First-principles study on mixed $Si_{n-1}N$ ($n = 1$–19) clusters

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ABSTRACT

The mixed $Si_{n-1}N$ ($n = 2$–19) clusters have been investigated systematically using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method and Amsterdam Density Functional (ADF) program with TZ2P basis set in conjunction with self-consistent field (SCF). Their ionization potentials (IPs), electron affinities (EAs), dipole moments μ, constant volume heat capacity per atom C_v are computed. Based on the Mulliken population analyses, it is found that some of charge is transferred from the Si atoms into the nitrogen atom. Compared with other structures, most of the substitutional structures with three Si–N bonds are more stable. Our calculated results suggest that the N impurity atom improves the stability of the mixed clusters.

1. Introduction

Investigation on semiconductor materials, in particular, pure silicon clusters, has been one subject of intensive research due to the technological relevance towards the development of semiconductor science over the past decades [1–12]. Recently, both experimentalists and theoreticians are devoted to the study of heteroatom-doped silicon clusters because of their potential applications [13–16]. Xiao and co-workers investigated the geometric, energetic and bonding properties of neutral and charged $CuSi_n$ ($n = 4, 6, 8, 10$ and 12) clusters by using a hybrid density functional method (B3LYP) [13]. Most of $CuSi_n$ isomers in their paper can be obtained from the ground state structures or low-lying isomers of Si_n or Si_{n+1} with Cu at various substitutional or adsorption sites. Their findings showed that the Cu–Si bond in $CuSi_n$ clusters is strong for the substitutional structures in the center-site, but weak for the adsorption structures. Khanna et al. reported the equilibrium geometries and their total energies of Cr encapsulated in the Si clusters. They found that $CrSi_{12}$ is more stable than its neighbors [14]. Analyzing the final product MSi_n^+ cluster ions ($n = 9, 14$–11) by the reacting of many kinds of transition metal ions M^+ (M = Hf, Ta, W, Re, Ir, etc) with silane

(SiH_4), Hiura and co-workers found that the metal atom is endohedral, and stabilizes the Si polyhedral cages [15].

In addition to the works described above, the nonmetal heteroatom-doped silicon clusters have also been considered [16–17]. Chu et al. investigated the influences of carbon heteroatom on Si_n ($n = 2$–19) clusters by using full-potential linear-muffin-tin-orbital molecular-dynamics (FP-LMTO-MD) method [16]. It has been found that the influence of the C impurity atom would decrease as the clusters size increases, and that the C heteroatom probably reverses the energy orderings of the Si isomers with the small energy difference. Nigam and co-workers had studied the geometric and electronic structures for PSi_{n-1}, Si_n^+ and Si_n^- clusters ($n = 2$–13) using the ab initio molecular orbital theory formalism [17]. They found that the geometries of the silicon clusters with substitutional P atom show similar growth as that of negatively charged Si_n clusters with small local distortions. For the isoelectronic PSi_{n-1} clusters, it is found that although the substitution of P atom improves the binding energy of Si_n clusters when $n < 4$, the effect is opposite for slightly larger Si_n clusters.

Nitrogen is contiguous to carbon, which is in the same main group of the periodic table as phosphorus. The influences of nitrogen in the bulk silicon on the physical as well as chemical properties are received increasing research interests [18–39]. In Ref. [34], it is found that silicon nitride-based compound provides high strength at high temperature, good thermal stress resistance,

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and excellent oxidation, corrosion, and erosion resistance. Therefore, from a more fundamental perspective, to study the nature of nitride silicon clusters and to find out the physical and chemical proprieties of the clusters are also important. Some authors have made the investigations toward this direction. Goldberg et al. used collision experiments and high-level ab initio calculations to characterize the neutral, cationic, and anionic Si_3N clusters molecules [31]. They also calculated the geometries and harmonic frequencies of Si_nN ($n = 1–3$) for neutral, positive, and negative species. Their calculations revealed that both of the Si_2N and Si_3N molecules form two isomeric structures, which differ by only a few kcal/mol, and coexist in the gas phase. But the other clusters like Si_2C, Si_2O and Si_3C possess one preferred structures. Ornellas and co-workers studied three isomeric forms of the species Si_2N [32] theoretically. It is found that the symmetric linear structure is the global minimum. Kerkines and Mavridis calculated the spectroscopic constants and energetics for the two lowest-lying states of SiN and SiN^- employing the coupled cluster methodology and very large basis sets accounting for core/valence correlation, one-electron Douglas–Kroll–Hess relativistic effects, and atomic spin-orbit couplings [33]. In Ref. [35], the structures and energetics of Si_nN_m ($n+m<7$) is investigated by all-electron full-potential density-functional method at both the local density approximation (LDA) and the generalized gradient approximation (GGA) levels of theory. They found that N-rich clusters are easy to form linear or quasi-linear structures, whereas Si-rich clusters favor planar or three-dimensional structures. It is evident that all of these works are limited to the small nitride silicon clusters. Jackson et al. investigated the structures and properties of Si_nN_m ($n+m = 20$) clusters using the density-functional-based tight binding technique [40]. The calculations indicated a transition in the basic geometrical structure of the substituted clusters from close-packed structures typical of pure Si clusters for <4 to cage-like structures for $m \geqslant 4$. Widjaja et al. investigated the reaction of atomic nitrogen on the $Si(100)–(2 \times 1)$ surface [41]. It was found that the structure with nitrogen atom bridge-bonded into the Si–Si dimer is the most thermodynamically stable. Even though the investigations above have been performed, our knowledge about the nature of the large nitride-doped silicon clusters is still little.

In this paper, we will report our result about the investigation of $Si_{n-1}N$ clusters ($n = 2–19$). Our main purpose is to explore how the impurity N atom affects the structures and bonding properties of the Si_n ($n = 2–19$) clusters.

2. Computational methods

Firstly, we performed geometrical optimization calculations on the initial structures above by means of the FP-LMTO-MD method, which is a self-consistent implementation of the Kohn–Sham equations in the local-density approximation [42–45]. During the molecular-dynamics calculations, space is divided into two parts: non-overlapping muffin-tin (MT) spheres centered at the nuclei, and the remaining interstitial region. LMTOs are augmented Hankel functions inside the MT spheres, but not in the interstitial region [46–49]. Self-consistent calculations are carried out with convergence criteria of 10^{-5} a.u. on the total energy and 10^{-3} a.u. on the force. The details of how the molecular dynamics method can be performed are described in Refs. [46–49]. This method is suitable for investigating the geometrical and electronic structures of semiconductor and nonmetal clusters [6,11,50]. The calculating results from the method are in good agreement with those obtained by some other advanced molecular dynamics methods [50].

Secondly, we re-optimized several promising candidates with larger binding energies by using the Amsterdam density functional (ADF) program [51], version (2007.01). In the ADF program, molecular orbitals (MOs) were expanded using a large, uncontracted set of Slater-type orbitals (STOs): TZ2P [52]. The TZ2P basis is an all-electron basis of triple-ζ quality, augmented by two sets of polarization functions. The frozen-core approximation for the inner-core electrons was used. The orbitals up to 2p for silicon and 1s for nitrogen were kept frozen. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately in each self-consistent field (SCF) cycle. Calculations have been made in the framework of the GGA by means of the Becke–Perdew functional, which uses Becke's [53] gradient correction to the local expression for the exchange energy and Perdew's [54] gradient correction to the local expression of the correlation energy. The SCF was converged to a value of 10^{-7}. Frequencies were computed using numerical differentiation of gradients computed in slightly displaced geometries.

3. Results and discussions

The calculations on the geometries and energetics of the $Si_{n-1}N$ ($n = 2–19$) clusters have been carried out using the sophisticated methods mentioned above. One important thing is to select some initial structures as seeds. Firstly, the initial atomic configurations of the $Si_{n-1}N$ clusters are of the substitutional, or adsorption, or endohedral types. The substitutional structures can be obtained by substituting one silicon atom in all the possible positions of the isomer structures for the Si_n clusters with large binding energy by using a nitrogen atom. The adsorption structures only arise from each possible adsorption of one N atom on the ground state structures of the Si_n clusters. The endohedral structures can be obtained by filling one N atom in the inside of some Si_n cages. Secondly, the initial atomic configurations are produced automatically within a three-dimensional box of real space by a random way. The separations of Si–Si, Si–N and N–N atoms are confined in 2.3–2.7 Å, 1.6–2.0 Å, and 1.1–1.5 Å. This range precludes the starting geometries that are too compressed, or not efficiently packed. Thirdly, the initial atomic configurations are constructed from some consideration of symmetry (such as double icosahedron, decahedron, octahedron, etc.). After the initial geometrical configurations are optimized, a number of stable structures are obtained. In many cases, the geometrical optimization of several different starting configurations is found to give the same geometrical parameters upon optimization. Only the stable structures with largest binding energies are presented in Fig. 1. In order to confirm the stability of the structures, the computation of frequencies on them was also carried out. Imaginary frequencies indicate that a structure is unstable. But, there are no imaginary frequencies in the structures. The calculated total binding energy E_b, ionization potentials (IPs), electron affinities (EAs), dipole moment μ, total constant volume heat capacity C_v, and Q transferred from Si atoms to N atom are presented in Table 1.

SiN, which is a dimer with different atoms, is the simplest and smallest molecule in silicon nitride family. The calculated Si–N bond length of SiN cluster is 1.61 Å, which is slightly larger than 1.57 Å obtained by Jungnickel and Frauenheim using all-electron full-potential density-functional method at both the LDA and the GGA levels of theory [35]. But, the value is in good agreement with 1.62 Å obtained by employing a B3LYP method of the Gaussian 03 program package with 6-311++G basis sets [36]. Further calculation finds that the Si–N bond length of SiN anion is