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A DFT study on the structures and stabilities of As-doped Si_{n-1} ($n = 2–15$) clusters

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ABSTRACT

The structures and relative stability of pure Si_n and $AsSi_{n-1}$ ($n = 2–15$) clusters have been investigated at the B3LYP/6-31++G(3d) level of density functional theory. In general, the As doping does not lead to fundamental changes in the geometry of the studied clusters; the effects are localized. Relative stabilities of these clusters have been analyzed based on the variation of their averaged binding energies (E_b), fragmentation energies (E_f), second differences in energy (Δ^2E), and the highest occupied and the lowest unoccupied molecular orbital (HOMO–LUMO) gaps (ΔE) with cluster size (n). The calculated values of E_f, Δ^2E, and ΔE shed light on the relatively high stability of clusters Si_{12} and Si_{14} in addition to the well-known magic numbers Si_6 and Si_{10}. According to E_b, Δ^2E, and E_f results both Si_n and $AsSi_{n-1}$ clusters with $n = 6$, 10, 12, and 14 exhibit high stability when compared to their neighbors. This has been discussed in terms of their close-packed structures rather than electronic pairing effect. The analysis indicates that ΔE of $AsSi_{n-1}$ clusters are significantly smaller than those of the corresponding Si_n clusters, especially for $n > 4$, which means that the metallic characters of $AsSi_{n-1}$ clusters are enhanced by As doping.

1. Introduction

The chemistry of silicon has shown dramatic expansion in recent years [1]. This is due to the importance of this chemical element in fields with high-level potential technological applications [2]. Atomic clusters form a link between molecules and solids with novel properties found neither in molecules nor in solids. As silicon is the most important semiconducting element for the microelectronics industry, device fabrication, and atomic scale engineering, it is important to understand the physical and chemical properties of silicon clusters with a few to a hundred of atoms. Extensive investigations on pure silicon clusters have been reported [3–38]. Although the structures of small silicon clusters ($n < 10$) have been extensively studied by theoretical methods [3–17] and experimentally confirmed [18–20], theoretical predictions for global-minimum structures of medium-sized silicon clusters Si_n ($n \geqslant 10$) are increasingly difficult because of the rapid increase of the number of low-energy isomers. These clusters have attracted much attention both theoretically [21–38] and experimentally [39–41].

The geometric structures of the transition-metal-atom doped silicon clusters have been studied [42–51]. It has been found that transition-metal atoms are good candidates to stabilize the pure Si cages by saturating their dangling bond. The mass spectrum of $CuSi_n$ ($6 \leqslant n \leqslant 12$) showed exceptional stability of $CuSi_{10}$ [42]. The geometric and electronic structures of mixed metal–silicon MSi_{16} (M = Sc, Ti, and V) clusters using mass spectrometry and photoelectron spectroscopy of anionic clusters have been studied [43]. In addition, several computational investigations on MSi_n (M = Cr, Mo, W) clusters are carried out [44–46]. Co and Fe encapsulating in Si_n ($n = 1–14$) clusters have been studied [47,48]. The geometric, energetic, and bonding properties of $CuSi_n$ ($n = 4$, 6, 8, 10, and 12) clusters have been investigated in detail [49] and the interaction of Sc and Cu atoms with small Si_n clusters has been compared [50]. The $AgSi_n$ ($n = 1–13$) clusters were found to be relatively stable when $n = 7$ and 10 [51].

The main-group element doped silicon clusters have also been investigated [52–56]. A theoretical study on the equilibrium geometry and energetics of Si_n and $AlSi_{n-1}$ clusters indicated that both Si_n and $AlSi_{n-1}$ clusters with $n = 4$, 6, and 10 demonstrating higher stability than their neighboring clusters [52]. The main-group element doped $NSi_n/AlSi_n/CSi_n$ silicon clusters have been extensively studied [53–55]. The geometric and electronic structures of Si_n, Si_n^- and PSi_{n-1} clusters ($2 \leqslant n \leqslant 13$) have been explored using ab initio molecular orbital theory formalism [56].

Many experimental and theoretical studies on the diffusion of the arsenic dopant in silicon have been reported [57–59]. To the best of our knowledge, we are aware of only two theoretical studies on the structures and properties of $AsSi_n$ [60] and As_2Si_n [61] ($n = 1–8$) have been recently reported during the preparation of the current work for publication. In the current work, the main

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objective is to investigate the effect of inclusion of As atom in Si_n clusters on the corresponding geometrical, stability, electronic and optical properties of silicon clusters. This objective is accomplished by studying the structures and energetics of As-doped $AsSi_{n-1}$ clusters ($n = 2–15$). The corresponding Si_n clusters are also investigated in the present work for comparison as well as to reexamine a number of low-energy geometric isomers of some medium-sized silicon clusters (Si_{11}–Si_{15}) that have been previously reported.

2. Computational details

DFT approaches have been used for many silicon cluster studies. The LDA (local density approximation) [25,62–64] and GGA (generalized gradient approximation) [25,62,65,66] approaches are the most employed. However, accumulated experience [67], recommends hybrid functional approaches; they yield more reliable energies and structures. Moreover, performance tests for different DFT functionals [68] supporting the use of a hybrid functional to obtain better results. It has been demonstrated that hybrid functionals such as B3LYP are necessary to get DFT results that can be expected to come close to those produced by methods in which electron correlation is considered explicitly. The calculations for both pure silicon clusters and As-doped silicon clusters were carried out using Becke's hybrid Hartree–Fock (HF) density functional method [69] with the Lee–Yang–Parr (LYP) correlation functional [70] (B3LYP) and the 6-31++G(3d) basis set as implemented in Gaussian03W package [71]. To obtain the local-minimum structures, a full geometry optimization without any symmetry constraints is undertaken at the B3LYP/6-31++G(3d) level. Vibration frequency calculations are performed at the same level of theory to confirm the nature of the stationary points. Therefore, the determination of the global minimum becomes an increasingly challenging task as the cluster size increases.

To justify our computational method, the ionization potentials (IPs) of Si and As atoms, and those of As_2 and Si_2 clusters were calculated at the B3LYP/6-31++G(3d) level. Our results are 8.11, 9.79, 9.65, and 7.61 eV for Si, As, As_2, and Si_2, respectively, which are in good agreement with the experimental values 8.11 [72], 9.81 [72], 9.51 [73], and 7.92 ± 0.05 eV [74], respectively. In addition, our optimized Si–Si and As–As bond lengths for the Si_2 and As_2 dimers are 2.273 Å and 2.099 Å, which are in good agreement with the experimental values of 2.246 Å and 2.103 Å, respectively [75]. On the other hand, the vibrational frequency of Si_2 dimer in the triplet state is 498.3 cm^{-1} that agrees with the reported experimental value, 510.98 cm^{-1} [75].

3. Results and discussion

A number of low-lying energy structures of $AsSi_{n-1}$ ($n = 2–15$) clusters are calculated at the B3LYP/6-31++G(3d) level to obtain the corresponding global minimum structures. The lowest-energy structures of pure Si_n are also calculated and depicted in Fig. 1 for comparison. They are well consistent with previous ab initio and DFT calculations results [3–25,28,32,33,37–39,56,63,64,66]. The global minima in addition to one or more of the lowest-energy structures of $AsSi_{n-1}$ are shown in Fig. 2. All structures presented have no imaginary frequencies, indicating that they are genuine minima. Two approaches have been adopted to generate initial structures for each As-doped silicon cluster size. The first one is the substitution of one Si atom in the lowest-energy structure of a pure Si_n cluster at selected positions with an As atom to create a new structure for an $AsSi_{n-1}$ cluster. The second approach involves As-capping a pure Si_{n-1} cluster or Si-capping the lowest-energy structure of $AsSi_{n-2}$ cluster at selected positions to create an $AsSi_{n-1}$ cluster.

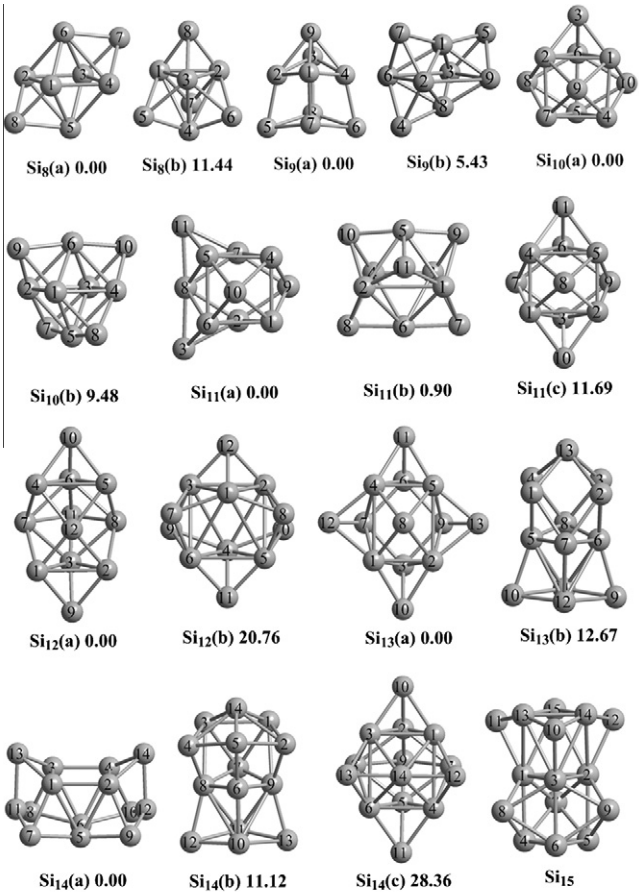
Si_8(a) 0.00 Si_8(b) 11.44 Si_9(a) 0.00 Si_9(b) 5.43 Si_{10}(a) 0.00
Si_{10}(b) 9.48 Si_{11}(a) 0.00 Si_{11}(b) 0.90 Si_{11}(c) 11.69
Si_{12}(a) 0.00 Si_{12}(b) 20.76 Si_{13}(a) 0.00 Si_{13}(b) 12.67
Si_{14}(a) 0.00 Si_{14}(b) 11.12 Si_{14}(c) 28.36 Si_{15}

Fig. 1. B3LYP/6-31++G(3d) optimized geometries of Si_n clusters ($n = 8–15$). The relative energies (kcal mol^{-1}) are indicated below the structures.

3.1. Equilibrium geometries

The DFT/B3LYP/6-31++G(d) ground states and two or three of the low-lying isomers of Si_n ($n = 8–15$) clusters are presented in Fig. 1 for comparison. These structures are consistent with the accepted low-lying structures of Si_n clusters previously established [3–20]. The ground states and several low-lying structures of $AsSi_{n-1}$ ($n = 2–15$) are shown in Fig. 2. The $AsSi_{n-1}$ ($n = 2–9$) clusters obtained in this work are consistent with those recently reported based on DFT/B3LYP/6-311+G(d) method [60]. However, there are some notices may be of interest to be mentioned here. It is worth to note that the As atom in each of the ground state structures of $AsSi_4$, $AsSi_5$, and $AsSi_6$ clusters prefers to occupy the base atom sites of the corresponding trigonal, face-capped trigonal, and pentagonal bipyramids, respectively. The structures in which the As atoms are substituted in the apex atom sites are less stable energetically (Fig. 2). The same site preference (base atom site) is found for the ground state structures of Si_4N and Si_6N [53] and for PSi_4, PSi_5, and PSi_6 [56] clusters where both nitrogen, phosphorous, and arsenic belong to group V in the periodic table. For $AsSi_7$, the ground state structure (7a) can be obtained by replacing the apex silicon atom in Si_8(c) isomer of Si_8 cluster (Fig. 1) with an As atom or by face-capping the trigonal bipyramid $AsSi_6$(c) isomer with one more silicon atom. Such ground state structure is similar to that proposed for NSi_7 [53] and PSi_7 [76]. Moreover, when the As atom migrates from the 3-coordinated to the 6-coordinated vertex