# CALCULATIONS ON THE STRUCTURES OF $SiGe_nSc^{0/-}$ ($n = 3, 4$) CLUSTERS

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## Abstract

*The structures of* $SiGe_nSc^{0/-}$ ($n = 3, 4$) *clusters were investigated by a combination of quantum chemical calculations, including the genetic algorithm (GA), the Perdew-Burke-Ernzerhof PBE functional, and coupled-cluster calculations (CCSD(T)). The geometrical structure, relative energy, harmonic vibrational frequency, adiabatic detachment energies were reported. The PBE functional is in good agreement with the CCSD(T) method. The stable structure of the* $SiGe_nSc^{0/-}$ ($n = 3, 4$) *clusters have a low spin multiplicity. The larger cluster can be formed by adsorbing the atom into the smaller cluster. The obtained results can contribute to the orientation of the nanomaterial formation for gas adsorption.*

**Keywords:** *GA-DFT, optimization, PBE functional,* $SiGe_3Sc^{0/-}$, $SiGe_4Sc^{0/-}$.

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# TÍNH TOÁN CẤU TRÚC CỦA CÁC CLUSTER $SiGe_nSc^{0/-}$ (*n* = 3, 4)

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## Tóm tắt

*Cấu trúc của các cluster $SiGe_nSc^{0/-}$ (n = 3, 4) được nghiên cứu bằng sự kết hợp của giải thuật di truyền, phiếm hàm PBE, lý thuyết chùm tương tác CCSD(T). Cấu trúc hình học, năng lượng tương đối, tần số dao động điều hòa, năng lượng tách electron của các đồng phân được báo cáo. Phiếm hàm PBE cho kết quả tính phù hợp tốt với các tính toán theo phương pháp CCSD(T). Các cấu trúc ổn định của các cluster $SiGe_nSc^{0/-}$ (n = 3, 4) có độ bôi spin thấp. Các cluster kích thước lớn có thể hình thành từ các cluster kích thước bé bằng cách nhận thêm nguyên tử vào. Kết quả nghiên cứu thu được góp phần định hướng cho việc tạo vật liệu hấp phụ khí.*

**Từ khóa:** *GA-DFT, sự tối ưu hóa, phiếm hàm PBE, $SiGe_3Sc^{0/-}$, $SiGe_4Sc^{0/-}$.*

## 1. Introduction

Germanium and silicon are semiconduction elements to design electronic device. These element can be used to synthesize the materials in pharmacy due to non-toxic and high bio-compatibility (McVey et al., 2017). The structures of germanium, scandium, silicon have been highly appreciated for their wide array of applications in electronic, adsorption, catalyst, pharmacy field and its depending on their size (Abel et al., 2013; Biswas et al., 2017; Carolan, 2017; McVey et al., 2017).

The structures of germanium, silicon, and scandium were studied by experimental methods and the theoretical methods. The nanowire heterostructures of germanium/silicon were synthesized with one-dimensional hole gas (Lu et al., 2005). The Ge/Si core/shell nanowire heterostructures are three to four times greater than state-of-the-art metal-oxide-semiconductor field-effect transistors and are the highest obtained on nanowire field-effect transistors. The performance of Ge/Si nanowire field-effect transistors is comparable to similar length carbon nanotube field-effect transistors and substantially exceeds the length-dependent scaling of planar silicon metal-oxide-semiconductor field-effect transistors (Xiang et al., 2006). The Ge nanowires are directly synthesized on glass via vapor-liquid-solid growth using chemical-vapor deposition (Nakata et al., 2015).

Combination of Si, Ge, Sc elements to form clusters were done by quantum chemical calculations as $ScGe_n^-$ ($n$ = 6 - 20) (Atobe et al., 2012, Borshch et al., 2015), $ScSi_n^{(0,-1)}$ ($n$ = 1 - 6) (Lu et al., 2014), $Si_xGe_{4-x}$ ($x$ = 0 - 4) (Nahali and Gobal, 2010), $Ge_nSi_m$ ($n + m \leq 5$) (Wielgus et al., 2008), $Si_{(1-x)}Ge_x$ (Abel et al., 2013). The stability and carbon monoxide adsorption of nanocluster $Si_xGe_{4-x}$ ($x$ = 0 - 4) was studied by the MPW1B95 functional (Nahali & Gobal, 2010). The results showed that there are two modes of adsorption including on-top and bridged; and the silicon atom generally makes a stronger bond with CO than germanium. The stable and properties of clusters can be increased by doping the transitional metal (Liu et al., 2018; Pham et al., 2019; Sajjad et al., 2019; Zhou et al., 2019).

The study on the structure of transitional metal doped-germanium silicon is still not performed. Since the 3d orbitals have near degeneration in energy, transition metal doped germanium silicon clusters can build many structures with equal stability. The quantity of isomers depends on the quantity of atom, elements in cluster. Therefore, the more atoms and elements there are, the more isomers the cluster has. In this study, we use the combinations of genetic algorithm and density functional theory (GA-DFT) to investigate the stable structures of $SiGe_nSc$ ($n$ = 3, 4) clusters. The GA-DFT method can find the global structure with high accuracy (Jennings & Johnston, 2013). The density functional theory can rapidly optimize the structure of cluster; a good reason in energy depends on the functional and basis set for specific system.

## 2. Methods

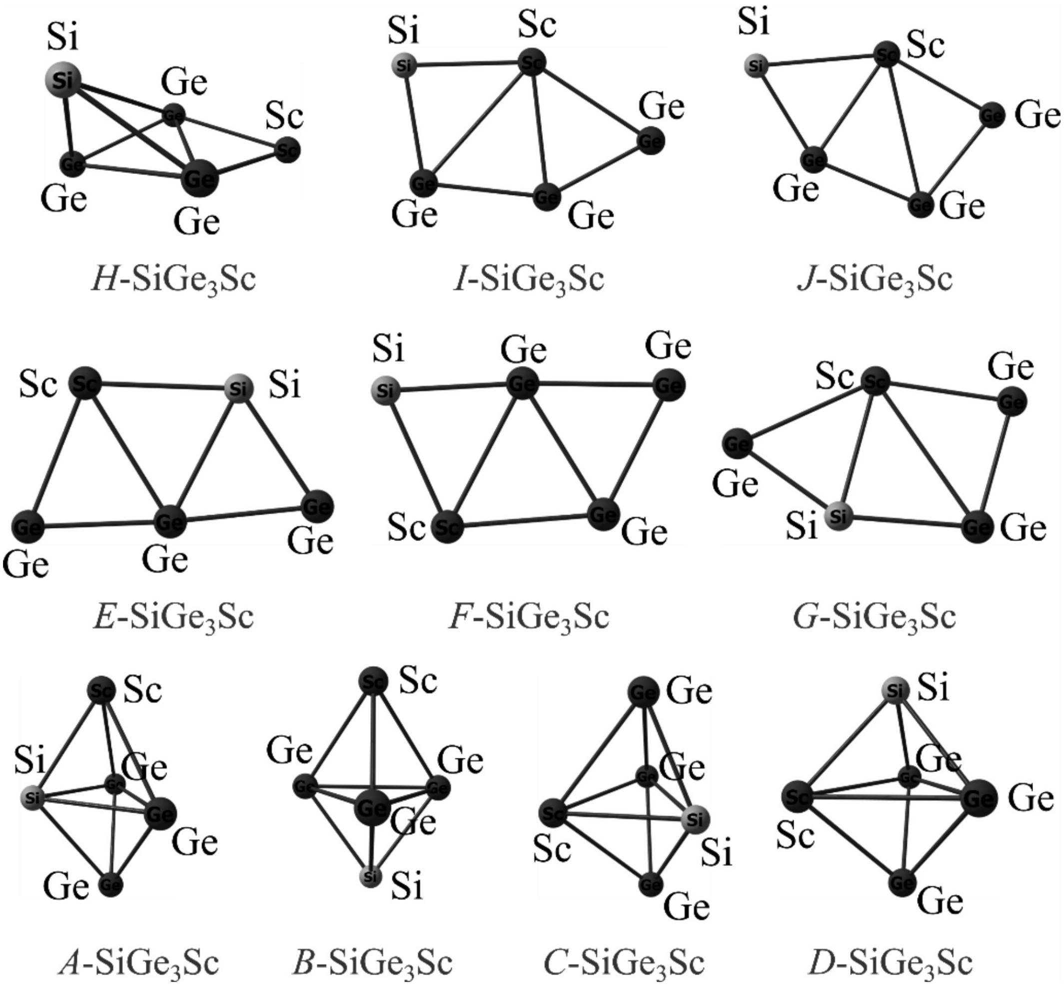
The structures of neutral cluster were investiagated by GA-DFT method (Hussein & Johnston, 2019; Jennings & Johnston, 2013). In this study, the initial generation of genetic algorithm include 20 randomly structures. In the next generations, 15 structures are calculated with 40% structures from previous generation, 20% mutation structures, 20% crossing structures, and 20% new random structures. The maximum generation of 10 are chosen. The stop condition of the process is 5 generations whose energy error does not surpass 0.01 eV or the maximum generation have been done. The GA process is performed by USPEX 10.3 code (AR et al., 2011; AR and CW, 2006; Lyakhov et al., 2013). The energies of these processes are calculated by pwSCF code of Quantum Espresso 6.0 package (Giannozzi et al., 2009). In addition, some local minimum structures are built from other references to reduce the loss of minimum structure.

All obtained structures are reoptimized by the PBE functional (Perdew et al., 1996). To save calculation time, the geometrical structures are optimized by small basis set def2-SVP. Then, re-optimization was done by larger basis set def2-TZVP. The anionic cluster were optimized from the neutral cluster at the same level. The relative energies are computed with the correctness of zero-point energy (ZPE) value. The relative energy and frequency values of optimized structures are obtained. The DFT calculations are performed by ORCA 4.2.1 code (Neese, 2012).

## 3. Results and discussion

### 3.1. The structure of $SiGe_3Sc$ cluster

The structure, geometrical symmetry, electronic state, relative energy, and harmonic vibrational frequencies of the isomers of $SiGe_3Sc$ cluster are presented in Figure 1 and Table 1. The harmonic vibrational frequency values of all of structures of $SiGe_3Sc$ isomers are from 31.97 cm$^{-1}$ to 463.28 cm$^{-1}$ that indicate these obtained structures is at the true minima on the potential energy surface.



*H*-$SiGe_3Sc$ *I*-$SiGe_3Sc$ *J*-$SiGe_3Sc$

*E*-$SiGe_3Sc$ *F*-$SiGe_3Sc$ *G*-$SiGe_3Sc$

*A*-$SiGe_3Sc$ *B*-$SiGe_3Sc$ *C*-$SiGe_3Sc$ *D*-$SiGe_3Sc$

**Figure 1. Ten isomers of the $SiGe_3Sc$ cluster**

To determine the reasonable values by the PBE functional, the single point calculations at the ROHF-CCSD(T) method with the def2-TZVP basis set are calculated with the optimized geometries at the PBE/def2-TZVP level. The CCSD(T) calculation is the gold standard of quantum chemical calculations (Varandas, 2021). The results indicated that the two methods have high fitness in relative energy. The relative energy values showed that the *A*-$SiGe_3Sc$ isomer is the global minimum structure. The *A*-$SiGe_3Sc$ isomer has a triangle bipyramid with one Sc atom at the top of the pyramid and one Si atom at the base. The *A*-$SiGe_3Sc$ isomer has the lowest energy at $^2A'$ state in the $C_s$ symmetry. The formation of the *A*-$SiGe_3Sc$ isomer can be performed by adsorbing a Sc atom and a Si atom on one side of the GeGeGe triangle.

If two atoms of Sc and Si add into two sides of GeGeGe triangle, the *B*-$SiGe_3Sc$ isomer is formed. The *B*-$SiGe_3Sc$ isomer has the relative energy value of 0.12 eV and 0.15 eV in the PBE functional and the CCSD(T) method, respectively. The geometrical structure of the *B*-$SiGe_3Sc$ isomer is a triangle bipyramid with a Sc atom and a Si atom at two tops of bipyramid. The point group symmetry of the

*B*-$SiGe_3Sc$ isomer is the $C_s$. The different energy of 0.04 eV showed that two bipyramid structures of the *B*-$SiGe_3Sc$ and the *C*-$SiGe_3Sc$ have the equivalent stability. The relative energy of the *D*-$SiGe_3Sc$ isomer is 0.31 eV than the global structure. This *D*-$SiGe_3Sc$ structure can be formed as the *A*-$SiGe_3Sc$ structure with the changing positions of Sc and Si atoms.

The *E*-*J* isomers of the $SiGe_3Sc$ cluster also have the $C_s$ symmetry with the structure of planar except *H*-$SiGe_3Sc$ isomer in $C_1$ point group symmetry. The relative energy values of these structures are respectively 0.65; 0.69; 0.87; 0.93; 1.07 and 1.09 eV as the calculated results by the PBE functional. At the CCSD(T) level, the relative energies of these isomers are 0.62; 0.61; 0.83; 0.94; 0.97; and 0.96 eV, respectively. These relative energies indicate that the same stability of *E* and *F* isomers with the small difference of 0.04 eV at the PBE functional and 0.01 eV at the CCSD(T) level.

**Table 1. The structure, symmetry, electronic state, relative energy, harmonic vibrational frequencies of the isomers of $SiGe_3Sc$ cluster**

| Structure | Sym. | State | RE (eV) | | Harmonic vibrational frequencies ($cm^{-1}$) |
|---|---|---|---|---|---|
| | | | PBE | CCSD(T) | |
| *A*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 0.00 | 0.00 | 87.41; 122.12; 140.45; 180.28; 217.94; 231.94; 239.23; 305.94; 371.12 |
| *B*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 0.12 | 0.15 | 100.87; 114.42; 141.37; 169.78; 183.65; 200.77; 248.94; 303.00; 360.55 |
| *C*-$SiGe_3Sc$ | $C_1$ | $^2A$ | 0.16 | 0.20 | 72.29; 103.84; 117.71; 136.32; 187.29; 209.52; 258.81; 324.19; 255.51 |
| *D*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 0.31 | 0.32 | 59.56; 127.23; 128.46; 177.99; 205.95; 240.47; 242.75; 300.09; 355.15 |
| *E*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 0.65 | 0.62 | 39.04; 92.30; 123.47; 168.01; 183.51; 228.76; 292.21; 327.44; 386.51 |
| *F*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 0.69 | 0.61 | 45.31; 104.16; 128.22; 158.06; 199.30; 245.17; 271.32; 300.26; 392.99 |
| *G*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 0.87 | 0.83 | 56.68; 82.30; 88.90; 132.59; 193.04; 238.18; 254.42; 337.10; 463.28 |
| *H*-$SiGe_3Sc$ | $C_1$ | $^2A$ | 0.93 | 0.94 | 31.97; 88.38; 121.12; 171.05; 187.43; 242.85; 280.37; 294.64; 368.01 |
| *I*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 1.07 | 0.97 | 51.11; 90.99; 98.94; 124.32; 182.88; 258.62; 303.94; 325.39; 357.87 |
| *J*-$SiGe_3Sc$ | $C_s$ | $^2A'$ | 1.09 | 0.96 | 48.34; 78.73; 87.45; 158.73; 202.39; 241.19; 257.82; 277.33; 418.12 |

All isomers of the $SiGe_3Sc$ cluster have a low spin multiplicity of 2. The irreducible presentation of electronic state in $C_s$ symmetry of isomers are also A′, except with *H*-$SiGe_3Sc$ in $C_1$ symmetry. The obtained relative energies from two calculation methods indicated that the PBE functional is suitable for studying the structure of clusters of Si, Ge, and Sc elements. So, this functional was used to study the structure of the $SiGe_4Sc$ cluster and their anion clusters.

### 3.2. The structure of $SiGe_4Sc$ cluster

By the GA-DFT calculations, the fifteen isomers of the $SiGe_4Sc$ cluster were found on the potential energy surface. The vibrational frequencies have values in the range of 23.75 $cm^{-1}$ to 450.19 $cm^{-1}$ which showed that these obtained structures are the minimum structures. The structure, symmetry, electronic state, relative energy, and vibrational frequency values at the PBE/def2-TZVP level were presented in Figure 2 and Table 2. The ten lowest stable isomers have also the bipyramid structure with or without the capping of one atom on the surface. These bipyramid structures can be formed from the smaller cluster as $SiGe_3Sc$ cluster or $Ge_4$ cluster. The *A*-$SiGe_4Sc$ isomer is the global minimum structure which has a triangle bipyramid with a Sc atom at the top of the pyramid and one Si atom covers at the ScSiGe surface. The geometrical structure of the *A*-SiGe$_4$Sc isomer has the symmetry of C$_1$ point group. The spin multiplicity of the *A*-SiGe$_4$Sc isomer is 2. This *A*-SiGe$_4$Sc isomer can be formed by adding a Ge atom to the side of the ScSiGe surface of the *A*-SiGe$_3$Sc isomer or SiGeGe surface of the *C*-SiGe$_3$Sc isomer.

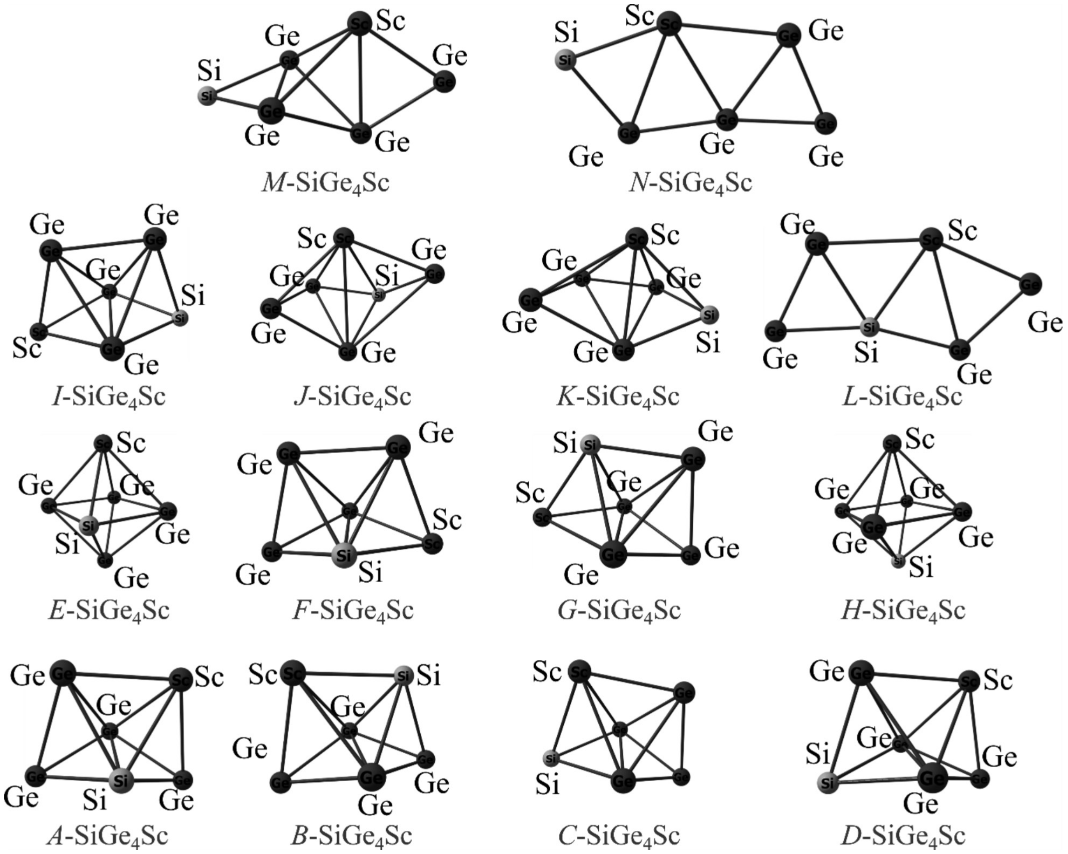


**Figure 2. Isomers of the SiGe$_4$Sc cluster**

In the same manner, adding one Ge atom in the different positions of the *A*-SiGe$_3$Sc isomer can produce the *B, F*-SiGe$_4$Sc isomers with the relative energy values of 0.17, 0.34 eV, respectively. The *B*-SiGe$_4$Sc isomer was formed by one Ge atom into the ScGeGe of *A*-SiGe$_3$Sc cluster or into the SiGeGe surface of *D*-SiGe$_3$Sc cluster. The capping a Ge atom at SiGeGe surface will produce the structure of the *F*-SiGe$_4$Sc isomer. The relative energies of the *C, G*, and *I*-SiGe$_4$Sc isomers are 0.24; 0.37; 0.51 eV than the global isomer, respectively. The *C*-SiGe$_4$Sc isomers can be produced by adding a Ge atom into the GeGeGe surface of the *D*-SiGe$_3$Sc isomer. The *A*-SiGe$_3$Sc structure was capped at the GeGeGe surface which create the *G*-SiGe$_4$Sc isomer. The *I*-SiGe$_4$Sc isomer can be formed from the bipyramid of ScGe$_4$ or SiGe$_4$ isomer by adsorbing one atom of Si or Sc element. On the other way, three structures of *C, G,* and *I*-SiGe$_4$Sc isomers can be created by adding one Sc atom and one Si atom on the surfaces of the tetrahedron Ge$_4$ cluster. By capping one Ge atom on the ScGeGe of the *B*-SiGe$_3$Sc isomer, the *D*-SiGe$_4$Sc isomer was created and its relative energy of 0.26 eV. Two isomers *E, H*-SiGe-$_4$Sc have the shape of a tetragonal bipyramid with a Sc atom at the top of the pyramid and they are higher at 0.28 and 0.43 eV than the A-SiGe$_4$Sc isomer.

The isomers *J, K, L, M*, and *N*-SiGe$_4$Sc have higher energy than the *A*-SiGe$_4$Sc isomer at least 0.94 eV. The *L*-SiGe$_4$Sc isomer and *N*-SiGe$_4$Sc isomer have the C$_s$ symmetry with the planar geometry structure and their relative energies are 1.46 and 1.76 eV, respectively. Except the *L* and *N*-SiGe$_4$Sc isomers, all isomers have the geometrical structures of 3D showed that the $sp^3$ hybrid is favour for Si and Ge elements. The energy of many isomers is equivalent and can be explained by the *d*-orbital of the Sc atom in structure.

**Table 2. The structure, symmetry, electronic state, relative energy (RE in eV), and harmonic vibrational frequencies of the isomers of $SiGe_4Sc$ cluster**

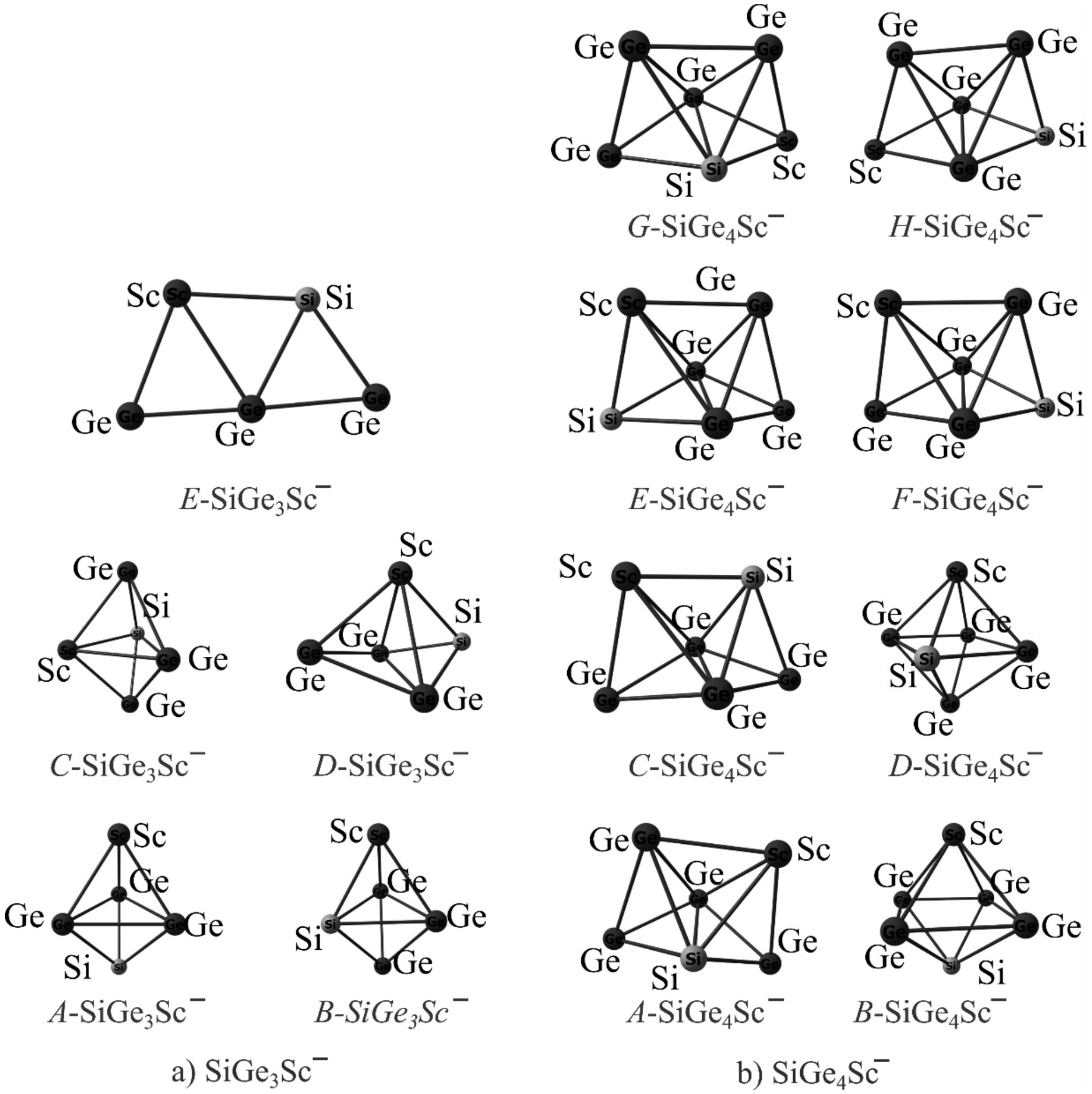
| Structure | Sym. | State | RE | Harmonic vibrational frequencies (cm-1) |
|---|---|---|---|---|
| *A*-$SiGe_4Sc$ | $C_1$ | $^2A$ | 0.00 | 70.27; 91.60; 138.60; 160.66; 178.34; 184.58; 209.82; 224.41; 255.27; 298.36; 329.20; 365.93 |
| *B*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 0.17 | 75.01; 95.29; 144.86; 159.33; 176.97; 206.38; 208.01; 217.96; 224.24; 263.58; 326.59; 352.02 |
| *C*-SiGe4Sc | $C_s$ | $^2A'$ | 0.24 | 79.72; 96.33; 151.65; 158.03; 174.86; 182.89; 190.63; 226.90; 244.97; 260.58; 283.32; 348.91 |
| *D*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 0.26 | 85.80; 86.26; 160.12; 168.93; 174.30; 181.68; 204.08; 218.32; 246.19; 249.33; 294.01; 357.13 |
| *E*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 0.28 | 86.25; 97.01; 105.20; 155.38; 168.14; 181.12; 186.36; 221.27; 241.39; 274.75; 320.22; 331.93 |
| *F*-$SiGe_4Sc$ | $C_1$ | $^2A$ | 0.34 | 58.78; 66.73; 123.09; 137.90; 164.81; 178.81; 208.01; 220.29; 245.55; 265.29; 307.66; 361.07 |
| *G*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 0.37 | 64.27; 74.23; 133.72; 147.10; 167.89; 181.41; 192.32; 214.30; 216.34; 253.43; 326.93; 361.54 |
| *H*-$SiGe_4Sc$ | $C_{2v}$ | $^2B_1$ | 0.43 | 77.87; 82.43; 108.13; 146.86; 181.17; 183.09; 186.60; 210.13; 239.54; 279.18; 280.58; 337.96 |
| *I*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 0.51 | 64.00; 79.85; 114.95; 137.05; 169.45; 172.94; 210.19; 212.03; 232.35; 235.59; 291.03; 352.42 |
| *J*-$SiGe_4Sc$ | $C_1$ | $^2A$ | 0.94 | 45.36; 67.02; 97.23; 122.07; 153.76; 174.73; 206.26; 219.09; 246.26; 275.19; 324.12; 417.11 |
| *K*-$SiGe_4Sc$ | $C_1$ | $^2A$ | 1.38 | 37.17; 69.28; 91.35; 127.06; 129.24; 164.71; 177.36; 208.43; 221.80; 230.47; 274.30; 333.86 |
| *L*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 1.46 | 23.75; 40.69; 84.71; 91.97; 106.08; 160.29; 212.79; 223.89; 256.70; 278.73; 337.45; 450.19 |
| *M*-$SiGe_4Sc$ | $C_1$ | $^2A$ | 1.71 | 26.29; 35.28; 80.59; 94.23; 127.01; 162.88; 185.99; 206.99; 242.08; 269.71; 279.34; 377.72 |
| *N*-$SiGe_4Sc$ | $C_s$ | $^2A'$ | 1.76 | 24.92; 38.33; 64.33; 85.39; 114.57; 154.49; 190.37; 226.47; 244.87; 295.73; 311.06; 360.20 |

### 3.3. The most stable structures of $SiGe_nSc^-$ ($n$ = 3, 4) clusters

The structure, symmetry, electronic state, relative energy, and the vibrational frequency of the most stable isomers of the $SiGe_nSc^-$ ($n = 3 - 4$) cluster are displayed in Figure 4 and Table 4. Because all vibrational frequencies of isomers of $SiGe_nSc^-$ ($n = 3 - 4$) clusters are not negative, so these structures are at the true minima on the potential energy surface.

The geometry of the isomers of *A, B, C, D*, and *E*-$SiGe_3Sc^-$ isomers are the triangle bipyramids. The *F*-$SiGe_3Sc^-$ has a planar geometry. Two isomers of *A* and *B*-$SiGe_3Sc^-$ are the most stable isomers with small energy difference is only 0.01 eV and 0.07 eV by the PBE and CCSD(T) calculations, respectively. The structure of the *A*-$SiGe_3Sc^-$ isomer has the triangle bipyramid with a Sc atom and a Si atom at two tops of pyramids. The geometrical structure of this isomer is the $C_{3v}$ symmetry, and the electronic state is the 1A' state in $C_s$ symmetry. The *B*-$SiGe_3Sc^-$ isomer has a triangle bipyramid with a Sc atom at the top and Si on the base of the pyramid. The one electron process from anion cluster is done. The adiabatic detachment energy (ADE) is difference in energy of the optimized geometrical structures of anion and neutral clusters. The ADE values of the *A*-$SiGe_3Sc^-$

and the *B*-$SiGe_3Sc^-$ clusters are 2.22 eV and 2.09 eV as the results of the computations by the PBE functional. These values at the CCSD(T) are obtained as 2.44 eV and 2.22 eV, respectively. The one electron detachment from the *A*-$SiGe_4Sc^-$ structure will form the *B*-$SiGe_3Sc$ structure. The *A*-$SiGe_3Sc$ can be created by one electron detachment from *B*-$SiGe_3Sc^-$ structure. Two isomers *C*-$SiGe_3Sc^-$ and the *D*-$SiGe_3Sc^-$ are also near degeneracy in energy with the difference of 0.03 eV base on the PBE calculations. The relative energies of the *C*-$SiGe_3Sc^-$, *D*-$SiGe_3Sc^-$, and *E*-$SiGe_3Sc^-$ isomers are 0.53, 0.56, and 0.93 eV, respectively. The structures of the *C*-$SiGe_3Sc^-$, *D*-$SiGe_3Sc^-$, and *E*-$SiGe_3Sc^-$ isomers are same with the neutral isomer of *C*-$SiGe_3Sc$, *D*-$SiGe_3Sc$, and *E*-$SiGe_3Sc$, respectively.



a) $SiGe_3Sc^-$ b) $SiGe_4Sc^-$

**Figure 3. The low-lying isomers of the $SiGe_nSc^-$ ($n$ = 3, 4)**

**Table 4. The structure, symmetry, electronic state, relative energy (RE), adiabatic energy (ADE), and harmonic vibrational frequencies of the low-lying isomers of the SiGe$_n$Sc$^-$ ($n$ = 3, 4) clusters**

| Structure | Sym. | State | RE (eV) | ADE (eV) | Harmonic vibrational frequencies (cm$^{-1}$) |
|---|---|---|---|---|---|
| SiGe$_3$Sc$^-$ | | | | | |
| $A$-SiGe$_3$Sc$^-$ | C$_s$ (C$_{3v}$) | $^1$A′ | 0.00 (0.00)* | 2.22 (2.44) | 127.89; 128.94; 170.03; 204.55; 206.53; 243.40; 243.55; 311.36; 363.76 |
| $B$-SiGe$_3$Sc$^-$ | C$_s$ | $^1$A′ | 0.01 (0.07) | 2.09 (2.22) | 113.85; 145.63; 167.76; 198.68; 214.55; 217.86; 263.49; 324.64; 361.15 |
| $C$-SiGe$_3$Sc$^-$ | C$_s$ | $^1$A′ | 0.53 | | 82.80; 113.86; 136.59; 177.66; 199.85; 213.09; 261.00; 334.97; 335.60 |
| $D$-SiGe$_3$Sc$^-$ | C$_s$ | $^1$A′ | 0.56 | | 75.02; 134.26; 163.00; 174.21; 182.30; 223.67; 237.38; 287.55; 352.63 |
| $E$-SiGe$_3$Sc$^-$ | C$_s$ | $^1$A′ | 0.93 | | 44.81; 90.22; 116.22; 170.43; 206.42; 235.39; 288.21; 346.94; 385.76 |
| SiGe$_4$Sc$^-$ | | | | | |
| $A$-SiGe$_4$Sc$^-$ | C$_1$ | $^1$A | 0.00 | 1.88 | 75.52; 89.42; 139.08; 148.18; 175.07; 190.02; 214.19; 252.31; 259.47; 302.80; 333.77; 371.19 |
| $B$-SiGe$_4$Sc$^-$ | C$_{4v}$ | $^1$A$_1$ | 0.16 | | 94.29; 94.30; 96.52; 164.09; 166.61; 173.45; 210.84; 210.84; 268.61; 274.60; 274.62; 326.38 |
| $C$-SiGe$_4$Sc$^-$ | C$_s$ | $^1$A′ | 0.18 | | 75.46; 91.37; 128.32; 174.43; 177.59; 195.37; 215.33; 227.45; 239.27; 273.62; 328.66; 361.67 |
| $D$-SiGe$_4$Sc$^-$ | C$_s$ | $^1$A′ | 0.20 | | 84.87; 99.44; 125.11; 155.18; 184.63; 190.49; 210.53; 218.35; 237.17; 242.85; 291.46; 323.05 |
| $E$-SiGe$_4$Sc$^-$ | C$_s$ | $^1$A′ | 0.27 | | 81.65; 92.49; 139.61; 156.35; 173.28; 197.65; 204.75; 216.60; 254.62; 269.20; 290.07; 354.28 |
| $F$-SiGe$_4$Sc$^-$ | C$_s$ | $^1$A′ | 0.30 | | 66.30; 108.57; 147.13; 157.89; 174.84; 176.80; 209.92; 229.56; 235.63; 265.26; 292.28; 364.10 |
| $G$-SiGe$_4$Sc$^-$ | C$_1$ | $^3$A | 0.59 | | 59.16; 65.23; 126.25; 161.99; 164.88; 179.53; 207.40; 212.77; 229.69; 253.74; 314.26; 348.77 |
| $H$-SiGe$_4$Sc$^-$ | C$_1$ | $^3$A | 0.73 | | 69.12; 79.15; 120.07; 155.76; 161.07; 181.02; 202.16; 217.01; 224.95; 234.20; 261.80; 354.99 |

** calculated at CCSD(T) level*

The $A$-SiGe$_4$Sc$^-$ isomer is the global structure of the SiGe$_4$Sc$^-$ cluster. The one-electron detachment from the $A$-SiGe$_4$Sc$^-$ isomer created the $A$-SiGe$_4$Sc isomer with an ADE value of 1.88 eV which was found by using the PBE calculations. The $B$-SiGe$_4$Sc$^-$, C-SiGe$_4$Sc$^-$ and $D$-SiGe$_4$Sc$^-$ isomers are 0.16, 0.18 and 0.20 eV higher than $A$-SiGe$_4$Sc$^-$, respectively. The $B$-SiGe$_4$Sc$^-$ and $D$-SiGe$_4$Sc$^-$ isomers are the same as the geometrical structures of *H*-$SiGe_4Sc$ and *E*-$SiGe_4Sc$ isomers. However, the *B*-$SiGe_4Sc^-$ structure has a $C_{4v}$ point group symmetry with the electronic state of $^1A_1$. The C-$SiGe_4Sc^-$ and *B*-$SiGe_3Sc$ structures are equivalent. The *E*-$SiGe_4Sc^-$ and *F*-$SiGe_4Sc^-$ isomers have near degeneracy energy with the relative energy of 0.27 and 0.30 eV, respectively. The geometrical structure of the *A, C, D, E,* and F isomers of $SiGe_4Sc^-$ cluster have the $C_s$ point group symmetry and their electronic state is the $^1A'$ state. The *G*-$SiGe_4Sc^-$ and *H*-$SiGe_4Sc^-$ have the same geometrical structures as the *F*-$SiGe_4Sc$ and *I*-$SiGe_4Sc$ isomer. The *G*-$SiGe_4Sc^-$ and *H*-$SiGe_4Sc^-$ are less stable 0.59 and 0.73 eV than the global structure. The above results showed that the order of the stability of anion clusters have different from those neutral clusters.

## 4. Conclusion

The structures of the $SiGe_nSc^{0/-}$ (*n* = *3, 4*) clusters are investigated by the genetic algorithm, density functional theory, coupled-cluster theory. The stable structures have a low spin multiplicity. The bipyramid structures with or without capping one atom on the surfaces are the main structures. The ADE values of the *A*-$SiGe_3Sc^-$, *B*-$SiGe_3Sc^-$ and *A*-$SiGe_4Sc^-$ at the PBE/def2-TZVP level are 2.22, 2.09, 1.88 eV, respectively. At the CCSD(T) level, the ADE values of the *A*-$SiGe_3Sc^-$, *B*-$SiGe_3Sc^-$ isomers are 2.44 and 2.22 eV. The changing of electron numbers in the cluster can change the order of stability between the neutral clusters and anion clusters. The bigger cluster can be formed from the smaller cluster that show the formation ability of the scandium doped germanium silicon nanomaterial. It can be used to apply in gas adsorption./.

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