^-$.

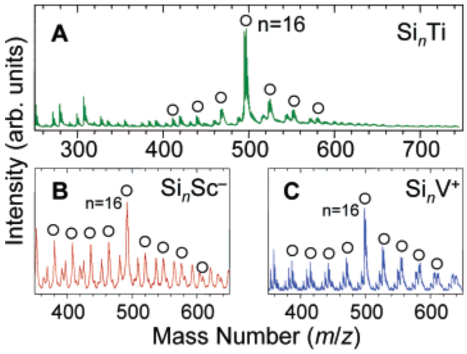

Figure 1. Mass spectra showing size-selective formation of (A) $TiSi_{16}$ neutrals, (B) $ScSi_{16}$ anions, and (C) VSi_{16} cations.

The details of our apparatus have been described elsewhere.[19] Metal atom doped silicon clusters were produced via dual laser vaporization of a pure metal and pure silicon targets with a helium carrier gas and were mass analyzed with time-of-flight mass spectrometry. Neutral metal−silicon clusters were photoionized with an F_2 laser (157 nm) for the mass spectrometry, while charged metal−silicon clusters were directly accelerated with a pulsed electric field. Figure 1 shows the mass spectra of titanium (Ti)−Si neutrals, scandium (Sc)−Si anions, and vanadium (V)−Si cations. In all of the mass spectra, MSi_{16} clusters were predominantly produced as "magic numbers", although the mass spectra in previous studies were dominated by pure silicon clusters where $n = 4−11$.[9−12] In the photoionization of MSi_n neutral, laser power dependence indicates that one-photon ionization occurs not with the ArF laser (6.43 eV) but with the F_2 laser (7.90 eV) for $n = 5−18$. The improvement of face-to-face laser vaporizations of two rods accelerated the mixing of the two elements significantly.[20] This magic numbers behavior became much less prominent in other charged states; in Sc−Si compounds, for example, the magic number MSi_{16} appears only in the anions (see Supporting Information). As a neutral species, $TiSi_{16}$ can be formed selectively by fine-tuning the source conditions, laser fluences, and flow rate of the He carrier. This selective formation is very similar to the initial finding of single-element clusters of C_{60}.[1] Since the efficient mixing of hot vapors with proper rapid cooling enhanced the selective formation, the $TiSi_{16}$ neutral cluster itself was formed selectively. As reported previously,[12] a chemical probe method is useful in deducing the structure of the MSi_n clusters. In fact, the adsorption reactivity of MSi_n clusters toward H_2O vapor can reveal the location of the metal atom in the cluster. None of the $ScSi_{16}^-$, $TiSi_{16}$, or VSi_{16}^+ compounds exhibit adsorption reactivity, leading to the suggestion that the metal atom is encapsulated inside the Si_n cage ($M@Si_{16}$; see Supporting Information).

To obtain magic clusters of MSi_n selectively at $n = 16$, the substitution of a Ti atom for a neighboring Sc or V requires a change in the total charge of the cluster. This demonstrates that MSi_{16} exhibits an electronic preference as well as geometric encapsulation, and the electron configuration of MSi_{16} is actually closed, with the valence electrons of Sc^-, Ti, and V^+. The plausible explanation is that $TiSi_{16}$ assumes a closed electron configuration with tetravalent Ti and completes the electron shell of 20 electrons with an electron

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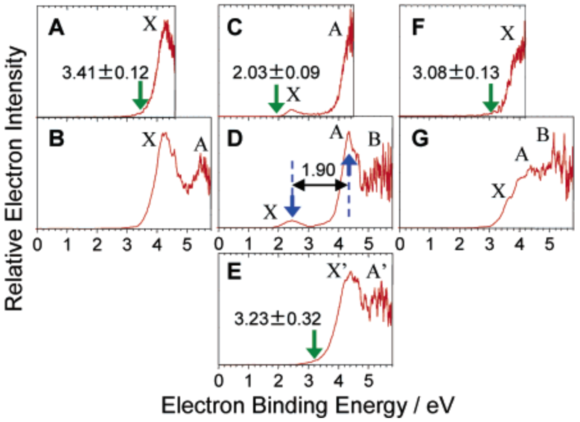

Figure 2. Photoelectron spectra of $ScSi_{16}^-$ (A and B), $TiSi_{16}^-$ (C and D), and VSi_{16}^- (F and G) at 266 nm (4.66 eV; top three spectra) and at 213 nm (5.82 eV; bottom four spectra). Comparison of the photoelectron spectrum of $TiSi_{16}^-$ with that of $TiSi_{16}F^-$ (E) enables us to assign the HOMO−LUMO gap. Photoelectrons were analyzed with a magnetic bottle-type photoelectron spectrometer calibrated using the known spectrum of Au^-.

in the $3p_z$ orbital of sp^2-hybridized Si atoms, although this conjecture should be examined by theoretical calculations.

The electronic states were probed using anion photoelectron spectroscopy. $TiSi_{16}^-$ clusters were selected and decelerated before photodetachment. Figure 2 shows the PES spectra of $ScSi_{16}^-$, $TiSi_{16}^-$, and VSi_{16}^- at two different photon energies. The 213 nm spectrum of $TiSi_{16}^-$ (Figure 2D) displays a weak peak around 2.4 eV (labeled X), followed by a large energy gap and more discrete transitions at higher binding energies (A, B, ...). The 266 nm spectrum yielded a vertical detachment energy (VDE) of 2.45 ± 0.06 eV and an adiabatic detachment energy of 2.03 ± 0.09 eV for $TiSi_{16}^-$. The latter is the electron affinity (EA) of $TiSi_{16}$.

This spectral feature is very different from those displayed by $ScSi_{16}^-$ and VSi_{16}^- in which the detachment peaks start in the higher energy region without a separate peak, such as peak X for $TiSi_{16}^-$. If peak X in the PES spectrum of $TiSi_{16}^-$ truly corresponds to a singly occupied MO (SOMO), this spectral pattern suggests that $TiSi_{16}$ neutral is a closed-shell molecule with a large HOMO−LUMO gap. Experimental verification of single occupation was achieved by our established technique of halogen atom doping.[21] Briefly for the nondegenerate SOMO in geometrically rigid clusters, a halogen atom can remove the one electron from the SOMO without any serious distortions.

As shown in Figure 2E, the 213 nm spectrum of $TiSi_{16}F^-$ exhibits the disappearance of peak X in Figure 2D, while the other spectral features are maintained. The gap obtained in $TiSi_{16}$ is very large, about 0.3 eV greater than that in C_{60} (1.57 eV).[22] Since feature A corresponds to the lowest triplet state of the neutral compound, the A−X separation, measured to be 1.90 eV, represents the excitation energy of the first triplet states of neutral $TiSi_{16}$, which is also an approximate experimental measure of the HOMO−LUMO gap. Interestingly, the spectral features resemble roughly those of $TiSi_{16}F^-$ and $ScSi_{16}^-$, which is consistent with them both having an isoelectronic framework of MSi_{16}. What is surprising is the magnitude of the HOMO−LUMO gap; the HOMO−LUMO gap observed for $TiSi_{16}$ is the largest among those measured for single metal atom doped silicon clusters.[20] It is very comparable with that observed in the recently discovered 20 electron tetrahedral Au_{20} cluster.[23] The large HOMO−LUMO gap suggests that $TiSi_{16}$ should be very inert and may possess a highly symmetrical geometry. In fact, it has been proposed that $TiSi_{16}$ assumes the metal-encapsulated structure of a Frank−Kasper polyhedron,[24] being calculated to have an EA of 1.91 eV and a HOMO−LUMO gap of 2.35 eV.[13,14]

A “magic” cluster of a metal atom-encapsulated in a Si cage can be viewed as a superatom. To more conclusively determine whether MSi_{16} is a superatom in this sense, reactivity toward F_2 was examined. By carefully adjusting the flow of F_2, VSi_{16} was converted to the preferred product of $VSi_{16}F$.[20] It is noted that the VSi_{16}^+ cation is nonreactive toward F_2 as is the $TiSi_{16}$ neutral. The halogen atom addition suggests that VSi_{16} is an alkali atom-like species, and that $VSi_{16}F$ is an ionically bound superatom complex, where VSi_{16}^+ having a structure isoelectronic with $TiSi_{16}$, is electronically closed. Besides, the photoelectron spectra of $ScSi_{16}^-$ yielded a VDE of 4.25 eV and an adiabatic detachment energy of 3.41 eV, being much larger than those of other metal doped silicon clusters. This pronounced stability of $ScSi_{16}^-$ is very similar to that of Al_{13}^-,[25] where Al_{13} can be viewed as a superhalogen having high EA.[26] Current studies involving the reaction of metal atom-encapsulated silicon cages with halogen atoms suggest that it is possible to synthesize “cluster−salt crystals” as well as the theoretically predicted superatom salt of $Al_{13}K$.[26]

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Supporting Information Available: Mass spectra and adsorption reactivity toward H_2O for anions, neutrals, and cations of MSi_n (M = Sc, Ti, and V). This material is available free of charge via the Internet at http://pubs.acs.org.

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