Electronic and geometric stability of double titanium-doped silicon clusters

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Abstract

We performed the genetic algorithm (GA) incorporated with density functional theory (DFT) calculations to investigate the atomic and electronic properties of a series of Ti2Si
n (n = 3 = –24) clusters. Comprehensive consideration on the formation energy, the second difference in cluster energy and the addition energy of Si to a Ti2Si
n-1 cluster as well as the HOMO-LUMO gap, our results show that Ti2Si
4 cluster is the most stable one in the series of clusters, followed by the Ti2Si
1-, Ti2Si
21, Ti2Si
15 and Ti2Si
7 clusters, which can be understood by the combination of symmetry and electron shell filling rule. The silicon cage could be obviously enhanced by doping double Ti atoms making them promising nanoscale materials.

1. Introduction

Recently, Si clusters have drawn great investigation both experimentally [1] and theoretically [2–5] because silicon is a semiconducting element of great importance in microelectronics industry. Many investigations attempt to obtain a stable Si cluster building-block like Si cage with self-complete bonding, which is still a challenge because sp2 hybridization is highly unfavorable in silicon [6]. A most studied approach is to locate a guest atom, especially a single transition metal (TM) atom, in the Si cage and some size-selective TMSi
n clusters are stable to be capable of building blocks of self-assembly semiconductor nanomaterials [7–13]. Furthermore, first-principles calculations show that the TMSi
n clusters have enhanced stabilities and strong size selectivity in comparison with pure Si cage.

To understand the stability of TMSi
n clusters, Hiura et al [14] found that WSi
12 cluster could be explained by 18-electron counting rule, in which each Si atom contributes one electron to the central W atom and W atom possesses 6 valence electrons to totally form a closure electron shell. Khanna et al [15] concluded that 12 is the magical number of CrSi
n cluster for creating a closed 18-electron shell as well as FeSi
16 [16] and CoSi
17. While Guo et al [18] argued that the electron shell filling rule is just one of the factors to the stabilize the TMSi
n clusters, and the atomic size of TM, pd hybridization and symmetry are also very important to understand their stabilities. Abreu [19] critically examined the bonding and nature of stability of CrSi
12, and showed that its electronic structure does not conform to the 18-electron rule while CrSi
14 is shown to follow the 18-electron rule and exhibits all conventional markers characteristic of a magic cluster. Besides one guest atom case, more and more groups extend to locate two TM atoms inside the Si cage and very stable TM2Si
n clusters can also be realized. For instance, Wang [20] investigated Zr2Si
n (n = 16–24) using UB3LYP/LanL2DZ approach and concluded that the magic number of n in Zr2Si
n clusters are 18, 20 and 22 and the HOMO-LUMO gaps of the Zr2Si
n (n = 16–24) are larger than 1 eV, which suggests that Zr2 is favorable to increase the stability of large sized silicon cage. Ji et al [21] investigated a series of TM2Si
18 (TM = Ti–Zn) clusters, and they concluded that Co2Si
18 is the most stable clusters among all 3d doped TM2Si
18 clusters which correspond to the formation of double shell closure. Zhao et al [22] investigated Pd2Si
n (n = 10–20), which indicated that Pd2Si
16 is the most stable clusters and Pd2Si
17 has the largest HOMO-LUMO gap, while this could not be explained by the 18 or 20 electrons counting rule.

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To our best knowledge, the physical mechanism for the stability of TM$_2$Si$_n$ clusters has not been well revealed yet. Here we systematically investigated the structural and electronic properties of Ti$_2$Si$_n$ ($n = 3$–24) clusters using the genetic algorithm (GA) incorporated with density functional theory (DFT) calculations. Our results show that Ti$_2$Si$_4$ cluster is the most stable one in the series of clusters, followed by the Ti$_2$Si$_{13}$, Ti$_2$Si$_{12}$, Ti$_2$Si$_{15}$ and Ti$_2$Si$_7$ clusters.

2. Computational details

In order to determine the minimum energy structure of Ti$_2$Si$_n$ clusters, we performed the genetic algorithm (GA) [23, 24] incorporated with density functional theory (DFT) calculations, which is quite different with most of the former artificial speculation studies to investigate the structure in certain symmetries. In the GA unbiased global search, a number of initial configurations (12 isomers in this work) were generated from scratch with 3000 GA iterations to ensure the global minimum. As to the detail of DFT, we performed our calculations by the Vienna Ab-initio Simulation Package (VASP) code [25–28]. The Kohn–Sham equations have been solved variationally in a plane wave basis set using the projector-augmented-wave (PAW) method. The exchange-correlation energy was described by the functional of Perdew, Burke, and Ernzerhof (PBE) [29] based on the generalized gradient approximation (GGA). To determine the stability of Ti$_2$Si$_n$ Clusters, we have calculated the binding energy (BE) per atom of the ground state of the Ti$_2$Si$_n$ cluster,

$$\text{BE} = \frac{[nE(\text{Si}) + 2E(\text{Ti}) - E(\text{Ti}_2\text{Si}_n)]}{(n + 2)}$$

(1)

the addition energy of a Si atom to a Ti$_2$Si$_{n-1}$ cluster,

$$E_\text{add}(\text{Ti}_2\text{Si}_n) = E(\text{Ti}_2\text{Si}_{n-1}) + E(\text{Si}) - E(\text{Ti}_2\text{Si}_n)$$

(2)

and the second difference of the cluster energy,

$$E_\text{2nd}(\text{Ti}_2\text{Si}_n) = E(\text{Ti}_2\text{Si}_{n+1}) + E(\text{Ti}_2\text{Si}_{n-1}) - 2E(\text{Ti}_2\text{Si}_n)$$

(3)

Here $E(\text{Si})$, $E(\text{Ti})$ and $E(\text{Ti}_2\text{Si}_n)$ are the atom energy of Si, Ti and Ti$_2$Si$_n$ clusters, respectively.

3. Results and discussion

3.1. Geometries and stabilities

The genetic algorithm (GA) incorporated with density functional theory (DFT) calculations are used to investigate the atomic and electronic properties of a series of Ti$_2$Si$_n$ ($n = 3$–24) clusters. The two ($n = 3$–5) or three ($n = 6$–24) lowest-energy isomer structures and symmetries of Ti$_2$Si$_n$ clusters are shown in figure 1, and the ground states (GS), the first metastable states which are nearest to the ground states (NGS) and the second metastable states which are next nearest to the ground states (NNGS) are displayed in order of energy.

We find that some of the GS clusters possess high symmetry, such as Ti$_2$Si$_4$ (D$_{4h}$), Ti$_2$Si$_6$ (C$_{2v}$), Ti$_2$Si$_7$ (C$_{2v}$), Ti$_2$Si$_{14}$ (C$_v$) and Ti$_2$Si$_{15}$ (C$_v$), while the other GS structures prefer the low symmetry as $C_i$ or $C_1$. As to the NGS clusters, Ti$_2$Si$_{12}$ (C$_{4h}$) is a capped hexagonal prism wheel-like structure as Huang et al [30] referred. And for the NNGS cluster, Ti$_2$Si$_{19}$ is $D_{2h}$ symmetry and Ti$_2$Si$_{15}$ is $C_{3v}$ symmetry. It’s very interesting to observe the position modification of Ti atoms as the growth of Si clusters. When the number of Si atom ($n$) is smaller than 16, one Ti atom stays in the open Si cage while the other is out. The Ti atom which is out of the Si cage is then surrounded by the silicon atoms step by step with the increase of Si atoms and the cluster finally forms a closed cage until the number of Si atoms reaches to 23. As to Ti$_2$Si$_{22}$, with different exchange-correlation Sheng-Jie Lu et al found that the structures could form double cage configuration with each Ti atoms encapsulated in a buckled 12 Si atoms composed cage [31].

We also calculated the magnetic behavior of the Ti$_2$Si$_n$ clusters. As to the GS clusters, there is only one structure (Ti$_2$Si$_3$) possesses the magnetic moment of 2 $\mu_B$ while the other GS structures are singlet spin states. As to the NGS and NNGS, some clusters possess magnetic moment of 2 $\mu_B$ such as the NNGS of Ti$_2$Si$_{18}$ and Ti$_2$Si$_7$. In the NNGS of Ti$_2$Si$_{11}$, the cluster, the Ti atoms form a distorted and broken hexagonal prism, and the magnetic moment of the Ti in(outside) the prism is 0.310 $\mu_B$ (1.118 $\mu_B$). As to Ti$_2$Si$_{12}$, the GS is in $C_i$ symmetry, the NGS is in $C_{4v}$ symmetry and the NNGS is in $C_1$ symmetry. The NGS and NNGS are 0.046 eV and 0.177 eV higher than the GS in energy. The GS and NNGS are singlet spin states while the NGS has magnetic moment of 2 $\mu_B$. The Si atoms in the NGS form a hexagonal prism, the magnetic moment of the Ti in the prism is 0.366 $\mu_B$ and the magnetic moment of the outside Ti atom is 1.289 $\mu_B$. As to Ti$_2$Si$_{15}$, the GS is in $C_{3v}$ symmetry, the NGS is in $C_1$ symmetry and the NNGS is in $C_{3v}$ symmetry. The NGS and NNGS are 0.126 eV and 0.317 eV higher than the GS in energy. The GS and NNGS are singlet spin states while the NNGS has magnetic moment of 2 $\mu_B$. The magnetic moment of the Ti in the cage is 0.020 $\mu_B$ and the magnetic moment of the outside Ti atom is 1.194 $\mu_B$. We could
find that the magnetic moment of the Ti atom in the cage basically disappeared. The magnetic properties of Ti$_2$Si$_n$ disappear as the clusters form a closed cage structure.

As to the ground states of the Ti$_2$Si$_n$ clusters, the bond length between two Ti atoms (Ti–Ti) and the average bond length between Si and Si atoms (Si–Si) are shown in figure 2. We could find that the bond lengths of Ti–Ti are from 2.50 Å ($n = 14$) to 3.17 Å ($n = 24$), which are near the bulk bond length (2.997 Å) of Ti metal. The bond lengths of Si–Si are from 2.38 Å ($n = 7$) to 2.51 Å ($n = 18$), which are larger than the bulk bond length (2.36 Å) of Si semiconductor. The oscillation of bond length of Ti–Ti is much stronger than that of Si–Si as the growth of Ti$_2$Si$_n$ clusters. It’s quite different from the bulk Ti metal that the magnetism of Ti$_2$Si$_n$ clusters do not vary too much along with the big changes of the bond length of Ti–Ti. We may understand this from the form of cage of clusters as the number of Si atom increases. The bond length of Ti–Ti is adjusted by the competition of Si-Ti and Ti–Ti interaction.

As is shown in figure 3, we calculated the binding energy ($BE$) per atom for the GS of Ti$_2$Si$_n$ clusters and the addition energy of a Si atom to a Ti$_2$Si$_{n-1}$ cluster. The positive value of $BE$ means the cluster structure is stable and the larger the value is the more stable the structure is. From the density functional theory calculations, we conclude that all the values of $BE$ for the Ti$_2$Si$_n$ clusters are positive and when $n$ is 15 and 23, the $BE$ values correspond to the local maxima. When $n$ is larger than 12, the $BE$ is relative large comparing to the small clusters. In addition, the stability of the clusters about Si could be revealed by the data of $E_{ad}$ shown in figure 3, from which we could find that there are five local maxima when the number of Si atoms equal to 4 ($E_{ad} = 5.822$ eV), 7 ($E_{ad} = 5.426$ eV), 13 ($E_{ad} = 5.722$ eV), 15 ($E_{ad} = 5.508$ eV) and 21 ($E_{ad} = 5.439$ eV). The addition energy of the GS clusters show that Ti$_2$Si$_4$ is the most stable structure followed by Ti$_2$Si$_{13}$, Ti$_2$Si$_{15}$, Ti$_2$Si$_{21}$ and Ti$_2$Si$_7$. The dominant factor of the stability of the clusters is the second difference of the cluster energy $E_{2ad}$, which is
We could find that there are several large local maxima when the number of Si atoms equal to 4, 7, 10, 13, 15, 18 and 21. The result indicated that the clusters of Ti$_2$Si$_4$ is the most stable structure followed by Ti$_2$Si$_{13}$, Ti$_2$Si$_{15}$ and Ti$_2$Si$_{21}$, which is consistent with the conclusion from the value of $E_{ad}$. In order to get extended information of chemical stability, we calculated the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) which we defined as HOMO-
LUMO gap showing in figure 4. We could find that the HOMO-LUMO gap is largest when the number of Si atoms \( n \) is 4 followed by 7, 21, 10, 15. As is mentioned in figures 3 and 4, the Ti\(_2\)Si\(_n\) possesses the most favorable HOMO-LUMO gap and large \( E_{2nd} \) and \( E_{abd} \), it is an octahedron structure in \( D_{4h} \) symmetry. The Ti\(_2\)Si\(_7\) possesses the second most favorable HOMO-LUMO gap, and it is in \( C_2v \) symmetry.

As to the geometric stability of the Ti\(_2\)Si\(_n\) clusters, Ti\(_2\)Si\(_4\) with a high symmetry of \( D_{4h} \) is the most stable structure followed by Ti\(_2\)Si\(_{13}\), Ti\(_2\)Si\(_{15}\) and Ti\(_2\)Si\(_7\). As to the stability of the electronic structure, Ti\(_2\)Si\(_4\) is still the most stable, followed by Ti\(_2\)Si\(_7\), Ti\(_2\)Si\(_{13}\), Ti\(_2\)Si\(_{10}\) and Ti\(_2\)Si\(_{15}\). We could find that the silicon cage could be obviously enhanced by doping double Ti atoms. When \( n > 21 \), it could form closed cages, while they are weaker in stability from the result of \( E_{abd} \) in figure 3, it suggests that double Ti encapsulated in Si cages get saturated when \( n = 21 \) for Ti\(_2\)Si\(_n\) clusters.

As to single Ti encapsulated TiSi\(_n\) clusters, Guo et al [32] found that TiSi\(_6\) is the most stable size in range of \( n = 2 \sim 15 \) suggested from their second-order differences and HOMO-LUMO gap. The Si cage emerges from size of \( n = 9 \), and the cage is close to our result of Ti\(_2\)Si\(_n\). As to Pd\(_2\)Si\(_n\) [22] the most stable size is Pd\(_2\)Si\(_{16}\) from the energy of fragmentation energy, and it forms a closed cage with double buckled pentagonal prism. As to Zr\(_2\)Si\(_n\), [20] the most stable size is Zr\(_2\)Si\(_{22}\), and the Zr atoms are also encapsulated in Si cage, whose structure is similar with our result. While both Pd\(_2\)Si\(_{16}\) and Zr\(_2\)Si\(_{12}\) are not subject to Jellium model, which we will discuss below. In addition, our results of formation energy, the second difference and HOMO-LUMO gap are consistent, while Pd\(_2\)Si\(_{16}\) and Zr\(_2\)Si\(_{22}\) are not consistent. It suggests that our results are more stable.

According to the theory of Jellium model [33, 34], the infinitely deep spherical well and the harmonic well are the simplest forms of the potential, in which the former possesses magic numbers of 2, 8, 18, 20, 34, 40, 58, ..., and 2, 8, 20, 40, 70, ... for the later. Such as TiSi\(_{16}\), Sc\(^+\)Si\(_{16}\) and V\(^+\)Si\(_{16}\) [35, 36] all of which are subject to the 68 electrons counting rule. If we adopt this model in the Ti\(_2\)Si\(_n\) clusters, we would expect that the number of Si in the relative stable clusters should be 3, 8, 15 and 21, in which the total valence electrons are 20, 34 and 92 respectively. While the result show that in the small size, the most stable clusters are Ti\(_2\)Si\(_4\) and Ti\(_2\)Si\(_7\), the stabilities of Ti\(_2\)Si\(_n\) clusters are mainly dominated by the symmetry. However, accompanied by the growth of clusters, the electron shell filling factor gradually dominates the stability of Ti\(_2\)Si\(_{13}\) and Ti\(_2\)Si\(_{21}\) clusters as a closure electron shell. In addition, we could also find that the Ti\(_2\)Si\(_{13}\) is quite stable, which has 60 valence electrons, we suppose that it is the result of the combination of geometry and electrons, which is interesting and also revealed by Pham et al [37].

3.2. Photoelectron spectroscopy and electronic properties
The usually experiment method of exploring the electronic properties is the photoelectron spectroscopy, which is a useful technique to ensure the cluster structure by comparing with the simulation of DFT method. In order to calculate the photoelectron spectra of Ti\(_2\)Si\(_n^−\) clusters, we studied the geometric structure of the Ti\(_2\)Si\(_n^−\) anion clusters based on the genetic algorithm (GA) incorporated with density functional theory (DFT) calculations.

![Figure 4](image.png)

Figure 4. The second difference of the cluster energy \( E_{2nd} \) and the HOMO-LUMO gap of the GS clusters.
Our results show that all of the anion structure of Ti$_2$Si$_n$ clusters are almost the same as the neutral ones. As mentioned above, the Ti$_2$Si$_{4}$, Ti$_2$Si$_{7}$, Ti$_2$Si$_{13}$ and Ti$_2$Si$_{21}$ are relative stable, for which the photoelectron spectra of Ti$_2$Si$_n$ (n = 4, 7, 13, 21) anion clusters are simulated using the PBE, B3LYP and BPW91 calculation schemes showing in figure 5. The result showed that the spectra differences of different method in Ti$_2$Si$_4$ are much larger than the other three structures. And the spectra of B3LYP and BPW91 are similar for Ti$_2$Si$_{7}$, Ti$_2$Si$_{13}$, Ti$_2$Si$_{21}$ anion clusters. The density of states (DOS) of Ti$_2$Si$_{13}$ and Ti$_2$Si$_{21}$ clusters are shown in figures 6(a) and 6(b). It suggests that the HOMO is mainly from the hybridization of Si $p$ orbital and Ti $d$ orbital. The deeper energy states are mainly from the hybridization of Si $s$ orbital and Si $p$ orbital. It can also be observed that in figure 6(a) the interior Ti atom has stronger $p$−$d$ hybridization with the surrounding Si atoms than with the surface Ti atom, and we could find that in figure 6(b) the nearest energy level to Fermi level is mainly from the $p$−$d$ hybridization of the Ti atom, which locates in the open cage rather than the one in the closed cage. It indicates that the stronger hopping decreases the electron energy level.

We further plotted the DOS of the GS and NGS isomers of Ti$_2$Si$_{12}$ in figures 7(a) and (b) to discuss why the GS is no magnetic while the NGS shows ferromagnetic properties. We could find that there is no spin split for the GS isomer which is shown in figure 7(a), and the $d$ electrons of both of the Ti atoms hybridize with $s$ and $p$ electrons of Si atoms strongly. While for the NGS which is shown in figure 7(b), the spin splitting is mainly from the HOMO and LUMO orbital of the outer Ti $3d$ electrons, the hybridization between Si and the inner Ti (denoted as Ti-in) is obviously stronger than that of the outer Ti atom (denoted as Ti-out). It means that for the outer Ti atom, the two $d$ electrons are less hybridized and showing more localizing property. The magnetism is mainly from the outer Ti atom. We could find that most isomers are not magnetic, Ti atoms are surrounded by Si atoms and the magnetic of Ti atoms disappeared because of the hybridization of electrons between Si and Ti.

Figure 5. Photoelectron spectra of Ti$_2$Si$_n$ (n = 4, 7, 13, 21) clusters simulated using the PBE, B3LYP and BPW91 calculation schemes.
Figure 6. (a) Density of states of the Ti$_2$Si$_{13}$ cluster; (b) Density of states of the Ti$_2$Si$_{21}$ clusters. Ti-out shows the $d$ orbital of the surface Ti atom and Ti-in displays the $d$ orbital of the inner Ti atom.

Figure 7. (a) Density of states of the GS in the Ti$_2$Si$_{12}$ clusters; (b) Density of states of the NGS in the Ti$_2$Si$_{12}$ clusters. Ti-out shows the $d$ orbital of the surface Ti atom and Ti-in displays the $d$ orbital of the inner Ti atom.
4. Conclusions

In summary, we investigated a series of Ti$_2$Si$_n$ ($n = 3$–24) clusters performed with GA-DFT method of the structures, stabilizes, and electronic properties. The most stable cluster is Ti$_2$Si$_{13}$ followed by Ti$_2$Si$_{13}$, Ti$_2$Si$_{21}$, Ti$_2$Si$_{13}$ and Ti$_2$Si$_7$ which can be understood by the combination of symmetry and electron shell filling rule. The calculations show that the stability becomes weaker and weaker when the number of Si is larger than 21 in the cage suggesting that the double Ti encapsulated Si cage is saturated when the number reaches 21. The magnetization of Ti atoms in the clusters are basically quenched by surrounding Si atoms because of the hybridization. The silicon cage could be obviously enhanced by doping double Ti atoms and it is very promising for nanoscale materials.

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