Anion Photoelectron Spectroscopy and Theoretical Investigation on Nb$_2$Si$_n$ $^{−/0}$ ($n = 2–12$) Clusters

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ABSTRACT: We measured the photoelectron spectra of Nb$_2$Si$_n$$^{−}$(n = 2–12) anions and investigated the geometric structures and electronic properties of Nb$_2$Si$_n$$^{−}$ anions and their neutral counterparts with ab initio calculations. The most stable structures of Nb$_2$Si$_n$$^{−/0}$ (n = 2–12) clusters can be regarded as a central axis of Nb$_2$ surrounded by the Si atoms. The most stable isomers of Nb$_2$Si$_n$$^{−}$ anions are in spin doublet states, while those of the neutral clusters are in spin singlet states. The results showed that the two Nb atoms in Nb$_2$Si$_n$$^{−/0}$ clusters incline to form a strong Nb−Nb bond and also prefer to occupy the high coordination sites to form more Nb−Si bonds. The most stable isomers of anionic and neutral Nb$_2$Si$_n$ are $D_{3h}$-symmetric trigonal bipyramid structures, and that of Nb$_2$Si$_6$$^{−}$ has $C_{2h}$ symmetry with the six Si atoms forming a chair-shaped structure. The ground state structure of the Nb$_2$Si$_{12}$$^{−}$ anion is a $C_{6v}$-symmetric capped hexagonal antiprism in which one Nb atom is encapsulated inside the Si$_{12}$ cage and the second Nb atom caps the top of the hexagonal antiprism. It is found that the atomic dipole moment-corrected Hirshfeld population (ADCH) charge distributions on the two Nb atoms not only depend on the electronegativities of Si and Nb atoms but also relate with the structural evolution of Nb$_2$Si$_n$$^{−}$ clusters. The molecular orbital analyses of Nb$_2$Si$_5$$^{−}$, Nb$_2$Si$_6$$^{−}$, and Nb$_2$Si$_{12}$$^{−}$ anions indicate that the delocalized Nb−Si$_n$ ligand interactions and the strong Nb−Nb bonds play important roles in their structural stability.

INTRODUCTION

Silicon is widely used in modern microelectronics devices. Many experimental and theoretical works have been conducted to understand the structures and properties of transition-metal (TM) doped silicon clusters because these clusters not only are useful for silicon-based catalysts, solar cells, and lithium-ion batteries$^{1−5}$ but also can be used as building blocks of cluster-assembled materials.$^{6−12}$ Compared to single-TM atom-doped silicon clusters, multiple-TM atom-doped silicon clusters may hold very special geometric structures such as tubular, pearl-chain style, wheel-like, stacked naphthalene-like, or dodecahedral structures.$^{13−18}$ and have special magnetic properties such as ferromagnetism or antiferromagnetism.$^{12,15,19−22}$

Niobium-doped silicon clusters have attracted great attention because niobium is widely used in the alloy industry and superconducting materials. Amorphous thin Nb$_2$Si$_{12}$ films can be used to probe the mechanisms of superconductor−insulator transitions (SIT).$^{23−26}$ Niobium silicide films or alloys can be used in digital superconducting electronics (SCE)$^{27}$ and in bolometers for astrophysical particle detection.$^{28−31}$ Nb−Si-based superalloys may be used as high-temperature materials in aircraft turbine engines and rockets because of their excellent mechanical properties at high temperature.$^{32−40}$ The structures of silicon clusters doped with one or two Nb atoms have been studied previously by several theoretical calculations.$^{41−48}$ The diatomic NbSi$^−$ anion was studied by photoelectron imaging experiments and ab initio calculations,$^{49}$ and the NbSi$^−$ anions in the size range of n = 3–18 were investigated with anion photoelectron spectroscopy.$^{50,51}$ The NbSi$_6^+$ (n = 6–20) and Nb$_2$Si$_n^+$ (n = 13–19) cations were studied with mass spectrometry and H$_2$O adsorption reactivity experiments.$^{52}$ The NbSi$_n^+$ (n = 4–12) cations were also investigated using argon-tagged infrared multiphoton dissociation (IR-MPD) experiments and density functional theory (DFT) calculations.$^{53}$ In order to get more detailed information regarding the geometric structures and electronic properties of Nb$_2$Si$_n$ clusters, in this work we investigated Nb$_2$Si$_n$$^{−/0}$ (n = 2–12) clusters with size-selected anion photoelectron spectroscopy and ab initio calculations. It is found that the two Nb atoms in Nb$_2$Si$_n$$^{−/0}$ clusters form a strong Nb−Nb bond and the Nb$_2$Si$_3$$^{−/0}$, Nb$_2$Si$_6$$^{−}$, and Nb$_2$Si$_{12}$$^{−}$ clusters have high symmetric geometric structures.
EXPERIMENTAL AND THEORETICAL METHODS

Experimental Method. The experiments were conducted on a home-built apparatus consisting of a laser vaporization cluster source, a time-of-flight mass spectrometer, and a magnetic-bottle photoelectron spectrometer, which has been described elsewhere.\(^5^4\) The Nb\(_{2}\)Si\(_{n}^-\) cluster anions were produced with the laser vaporization source by laser ablation of a rotating and translating Nb/Si disk target (Nb:Si mole ratio 1:1, 13 mm diameter) with the second-harmonic light (532 nm) pulses from a nanosecond Nd:YAG laser (Continuum Surelite II-10), while helium carrier gas with ~0.4 MPa backing pressure was allowed to expand through a pulsed valve (General Valve Series 9) into the source to cool the Nb\(_{2}\)Si\(_{n}^-\) clusters. The clusters anions were mass analyzed by the time-of-flight mass spectrometer. The Nb\(_{2}\)Si\(_{n}^-\) anions were each size selected with a mass gate and decelerated by a momentum decelerator before crossing with the laser beam of the fourth-harmonic light (266 nm) pulses from the other Nd:YAG laser at the photodetachment region. The resulting electrons were energy analyzed by the magnetic-bottle photoelectron spectrometer. The photoelectron spectra were calibrated with the spectra of Cu\(^+\) and Au\(^+\) ions taken under similar conditions. The resolution of the magnetic-bottle photoelectron spectrometer was about 40 meV for electrons with 1 eV kinetic energy.

Theoretical Method. Full structural optimizations and frequency analyses of Nb\(_{2}\)Si\(_{n}^-\) anions and their neutral counterparts were carried out employing density functional theory (DFT) with the Beck’s three-parameter and Lee–Yang–Parr’s gradient-corrected correlation hybrid functional (B3LYP).\(^5^5,^5^6\) as implemented in the Gaussian 09 program package.\(^5^7\) The exchange-correlation potential and effective core pseudopotential LanL2DZ basis set\(^5^8\) was used for the Nb atoms, and the Pople’s all-electron 6-311+G(d) basis set\(^5^9\) was used for the Si atoms. No symmetry constraint was imposed during the geometry optimizations for both anionic and neutral clusters. For all clusters, numerous initial structures reported in the literature were taken into account at all possible spin states. Additionally, the swarm-intelligence-based CALYPSO structure prediction software\(^6^0\) was used to search the global minima for both anionic and neutral clusters. CALYPSO is an efficient structure prediction method. This approach requires only chemical compositions for a given cluster to predict stable or metastable structures at given external conditions. The success of CALYPSO is due to the integration of several major techniques, which include structural evolution through PSO algorithm, symmetry constraint during structure generation, the Metropolis criterion, atom-centered symmetrical function, and bond characterization matrix (BCM). These critical techniques can enhance the capability of CALYPSO in dealing with more complex systems and can also accelerate the structural optimization process, reduce searching space, enhance the structural diversity, and eliminate similar structures on the potential energy surfaces to enhance searching efficiency. Harmonic vibrational frequency analyses were performed to verify that the optimized structures are the true minima on the potential energy surfaces. The theoretical vertical detachment energies (VDEs) were calculated as the energy differences between the neutrals and the anions both at the geometries of anionic species, while the theoretical adiabatic detachment energies (ADEs) were calculated as the energy differences between the neutrals and the anions relaxed to the nearest local minima using the geometries of the corresponding anions as initial structures. The single-point energies of Nb\(_{2}\)Si\(_{12}^-\)–12\(^7^0\) clusters were calculated by using the coupled-cluster methods including single, double, and perturbative triple excitation [CCSD(T)]\(^6^1,^6^2\) to obtain more accurate relative energies of the low-lying isomers in which the aug-cc-pVDZ-PP basis set\(^6^3\) was used for the Nb atoms and cc-pVDZ basis set\(^6^4\) was used for the Si atoms. Zero-point energy (ZPE) corrections obtained from the B3LYP functional were included in all calculated energies. To gain insight into the charge distributions of Nb\(_{2}\)Si\(_{12}^-\) anions, we used the program Multiwfn\(^6^5\) to conduct the atomic dipole moment-corrected Hirshfeld population (ADCH) analyses. The ADCH charge is proposed by Lu et al.\(^6^6\) and is an improved version of Hirshfeld charge to resolve many inherent drawbacks of Hirshfeld charge, such as the poor dipole moment reproducibility.\(^6^7\) Also, it has many advantages over the Mulliken, NPA, and AIM charges in dealing with atomic charge distributions of clusters. The program Multiwfn was also employed to analyze the orbital compositions by using the natural atomic orbital method.

EXPERIMENTAL RESULTS

The photoelectron spectra of Nb\(_2\)Si\(_n^-\) (n = 2–12) clusters recorded with 266 nm photons are presented in Figure 1, and the experimental VDEs and ADEs of these clusters obtained from their photoelectron spectra are summarized in Table 1. The experimental VDEs of these clusters were estimated from the maxima of the first peaks. We drew a straight line along the rising edge of the first peaks and made the straight line intersect with the baseline of the experimental spectra. The electron binding energy (EBE) values at the intersection points plus the instrumental resolution were assigned as the experimental ADEs.

The experimental peaks in the photoelectron spectra of Nb\(_2\)Si\(_n^-\) shift to the higher EBE region with increasing number of Si atoms. Due to the existence of the second Nb atom, the spectral features of Nb\(_2\)Si\(_n^-\) are more complex than those of Nb\(_n^-\) and the VDEs of Nb\(_2\)Si\(_n^-\) are relatively lower than those of corresponding Nb\(_n^-\).\(^5^4\)

The photoelectron spectrum of Nb\(_2\)Si\(_2^-\) reveals five major peaks centered at 1.95, 2.51, 3.06, 3.44, and 3.83 eV, respectively. In the spectrum of Nb\(_2\)Si\(_3^-\), there is a low-intensity shoulder peak at 2.13 eV, followed by five major peaks centered at 2.52, 2.66, 2.92, 3.50, and 3.91 eV, respectively. The spectrum of Nb\(_2\)Si\(_4^-\) displays a broad shoulder peak at 2.23 eV and a high-intensity peak at 2.68 eV, followed by four barely resolved broad peaks at 3.23, 3.48, 3.65, and 4.15 eV, respectively. As for the spectrum of Nb\(_2\)Si\(_5^-\), there is a low-intensity peak centered at 2.37 eV, a high-intensity broad peak centered at 3.19 eV, a shoulder peak between 2.37 and 3.19 eV, a major peak centered at 3.50 eV, followed by two barely distinguishable peaks at 3.95 and 4.20 eV. The spectrum of Nb\(_2\)Si\(_6^-\) has a low-intensity peak centered at 2.62 eV and three high-intensity peaks centered at 2.98, 3.41, and 3.82 eV. A low-intensity peak centered at 2.71 eV and two high-intensity peaks centered at 3.34 and 3.96 eV can be observed in the spectrum of Nb\(_2\)Si\(_7^-\).

The spectrum of Nb\(_2\)Si\(_8^-\) displays a low-EBE tail in the range of 2.4–2.8 eV, a major peak centered at 3.08 eV, and another high-intensity broad peak in the range of 3.25–4.25 eV. The spectrum of Nb\(_2\)Si\(_9^-\) possesses a low-intensity peak centered at 2.94 eV followed by three barely resolved peaks centered at 3.56, 3.81, and 4.13 eV, respectively. In the spectrum of
In the DOS spectra, each transition is treated equally in the simulations.

**Nb$_2$Si$_n^-$ ($n = 2–12$) Anions.** Nb$_2$Si$_2^-$ is the most stable isomer of Nb$_2$Si$_n^-$ ($n = 2$) and is a C$_{3v}$-symmetric tetrahedron structure. Its theoretical VDE (1.81 eV) is in reasonable agreement with the experimental value (1.95 eV), and its simulated DOS spectrum can roughly reproduce the peak positions and patterns of the experimental spectrum, although the intensity of the high EBE part of the DOS spectrum is slightly higher than that of the experimental spectrum. The existence of isomer 2B can be ruled out because it is much higher in energy than isomer 2A by 0.44 eV. Therefore, we suggest that isomer 2A is the most likely structure observed in our experiments.

Nb$_2$Si$_3^-$ is the most stable isomer (3A) of Nb$_2$Si$_n^-$ and can be viewed as adding a Si atom to cap the triangular face of isomer 3B. The calculated VDE (2.14 eV) is in excellent agreement with the experimental value (2.13 eV), and its simulated DOS spectrum can roughly reproduce the peak positions and patterns of the experimental spectrum. Isomer 3B is higher in energy than isomer 3A by 0.10 eV. The existence of isomers 3C and 3D can be ruled out because they are much higher in energy than isomer 3A by at least 0.53 eV. Thus, we suggest isomer 3A to be the most probable structure contributing to the photoelectron spectrum of Nb$_2$Si$_3^-$ and isomer 3B may have some contribution to the higher electron binding energy (EBE) sides of the photoelectron spectrum.

Nb$_2$Si$_4^-$ is the most stable isomer (4A) of Nb$_2$Si$_n^-$ and can be viewed as adding a Si atom to cap the triangular face of isomer 4B. The theoretical VDEs (2.23 and 2.13 eV) of isomers 4A and 4B are both in excellent agreement with the experimental value (2.23 eV), and the energy difference between 4A and 4B is only 0.05 eV. The simulated spectrum of isomer 4A can match most of the experimental peaks, and that of isomer 4B is in reasonable agreement with the experimental peaks at 3.23 and 3.65 eV. The combination of the DOS spectra of isomers 4A and 4B can reproduce the peak positions and patterns of the experimental spectrum. Isomers 4C and 4D are impossible to present in our experiments because they are much higher in energy than isomer 4A by at least 0.30 eV. Thus, isomers 4A and 4B are suggested to be the most probable structures detected in our experiments.

Nb$_2$Si$_5^-$ is the most stable isomer (5A) of Nb$_2$Si$_n^-$ and can be viewed as adding another Si atom to cap the triangular face of isomer 5B. The calculated VDE (2.38 eV) of isomer 5A is in excellent agreement with the experimental value (2.37 eV), and its simulated DOS spectrum fits the peak positions and patterns of the experimental spectrum very well. Isomer 5B is higher in energy than isomer 5A by 0.18 eV. The existence of isomers 5C and 5D can be ruled out because they are much higher in energy than isomer 5A by at least 0.66 eV. Thus, we suggest isomer 5A to be the most probable structure contributing to the photoelectron spectrum of Nb$_2$Si$_5^-$, and isomer 5B may have some contribution to the higher EBE sides of the photoelectron spectrum.

Nb$_2$Si$_6^-$ is the most stable isomer (6A) of Nb$_2$Si$_n^-$ and can be viewed as adding two Si atoms to cap the rhombic Nb$_2$Si$_{12}^-$ unit of isomer 6B. The theoretical VDE (3.14 eV) of isomer 6A is in good agreement with the experimental value (2.98 eV), and that (3.62 eV) of isomer 6B is consistent with the experimental peak at 2.62 eV. Isomer 6B is slightly higher in energy than isomer 6A by 0.13 eV.
Table 1. Relative Energies, Theoretical VDEs and ADEs of the Low-Lying Isomers of Nb2Si− (n = 2−12) Clusters, and Experimental VDEs and ADEs Estimated from Their Photoelectron Spectra

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<th>Sym</th>
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<th>ADE (eV)</th>
<th>VDE (eV)</th>
<th>ADE (eV)</th>
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“*The isomers labeled in bold are the most probable isomers in the experiments.*

The $\Delta E$s are calculated at the CCSD(T)//cc-pVQZ/Si/aug-cc-pVQZ/Nb level of theory. The ADEs and VDEs are calculated at the B3LYP//6-311+G(d)/Si/LanL2DZ/Nb level of theory. The uncertainties of the experimental VDEs and ADEs are ±0.08 eV.

simulated DOS spectrum of isomer 6A can match the experimental peaks centered at 2.98 and 3.82 eV, while that of isomer 6B is in good agreement with the experimental peaks centered at 2.62 and 3.41 eV. The combination of the DOS spectra of isomers 6A and 6B is in good agreement with the experimental spectrum. The existence of isomers 6C and 6D can be ruled out because they are much higher in energy than isomer 6A by at least 0.32 eV. Therefore, isomers 6A and 6B might coexist in our experiments.

$\text{Nb}_2\text{Si}_{12}^-$. The lowest lying isomer of $\text{Nb}_2\text{Si}_{12}^-$ (7A) can be described as an additional Si atom face capping the $\text{Nb}_2\text{Si}_5$ rhombus of $\text{Nb}_2\text{Si}_6^-$. The calculated VDE (2.71 eV) of isomer 7A agrees well with the experimental value (2.71 eV), and its simulated DOS spectrum can duplicate the spectral features of the experimental spectrum. The existence of isomers 7B, 7C, and 7D can be ruled out because they are much higher in energy than isomer 7A by at least 0.48 eV. Thus, isomer 7A is suggested to be the most probable structure detected in our experiments.

$\text{Nb}_2\text{Si}_{10}^-$. The most stable isomer of $\text{Nb}_2\text{Si}_{10}^-$ (8A) can be viewed as a $\text{Si}_5$ five-membered ring penetrated by the vertical Nb−Nb axle and adding a $\text{Si}_1$ triangle at the bottom. The calculated VDEs (2.99, 3.03, and 2.96 eV) of isomers 8A, 8B, and 8C are all in reasonable agreement with the experimental value (3.08 eV), and that of isomer 8D is calculated to be 2.73 eV. The simulated DOS spectra of isomers 8A, 8B, and 8C are consistent with the experimental peak at 3.08 eV and the high-intensity broad peak in the range of 3.25−4.25 eV, while that of isomer 8D is in reasonable agreement with the low-EBE tail in the range of 2.4−2.8 eV. Isomers 8B, 8C, and 8D are higher in energy than isomer 8A by 0.07, 0.17, and 0.20 eV. Thus, we suggest that isomer 8A is the major one detected in the experiments, and isomers 8B, 8C, and 8D are the minor species contributed to the photoelectron spectrum of $\text{Nb}_2\text{Si}_{10}^-$. Multiple isomers coexisting in the experiments can explain why the spectral features of $\text{Nb}_2\text{Si}_{10}^-$ are very broad.

$\text{Nb}_2\text{Si}_{10}^-$. As the ground state structure of $\text{Nb}_2\text{Si}_{10}^-$, isomer 9A can be considered as a $\text{Si}_5$ rhombus and a $\text{Si}_5$ pentagonal ring bridged by the Nb−Nb bond, which is perpendicular to the $\text{Si}_4$ and $\text{Si}_5$ subunits. The calculated VDE (2.97 eV) of isomer 9A is in excellent agreement with the experimental value (2.94 eV), and its simulated DOS spectrum fits the peak positions and patterns of the experimental spectrum very well. The calculated VDE of isomer 9B is 2.66 eV, which is much smaller than the experimental value, and its simulated DOS spectrum is also different from the experimental spectrum. The existence of isomers 9C and 9D can be ruled out because they are much higher in energy than isomer 9A by at least 0.41 eV. Thus, isomer 9A is considered as the most probable structure observed in our experiments.

$\text{Nb}_2\text{Si}_{10}^-$. The lowest lying isomer of $\text{Nb}_2\text{Si}_{10}^-$(10A) can be regarded as deriving from isomer 8A by adding a Si atom to cap the triangle face of $\text{Nb}_1\text{Si}_5$ and an additional Si atom to face cap the folded $\text{Nb}_2\text{Si}_5$ rhombus. The calculated VDE (3.02 eV) of isomer 10A is in excellent agreement with the experimental value (3.07 eV), and its DOS spectrum matches the peak positions and patterns of the experimental spectrum very well. The existence of isomers 10B, 10C, and 10D can be ruled out because they are much higher in energy than isomer 10A by at least 0.38 eV. Therefore, we suggest isomer 10A to be the most probable structure contributing to the photoelectron spectrum of $\text{Nb}_2\text{Si}_{10}^-$. $\text{Nb}_2\text{Si}_{11}^-$. The most stable structure of $\text{Nb}_2\text{Si}_{11}^-$(11A) is formed by the upper $\text{Si}_6$ hexagon and the lower $\text{Si}_5$ pentagon.
interacted with the Nb−Nb bond, which is vertical to the Si₆ and Si₅ subunits. Isomer 11A can also be obtained by two additional Si atoms face capping the upper Si₄ rhombus of isomer 9A. The calculated VDE (3.07 eV) of isomer 11A agrees well with the experimental value (3.09 eV), and its simulated DOS spectrum fits the peak positions and patterns of the experimental spectrum very well. Isomer 11B has a similar structure with its competitive isomer 11A with the upper Si₆ hexagon being slightly distorted. The calculated VDEs (2.96 and 3.00 eV) of isomers 11B and 11C are both in reasonable agreement with the experimental values.

**Figure 2.** Typical low-lying isomers of anionic Nb₂Siₙ⁻ (n = 2–12) clusters. ΔE values are calculated at the CCSD(T)/cc-pVDZ/Si/aug-cc-pVDZ-PP/Nb level of theory. Green and red balls stand for the Si atoms and Nb atoms, respectively.
agreement with the experimental value, and they are higher in energy than isomer 11A by 0.03 and 0.21 eV. Isomer 11D is likely to be detected because it is much higher in energy than isomer 11A by 0.46 eV. Thus, we suggest that isomer 11A is the most probable structure contributing to the experimental spectrum of Nb$_2$Si$_{11}^{−}$. Nb$_2$Si$_{12}^{−}$. The most stable isomer of Nb$_2$Si$_{12}^{−}$ (12A) is a C$_{6v}$-symmetric capped hexagonal antiprism with one Nb atom encapsulated inside the Si$_{12}$ cage and the second Nb atom face capping the top of the hexagonal antiprism, similar to the structure of V$_2$Si$_{12}^{−}$. Isomer 12A can also be regarded as stemming from isomer 11A by an additional Si atom capping the Si–Si bond of the bottom Si$_5$ five-membered ring. The VDE of isomer 12A is calculated to be 3.41 eV, which is in excellent agreement with the experimental value (3.45 eV), and its simulated DOS spectrum is in line with the experimental spectrum, although the intensity of the high-EBE part of the DOS spectrum is slightly lower than that of the experimental spectrum. Although isomer 12B is higher in energy than isomer 12A by only 0.04 eV, the existence of isomer 12B can be ruled out because its calculated VDE (2.99 eV) is much smaller than the experimental value. Isomer 12C is higher in energy than isomer 12A by 0.09 eV. The existence of isomer 12D can be ruled out because it is much higher in energy than isomer 12A by 0.93 eV. Therefore, we suggest isomer 12A to be the most likely structure detected in our experiments, and isomer 12C may have a minor contribution to the photoelectron spectrum of Nb$_2$Si$_{12}^{−}$. The previous DFT calculations suggested that the structure of Nb$_2$Si$_{12}^{−}$ is also a C$_{6v}$-symmetric capped hexagonal antiprism, similar to isomer 12A.  

### Discussion

The most stable structures of Nb$_2$Si$_{12−6}$ found in this work are in line with the previous theoretical results of Nb$_2$Si$_{12−6}^{−}$ (n = 2−6). We found that the two Nb atoms in Nb$_2$Si$_{12−6}^{−}$ (n = 2−12) clusters tend to stay close to form a Nb−Nb bond, similar to the theoretical results of T$_2$Si$_{12−8}$ (T = Fe, Co, Ni) and M$_2$Si$_{12}$ (M = Nb, Ta, Mo, W). The metal−metal bond is also found in our previous works of V$_2$Si$_{12−6}^{−}$ investigated by anion photoelectron spectroscopy and DFT calculations. In addition, the two Nb atoms in Nb$_2$Si$_{12−6}^{−}$ prefer to occupy the high coordination sites to form more Nb−Si bonds. That is more likely due to the existence of unfilled d orbitals in the Nb atom. The Nb−Nb bond length in Nb$_2$Si$_{11−6}^{−}$ (n = 2−12) clusters are between 2.37 and 2.68 Å, which are longer than the Nb−Nb bond length of 2.08 Å in the niobium dimer (Nb$_2$) but shorter than the nearest neighbor distance of 2.86 Å in the metallic niobium. This suggests that there are strong interactions between the two Nb atoms in Nb$_2$Si$_{11−6}^{−}$ (n = 2−12) clusters. As for neutral Nb$_2$Si$_{11}$ clusters, the Nb−Nb distances are in the range of 2.39−2.68 Å at n = 2−11, which are also longer than the Nb−Nb distance in the niobium dimer and shorter than the nearest neighbor distance in the metallic niobium. However, the Nb−Nb distance in neutral Nb$_2$Si$_{12}$ is about 2.95 Å, which is even longer than the Nb−Nb distance in the metallic niobium. That indicates that the removal of the excess electron from Nb$_2$Si$_{12}$ anion weakens the Nb−Nb bond (which can be confirmed by the analyses of molecular orbitals).

It is interesting to compare the structures of Nb$_2$Si$_{12−6}^{−}$ with those of V$_2$Si$_{12}^{−}$. The structures of V$_2$Si$_{12}^{−}$ have been reported by Xu et al. and V$_2$Si$_{12}^{−}$ reported by Huang et al. At n = 3−
6, the photoelectron spectra of Nb2Si\textsuperscript{n−} are similar to those of V2Si\textsuperscript{n−} except that the VDEs of Nb2Si\textsuperscript{n−} are slightly lower than those of V2Si\textsuperscript{n−}. The most stable isomers of Nb2Si\textsuperscript{n−} and V2Si\textsuperscript{n−} are all regarded as the metals face capping the Si\textsubscript{n} frameworks and occupying the high coordination sites. Their similar geometric structures can explain why Nb2Si\textsuperscript{n−} and V2Si\textsuperscript{n−} have similar spectral features. The Si\textsubscript{6} chair-shaped structure of Nb2Si\textsubscript{6}− is slightly distorted to the lower C\textsubscript{2h} symmetry compared to the D\textsubscript{3d} symmetry of V2Si\textsubscript{6}−, and the Si−Si bond lengths (2.42−2.55 Å) in Nb2Si\textsubscript{6}− are longer than those (2.38−2.44 Å) in V2Si\textsubscript{6}−, probably because the atomic radius of the Nb atom (1.47 Å) is larger than that of the V atom (1.35 Å). At n = 12, the spectral feature of Nb2Si\textsubscript{12}− is also similar to that of V2Si\textsubscript{12}−, but the experimental VDE of Nb2Si\textsubscript{12}− is lower than that of V2Si\textsubscript{12}− by 0.21 eV. The global minima of both Nb2Si\textsubscript{12}− and V2Si\textsubscript{12}− are a capped hexagonal antiprism with one metal atom encapsulated into the Si\textsubscript{12} cage and the other metal atom face capping the top of the hexagonal antiprism. The height and sides (2.57 and 2.45 Å) of Nb2Si\textsubscript{12}−-capped hexagonal antiprism are slightly longer than those (2.53 and 2.43 Å) of V2Si\textsubscript{12}−, which is because the atomic radius of the Nb atom is larger than that of the V atom.

To give insight into the charge distributions of Nb\textsubscript{2}Si\textsubscript{n−} clusters, we conducted the atomic dipole moment-corrected Hirshfeld population (ADCH) analyses on the most stable isomers of Nb\textsubscript{2}Si\textsubscript{n−} (n = 2−12) clusters and presented them in Figure 5. The ADCH charge on the Nb1 atom ranges from −0.12 e to 0.45 e, while that on the Nb2 atom is in the range of −0.12 e to 0.34 e. The ADCH charge distributions on the two Nb atoms are very similar at n = 2−6 and display no significant changes, which is probably due to the two Nb atoms interacting with nearly the same number of Si atoms in these clusters. For cluster sizes of n = 7−12, the two Nb atoms begin to bond with different number of Si atoms, resulting in the different ADCH charge distributions on the two Nb atoms. In particular, at n = 12, the ADCH charge on the Nb1 atom is 0.45 e and that on the Nb2 atom is 0.06 e, more likely related to the formation of a C\textsubscript{6v}-symmetric capped hexagonal antiprism. Except for Nb2Si\textsubscript{2}−, the ADCH charge distributions on the two Nb atoms are positive values, which is more likely due to the electronegativity of the Si atom (\(\chi = 1.90\)) being stronger than that of the Nb atom (\(\chi = 1.60\)).\textsuperscript{73} This also implies that there is slight charge transfer from the two Nb atoms to the Si\textsubscript{n} frameworks. It seems that the ADCH charge distributions on the two Nb atoms are associated with the structural evolution of Nb\textsubscript{2}Si\textsubscript{n−} clusters and the electronegativities of the Si and Nb atoms.

To further understand the bonding nature in Nb\textsubscript{2}Si\textsubscript{n−} clusters, we calculated the Wiberg bond orders and Mayer

![Figure 3. Comparison between the experimental photoelectron spectra and the simulated DOS spectra of the low-lying isomers of Nb\textsubscript{2}Si\textsubscript{n−} (n = 2−12) clusters. Simulated spectra were obtained by fitting the distribution of the transition lines with the unit area Gaussian functions of 0.20 eV full widths at half-maximum.](image-url)
The calculations show that the Wiberg bond orders of the Nb–Nb bonds in Nb$_2$Si$_3^-$, Nb$_2$Si$_6^-$, and Nb$_2$Si$_{12}^-$ are 2.05, 1.71, and 1.47, respectively, whereas the Mayer bond orders are 1.89, 1.87, and 1.39, respectively. The high Nb–Nb bond orders reveal that the interactions between the two Nb atoms are very strong in these clusters. We also conducted detailed analyses on the molecular orbitals of Nb$_2$Si$_3^-$, Nb$_2$Si$_6^-$, and Nb$_2$Si$_{12}^-$ and presented them in Figure 6. From Figure 6 it can be seen that the singly occupied molecular orbital (SOMO)
of Nb$_2$Si$_3^-$ displays a large overlap between the 4d$_z$ orbitals of the Nb atoms. From the HOMO-3 and HOMO-4 of Nb$_2$Si$_3^-$ it can be seen that there are large overlaps between the 4d$_x$ and the 4d$_{2z}$ orbitals of the Nb atoms, respectively. The SOMO and HOMO-1 of Nb$_2$Si$_3^-$ show large overlaps between the 4d$_y$ and the 4d$_{2z}$ orbitals of the Nb atoms, respectively. As for Nb$_2$Si$_{12}^-$, the SOMO and HOMO-8 reveal large overlaps between the 4d$_x$ orbitals of the Nb atoms, the HOMO-3 and HOMO-4 display overlaps between the 4d$_x$ and 4d$_y$ of the Nb atoms, respectively, and the HOMO-6 and HOMO-7 show overlaps between the 4d$_x$ and the 4d$_{2x}$ orbitals of the Nb atoms, respectively. The strong interactions between the 4d orbitals of the two Nb atoms are consistent with the high Nb–Nb bond orders and the short Nb–Nb bond lengths (2.37–2.68 Å) found in Nb$_2$Si$_n^-$ clusters. It is also worth mentioning that the SOMOs of Nb$_2$Si$_3^-$, Nb$_2$Si$_6^-$, and Nb$_2$Si$_{12}^-$ are mainly composed by the 4d orbitals of the Nb atoms and the 3s3p hybridized orbitals of the Si$_n$ frameworks, and the electron densities are delocalized over the whole clusters, suggesting that there are delocalized Nb–Si ligand interactions between the Nb atoms and the Si$_n$ frameworks. Overall, the strong Nb–Nb bonds and the delocalized Nb–Si ligand interactions play important roles in the stability of the D$_{3h}$-symmetric trigonal bipyramid structure of Nb$_2$Si$_3^-$, the C$_{3v}$-symmetric Si$_6$ chair-shaped structure of Nb$_2$Si$_6^-$, and the C$_{6v}$-symmetric capped hexagonal antiprism of Nb$_2$Si$_{12}^-$. 

### CONCLUSIONS

We conducted a combined anion photoelectron spectroscopy and theoretical study on bi-Nb-doped silicon clusters. We found that the two Nb atoms in Nb$_2$Si$_n^-/0$ ($n = 2–12$) clusters tend to stay close to form a Nb–Nb bond and occupy the high coordination sites to interact with more Si atoms. The most stable structures of Nb$_2$Si$_n^-/0$ ($n = 2–12$) clusters can be regarded as a central axis of Nb surrounded by the Si atoms. The most stable isomers of Nb$_2$Si$_n^-$ anions are all in spin doublet states, while those of the neutral clusters are all in spin singlet states. The most stable isomers of anionic and neutral Nb$_2$Si$_n$ are D$_{3h}$-symmetric trigonal bipyramidal structures, that of Nb$_2$Si$_4^-/0$ has C$_{3h}$ symmetry with the six Si atoms forming a chair-shaped structure, and that of Nb$_2$Si$_{12}^-$ has a C$_{6v}$-symmetric capped hexagonal antiprism structure. According to the atomic dipole moment-corrected Hirshfeld population (ADCH) analyses, the ADCH charge distributions on the two Nb atoms are not only associated with the structural evolution of Nb$_2$Si$_n^-$ clusters but also related to the electronegativities of Si and Nb atoms. Additionally, we analyzed the molecular orbitals of Nb$_2$Si$_3^-$, Nb$_2$Si$_6^-$, and Nb$_2$Si$_{12}^-$ anions and confirmed that the strong Nb–Nb bonds and the delocalized Nb–Si ligand interactions are important for their structural stability. The current study may provide insights into the structural and bonding properties of Nb–Si-based films and alloys at the molecular level.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b01904.

Cartesian coordinates of the low-lying isomers of Nb$_2$Si$_n^-/0$ ($n = 2–12$) clusters (PDF)

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