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Introduction

Silicon is the most important fundamental element in the modern microelectronics industry. The fast pace towards further miniaturization of nanoelectronic devices has motivated tremendous interest in investigating Si clusters.¹⁻¹¹ However, the existence of dangling bonds in pure silicon clusters makes them chemically reactive, and so they are unsuitable to serve as building blocks of nanodevices.⁹⁻¹¹ As an alternative, transition-metal (TM)-doped Si clusters have attracted great attention due to the fact that inserting a TM atom not only can enhance the stability of Si clusters,¹²⁻¹⁸ but also produce extraordinary physical properties such as large HOMO-LUMO gaps^{13,19} and high intrinsic magnetic moments.²⁰⁻²³

In the last few decades, TM-doped silicon clusters have been extensively investigated. For instance, a mass spectrometric study revealed the outstanding abundance of MSi_{15-16}^+ clusters



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We present a systematic study of the structures and electronic properties of vanadium-doped silicon cluster anions, VSi_n^- (n = 14-20), by combining photoelectron spectroscopy (PES) measurements and density functional theory (DFT) based theoretical calculations. High resolution PES of low temperature (10 K) clusters are acquired at a photon wavelength of 248 nm. Low-lying structures of VSi_{14-20}^- are obtained by a genetic algorithm based global minimum search code combined with DFT calculations. Excellent agreement is found between the measured PES and the simulated electron density of states of the putative ground-state structures. We conclude that clusters with sizes n = 14 and n = 15 prefer cage-like structures, with the encapsulated vanadium atom bonding with all silicon atoms, while a fullerene-like motif is more favorable for $n \ge 16$. For the sizes n = 16 to 19, the structures consist of a V@Si₁₄ with two, three, four, and five Si atoms on the surface of the cage. For n = 20 the structure consists of a V@Si₁₅ with five Si atoms on the surface of the cage. VSi₁₄⁻ has the highest stability and stands out as a simultaneous closing of electronic and geometrical shells.

of MSi_n^+ (M = Cr, Mo, W)^{24,25} which indicates their high stability. A study of single TM (Sc, Ti, V, Y, Zr, Nb, Hf) and lanthanide (Lu, Tb, Ho, Ta) doped Si₆₋₂₀ clusters using mass spectrometry (MS) and PES measurements showed, e.g., that $ScSi_{16}^{-}$, TiSi₁₆, and VSi_{16}^{+} are very stable species, which is due to a simultaneous electronic and geometric shell closing^{13,26,27} Further studies of small sized $TMSi_n$ clusters (TM = Sc_{1-2} ,^{28,29} V_{1-3} , 21,30,31 Cr_{1-3} , 20,23,32 Cu, 33 Nb_{1-2} , 34,35 Ag, 36 Au_{1-2} , 37,38 $n \leq 18$) uncovered many geometrical structures through a combination of PES and DFT calculations. Additionally, purely theoretical studies were conducted on the structural evolution, electronic and magnetic properties of TMSi_n clusters including and NiSi₁₋₈.⁴⁶ Electron counting rules have been investigated in detail for a number of clusters, like TMSi₁₂ (TM = Sc-Ni); here the enhanced stability of CrSi₁₂ and FeSi₁₂ clusters can be explained by a phenomenological shell model.⁴⁷ In principle, a 20-electron counting rule can explain the high stability and chemical inertness of CrSi₁₄ among the MSi₁₄ clusters (M = Sc-Ni),⁴⁸ but for this system it was also shown that such counting rules have to be applied with care.49 For more detailed theoretical and experimental studies on TM doped Si clusters, please refer to the two recent reviews.50,51

Regarding V-doped Si clusters, small sizes have been systematically studied, including their structural evolution, magnetic,

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electronic and optical properties. For instance Si3-6 doped with one and two V atoms were studied by PES and DFT calculations, showing the existence of a strong V-V bond in $V_2 Si_{3-6}$ ^{-.30} Combined PES measurements and DFT calculations of $V_3Si_{3-14}^{-31}$ and $V_{1-3}Si_{12}^{-21}$ allowed identification of their structures and lead to the discovery of ferrimagnetic order in $V_3Si_{12}^{-}$. The structures of VSi_n^+ with n = 6-9 and 12-16 were determined by comparing measured infrared multiple photon dissociation spectra with simulated infrared absorption spectra.⁵²⁻⁵⁴ Among the fewer studies of larger clusters, a combination of PES and DFT calculations showed that $V_2Si_{20}^{-}$ adopts a fullerene-like Si_{20} cage with a V_2 unit encapsulated inside.55 Another theoretical study has predicted the structures of Si₁₄₋₁₈V⁺.⁴⁰ However, there is lack of experimental data for VSi_n and VSi_n⁻ for $n \ge 14$. Here, we present a systematic study of the medium-sized Si clusters doped with single V atom, VSi_n^{-} (*n* = 14–20), based on both PES measurements and DFT calculations.

Experimental method

The experiments were performed in a magnetic-bottle PES apparatus equipped with a magnetron sputtering gas aggregation cluster source, which has been described in detail elsewhere.⁵ V-doped Si cluster anions were produced from a sandwiched V-Si target. A liquid nitrogen cooled mixture of helium and argon (ratio 3:1) with a total pressure of about 0.5 mbar was used as buffer gas. The clusters leave the aggregation tube through an adjustable iris, and are transferred by a radio-frequency (RF) hexapole ion guide into a differentially pumped vacuum chamber where they are fed into a 12pole RF cryogenic ion trap cooled to about 10 K. In this trap, the clusters are thermalized by collisions with helium buffer gas with a pressure of around 10^{-3} mbar. Bunches of cluster anions are then extracted from the trap and introduced into a high resolution, double reflection time-of-flight mass spectrometer, where they are selected by a multiwire mass gate located at the focal point of the first reflector with a resolution of about $m/\Delta m = 2000$. The size-selected clusters are then reflected and re-bunched by the second reflector, and decelerated by a pulsed electric field. Then, they enter into the photo-detachment region of a magnetic bottle time-of-flight photoelectron spectrometer, where they are irradiated by an excimer laser (KrF: 248 nm). The photoelectron spectra were averaged over 30 000 laser shots with a repetition rate of 100 Hz. The machine was calibrated by measuring spectra of platinum anions, which ensures error of measured binding energies of less than 30 meV.

Theoretical method

To obtain the ground-state structures of VSi_n^- (n = 14-20) clusters, the global search was conducted through a homemade genetic algorithm code incorporated into the ORCA quantum chemistry package.^{56,57} Generally, 20 clusters are generated to

form an initial population. In order to fully search the potential energy surface, the maximum iteration number is not less than 2000 for clusters. The mutation rate is set to 0.2. The roulette method is used to select a "father" or "mother" cluster. The mutation operator refers to a previous article.⁵⁸ In the crossover operator, a modified "cut and splice" method is adopted. Different from the conventional crossover operator,⁵⁹ here, the cut plane can randomly passes through the parent cluster instead of fixing at their center of mass.

During the search, the BP86 functional^{60,61} and the valence double-zeta def2-SVP basis set^{62,63} were applied for energy calculations. We tested a range of functionals (BP86,60,61 PBE,⁶⁴ BLYP,^{61,65} PBE0,⁶⁶ M06,⁶⁷ M06-2X,⁶⁷ B3P⁶⁸) and found that B3P with the aug-cc-pVDZ basis set obtained vertical detachment energy (VDE) values close to the experimental ones for all the VSi_n⁻ (n = 14-20) clusters. Therefore, considering the efficiency and rationality, we choose B3P functional combined with cc-pVDZ^{69,70} basis set to optimize the structures of the 10-20 lowest energy isomers, and B3P functional combined with aug-cc-pVDZ^{69,70} basis set is used to get more accurate electronic energy of these isomers. In order to reduce the computational cost, the resolution of the identity (RI) approximation⁷¹ and RIJCOSX method⁷² are always adopted in calculations. Vibration analyses show that the structures have no imaginary frequencies. Zero-point-energy (ZPE) corrections were included for the relative energy calculations. The Visual Molecular Dynamics (VMD) software⁷³ were used to produce the graphs of the clusters. The simulated PESs were calculated according to the generalized Koopmans' theorem.⁷⁴ First, the vertical detachment energy (VDE) is calculated from the total energy difference between the anionic and the neutral charge state of a cluster with the relaxed structure of the anionic state. Each line of the calculated Kohn-Sham (KS) eigenvalue spectrum was shifted to align the highest occupied KS molecular orbital with the calculated VDE, and then the simulated photoelectron spectrum is obtained by Gaussian broadening of these translated energy levels with a FWHM of 0.06 eV with is corresponding to the resolution of measured PES experimentally.

Results and discussion

The photoelectron spectra of VSi_n^- (*n* = 14–20)

The experimental photoelectron spectra of VSi_n⁻ (n = 14-20) recorded with 248 nm photons are displayed in Fig. 1. For VSi₁₄⁻, the experimental spectrum has only one characteristic peak X at about 4.4 eV, which is very similar to the experimental spectrum of TiSi₁₄⁻.⁷⁵ Similarly, the experimental spectrum of VSi₁₅⁻ has only one band, but there are three identifiable peaks in the band. VSi₁₆⁻ has four clear peaks (X, A, B and C) centered 3.73 eV, 3.90 eV, 4.25 eV and 4.51 eV in the experimental spectra. Similarly, VSi₁₇⁻ also shows four clear peaks located at 3.70 eV, 4.08 eV, 4.24 eV and 4.48 eV.

For VSi_{18}^{-} there are four well-resolved peaks (X: 3.48 eV, A: 3.85 eV, B: 4.01 eV and C: 4.31 eV) as well as a shoulder at 4.50 eV. Three well-resolved peaks (X, B and C) are observed in



Fig. 1 The experimental photoelectron spectra (red lines) of VSi_n^- (n = 14-20) measured at a photon energy of 5.0 eV, compared with the calculated spectra (blue lines) for the structures shown in Fig. 2.

the spectrum of VSi₁₉⁻, centered at 3.50 eV, 4.08 eV and 4.35 eV, along with a peak A centered at 3.85 eV between peaks X and B. The spectrum of VSi₂₀⁻ has a well resolved X peak centered at 3.60 eV, followed by a prominent peak A, and a broad peak B centered at 4.1 and 4.50 eV, respectively.

In order to obtain detailed structural information and the electronic properties of these clusters, low-lying structures have been searched globally as described above; the results are shown in Fig. 2. Here for all sizes the three lowest energy isomers identified by the extensive search are shown together with their calculated relative energies. The photoelectron spectra calculated for these structures are compared to the measured ones in Fig. 1 (more structures and simulated spectra are displayed in the ESI†). As shown in Fig. 1, the spectra of all lowest energy structures conform well to the experimental spectra except for VSi₁₅⁻.

The calculated spectrum of 15A can produce three peaks, but the X (4.08 eV) is larger than the experimental one (4.00 eV), while for 15B it has X (3.96 eV) and B, but not A. Considering their minute energy difference (9 meV), these two isomers as well as isomer C should be present in the cluster beam and contribute to the measured PES, which could explain why the spectrum lacks discernible structure.

Structures of the VSi_n^- (*n* = 14–20)

The low-lying geometric structures of VSi_n^- (n = 14-20) optimized at B3P/cc-pVDZ level are displayed in Fig. 2. Our calculations show that, as the ground-state structure, the geometry of

VSi₁₄⁻ adopts a bicapped pentagonal prism motif with two Si atoms inserted into the waist of the prism with C_{2v} symmetry. This structure of VSi_{14}^{-} is also adopted by $TiSi_{14}^{-75}$ and CrSi₁₄^{0/-} clusters.^{23,76} The isomer 14B exhibits a structure reminiscent of carbon fullerenes with the V atom embedded inside. Unlike the two neighboring Si atoms in the waist of 14A, the two Si atoms in the waist of 14C isomer are very far apart. For n = 15, there are three nearly energetically degenerate isomers. The lowest-energy structure, 15A, adopts a Si₁₅ cage as the structural motif enclosed a V atom. 15B is 9 meV higher in energy and has the same structural motif as the lowest-lying of VSi14⁻ with three instead of two Si atoms inserted in the waist of the pentagonal prism, leading to $C_{\rm s}$ symmetry. The 15C isomer is a deformed version of 15A, showing C_2 symmetry. For the sizes n = 16-19, the lowest-energy structures adopt 14B $(V@Si_{14})$ as a core structural motif with two, three, four, and five additional Si atoms on the top, respectively. Moreover, 17B, 17C, 18B, 18C, 19B, 20B, and 20C also adopt this V@Si14 structure as the core structural motif with excess Si atoms attached to the surface. 16B can be obtained by adding one Si atom on the surface of 15C. The FK structure is worth discussing for VSi₁₆⁻. Our calculation show that the FK polyhedron is not stable upon geometry optimization, and transforms into the isomer 16F. Considering that VSi₁₆⁻ has one more electron than the FK TiSi₁₆⁻⁷⁵, it shows that one extra electron adding can significantly change its overall structure. The isomer 19C adopts 14A as a core structural motif with five extra Si atoms attached to the surface of the cage. For the lowest-lying VSi₂₀⁻,



Fig. 2 Optimized geometries of VSi_n^- (n = 14-20) clusters at B3P/cc-pVDZ level. For each cluster size, the energy difference of isomer with regard to the lowest energy isomer marked is provided and the symmetry is given in parenthesis. Gray and yellow balls represent V and Si atoms, respectively.

although it has a significantly different structure from the previous clusters, it still adopts a V $(@Si_{15}$ cage structure as a core structural motif with five extra Si atoms attached on the top.

Compared to the ground-state structures of pure Si_{14-20}^{-1} clusters,⁵ doping the clusters with one V atom can obviously result in significant structural reconstruction. In general, the V atom tends to stay inside the Si cage in the lowest-lying structures of VSi_n^{-1} (n = 14-20). For n = 14-15, the clusters prefer single cage-like structures, while larger ones ($n \ge 16$) adopt fullerene-like-structures with extra Si atoms on the outside of the cages.

Properties of the ground-state VSi_n^- (*n* = 14–20) clusters

To further verify the correctness of the structures discussed above, a systematic comparison between the calculated vertical detachment energy (VDE, the first peak in PES spectra) with the ones extracted from the measured spectra is shown in Table 1 and Fig. 3(a). It indicates that all the VDEs from theoretical calculations lie close to the experimental values, with a maximum deviation of 0.1 eV for size n = 16. The VDEs of VSi_n⁻ gradually decrease with a growing number of Si atoms, reach a minimum value at size n = 18, and then increases again. The trend of the HOMO–LUMO gap curve (in Fig. 3(c)) is consistent with that of the VDE. The high VDEs and HOMO–LUMO gaps at n = 14 and 15 signal that VSi₁₄⁻ and, to a slightly less extent, VSi₁₅⁻ are the most stable species. For VSi₁₄⁻ this is expected, as it is closely related to the highly stable neutral CrSi₁₄,⁷¹ with which it shares both geometric structure and electron count.

Table 1 Data of experimental (Expt.) and theoretical (Theo.) vertical detachment energies (VDE), binding energies (E_b), HOMO-LUMO gaps (Gap), and the second energy differences ($\Delta^2 E$) of VSi_n⁻ (n = 14-20) clusters

Cluster	VDE (eV)				
	Expt.	Theo.	$E_{\rm b}$ (eV)	Gap (eV)	$\Delta^2 E$ (eV)
VSi ₁₄ ⁻	4.35 ± 0.03	4.26	3.712	2.961	
VSi_{15}^{-}	4.00 ± 0.03	4.08	3.717	2.748	0.032
VSi ₁₆	3.73 ± 0.03	3.63	3.719	1.991	0.558
VSi ₁₇ ⁻	3.70 ± 0.03	3.67	3.690	1.419	-0.658
VSi ₁₈	3.48 ± 0.03	3.42	3.698	1.461	0.337
VSi ₁₉ ⁻	3.50 ± 0.03	3.47	3.689	1.651	-0.306
VSi_{20}^{-}	3.55 ± 0.03	3.50	3.696	1.708	

The stability of a VSi_n⁻ cluster can be characterized by its average binding energy (E_b) as $E_b(VSi_n^-) = [(n - 1)E(Si) + E(Si^-) + E(V) - E(VSi_n^-)]/(n + 1)$, where $E_b(VSi_n^-)$ is the energy of the anionic VSi_n⁻ cluster, E(Si), $E(Si^-)$ and E(V) are the total energies of the neutral Si atom, anionic Si atom, and neutral V atom, respectively. The second energy difference ($\Delta^2 E$) was calculated using the equation $\Delta^2 E(VSi_n^-) = E(VSi_{n+1}^-) + E(VSi_{n-1}^-) - 2E(VSi_n^-)$.

Fig. 3(b) shows E_b as a function of number of Si atoms *n*. The average binding energies of sizes n = 14-16 are significantly higher than that of sizes n = 17-20, which may be related to the closed cage structures of VSi₁₄₋₁₆⁻. Comparing to the pure neutral silicon clusters⁷⁷ (at B3LYP/6-311++G(2d) level) with the same size *n*, the incorporation of one V atom into a silicon cluster can increase the binding energy by ~0.5 eV. This evidences the efficient enhancement of stability by V atom insertion. The second energy difference ($\Delta^2 E$, in Fig. 3(d))



Fig. 3 (a) The measured (red spheres) and calculated (blue open squares) VDEs. (b) The average binding energies (E_b). (c) The HOMO–LUMO Gaps (Gap). (d) The second energy differences ($\Delta^2 E$).

shows obvious odd–even oscillation, with maximum values occurring at n =16 and 18.

Conclusions

A systematic study of the ground-state structures and electronic properties of the VSi_n⁻ (n = 14-20) clusters has been performed based on experimental anion photoelectron spectroscopy combined with first-principles calculations. It demonstrates a reasonable agreement between the experimental and simulated photoelectron spectra, which corroborates the lowest-energy structures found. In these clusters, the V atom always stays inside a cage-like structure. Sizes n = 14 and n = 15 prefer cagelike structures with the encapsulated vanadium atom bonding with all silicon atoms. A fullerene-like motif is more favorable for n = 16 to 19, which can be seen as a V@Si₁₄ with two, three, four and five Si atoms on the surface. n = 20 consists of a V@Si₁₅ with five Si atoms on the top of the cage. Doping a V atom into a silicon cluster can not only modify its equilibrium geometry, but also remarkably enhance its stability in general. In all studied cases, VSi₁₄⁻ stands out due to its simultaneous closing of both electronic and geometric shells.

Conflicts of interest

The authors declare no competing financial interest.

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