



## NEUTRAL AND CATIONIC TITANIUM-DOPED SILICON CLUSTERS: GROWTH MECHANISM AND STABILITY

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### ABSTRACT

We report ab-initio study on neutral and cationic titanium-doped silicon clusters  $\text{TiSi}_n^{0/+}$  ( $n = 1-10$ ). The growth patterns for both neutral and charged clusters are revealed. The neutral  $\text{TiSi}_n$  clusters follow a consistent rule of addition: the larger  $\text{TiSi}_n$  cluster is built up by adding a Si atom on the smaller  $\text{TiSi}_{n-1}$  cluster. However, the Ti atom prefers to substitute at a high-coordination position to form the cationic clusters. The neutral  $\text{TiSi}_n$  clusters is more stable than the pure  $\text{Si}_{n+1}$  clusters while the cationic  $\text{TiSi}_n^+$  is less stable than the pure ones. Both neutral and cationic clusters tend to loss Si atom rather than Ti atoms.

*Keywords:* doped-silicon clusters; growth mechanism; stability; density functional theory; cationic cluster.

### 1. INTRODUCTION

The importance of silicon in many technological applications together with the explosion of cluster science leads to an expansion of studies on silicon clusters in recent years [1 - 4]. There is currently a strong interest in the prospect of producing novel materials consisting of small atomic clusters, and in particular silicon clusters [5 - 7]. Many studies have been published on geometrical structures and spectroscopic properties of the pure silicon clusters. For instant, the most recent studies on pure silicon clusters done on ionization energy measurement [8], infrared spectra [9], or thermochemical parameters [10]. For large pure Si clusters, Song et al. found that the global minimum of  $\text{Si}_n$  clusters are all of the high coordination [11]. Pure silicon clusters, however, are unsuitable as building blocks because they are chemically reactive due to the existence of dangling bonds [12]. Beck first produced transition metal (TM = W, Mo, and Cr) doped silicon clusters and found that doped clusters are more stable than the pure Si clusters of the same size [13].

Since then, a large number of studies have devoted to understand the effect of transition metals to the structures and properties of silicon clusters. For example, Grubisic et al. [14] studied the photoelectron spectra of  $\text{EuSi}_n^-$  cluster anions ( $n = 3-17$ ) and proposed that a significant geometric reorganization due to the encapsulation of a europium atom occurs in this size range and is responsible for the detected changes in the electronic structure. Ohara et al. reported experimental photoelectron spectra and water reactivities of  $\text{TbSi}_n$  ( $n = 6-16$ ) [15, 16]. The knowledge about the structural identity of cluster is important since the all the fundamental cluster properties, specifically stability, depend on its geometry. Determination of geometries, stabilities, and electronic structures of doped clusters have immensely been investigated [12, 17 - 21]. Recently, the combination between experimental and theoretical studies allowed us to reveal the structural effects of V and Cu on the Si clusters [22].

Titanium has been attracted much attention and studies as a transition metal dopant in C [23], Al [24], and Au [25] clusters. The Ti-doped silicon clusters have appeared in few experimental and theoretical publications, but they mainly focus on the closed electronic shell and magic number of  $\text{TiSi}_{16}$  cluster [26, 27]. Kawamura and co-workers concluded that  $\text{TiSi}_n$  clusters form basket structures up to  $n = 12$  and cage structures from  $n = 13$  onwards [28]. Eventhough, a recent theoretical studies on neutral  $\text{TiSi}_n$  were performed using B3LYP functional and core potential LANL2DZ basis set, they could not draw a consistent growth mechanisms for these clusters [29]. Moreover, to the best of our knowledge, there is no study on cationic  $\text{TiSi}_n^+$  clusters. Therefore, in this paper, we investigate geometries, electronic structures and growth mechanism of both neutral and positively charged Ti-doped silicon clusters, and then reveal the charge effect on the geometrical and electronic structures of the clusters.

## 2. COMPUTATIONAL DETAILS

The optimizations of a large number of atomic arrangements are performed. All the structures of doped silicon clusters available in the literature are taken as initial configurations for the optimization. In addition, more starting geometries are obtained by a substitution of Si atom by one Ti atom on the low-lying  $\text{Si}_{n+1}$  isomers, or an addition of Ti atom to different sites of the  $\text{Si}_n$  isomers. The formation of initial structures by adding Si atoms to smaller doped isomers or removal Si atoms from larger one are also considered.

Quantum chemical calculations were performed using density functional theory (DFT) methods. Up to now, DFT is the most efficient computational method to study cluster at the molecular level. In this study we use the pure BP86 functional, which was proved to give good results on ground state structures and infrared spectra of the  $\text{VSi}_n^+$  clusters [22], isoelectronic systems of  $\text{TiSi}_n$ , to investigate geometrical and electronic structures of the clusters. The hybrid B3LYP and B3P86 functionals are also used in some test cases.

Geometries are optimized without any symmetry constraints starting from a number of initial configurations and for all the possible spin states. Identity of the structures is checked by calculating their harmonic vibrational frequencies. If an imaginary frequency is found, a relaxation along the coordinates of the imaginary vibrational mode is carried out until a true local minimum is reached. Adiabatic ionizations (AIEs) are evaluated from the differences in energy between the ground state of neutral and cationic ground state. The vertical ionization energies (VIEs) are calculated from the single-point electronic energies of both neutral and cationic structures at the optimized-geometry of the neutral. All the calculations are carried out by the GAUSSIAN 03 program package.

### 3. RESULTS AND DISCUSSION

Shapes, point groups, electronic states, and relative energies of the low-lying isomers of neutral and cationic  $\text{TiSi}_n$  ( $n = 2-10$ ) clusters are shown in Figures 1 and 2. For a convention, the lower-lying isomers are labeled hereafter by **nn.X** and **nc.X** where the first letter (n) stands for the cluster size ( $\text{TiSi}_n$ ), the second letter (*n* or *c*) for neutral or cation, and **X** for the label of isomers.

#### 3.1. Structures of $\text{TiSi}_n$ and $\text{TiSi}_n^+$ clusters

##### *TiSi<sub>2</sub> and TiSi<sub>2</sub><sup>+</sup>*

All the possible  $\text{TiSi}_2$  atomic arrangements with  $C_{2v}$ ,  $C_{\infty v}$ , and  $D_{\infty h}$  with allowed spin states ranging from singlet to septet are optimized. We found that the ground state structure of  $\text{TiSi}_2$  (**2n.1**) is an isosceles triangle ( $C_{2v}$ ) at triplet  $^3B_1$  state. This isomer can be formed by adding a Ti atom into  $\text{Si}_2$  cluster or substituting the central Si atom in the  $\text{Si}_3$  cluster [10]. The singlet state of  $C_{2v}$  shape is 0.61 eV less stable than the triplet state. This result is similar to the report of Guo et al. Removal of an electron from  $\text{TiSi}_2$  leads to the formation of  $\text{TiSi}_2^+$  for which a doublet  $C_{2v}$  ground state is derived. That means that the unpaired electron is removed. All the other structural isomers are energetically unfavorable for both neutral and cation, with more than 1.5 eV higher in energy than the ground state.

##### *TiSi<sub>3</sub> and TiSi<sub>3</sub><sup>+</sup>*

For  $\text{TiSi}_3$ , a  $C_{3v}$  pyramidal structure (**3n.1**) at triplet  $^3B_1$  state, which is built by adding a Ti atom to the  $\text{Si}_3$  triangle, is found to be the ground state. At this size, our result is different from Guo et al.'s work where the  $C_{2v}$  planar rhombus (**3n.2**) was identified as the lowest-lying isomer at the B3LYP/LANL2DZ level of theory<sup>29</sup>. Our calculations at the B3LYP, B3P86 and BP86 functionals in combination with an all-electron 6-311+G(d) basis set show that **3n.2** is 0.15, 0.24 and 0.55 eV higher than the **3n.1** ground state. Moreover, the isoelectronic  $\text{VSi}_3^+$  was predicted to be a  $C_{3v}$  pyramid [22]. This means that the LANL2DZ is too simple to reasonably predict the energetic ordering of different isomers of this cluster. The other rhombic isomer (**3n.3**) lies even higher than the rhombic **3n.2**. At this size, all the isomers are stable at high-spin states.

However, the  $\text{TiSi}_3^+$  cation adopts a  $C_{2v}$  planar rhombus (**3c.2**) at doublet  $^2A_2$  state as the lowest-lying isomer. The quartet and sextet states of the same shape are calculated to be higher in energy than the doublet state. The  $\text{TiSi}_3^+$  ground state can be described by adding a Ti atom into the pure  $\text{Si}_3$  cluster or substituting a Si atom by Ti atom from the pure  $\text{Si}_4$  cluster. The cation **3c.1**, which has the same shape as the neutral ground state, is 0.33 eV higher in energy than the cationic lowest-lying isomer (**3c.2**). The ground state structure of  $\text{TiSi}_3^+$  found in the current work is similar to that of the isoelectronic  $\text{ScSi}_3$  cluster in ref. [21].

##### *TiSi<sub>4</sub> and TiSi<sub>4</sub><sup>+</sup>*

Our results show that the most stable structure of  $\text{TiSi}_4$  is a  $C_{3v}$  triangular bipyramid with the Ti atom lying on axial position at singlet state (**4n.1**) which is formed by substituting a Si atom on the  $\text{Si}_5$  cluster by Ti atom. However, previous study at B3LYP/LANL2DZ predicted the distorted triangular bipyramid (**4n.2**) at triplet state is the lowest-lying isomer while the **4n.1** is 0.16 eV less stable than **4n.2** isomer [29]. Our calculations using the B3LYP, B3P86 functionals in combination with the 6-311+G(d) basis set show that these two isomers are almost degenerate, while the BP86/6-311+G(d) calculations suggest that **4n.2** is 0.40 eV higher in

energy than **4n.1**. Ref. [21] confirmed the  $C_{3v}$  trigonal bipyramid (similar to **4n.1**) as the ground state of  $VSi_4^+$  which is isoelectronic with  $TiSi_4$ . Thus it is very likely that **4n.1** is the ground state as predicted at the BP86/6-311+G(d) level of theory.

Shape of the lowest-energy isomer of  $TiSi_4^+$  (**4c.2**) is predicted to be different from that of  $TiSi_4$ . The **4c.2** isomer ( $C_{2v}$ ) has similar shape to the second-energy isomer **4n.2** of the neutral and can be formed by substituting Si atom at the horizontal position of the  $Si_5$  cluster. The **4c.1** isomer whose shape is similar to **4n.1** lies 0.1 eV than the cationic ground state **4c.2**.  $ScSi_4$  which is isoelectronic with  $TiSi_4^+$  also adopts the  $C_{2v}$  structure as the ground state [21].

#### ***TiSi<sub>5</sub> and TiSi<sub>5</sub><sup>+</sup>***

At this size, both neutral and cation adopt similar shapes as their ground states, namely **5n.1** and **5c.1** respectively. This face-capped trigonal bipyramidal structure can be described as substitution of the distorted octahedron  $Si_6$  by Ti atom. The  $VSi_5^+$  cluster, isoelectronic species of  $TiSi_5$ , and the  $ScSc_5$  cluster, the isoelectronic species of  $TiSi_5^+$ , also take up similar shape as their ground state structure [21,22]. Other isomers are built by replacing a Si atom on different fluxional forms of  $Si_6$  by Ti atom.

#### ***TiSi<sub>6</sub> and TiSi<sub>6</sub><sup>+</sup>***

The Si-face-capped tetragonal bipyramid with Ti on the axial position (**6n.1**) is found to be the ground state structure of the neutral  $TiSi_6$  cluster. This result is consistent with Guo's report [29]. Two other low-lying isomers (**6n.2** and **6n.3**) are formed by substitution of a Si atom by Ti from the pure silicon cluster  $Si_7$  [30] leading to the pentagonal bipyramidal structures with Ti atom at different positions. They are both obviously higher in energy than the lowest-lying isomers by 0.47 and 0.52 eV.

Different from the neutral, the cationic  $TiSi_6^+$  adopts a pentagonal bipyramid within Ti is situated at horizontal position as the global minimum (**6c.3**). The cationic isomer **6c.1** which has the same shape with the neutral ground state is higher in energy than the lowest-lying isomer **6c.3** by 0.26 eV. The ground state structure of the isoelectronic  $ScSi_6$  cluster is also similar to that of  $TiSi_6^+$  [21].

#### ***TiSi<sub>7</sub> and TiSi<sub>7</sub><sup>+</sup>***

Our calculations found two quasi-degenerate isomers (**7n.1** and **7n.2**) of  $TiSi_7$ . The energy differences between the two isomers are 0.01, 0.07 and 0.05 eV using the BP86, B3LYP and B3P86, respectively. On the other hand, these two structures are very similar, they are both built up by substitution of Si of the  $Si_8^+$  by Ti atom and following by a relaxation. The difference is that **7n.1** has a Si atom capped on a Si-Si-Ti face while the **7n.2** has a Si atom capped on a Si-Si-Si face, thus leading to the difference in coordination number of the Ti atom. Interestingly, the isoelectronic  $VSi_7^+$  cluster was concluded that to have both structures in the molecular beam of the infrared measurements [22]. Therefore, it is likely that both isomers are quasi-degenerate and competitive for the ground state. However, the previous investigation [29] using B3LYP/LANL2DZ found only **7n.1** as the lowest-lying isomer. Other isomers located in this study have either pentagonal bipyramidal motif or bicapped octahedral motif.

The most stable structure of the cationic  $TiSi_7^+$  cluster (**7c.2**) is similar to **7n.2** of the neutral. **7c.1** isomer which is similar to **7n.1** of the neutral lies 0.14 eV higher in energy than the ground state of the cation. Thus, the isomeric selection can be done using the ionization process.

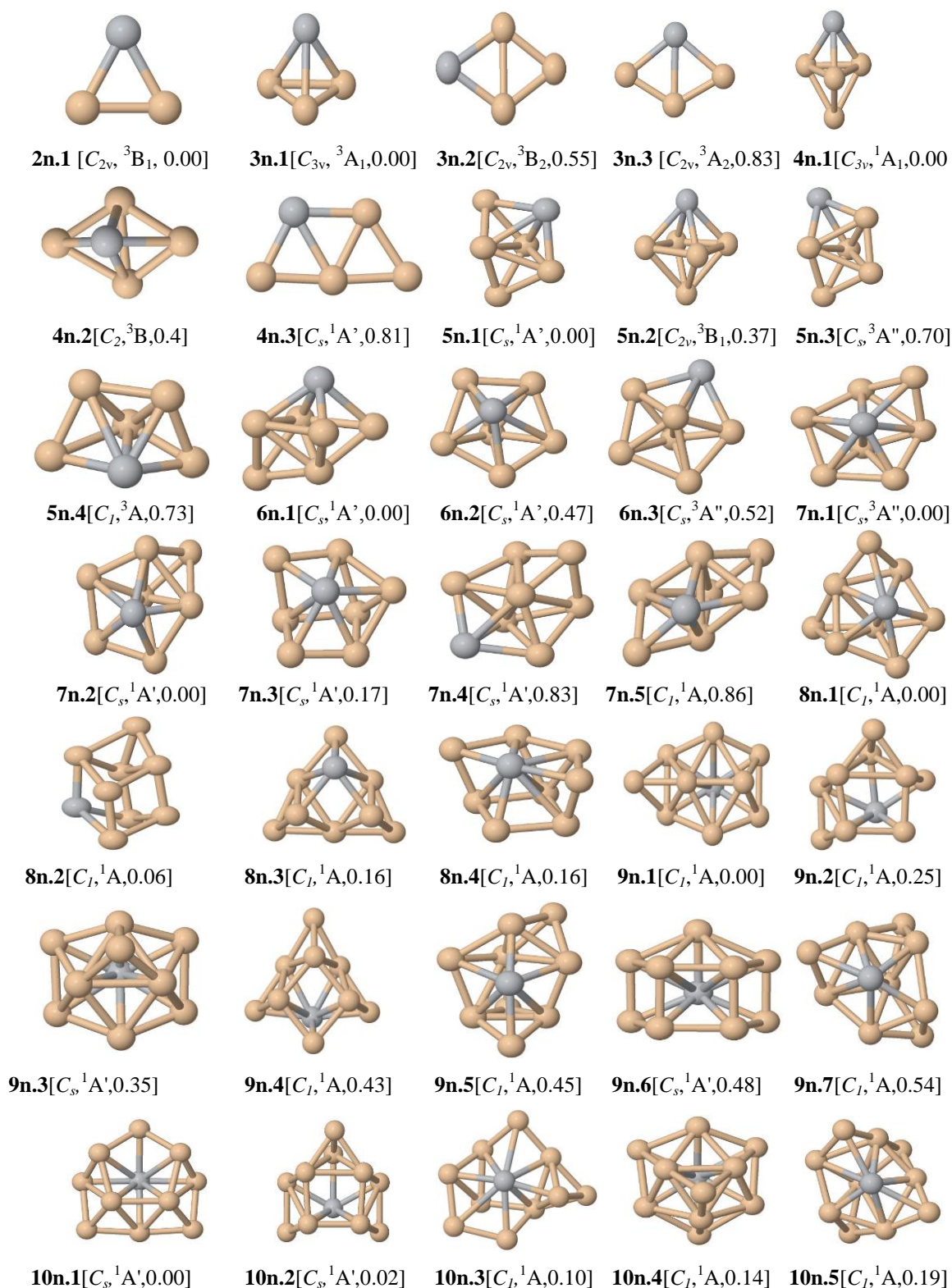


Figure 1. The low-lying isomers of the neutral  $TiSi_n$  clusters. Relative energies are given in eV.

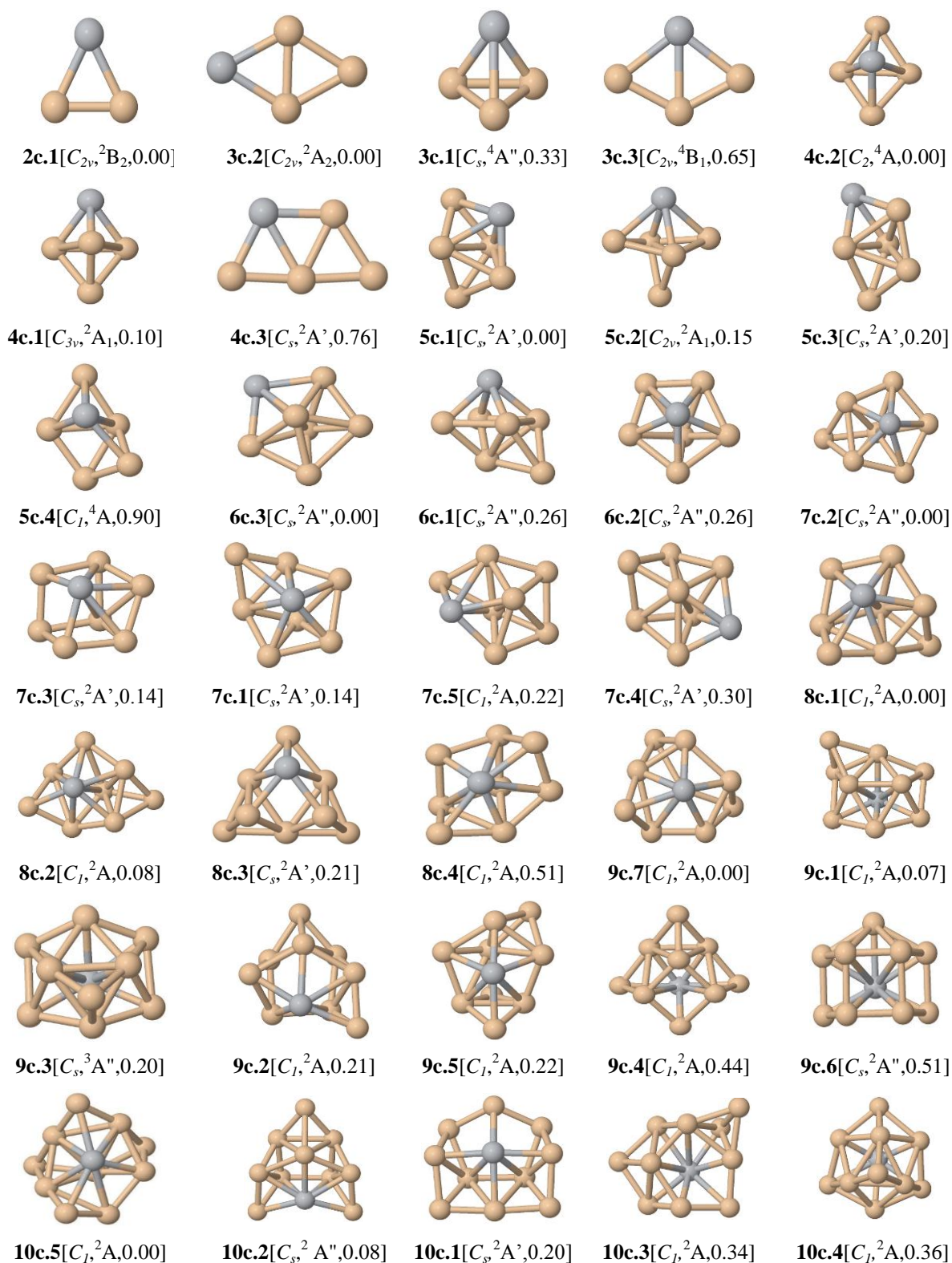


Figure 2. The low-lying isomers of the  $TiSi_n^+$  clusters. Relative energies are given in eV.

### *TiSi<sub>8</sub> and TiSi<sub>8</sub><sup>+</sup>*

The global minimum **8n.1** of the neutral can be described as a bicapped pentagonal bipyramid with Si atom at axial position. A substitutive derivative of the bicapped pentagonal bipyramid ground state of the C<sub>2v</sub> structure of Si<sub>9</sub> leads to the distorted isomer **8n.2** which is only 0.06 eV higher in energy than the **8n.1** ground state structure. **8n.4** which is previously reported by Guo et. al. [29] and Kumar et. al. [28] as their lowest isomer of TiSi<sub>8</sub>, is higher in energy than **8n.1** by 0.16 eV. Our calculations at the B3LYP and B3P86 levels with the same basis set 6-311+G(d) confirmed that **8n.4** is energetically higher than **8n.1** by 0.25 eV and 0.34eV, respectively. Interestingly, the far infrared measurements determined 8n.1 as the ground state structure of VSi<sub>8</sub><sup>+</sup> which is isoelectron of TiSi<sub>8</sub>.

All of cationic isomers of TiSi<sub>8</sub><sup>+</sup> keep the similar shape to the corresponding neutral. Upon removal of one electron from the lowest-lying isomers of the neutral **8n.1**, the ground-state of cationic cluster TiSi<sub>8</sub><sup>+</sup>, which is in a doublet state, is obtained. Another face-capped pentagonal bipyramid isomer (**8c.2**) is only 0.08eV less stable than **8c.1**. Several other isomers are unfavorable with at least 0.21 eV higher in energy than the ground state.

### *TiSi<sub>9</sub> and TiSi<sub>9</sub><sup>+</sup>*

The most stable **9n.1** isomer of the neutral is formed by capping TiSi<sub>8</sub> with one additional Si atom. The **9n.6** isomer, which is reported in previous studies by Guo et. al.[29] and Kumar [28] as ground state of TiSi<sub>9</sub>, is 0.48eV less stable than **9n.1**. The calculations using other functionals also confirmed that 9n.6 is much higher in energy than **9n.1**. It should be noted that 9n.1 is also assigned for the ground state of VSi<sub>9</sub><sup>+</sup> (isoelectronic with TiSi<sub>9</sub>) using infrared spectra. Other isomers are higher in energy than the most stable at least 0.35eV.

For TiSi<sub>9</sub><sup>+</sup>, tricapped the pentagonal bipyramid structure (**9c.7**) is the most stable isomer. **9c.1**, which has similar shape to neutral ground state TiSi<sub>9</sub>, is only 0.07eV less stable than cationic ground state. The Ti atom in all isomers of cation cluster TiSi<sub>9</sub><sup>+</sup> occupies in the interior site and is favorable high-coordinated position.

### *TiSi<sub>10</sub> and TiSi<sub>10</sub><sup>+</sup>*

The two lowest-lying isomer of the neutral TiSi<sub>10</sub> cluster is **10n.1** and **10n.2** with a marginal energy difference of 0.02 eV. They both are of C<sub>s</sub> symmetry. The **10n.2** isomer is built up basing on the trigonal prismatic motif with a Ti atom at a high-coordination position, while **10n.1** is a newly constructed structure basing on trigonal bipyramidal motif. Other higher-lying isomers (**10n.3**, **10n.4**, and **10n.5**) are based on the pentagonal bipyramidal building block.

Different from the neutral, the cation adopts the pentagonal bipyramidal shape to be the lowest-lying isomer (**10c.5**). The trigonal-prism-based structure (**10c.2**) lies only 0.08 eV higher in energy than the cationic ground state. The isomer having similar shape to the lowest-lying isomer of neutral (**10c.1**) is 0.2 eV less stable than the **10c.5** isomer.

## **3.2. Growth Mechanisms**

We now summarize the lowest-lying isomers of all the neutral and cationic TiSi<sub>n</sub><sup>0/+</sup> (n = 2-10) clusters in Figure 3 to investigate growth behavior of the cluster structures.

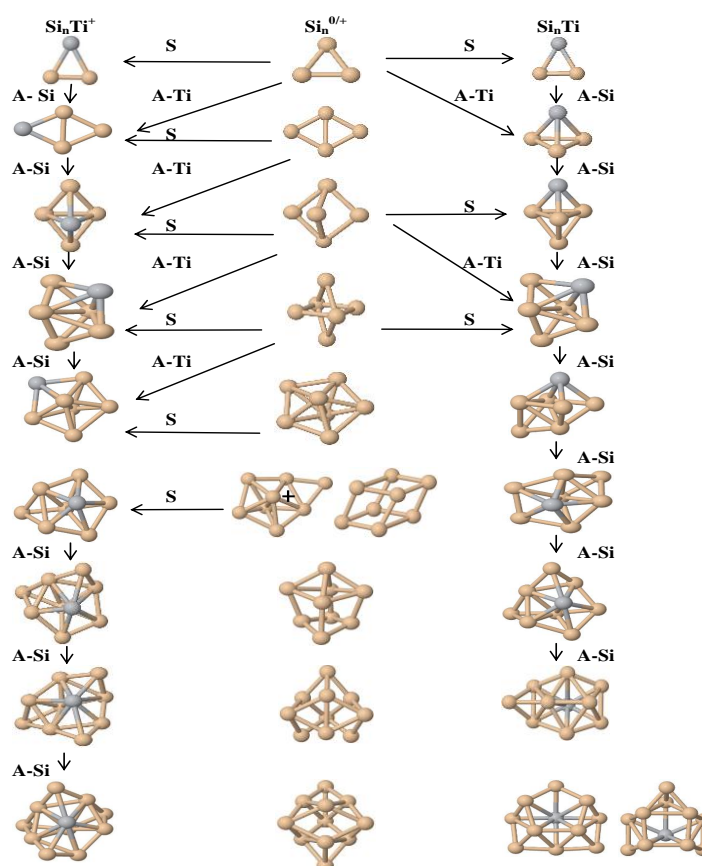


Figure 3. Growth mechanisms of the neutral  $\text{TiSi}_n$  (right column) and cationic  $\text{TiSi}_n$  (left column) with bare  $\text{Si}_n$  cluster (middle column). **S** stands for a substitution, **A-Ti** stands for an adsorption of a Ti atom and **A-Si** stands for the adsorption of a Si atom.

In general, structures of the neutral and cationic cluster are different. Thus they follow different growth mechanisms. In few cases, the structures of  $\text{TiSi}_n$  ( $n = 2, 4, 5$ ) clusters can be described either as a substitution of Ti atom on  $\text{Si}_{n+1}$  cluster or as an addition of Si atom on the smaller  $\text{TiSi}_{n-1}$  cluster. Totally, the  $\text{TiSi}_n$  clusters follow a consistent rule of addition, meaning that the larger  $\text{TiSi}_n$  cluster is built up by adding a Si atom on the smaller  $\text{TiSi}_{n-1}$  cluster. The growth patterns of the neutral  $\text{TiSi}_n$  clusters are similar to that of the isoelectronic  $\text{VSi}_n^+$  clusters [21].

In small cationic  $\text{TiSi}_n^+$  clusters ( $n = 2-7$ ), the ground state structures are formed by substituting a Si atom on  $\text{Si}_{n+1}$  clusters. For  $n = 8-10$ , the Si atom prefers to cap on a face of  $\text{TiSi}_{n-1}^+$  leading the  $\text{TiSi}_n$  cluster and Ti occupies a top of one pyramidal side. The growth behaviors of this cationic series are similar to that of the isoelectronic neutral  $\text{ScSi}_n$  clusters.

### 3.3. Energetic Parameters

In order to understand the variation of stabilities of the neutral and cationic Ti-doped silicon cluster, average binding energy ( $E_b$ ) and fragmentation energy. The average binding energy is calculated according to the following formulae:

$$E_b(n) = [E(\text{Ti}) + nE(\text{Si}) - E(\text{TiSi}_n)]/(n+1)$$



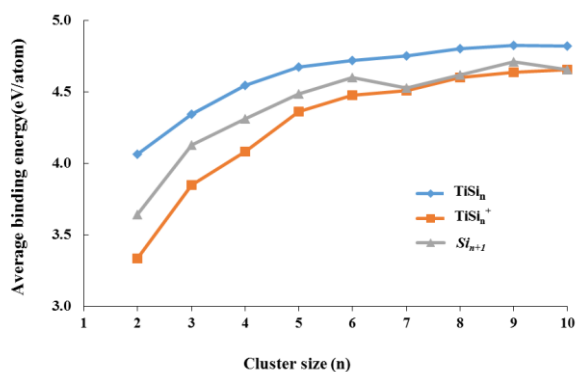


Figure 4. Size dependence of the binding energies of  $TiSi_n$  and  $TiSi_n^+$ , compared with the bare  $Si_{n+1}$  clusters.

The size dependence of average binding energy ( $E_b$ ) for the lowest-energy isomers of the neutral and cationic  $TiSi_n^{0/+}$  ( $n = 2-10$ ) clusters is plotted in Figure 4. The plots show that the average binding energy gradually increases with cluster size  $n$ , meaning that the stability of  $TiSi_n$  ( $n = 2-10$ ) clusters is enhanced as the size of clusters increases. In comparison with pure silicon clusters, the binding energies of neutral  $TiSi_n$  clusters are larger than those of the pure  $Si_{n+1}$ , whereas the cationic  $TiSi_n^+$  clusters generally less stable than the pure ones. That means the Ti-doping enhanced stability of the silicon clusters but the removal of electron from the neutral  $TiSi_n$  clusters significantly decreases the stability of the clusters.

Fragmentation energy of a cluster is another energetic parameter to investigate stability of the cluster. We calculate two dissociation paths for the neutral clusters and three dissociation paths for the cationic clusters as follows:

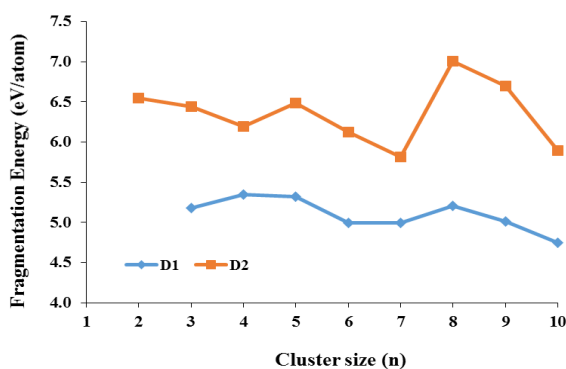
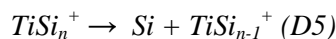
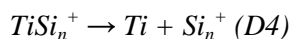
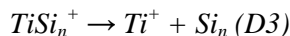
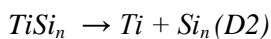


Figure 5. Size dependence of fragmentation energies in the processes of losing a Ti atom or a Si atom from the  $TiSi_n$  clusters.

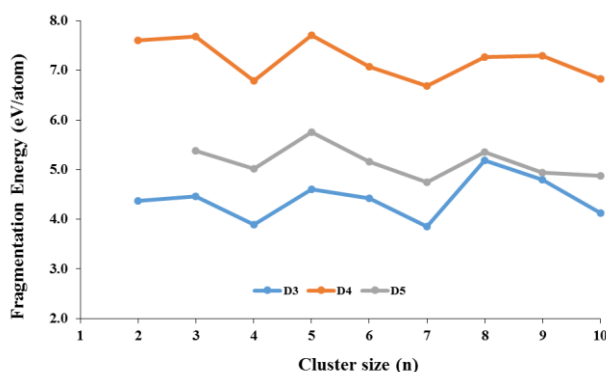


Figure 6. Size dependence of fragmentation energies in the processes of losing a  $\text{Ti}^+$  cation or a Ti atom or a Si atom from the  $\text{TiSi}_n^+$  clusters.

The dependence of the fragmentation energies on cluster size are plotted in Figures 5 and 6 for the neutral and cationic clusters, respectively. Figure 5 shows that the dissociation energies D1 are consistently lower than D2. That means that it is easier to lose a Si atom than a Ti atom from the  $\text{TiSi}_n$  clusters. This can be understood from the growth patterns of the neutral clusters. Indeed, the large  $\text{TiSi}_n$  clusters are built up by adding an extra Si atom on the smaller  $\text{TiSi}_{n-1}$  as discussed above. Thus removing the extra Si atom on surface of the smaller cluster should be easier than removing Ti atom which is always situated at a high-coordination position.

We investigate three dissociation paths for the cationic clusters as plotted in Figure 6. The figure clearly shows that the energy required for the process  $\text{TiSi}_n^+ \rightarrow \text{Ti}^+ + \text{Si}_n$  (D3) is lower than the dissociation energy D5 for the process  $\text{TiSi}_n^+ \rightarrow \text{Si}_{n-1}\text{Ti} + \text{Si}$  which in turn is lower than the energy D4 for  $\text{TiSi}_n^+ \rightarrow \text{Ti} + \text{Si}_n^+$ . This mean  $\text{TiSi}_n^+$  clusters prefer to loss of the  $\text{Ti}^+$  cation, referring that the positive charge is localized on the Ti center. Moreover, the removing Si atom from the cationic cluster is also easier than removing Ti atom. This is also because there is always Si atoms on surface of the doped clusters while the Ti atom is located at the high-coordination positions.

#### 4. CONCLUSION REMARKS

We have performed *ab-initio* calculations of titanium-doped silicon clusters at the neutral and positively charged states and resulted in some concluding remarks as follows:

- The pseudo-potential LANL2DZ basis set (used in ref.21) is not suitable to predict relative energies of various isomers of the neutral and cationic  $\text{TiSi}_n$  clusters. The large all-electron basis set, such as 6-311+G(d), should be used to obtain reasonable results.

- A clear picture of the growth patterns for both neutral and charged clusters is presented. The neutral  $\text{TiSi}_n$  clusters follow a consistent rule of addition, meaning that the larger  $\text{TiSi}_n$  cluster is built up by adding a Si atom on the smaller  $\text{TiSi}_{n-1}$  cluster. In the cationic clusters, Ti prefers to substitute at a high-coordination position.

- The neutral  $\text{TiSi}_n$  clusters is more stable than the pure  $\text{Si}_{n+1}$  clusters while the cationic  $\text{TiSi}_n^+$  is less stable than the pure ones.

- Both neutral and cationic clusters tend to lose Si atom rather than Ti atoms. Losing  $\text{Ti}^+$  cation from the cationic  $\text{TiSi}_n^+$  clusters is easier than losing Ti or Si atom.

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