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Study on structural, electronic and magnetic properties of Sn atom adsorbed on defective graphene by first-principle calculations

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ABSTRACT

The structural, electronic and magnetic properties of the Sn atom adsorption on pristine and defective graphene are comparatively studied by first-principle calculations with the generalized gradient approximation and local density approximation. For Sn atom adsorbed on pristine graphene, minimal adsorption energies and small charge transfer denotes the ionic bonding. The adsorption tune the Fermi level up but the unique Dirac point structure remains intact. Also the semiconductor graphene with zero bandgap becomes metallic and obtains a magnetic moment. For Sn atom adsorbed on defective graphene, the large adsorption energies and the bond lengths which smaller than the sum of covalent bond length indicate that the bonding is covalent bonding. Moderate and no bandgap were observed at the Fermi level in the Sn atom adsorbed on single vacancy and double vacancies graphene system, respectively. The zero bandgap semiconductor character of pristine graphene is dramatically changed due to the substitution of Sn. Sn atom adsorbed on defective graphene show nonmagnetic characters as pristine graphene.

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1. Introduction

Graphene, a single-layered of graphite, has attracted intense attentions since its first discovery in experiment in 2004 [1]. Each carbon atom of graphene connected with three neighbor carbon atoms by three σ bonds and the p_z electrons form the delocalized π bond. Graphene have unusual transport and electronic properties along with high crystal qualities [1,2] due to its unique zero bandgap with linear and symmetric dispersion relation close to the Dirac points. A surge of experimental and theoretical researches focused on the application of graphene in sensors [3–5], nanoelectronic devices [6,7], spin electronic devices [8], catalysis [9] and energy storage [10–12].

In order to supply wide applications in devices, one of the effective methods is to adsorb atoms on pristine or defective graphene. The direct evidence of experimental for the existence of metal–graphene structures have been provided by many works [13–17]. Graphene with small metal adatom can be created on a TEM grid by coevaporation [13–17]. Theoretically, it was found that the metal elements from groups I to III of the periodic table, the results are consistent with ionic bonding, and the adsorptions are characterized by minimal change in the graphene electronic states [18–21]. For transition metals (TM), the adsorbed energies and the bond lengths are consistent with covalent bonding, and the adsorbed is characterized by strong hybridization between adatom and graphene electronic states. The hollow site is found to be the more stable one for 3d TM [22,23]. In particular, noble metals prefer top site rather to hollow site. Their adsorption behavior is characterized as weak bonding interaction [18,19]. Defects of graphene provide good anchoring for isolated atoms [24,25]. Using the TEM with a focused (down to 1 Å in diameter) electron beam [26], C atoms can be displaced with atomic precision and create an array of vacancies. Then the temperature can be raised, so that the adatom become mobile unless they are pinned by the vacancies [25]. Theoretically, all transition metals and noble metals are strongly binding to the defective graphene [25]. Interestingly, metal–graphene (defective) systems show attractive electronic and magnetic properties [27]. Some metal–graphene systems open a finite bandgap and obtains a magnetic moment [25,27].

Among vast amount of studies on metal atoms adsorbed on graphene, the adsorption of Sn and Pb atoms on pristine and defective graphene is relatively less studied. The Sn and Pb atoms bonded weakly with pristine graphene and characterized as ionic bonding. They favor both directly above a carbon atom and the bond between two neighbor carbon atoms. The diffusion barrier between the two sites is vanishingly small [18,19,28,29]. The interaction between

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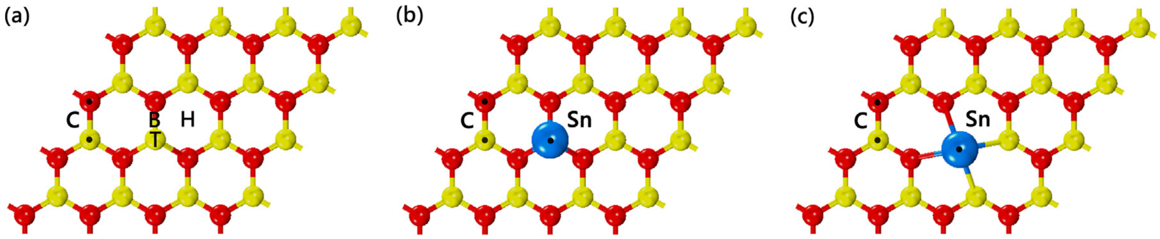

Fig. 1. Sn atom adsorbed on pristine and defective graphene: (a) three adsorption sites on pristine graphene: top (T) site, bridge (B) site, and hollow (H) site. (b) Sn atom adsorbed on single vacancy graphene. (c) Sn atom adsorbed on double vacancies graphene. The red and yellow atoms denote two different carbon atoms in the supercell and the blue atom denotes Sn atom. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the Sn or Pb atom and defective graphene is significantly strong [30]. When Pb adsorbed on pristine graphene, the Pb-graphene system shows metallic character and obtains a magnetic moment [28,29]. However, the system becomes semiconductor when the Sn or Pb atom adsorbed on defective graphene [30]. Experimentally, Pb growth on graphene have been in-depth studied [19,28,31], aiming at improving and manipulating the electronic and magnetic properties of graphene to meet various requirements in device applications. It is clear that Pb diffusion is extraordinarily fast since all the deposited atoms form the big crystalline islands even at very low temperature [31]. Sn-graphene nanocomposite is also studied by many researchers [10–12]. As above mentioned, few theoretical studies have been reported the electronic and magnetic properties with respect to Sn atom adsorbed on pristine and defective graphene.

2. Computational details

The geometric, electronic structure and magnetic properties of the Sn atom adsorbed on graphene is calculated by the density functional theory (DFT) in the generalized gradient approximation (GGA) implemented in the Vienna ab-initio simulation Package (VASP) [32,33] in which the projected augmented wave method [34] and Perdew, Burke, and Ernzernhof (PBE) [35] of exchange-correlation are used. The VASP was also used within local density approximation (LDA) to compare the adsorbed energy and geometric parameters obtained with PBE calculation to assess the quality of the results. In order to study the adsorbed on pristine and defective (both single and double vacancies) graphene, a $4 \times 4 \times 1$ supercell of graphene, 32 carbon atoms plus one adatom, 31 carbon atoms plus one adatom and 30 carbon atoms plus one adatom in the simulation cell are built for the adsorption on pristine, single and double vacancies graphene, respectively. This supercell is found to be adequate because previous works also use this supercell to study Sn or Pb atoms adsorbed on graphene [18,29]. In the direction perpendicular to the graphene plane, a large vacuum of 15 Å is used which allows a vacuum region of about 12 Å to eliminate the influence between the atom in the supercell and its replica. The semi core d states of Sn are treated as valence electrons. A plane-wave basis set with maximum plane-wave energy of 550 eV is used for the valence electron wave functions. In the geometrical structure optimization and self-consistent calculation, the Brillouin zone is sampled with a $9 \times 9 \times 1$ Γ-centered k-point grid, and the Gaussian smearing width is 0.05 eV. For calculation of density of states (DOS), a slightly large number of k-points are used, a $25 \times 25 \times 1$ Γ-centered k-point grid sampling of the Brillouin zone. The Hellmann-Feynman forces and conventional minimization techniques are used to determine the equilibrium structures. After the ionic relaxation, the Hellmann-Feynman forces are smaller than 0.01 eV/Å. The lattice constants are kept fixed through the optimization, all internal coordinates including the carbon atoms and the adatom are allowed to be relaxed.

The total energy calculation of an isolated atom is applied in a length of 15 Å cubic with a single atom placed at the original site. Spin-polarized calculation is implemented and only the Γ point is sampled in Brillouin zone.

In the systems of Sn atom adsorbed on pristine graphene (Sn&PG), because of the high symmetry hexagonal structure of graphene, the possible sites for Sn atom adsorbed on can be reduced into three types: the top (T), bridge (B), and hollow (H) sites, as shown in Fig. 1. In the top site adsorption, the Sn atom is located directly above one of carbon atom in graphene. In the bridge site adsorption, the Sn atom is located above the middle of the C–C bond. While in the hollow site adsorption, Sn atom is located just above the center of the hexagon of graphene.

In the systems of Sn atom adsorbed on defective graphene, containing single and double vacancies (Sn&SV and Sn&DV), initial sites used for structural optimization are shown in Fig. 1(b) and (c).

In order to compare the stability between the adsorption sites and different configurations, we calculated the adsorption energy, which is defined as follows:

$$E_{ad} = (E_{sn} + E_{Graphene}) - E_{Total} \tag{1}$$

In formula (1), E_{ad} is the adsorption energy; E_{sn} is the energy of an isolated Sn atom; $E_{Graphene}$ is the total energy of the graphene (including pristine and defective graphene); E_{Total} is the total energy of the system (including adatom and graphene).

Of all the sites, the site which has the maximum adsorption energy is considered as the most stable site. We also estimate a diffusion barrier for Sn atom adsorbed on graphene, which is estimated by the energy difference between the two configurations [18–21]. More accurate calculation of diffusion barrier needs the nudged elastic band method [36–38].

In order to study the geometry properties of Sn atom adsorbed on graphene, the adsorption height h is calculated, the adsorption height is defined: $h = Z_{\mathrm{ad}} - Z_{\mathrm{ave}}$, Z_{ave} is the mean value of z coordinate of the carbon atoms in graphene. The bond length between Sn atom and the nearest carbon atom in graphene (d_{ac}) is defined. To further study the interaction between the Sn atom and graphene, the distortion of graphene is also calculated, $\Delta h = Z_{\mathrm{max}} - Z_{\mathrm{ave}}$ in the graphene, where Z_{max} is the maximum value of z coordinate of the carbon atoms in graphene and Z_{ave} is the mean value of z coordinate of the carbon atoms in graphene. In the calculation of different sites, the initial height of Sn atom is set to 2.5 Å, and the adsorption height h, the bond length between Sn atom and the nearest carbon atom in graphene d_{ac}, the distortion of graphene Δh is obtained after full optimization.

3. Results

3.1. Structural

Table 1 summarizes the adsorption energy (define in Eq. (1)) and geometry structure of graphene (both pristine and defective)

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