

Experimental and theoretical investigation on binary semiconductor clusters of B/Si and Al/Si

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ASi_n^- (A = B and Al; $n = 1-6$) binary cluster anions were generated by laser ablation of samples composed of mixtures of Si and A (A = B and Al), and studied in the gas phase by tandem time-of-flight mass spectrometry. Some abundant ions are present in the mass spectrum, indicating that the clusters with these ions have stable structures. The structures of ASi_n^- clusters were investigated theoretically by the density functional theory (DFT) method and the energetically lowest-lying structures were obtained. The binary clusters BSi_n^- and AlSi_n^- , with the same number of n , share different geometric structures except for ASi_n^- with $n = 1$ and 6, which have the same geometric structures in the ground state. For all the anionic clusters ASi_n^- , the lower spin state is lower in energy than the higher spin state in their optimized structures except for the linear ASi^- anions, for which the triplet state is lower in energy than the singlet. Calculations of the bonding energy (BE), energy gain (Δ) and HOMO-LUMO energy gaps confirm that the cluster ASi_5^- has a very stable structure, which agrees well with the experimental results. Copyright © 2007 John Wiley & Sons, Ltd.

The study of atomic clusters has become an active area of research during the last two decades and, among these, semiconductor clusters have been extensively investigated for both their fundamental and technological interest. As important semiconductor materials, silicon clusters have been studied most extensively both theoretically and experimentally for the development of nanoelectronics.¹⁻⁴ Photodissociation⁵⁻⁷ and collision-induced dissociation^{8,9} experiments have shown that both Si_6 and Si_{10} have exceptional stability, consistent with their 'magic' behavior observed in the mass spectra of Si clusters.¹⁰ Several spectroscopic studies, such as photoelectron, Raman and infrared, have been carried out to understand the structures of small silicon clusters.¹¹⁻¹⁴

Boron-silicon (B/Si) and aluminum-silicon (Al/Si) binary clusters are of great interest in theoretical and experimental studies of semiconductor. B/Si alloys were reported to have potential application as semiconductors,^{15,16} and the interaction of an Al atom with Si nanowire significantly enhanced its electrical conductivity.¹⁷ Al atoms have also been reported to form an ordered array of magic clusters¹⁸ on the surfaces of Si(111) and to form Al-Si nanowires.¹⁹

Many studies have been carried out of precursor compounds used for chemical vapor deposition of boron-

doped silicon. Hu *et al.*^{20,21} studied the reactions of SiH_4 and B_2H_6 , and the interactions of SiH_4 and BH_3 . Bharatam *et al.*²² studied H-bridging bonds in SiBH_5 compounds. Bock *et al.*²³ studied the formation of silylboranes as intermediates in the decomposition of silane-diborane mixtures. Subramanian *et al.*²⁴ also studied SiBH_4 , Si_2BH_3 and $\text{Si}_2\text{B}_2\text{H}_4$. However, few B/Si binary cluster studies have been carried out. Bernardo and Morrison studied the structures of cationic SiB_n ($n = 1-4$).²⁵ Verhaegen *et al.*²⁶ and Viswanathan *et al.*²⁷ investigated the thermochemistry of BSi , BSi_2 and BSi_3 . Boldyrev and Simons²⁸ carried out a theoretical study of the electronic states of the BSi dimer and their results were confirmed experimentally by Knight *et al.*²⁹ Davy *et al.*³⁰ carried out a theoretical study of the isomers of the simplest clusters, B_2Si , BSi_2 and B_2Si_2 , and predicted that the formation of B_2Si_2 from the smaller clusters would be thermodynamically favored. Al/Si binary clusters have also been studied recently. Chiranjib and Kulshreshtha³¹ made a systematic theoretical study of the equilibrium geometry and energetics of AlSi_n ($n = 1-10$) clusters, and revealed that clusters with $n = 3, 5$ and 9 showed higher stability, reflecting the magic behavior of these clusters.

A cluster is an intermediate phase between a single atom and bulk materials. The fundamental aim of cluster science is to determine how the geometric and electronic structures of clusters change as the cluster size increases from a single atom to bulk materials. With the current trend of miniaturization, miniature electronic devices will soon approach the

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size of atomic clusters, and stable clusters may be used as the building blocks for cluster-assembled materials. In this work, a series of binary anionic clusters ASi_n^- ($A=B$ and Al ; $n=1-6$) produced by laser ablation has been studied both experimentally with tandem time-of-flight mass spectrometry (TTOFMS) and theoretically with density functional theory (DFT) calculations. Although boron and aluminum have the same outer covalent electrons, they have different physical and chemical properties. Do BSi_n^- and $AlSi_n^-$ anionic clusters have the same geometrical and electronic structures?

EXPERIMENTAL

Binary semiconductor cluster ions composed of group III elements A ($A=B$ and Al) and Si were generated and analyzed under the following conditions. The samples were prepared with A (boron purity: 99%, aluminum purity: 99%) and silicon (purity: 99%) powders, mixed well in different atomic ratios and pressed into round tablets (diameter = 12 mm).

Production and detection of A/Si binary cluster ions were performed using a vaporization laser together with the first stage of a home-made tandem time-of-flight mass spectrometer. A detailed description of the mass spectrometer has been given elsewhere.³² Briefly, the second harmonic of a Q-switched Nd:YAG laser (typical power of 10–30 mJ/pulse, 5 pulses/s, 10 ns FWHM, operating at 532 nm) was focused on the surface of a tablet sample held in the vacuum chamber of the spectrometer to produce the cluster ions and the targets were rotated manually during the experiment process. The mass spectrometer is of the Wiley-McLaren type.³³ The cluster ions were extracted and accelerated with pulse voltages of 0.1 and 1.1 kV, respectively, and then allowed to drift in a field-free region, 3.5 m long. The ions were detected by a dual microchannel plate (MCP) detector at the end of the field-free region, and recorded to give the mass spectrum. The output signal was amplified and recorded by a 100 MHz transient recorder (USTC, Anhui, China), then stored by a computer. The timing of the laser vaporization, pulse acceleration and recording was optimized in a digital delay pulse generator (DG535; Stanford Research, Menlo Park, CA, USA). Typically, the final digitized mass spectrum was obtained with the average of 500 laser shots, and the mass resolution of the first stage of the TTOFMS instrument ($m/\Delta m$) is about 300 under the present conditions.

The source chamber and the first-stage detecting region were differentially pumped with turbomolecular pumps and mechanical pumps, and the operating pressures were all around 10^{-4} Pa.

THEORETICAL METHOD

In this work, geometric and electronic structural calculations on these binary clusters were performed using B3LYP functions,^{34,35} a widely used hybrid DFT-HF method.

Two basis sets, 6-311G(d) and 6-311+G(d), were used in both the geometry and the frequency calculations. The 6-311G specifies the standard split-valence triple- ζ 6-311G basis sets for the B atom and the McLean-Chandler (12s9p)/

[6s5p] basis sets for all second-row atoms (Al and Si).^{36,37} Initial geometrical optimizations were performed with singlet and triplet states at the B3LYP/6-311G(d) level without any symmetry constraints. These lowest-energy BSi_n^- and $AlSi_n^-$ structures were further optimized using the B3LYP/6-311+G(d) method. Because of the calculations of anions in this study, the 6-311G basis sets were augmented with *d*-polarization functions and diffuse *sp*-functions. It has been shown that such basis sets are able to give accurate results for B/Si and Al/Si clusters.^{30,38}

To assess the nature of the stationary points, harmonic vibrational frequencies were computed from analytic gradient techniques. All the most stable charged clusters were characterized as energy minima and without imaginary frequencies. All calculations were carried out with the GAUSSIAN 98 program suite.³⁹

RESULTS AND DISCUSSION

Product analysis with the mass spectrometer

Figures 1(a) and 1(b) present the TOF mass spectra of the cluster anions obtained by direct laser (the combined 1064 and 532 nm beams) ablation of B/Si and Al/Si samples, respectively. The resolution of our mass spectrometer allows the identification of the isotopic distribution in the mass spectra. In these experiments, clusters with magic numbers are observed.

From Fig. 1(a), we can see three different series of products: Si_{n+1}^- , BSi_n^- and $B_2Si_n^-$. The relative signal intensities of the Si_{n+1}^- and BSi_n^- series in the mass spectrum are greater

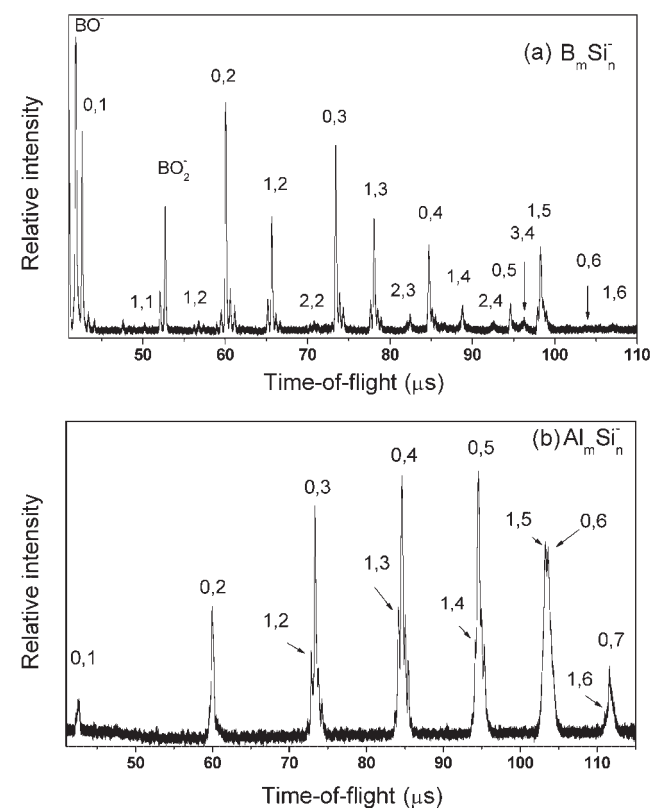


Figure 1. TOF mass spectra of binary cluster anions produced by laser ablation on mixed samples of (a) B/Si (atomic ratio 1:10) and (b) Al/Si (atomic ratio 1:1).

than that of the $B_2Si_n^-$ series. In the BSi_n^- series ($n=1-6$), the BSi_5^- is the individual species with a magic number, because its relative intensity is much greater than that of its neighboring clusters BSi_4^- and BSi_6^- , suggesting that it has a very stable structure. Comparing the Si_{n+1}^- and the BSi_n^- series, the relative intensities of the members of the BSi_n^- series are smaller than those of the Si_{n+1}^- series except for $n=5$.

In the mass spectra of $AlSi_n^-$ binary clusters, we can identify two different series of Si_n^- and $AlSi_n^-$, although the mass of Al is just one less than Si. In the $AlSi_n^-$ series ($n=2-6$), $AlSi_5^-$ is also the magic number species with its intensity being greater than that of its neighboring clusters $AlSi_4^-$ and $AlSi_6^-$. The relative intensities of $AlSi_n^-$ are also smaller than those of the Si_{n+1}^- series except for $n=5$.

To make these trends more clear, the relative intensities of the cluster series BSi_n^- and $AlSi_n^-$ ($n=1-6$), measured from Fig. 1, are plotted in Fig. 2. For the BSi_n^- series, the clusters with $n=2, 3, 5$ have greater signal intensity than the clusters with $n=1, 4, 6$. Obviously the intensity of BSi_5^- is higher than that of its neighbors BSi_4^- and BSi_6^- , so BSi_5^- presents magic number behavior. It has previously been reported^{5,9,10} that Si_6 has exceptional stability and presents magic number behavior. Here we show that with a Si atom in Si_6 replaced by a B atom, the cluster BSi_5^- also presents magic number behavior. For the $AlSi_n^-$ series, the distribution of peak signal intensities shows a parity effect: the clusters with odd values of n (3 or 5) have greater intensities than the ones with even values of n (2, 4 or 6), and $AlSi_1^-$ is not detected in the mass spectrum. The highest mass cluster is $AlSi_5^-$ and this is the species with a magic number. So, with a Si atom replaced by an Al atom, the cluster $AlSi_5^-$ also presents magic number behavior.

Structure by DFT calculations

We have optimized a number of various initial structures with the different spin states, and the normal vibrational frequencies at the optimized geometries have also been checked to rule out imaginary frequencies at the same theoretical level.

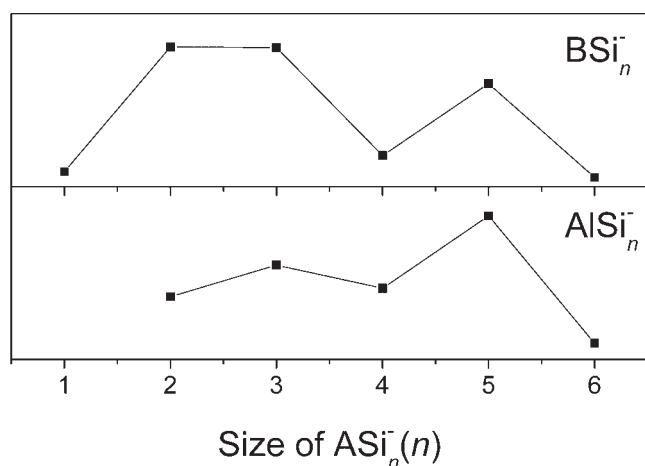


Figure 2. Relative intensities of binary cluster anions ASi_n^- ($A = B$ and Al , $n = 1-6$).

BSi_n^- ($n = 1-6$)

The optimized low-lying energy isomer structures for these species are depicted in Fig. 3, and they are within an energy difference of ~ 2.0 eV for $n=1-6$. All BSi_n^- binary anions have singlet ground states with the 6-311G(d) or 6-311+G(d) basis sets by B3LYP methods except for linear BSi^- , for which the triplet state ($^3\Pi$) (a) is 0.75 eV and 1.09 eV lower in energy than the singlet ($^1\Sigma^-$) (b) with the 6-311G(d) and 6-311+G(d) basis sets, respectively. All the optimized lowest-lying energy structures of the BSi_n^- anion are similar to those of the Si_nC neutral clusters,⁴⁰ as they are isoelectronic species. BSi_2^- and BSi_3^- have the 1A_1 ground state with planar C_{2v} symmetry. The C_s flexing line structure (b) of BSi_2^- ($^1A'$) is 1.78 eV and 1.72 eV higher in energy than the triangular one (a) with 6-311G(d) and 6-311+G(d) basis sets, respectively. The rhombus structure (b) of BSi_3^- is 1.67 eV and 1.61 eV higher in energy than the butterfly structure (a). For the BSi_4^- anion, we have investigated several isomeric structures which are obtained for Si_5^{41} and Si_4C^{40} clusters. The singlet state (1A_1) of the C_{3v} trigonal bipyramid isomer (a) is the most stable structure. The capped bent rhombus isomer (b) is 1.22 eV and 1.19 eV above the ground state with 6-311G(d) and 6-311+G(d) basis sets, respectively. Several initial structures which refer to the structures of Si_6^{41} and Si_5C^{40} clusters were considered to obtain the ground state structures of the BSi_5^- anion. The tetragonal bipyramidal structure (1A_1) (a) is the ground state and is 2.15 eV and 2.12 eV lower in energy than the edge-capped trigonal bipyramidal one (1A_1) (b) with 6-311G(d) and 6-311+G(d) basis sets, respectively. For the BSi_6^- anion, several isomers with a pentagonal bipyramid structure and a capped octahedron were considered. The lowest energy isomer shows the pentagonal bipyramid (PBP) structure (a) with the B atom occupying the top of it and the capped octahedron is >3.0 eV higher in energy than the PBP structure. The PBP structure (b) with the B atom occupying one corner of the base pentagon has one imaginary frequency.

Table 1 shows the B-Si and Si-Si bond lengths of the lowest-energy structures of BSi_n^- ($n=1-6$). The B-Si bond lengths in these stable structures are in the range 1.87 to 2.10 Å, in accord with Davy's report.³⁰ In BSi^- and BSi_2^- , the B-Si bond length is 1.87 Å, which is the shortest in the BSi_n^- series. In BSi_3^- there are two B-Si bond lengths, 1.89 and 2.09 Å, respectively. With an increase in the number of Si atoms, the B-Si bond length becomes subsequently longer, reaching 1.98 Å in BSi_5^- and 2.10 Å in BSi_6^- . Apparently the B-Si bond stretches as the number of Si atoms increases. The change in Si-Si bond length with increasing of number of Si atoms is similar to that observed for the B-Si bond.

$AlSi_n^-$ ($n = 1-6$)

The optimized isomer structures with low-lying energy for these species are depicted in Fig. 4, with an energy difference of less than 1.0 eV for $n=1-6$. All $AlSi_n^-$ binary anions have singlet ground states with the 6-311G(d) or 6-311+G(d) basis sets by B3LYP methods except for linear $AlSi^-$, for which the triplet state ($^3\Pi$) (a) is 0.67 eV and 0.70 eV lower in energy than the singlet ($^1\Sigma^-$) (b) with 6-311G(d) and 6-311+G(d) basis sets, respectively. Most of the optimized structures of $AlSi_n^-$ anions with the lowest-lying energy are similar to the

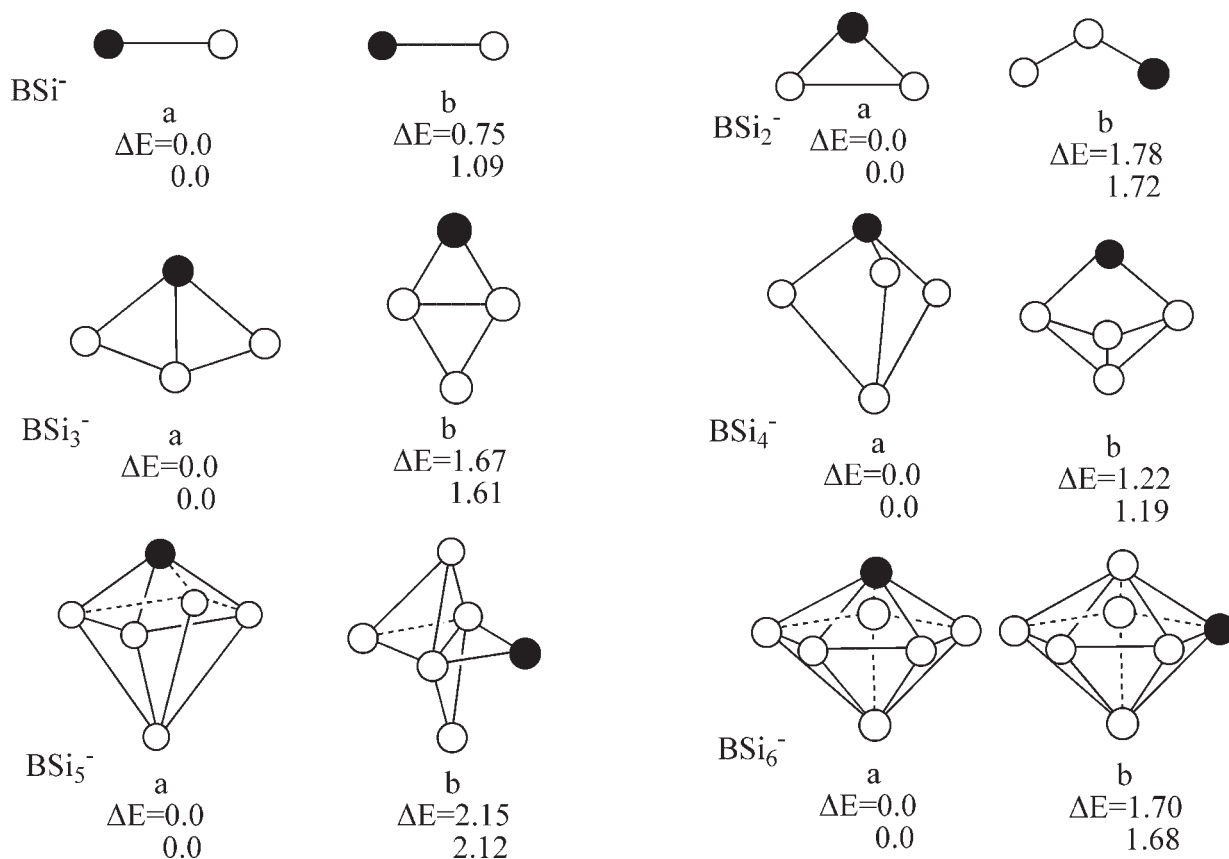


Figure 3. Geometries of the low-lying isomers of the BSi_n^- binary cluster anions ($n=1-6$). Open circles represent Si atoms and the solid ones stand for B atoms. The first line of ΔE is calculated with the 6-311G(d) basis set and the second line of ΔE is with the 6-311G(d) basis set using the B3LYP method.

ones of AlSi_n neutral clusters.³¹ AlSi_2^- and AlSi_3^- have the $^1\text{A}_1$ ground state with planar C_{2v} symmetry. The C_s flexing line structure (a) of AlSi_2^- ($^1\text{A}'$) is 0.91 eV and 0.90 eV lower in energy than the triangular structure (b) with the 6-311G(d) and 6-311+G(d) basis sets, respectively. The rhombus structure (a) of AlSi_3^- is 0.56 eV and 0.58 eV lower than the C_{2v} butterfly structure ($^1\text{A}_1$) (b). For the AlSi_4^- anion, we have investigated several isomeric structures and these were compared with the structures of the Si_5 clusters.⁴¹ The singlet state ($^1\text{A}_1$) of the capped bent rhombus isomer (a) is the most stable structure. The C_{3v} trigonal bipyramid isomer (b) is 0.37 eV and 0.33 eV above the ground state ($^1\text{A}_1$) with the 6-311G(d) and 6-311+G(d) basis sets, respectively. Several initial structures were considered to obtain the ground state

Table 1. The B–Si and Si–Si bond lengths (in Å) of the lowest-energy structures of BSi_n^- ($n=1-6$) with the 6-311G+(d) basis set

Cluster ions	Symmetry	State	B–Si bond	Si–Si bond
BSi^-	$\text{C}_{\infty v}$	$^3\Pi$	1.87	—
BSi_2^-	C_{2v}	$^1\text{A}_1$	1.87	2.32
BSi_3^-	C_{2v}	$^1\text{A}_1$	1.89	2.42
			2.09	—
BSi_4^-	C_{3v}	$^1\text{A}_1$	1.95	2.40
BSi_5^-	C_{4v}	$^1\text{A}_1$	1.98	2.49
			—	2.58
BSi_6^-	C_{5v}	$^1\text{A}_1$	2.10	2.39
			—	2.66

structures of the AlSi_5^- anion, which were compared with the structures of the Si_6^{41} clusters. The edge-capped trigonal bipyramidal structure ($^1\text{A}_1$) (a) is the ground state, 0.59 eV and 0.54 eV lower in energy than the tetragonal bipyramidal structure ($^1\text{A}_1$) (b) with the 6-311G(d) and 6-311+G(d) basis sets, respectively. For the AlSi_6^- anion, several isomers, similar in structure to neutral Si_7 and AlSi_6 reported recently,^{31,38} were considered. The lowest energy isomer shows a C_{5v} PBP structure (a) with the Al atom occupying the top position, and this is 0.20 eV and 0.24 eV lower in energy than the one (b) with the Al atom occupying the corner of the base pentagon. The edge-capped octahedron isomer is ~ 3.0 eV higher in energy than the PBP structure.

Table 2 shows the Al–Si and Si–Si bond lengths of AlSi_n^- ($n=1-6$) with the lowest energy structures. The Al–Si bond lengths in these stable structures are in the range from 2.34 to 2.57 Å, in accord with Chiranjib and Kulshreshtha's report.³¹ In AlSi^- and AlSi_2^- , the Al–Si bond lengths are 2.33 and 2.34 Å, respectively. With an increase in the number of Si atoms, the Al–Si bond becomes much longer and is now over 2.50 Å. Apparently the Al–Si bond stretches as the number of Si atoms increases, and the Si–Si bond lengths become subsequently longer with an increase in the number of Si atoms, reaching 2.51 Å in AlSi_6^- .

From the above results, we can see that the BSi_n^- and AlSi_n^- ($n=1-6$) cluster anions have different ground state structures, although both B and Al belong to group III. The B atom is more prone to bond to the Si atom than to the Al atom.

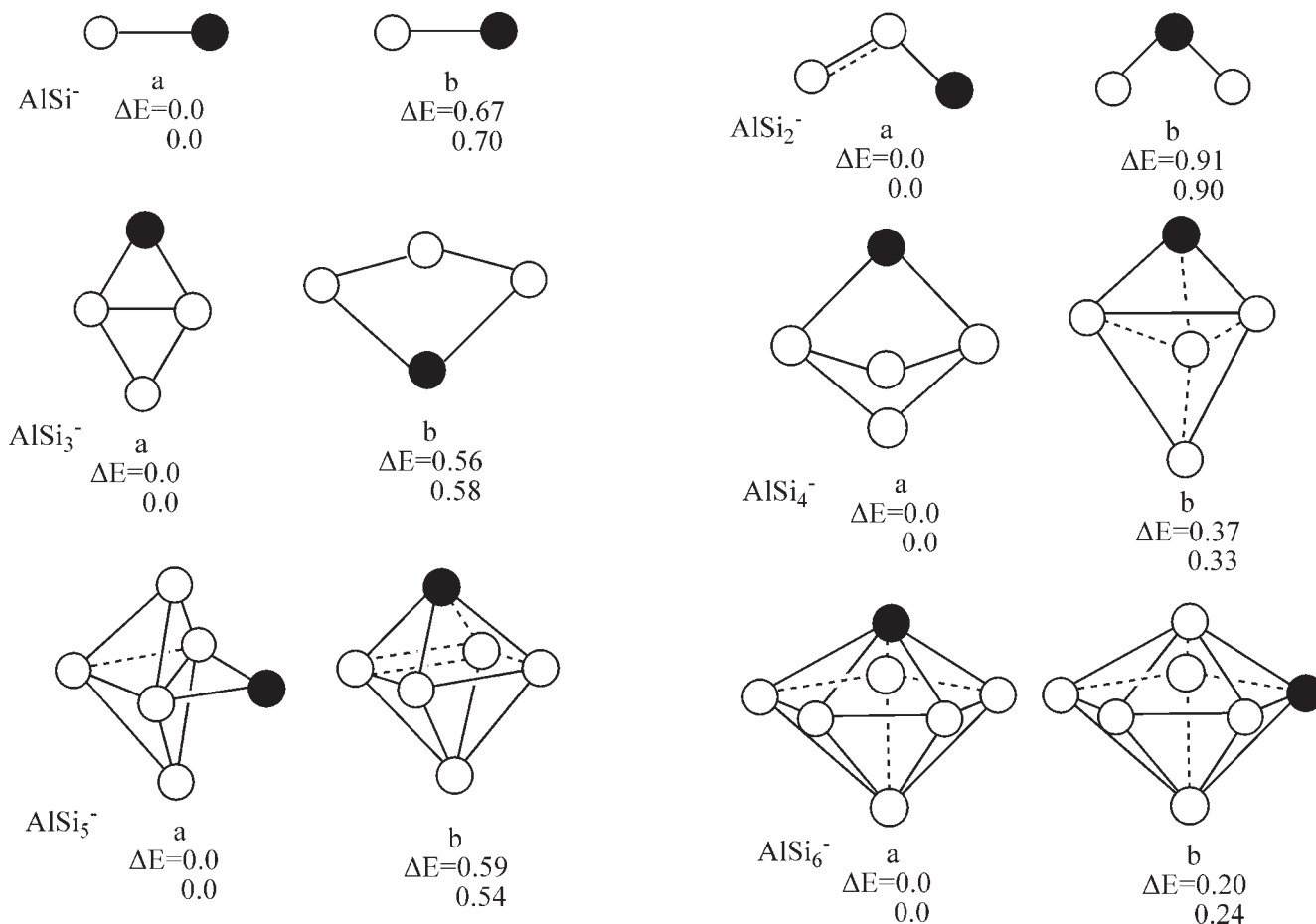


Figure 4. Geometries of the low-lying isomers of the AlSi_n^- binary cluster anions ($n=1-6$). Open circles represent Si atoms and the solid ones stand for Al atoms. The first line of ΔE is calculated with the 6-311G(d) basis set and the second line of ΔE is with the 6-311G(d) basis set using the B3LYP method.

Stability

In order to test the stability of ASi_n^- ($A = \text{B and Al}$; $n=1-6$) further and to obtain an understanding how the energy changes with increased cluster size, we calculated the binding energy (BE), energy gain (Δ) and HOMO-LUMO energy gap of all the lowest-energy structures of clusters ASi_n^- .

Binding energy

The binding energy (BE) of ASi_n^- is defined as follows:

$$\text{BE} = -[E(\text{ASi}_n^-) - E(\text{A}) - nE(\text{Si})]/(n+1)$$

Table 2. The Al-Si and Si-Si bond lengths (in Å) of the lowest-energy structures of BSi_n^- ($n=1-6$) with the 6-311G+(d) basis set

Cluster ions	Symmetry	State	Al-Si bond	Si-Si bond
AlSi^-	$C_{\infty v}$	$^3\Pi$	2.34	—
AlSi_2^-	C_{2v}	$^1A'$	2.44	2.16
AlSi_3^-	C_{4v}	1A_1	2.57	2.31
			—	2.39
AlSi_4^-	C_{2v}	1A_1	2.52	2.34
AlSi_5^-	C_{3v}	1A_1	2.57	2.41
			—	2.50
			—	2.64
AlSi_6^-	C_{5v}	1A_1	2.56	2.49
			—	2.51

Figure 5 shows the BE plotted for the structures of ASi_n^- ($A = \text{B and Al}$; $n=1-6$) cluster anions with the lowest energy calculated with (a) 6-311+G(d) and (b) 6-311G(d) basis sets using the B3LYP method, and the detailed numerical values of BE are presented in Table 3. It is clear from Fig. 5 that the BE increases as the size of the cluster anion grows. The increase (~ 0.2 eV) in BE from AlSi_4^- to AlSi_5^- is prominently larger than that (< 0.05 eV) from AlSi_5^- to AlSi_6^- (from Table 3).

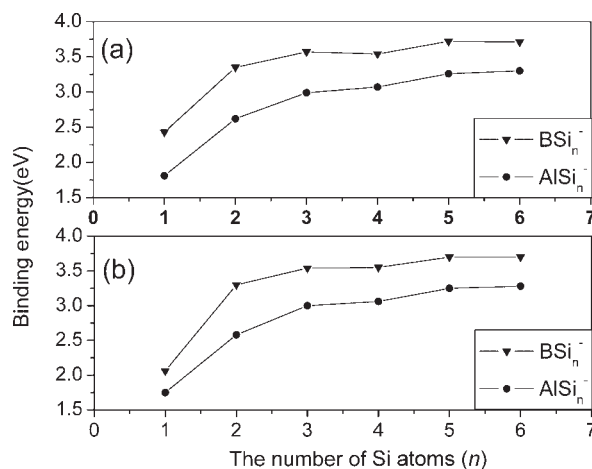


Figure 5. The binding energies of ASi_n^- cluster anions ($A = \text{B and Al}$; $n=1-6$) with 6-311+G(d) (a) and 6-311G(d) (b) basis sets using the B3LYP method.

Table 3. The binding energy (eV) of ASi_n^- ($A = \text{B}$ and Al ; $n = 1-6$) cluster anions by the B3LYP method with different basis sets

Cluster anions	Basis sets		Cluster anions	Basis sets	
	6-311G*	6-311+G*		6-311G*	6-311+G*
BSi_1^-	2.06	2.43	AlSi_1^-	1.75	1.81
BSi_2^-	3.30	3.35	AlSi_2^-	2.58	2.62
BSi_3^-	3.54	3.57	AlSi_3^-	3.00	2.99
BSi_4^-	3.53	3.45	AlSi_4^-	3.06	3.07
BSi_5^-	3.71	3.72	AlSi_5^-	3.25	3.26
BSi_6^-	3.70	3.71	AlSi_6^-	3.28	3.30

So the ASi_5^- ($A = \text{B}$ and Al) anionic cluster presents magic number behavior and is more stable than its adjacent cluster anions ASi_4^- and ASi_6^- . This agrees well with our experimental results.

Energy gain

The energy gain (Δ) is a very important criterion for cluster stability. The Δ of ASi_n^- is calculated as follows:

$$\Delta = -[E(\text{ASi}_n^-) - E(\text{Si}) - E(\text{ASi}_{n-1}^-)]$$

The energy gains of ASi_n^- ($A = \text{B}$ and Al ; $n = 1-6$) cluster anions calculated with (a) 6-311+G(d) and (b) 6-311G(d) basis sets using the B3LYP method are shown in Fig. 6. We can see that the energy gains of the ASi_n^- cluster anions for $n = 2, 3, 5$ are larger than for $n = 1, 4, 6$, which is similar to what is shown in Fig. 2. For the cluster anions with $n > 2$, the energy gain with $n = 5$ is the largest. This also indicates that the ASi_5^- cluster anion is more stable than the others and it presents magic number behavior.

The HOMO–LUMO energy gap

All the ASi_n^- ($A = \text{B}$ and Al , $n = 1-6$) cluster anions are closed-shell structures. We thus also calculated the HOMO–LUMO energy gap of these anions. Table 4 shows the values for the HOMO–LUMO energy gap of ASi_n^- ($A = \text{B}$ and Al ; $n = 1-6$) cluster anions by the B3LYP method with different

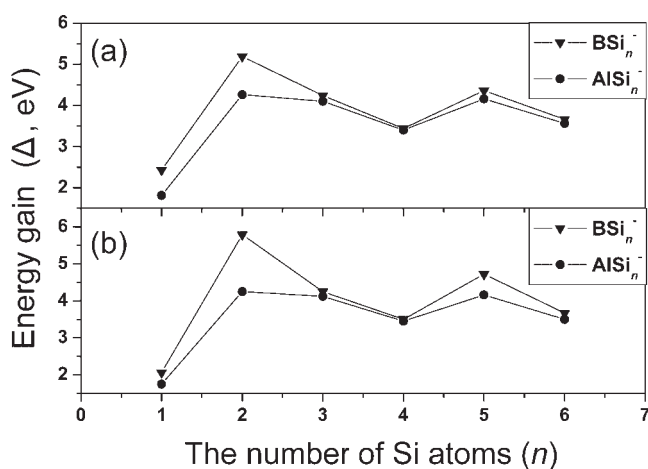


Figure 6. The energy gain of ASi_n^- cluster anions ($A = \text{B}$ and Al ; $n = 1-6$) with (a) 6-311+G(d) and (b) 6-311G(d) basis sets using the B3LYP method.

Table 4. The HOMO–LUMO energy gap (eV) of ASi_n^- ($A = \text{B}$ and Al ; $n = 1-6$) cluster anions by the B3LYP method with different basis sets

Cluster anions	Basis sets		Cluster anions	Basis sets	
	6-311G*	6-311+G*		6-311G*	6-311+G*
BSi_1^-	3.43	3.61	AlSi_1^-	2.83	2.71
BSi_2^-	3.15	3.10	AlSi_2^-	2.38	2.21
BSi_3^-	2.43	2.44	AlSi_3^-	2.26	2.27
BSi_4^-	3.55	3.45	AlSi_4^-	2.83	2.76
BSi_5^-	4.03	3.97	AlSi_5^-	3.25	3.20
BSi_6^-	3.92	3.80	AlSi_6^-	3.17	3.16

basis sets. Much work has shown that clusters with large HOMO–LUMO energy gaps tend to be highly stable.^{42–46} In Table 4, the HOMO–LUMO energy gap of ASi_5^- is the largest in the ASi_n^- series. We therefore suggest that the ASi_5^- cluster anion has relatively high stability and shows magic number behavior.

CONCLUSIONS

ASi_n^- ($A = \text{B}$ and Al ; $n = 1-6$) cluster anions are produced by laser ablation and analyzed by tandem time-of-flight mass spectrometry (TTOFMS) in the gas phase. The most possible structures of ASi_n^- are obtained by DFT calculations. Full structural optimization and frequency analysis reveal that BSi_n^- and AlSi_n^- cluster anions have different structural patterns in the ground state except for $n = 1$ and 6. Calculations of bonding energy (BE), energy gain (Δ) and HOMO–LUMO energy gaps confirm that the clusters ASi_5^- have relatively high stability and show magic number behavior in these anionic species, which agrees well with the experimental results.

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