First principles investigation of interaction between impurity atom (Si, Ge, Sn) and carbon atom in diamond-like carbon system

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ABSTRACT

The interaction between impurity atom (Si, Ge, and Sn) and carbon atom in diamond-like carbon (DLC) system was investigated by the first principles simulation method based on the density functional theory. The tetrahedral configuration was selected as the calculation model for simplicity. When the bond angle varied in a range of 90°–130° from the equivalent state of 109.471°, the distortion energy and the electronic structures including charge density of the highest occupied molecular orbital (HOMO) and partial density of state (PDOS) in the different systems were calculated. The results showed that the addition of Si, Ge and Sn atom into amorphous carbon matrix significantly decreased the distortion energy of the system as the bond angles deviated from the equilibrium one. Further studies of the HOMO and PDOS indicated that the weak covalent bond between Si(Ge, Sn) and C atoms was formed with the decreased strength and directionality, which were influenced by the electronegative difference. These results implied that the electron transfer behavior at the junction of carbon nano-devices could be tailored by the impurity element, and the compressive stress in DLC films could be reduced by the incorporation of Si, Ge and Sn because of the formation of weaker covalent bonds.

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1. Introduction

Carbon-based nanostructure materials including diamond-like carbon (DLC), carbon nanotubes, graphene and so on, have attracted extensive research interests because of their unique structures and electronical, optical, and magnetic properties [1–3]. Especially DLC films owning high hardness, low coefficient of friction, superior optical property and extremely good chemical inertness as well as biocompatibility, have been widely used in the industrial fields of molds, cutting tools, biology and nano-devices etc. [4–7]. However, to reduce the high residual compressive stress formed during the deposition process is still a key issue to spread the potential applications of DLC films. Adding a third element into DLC film is one of the effective methods to reduce the residual stress, but different incorporated atoms have different effects on the physical properties leading to the complexity of stress reduction mechanism. For example, the addition of N, Si or W into amorphous carbon matrix led to the stress reduction significantly without serious change of hardness [8–11], while the addition of Al reduced both the stress and hardness drastically [12]. This attributes to the limitation of experimental characterization of atomic bond structure which is closely related with high level of residual stress, leading to insufficient understanding of the mechanism of

the stress reduction by third element addition is yet to be understood. Especially, when DLC films are used for nano-devices where the electrode metal element or other impurity atom is usually incorporated into system at the junction of carbon nano-devices, the evolution insight of electronic structure such as the electron transfer behavior and bonding characteristic caused by the third element incorporation is of great importance for optimizing the design strategies and operating performance of the nano-device.

In the present work, we carried out first principles studies to investigate the electronic structure of atomic bond between the impurity and carbon atoms and the total energy change of the system with bond angle distortion. Si was selected as impurity element in carbon-based system because it is not only used in semiconductors frequently, but also used for the stress reduction in DLC films [11,13,14]. For more systematic understanding, the additions of Ge and Sn elements which have the same outermost electrons as Si were also done for comparison. We measured the distortion energy as a function of bond angle deviated from the equivalent state of 109.471°; the effect of impurity on electronic structure was evaluated by the charge density of high occupied molecular orbital (HOMO) and partial density of state (PDOS). The results suggested that the addition of impurity atoms (Si, Ge or Sn) can result in the changes of electron distribution and bond characteristic with a smaller distortion energy, which can explain the observed change in the residual stress of carbon-based materials during the experimental research.

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2. Calculation strategy

The tetrahedral bond model was used in the present study for the calculation simplicity, as shown in Fig. 1 [15]. The four carbon atoms were located at the corners of the tetrahedron, with an impurity atom or a carbon atom in the central position. Each carbon atom at the corner was passivated by three hydrogen atoms. Three of bond angles between the central atom (C, Si, Ge or Sn) and the corner carbon atom were changed from the equivalent state of 109.471° to 90°, 100°, 120° and 130°, respectively, in order to obtain the distorted structure. During the calculations, these three bond angles were fixed to consider the effect of bond angle distortion on the electronic structures only without constraining the C(Si, Ge, Sn)–C bond distance.

The DMol^3 software package based on the density functional theory (DFT) was employed with a generalized gradient approximation for the exchange-correlation potential defined by Perdew, Burke, and Ernzerhof [16]. The geometry optimization and energy calculation were done without taking into account spin-polarization. The self-consistent convergence criterion was that the total energy difference between two continuous iterating steps was less than 10^{-5} eV. During the geometry optimization, the convergence thresholds for energy change, maximum force, and maximum displacement between optimization cycles were 10^{-5} eV, 0.01 eV/Å and 0.005 Å, respectively. A gamma point and an all electron calculations were performed on the periodic supercell with a size of $15 \times 15 \times 15$ Å^3. The wave functions of atomic orbitals were expanded using a double-numerical polarization basis set with an orbital cutoff of 9 Å to guarantee the convergence. The evolution of total energy, charge density of HOMO and PDOS for each structure were calculated for the various central atoms units.

3. Results and discussion

For different central atoms, the total energy change of ΔE as a function of bond angle (hereafter referred to as distortion energy) was carried out when the bond angles of C(Si, Ge, Sn)–C tetrahedron deviated from the reference angle 109.471°, as illustrated in Fig. 2. For the pure carbon-based system, where carbon atom is located at the center of the tetrahedron, the distortion energy increases significantly as the bond angles change in the range of 90–130°. However, with the substitution of the central C atom by Si, Ge, or Sn atoms, the increase in the total energy is less than that of the pure C–C tetrahedron.

The residual stress of the amorphous covalent system such as diamond-like carbon would be essentially caused by the deviation in either bond length or bond angle. Even if we only focused on the bond angle in the present work, this result would provide a reasonable explanation of the previous experimental results of the stress reduction of amorphous carbon film by Si incorporation [14]. It must be also noted that if the distortion energy becomes small, an impurity atom of large size can be easily incorporated into the amorphous carbon network by distorting the nearby atomic configuration. So it could be deduced that doping the Si, Ge or Sn elements to amorphous
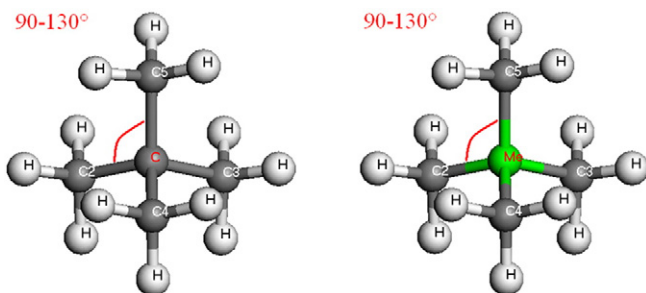
carbon matrix would reduce the residual stress according to the lowered distortion energy in case of the bond angle distortion.

To further clarify the relationship between the total energy changes and the electronic structures, the strength and directionality of bonds between the impurity atom (Si, Ge, Sn) and corner carbon atoms were investigated. For comparison, the characteristic of C–C bond was also performed. Fig. 3 shows the isosurface of electron density in the unit of electrons/Å^3 before the isosurfaces of the central and the corner carbon atoms are spatially separated. Herein, d is the bond length of C–C, Si–C, Ge–C or Sn–C, and ρ_{max} is the electron density of the isosurface. For the C–C case, the isosurface at the electron density 1.5391 electrons/Å^3 displays the strongest angular shape which implies the highest strength and directionality between the C–C bonds, leading to the higher distortion energy. When Si, Ge or Sn replaces the central carbon atom in the unit, the bond lengths increase to 1.89 Å, 1.98 Å and 2.20 Å, respectively. On the other hand, the increased isotropic characteristics of isosurface are observed and the corresponding ρ_{max} decreases monotonically to 0.78 electrons/Å^3, 0.7695 electrons/Å^3, and 0.5977 electrons/Å^3, respectively. Taking into account the total energy behaviors shown in Fig. 2, it can be thus said that the decreased bond strength and the decreased anisotropic characteristics of the chemical bond between the central impurity atom and the corner carbon atoms greatly contribute to the decreased distortion energy.

The changes in the bond characteristics can be understood by analyzing the PDOS and the electron transfer behavior between two atoms. Fig. 4 shows the PDOS for the various systems, and the insets show the charge density of HOMO between two corner carbon atoms and the central C or impurity atoms. For the C–C tetrahedral configuration (Fig. 4(a)), the charge density of HOMO indicates that the central carbon atom and the corner carbon atoms are connected by the charge distribution, which is the typical feature of the covalent bond with the high strength and directionality. Analysis of the PDOS shows that the HOMO is hybridized by the C-2p orbitals. According to the molecular orbital theory, two atomic orbitals can form two molecular orbitals when they possess the same symmetry, similar energy and maximum overlap of orbitals. If the energy of molecular orbital is less than that of atomic orbital, it is the bonding orbital; otherwise it is the anti-bonding orbital, while non-bonding orbital is always gained if two interactive atomic orbitals have the same energy. When the electrons fill the bonding orbital, it is a benefit in improving the stability of system configuration. On the other hand, the system stability can be weakened by the anti-bonding orbitals. By comparing the energy of HOMO and C-2p orbital in the C–C model, it could be said that the HOMO is dominated by the bonding orbital and as a consequence, the significant energy change is observed during the bond angle distortion.
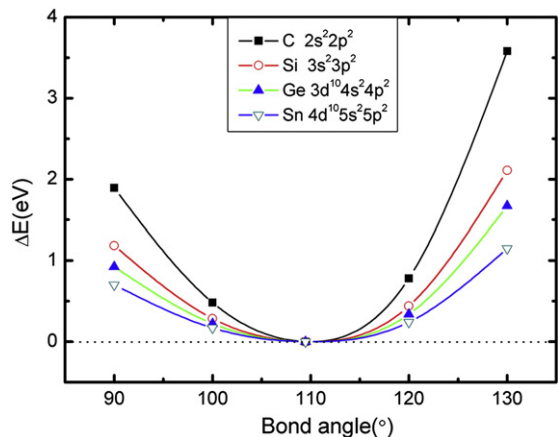

Fig. 1. Used tetrahedral bond model [15].

Fig. 2. Energy change via bond angle distortion from 109.471° to 90°, 100°, 120°and 130°.
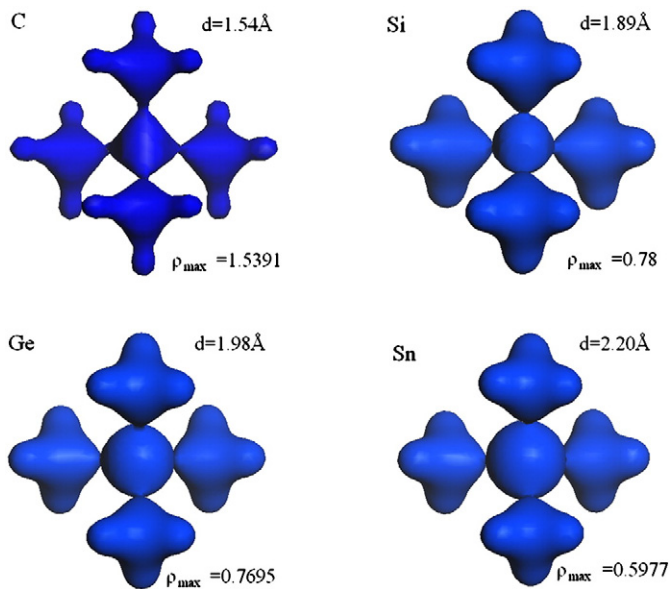
Fig. 3. Isosurface of electron density before the isosurface between central atom and corner C atoms is separated.

When the central carbon atom is replaced by the Si atom, the HOMO is hybridized by the Si-3p and C-2p atomic orbitals, as shown in Fig. 4(b). The charge density of HOMO shows similar covalent bond feature between Si and C atoms, but the charge density has the tendency to shift to be around the corner C atoms and the bond strength and directionality decrease. The effect of electron transfer behavior, induced by the difference in the electronegativity, can be described by ionicity determined by Pauling theory [17]. The value

of iconicity is 0.10 for the Si–C bond, indicating the contribution from the partial ionic characteristics of the bond. The ionic characteristics of the Si–C bond would contribute to the smaller total energy increased by the bond angle distortion, which agrees well with the experimental results reported elsewhere [11]. Fig. 4(c) and (d) reveals that for Ge–C or Sn–C tetrahedron, the HOMO is composed by the Ge-4p and C-2p atomic orbitals or by Sn-5p and C-2p atomic orbitals, but the weaker covalent bond is also generated as Si–C tetrahedron due to the electronegative difference between impurity atoms and C atom.

4. Conclusions

By using the simplified tetrahedral configuration model, the first principles calculation based on the DFT theory was undertaken to investigate the interaction between the impurity atom (Si, Ge and Sn) and C atom. When the atom of Si, Ge or Sn substitutes the central carbon atom in the tetrahedral structure, the increase in the energy of the various (Si, Ge and Sn)–C units is less than that of the pure C–C unit, as the bond angle distorted in the range of 90–130° from the tetrahedron's equilibrium value of 109.471°. The PDOS and HOMO results indicate that, comparing to the strong covalent bond of C–C model, the bonding feature can be classified by the weak covalent bond for Si–C, Ge–C or Sn–C tetrahedron. In addition, the electrons tend to be transferred around the high electronegative carbon atom with the incorporation of Si, Ge and Sn, so that the contribution from ionic character reduced the bond strength and thus directionality of bonds.
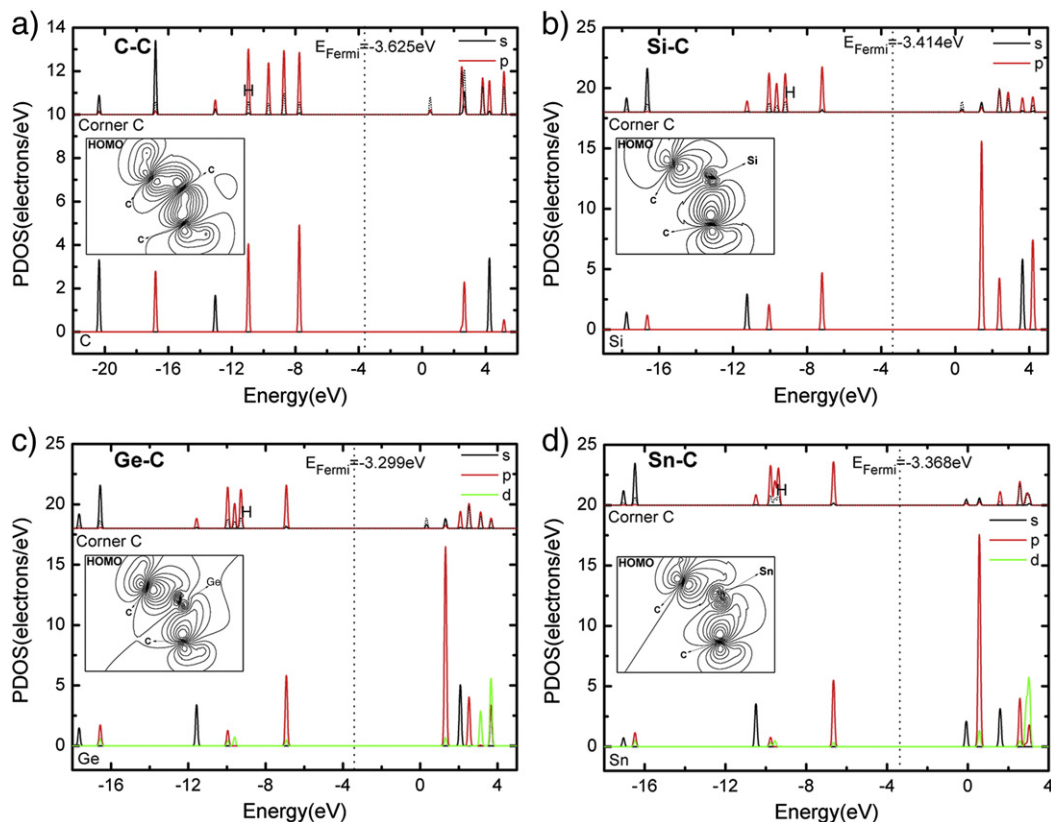
Fig. 4. PDOS for each tetrahedron unit (a) C–C, (b) Si–C, (c) Ge–C, and (d) Sn–C. The Fermi level is shown as a dotted line and the insets show the contour plots of charge density of HOMO passing through C(Si, Ge, Sn) and two corner C atoms.

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