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Shallow donors in diamond: Be and Mg

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ABSTRACT

The electronic properties of the impurities Be, Mg and the hydrogen complexes Be–H, Mg–H in diamond have been investigated by first-principle calculations. It is found that the interstitial Be- or Mg- doped diamond are of n-type metal conductivity character. Even at low impurity concentration the doped diamond also appears n-type behavior. The further results indicate that the interstitial Be or Mg doping diamond should be synthesized at H-poor conditions to obtain the n-type material because most of hydrogen atom may result in interstitial Be- and Mg- doped diamond p-type semiconductor or insulator. The substitutional Be and Mg show acceptor behaviors and may compensate other interstitial donors in diamond. Our results are very helpful to the research of n-type doping in diamond for the future experimental work.

1. Introduction

Diamond has recently attracted much attention due to its outstanding physical properties suitable for electronic device applications. The p-type material is easily achieved by boron doping. However, the lack of available n-type diamond material has hindered the use of diamond-based devices in electronic applications. It is crucial for diamond to attain an effective donor dopant. Various desired dopants, such as group I elements Li and Na, group V elements N, P, As and Sb, group VI elements O, S, Se and Te, have been independently doped or co-doped into diamond as donor dopants [1–12]. However, the expected n-type diamond material has not yet been obtained, which is one of the biggest challenges in diamond device development.

For diamond, substitutional phosphorus (P_s) with a donor level at E_c −0.6 eV is the best donor to date, however, such a deep donor is problematic for application at room temperature [13–15]. Recently, Koizumi [16] has succeeded in growing high quality P-doped diamond. However, the ionization energy of the phosphorus donor is large (0.57 eV), which is not suitable yet for application at room temperature. Nitrogen in diamond creates a deeper donor levels at E_c −1.7 eV due to the localization of the unpaired electron on a carbon dangling bond [4,17]. Consequently, the N-doped diamond is not expected to yield useful conductivities at room temperature. It has been reported that sulfur (S) can generate a "shallow" donor state below the conduction band and may become a good donor dopant, but these results have not yet been reproduced unambiguously; and in theory it is still controversial whether the substitutional sulfur is a "shallow" or "deep" donor [8,18–20]. Prins has obtained an n-type layer with donor level of E_c −0.32 eV in oxygen-implanted diamond [2]. But hardly any theoretical work explains the phenomenon and the subsequent report on O-doped n-type diamond is little. For the study of Li and Na in diamond, the results showed that a deep level is introduced in the band gap of diamond, which indicated that Li and Na in diamond are unlikely to produce the valid n-type material [4,21,22]. Simultaneously, studies on the interaction between hydrogen and these donor candidate dopants [23–26] have been carried out to research the effects of hydrogen on the gap states associated with defects and related electronic properties. The available n-type diamond material has not yet been obtained. In addition, a shallow n-type material with activation energy of around 0.23 eV has been obtained by deuteration of p-type B-doped diamond [27–30]. However, the origin of shallow donor level is controversial [31–36], which hampers the valid controlling of n-type material synthesis.

Despite the recent progress in the study of n-type diamond, it is not available and a hunt for effective donor dopants continues. Compared with the donor dopants mentioned above, group II elements Be and Mg have never received attention for several decades in the n-type doping of diamond both experimentally and theoretically, although they have been widely used in doping GaAs and AlxGa(1−x)As [37–39].

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In the present work, the geometry and electronic properties of diamond doped with Be, Mg and hydrogen complexes, respectively, have been studied by means of density functional theory. The results show that the interstitial Be- (Be_i-) and Mg- (Mg_i-) doped diamond appear n-type behaviors with metallic character. Even if the impurity concentration is low, the diamond doped with Be_i and Mg_i also appear n-type characters. It is found that hydrogen atom may result in Be_i- and Mg_i- doped diamond p-type semiconductor or insulator, which denotes that the impurity doping into diamond should be carried out at H-poor conditions. Both substitutional Be (Be_s) and Mg (Mg_s) in diamond show acceptor behaviors and act as compensation centers for n-type conductivity.

2. Method

In the present work, the calculations have been performed by the CASTEP code [40], in which a plane-wave basis set and a conjugated gradient electronic minimization were used. The conjugated gradient approximation (GGA) with ultrasoft pseudopotentials in reciprocal space was adopted and exchange-correlation potential was parametrized by the Perdew–Burke–Ernzerhof scheme (PBE) [41]. A cubic 64-atom supercell was used and all atoms in the supercell were allowed to move freely during the geometry optimization. Using periodic boundary, a plane-wave cutoff energy of 310 eV was employed. It has been shown that the results were well converged at this cutoff energy. The calculations were performed using the Monkhorst-Pack scheme for sampling in the Brillouin zone with a mesh of $4 \times 4 \times 4$ special k points [42].

3. Results and discussion

3.1. Interstitial defect atom X_i

Interstitial defect atom X_i (X represents Be or Mg) was placed at various initial sites including tetrahedral interstitial (T_d) site. All atoms were allowed to move freely until the energy was minimized and the optimized structure is shown in Fig. 1. After geometry optimization, we find that the equilibrium location of X_i is the T_d site. For the defect Be_i with T_d symmetry displayed in Fig. 1(a), the optimal bond length of Be_i–C is 1.67 Å and the bond angle of C–Be_i–C is 109.47°. For Mg_i with T_d symmetry shown in Fig. 1(b), the Mg_i–C bond length and the C–Mg_i–C bond angle are 1.75 Å and 109.47°, respectively.

Figs. 2(a) and (b) show the calculated band structures of the diamond doped with Be_i and Mg_i, respectively. For the sake of the completeness and comparison purposes, the band structure of pure diamond (as seen in Fig. 2(c)) is also shown as a reference. In Fig. 2(a) for the diamond doped with Be_i, it can be seen that the Be_i introduces donor states mixing with the conduction band (CB) and the Fermi level E_F lies in the CB, which means the Be_i-doped diamond is of n-type metal conductivity character. The band structure of Mg_i-doped diamond is displayed in Fig. 2(b). Similar as Be_i doping, the introduced Mg_i-related impurity states also locate near and overlap with the CB. The Fermi level is pinned in the conduction band, which presents that the diamond doped with Mg_i is of good n-type conductivity behaviors.

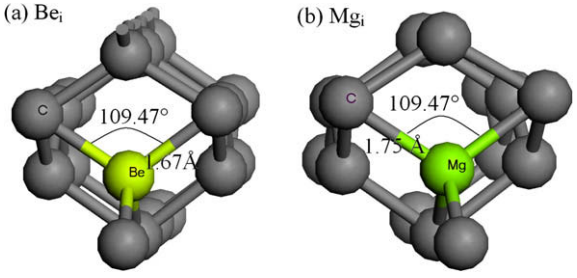

Fig. 1. Optimized structures for diamond doped with (a) interstitial dopants Be_i and (b) Mg_i.

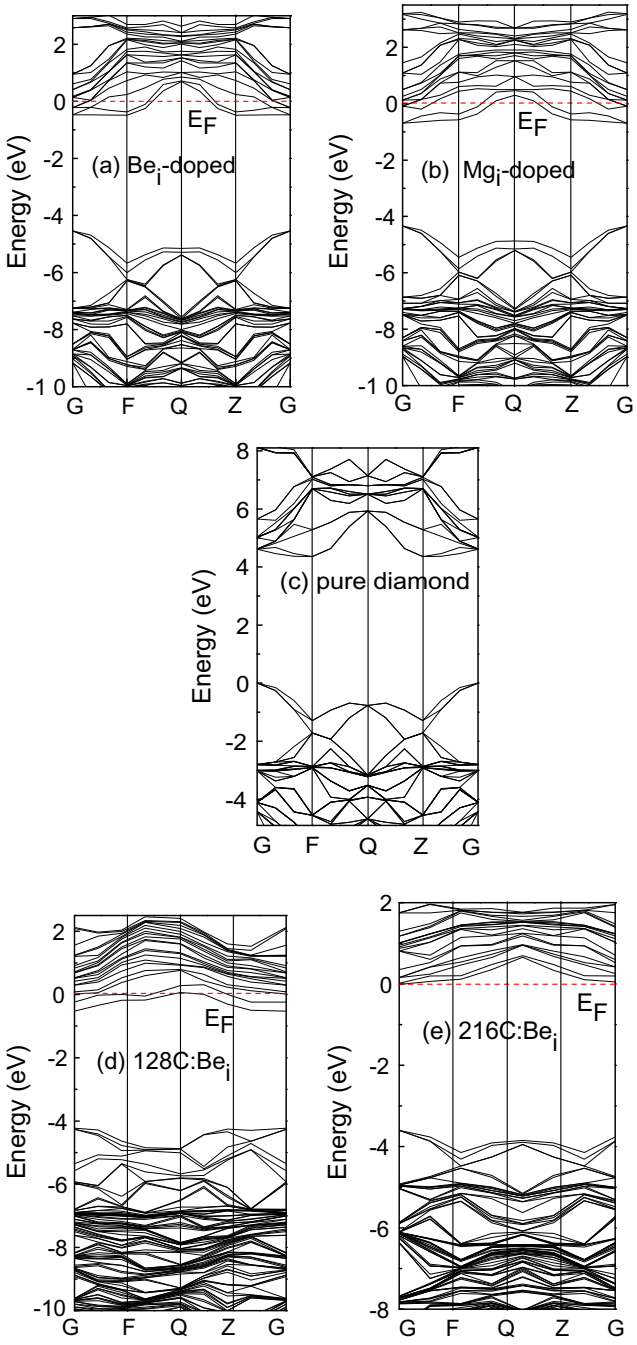

Fig. 2. The band structures of diamond with (a) Be_i doping, (b) Mg_i doping, (c) pure, (d) Be_i doping consisting of 128 C atoms and (e) Be_i doping consisting of 216 C atoms. The dot line represents the Fermi level E_F.

To investigate the influence of Be_i and Mg_i doping concentration on the electronic properties of diamond, the geometry and electronic properties of the doped diamond consisting of 128 and 216 C atoms have been studied by the method mentioned above. Considering the similar electronic properties of Be_i with Mg_i, we only describe the electronic properties of Be_i in 128- and 216-C supercells in detail. The optimized structures of the Be_i-doped dia-