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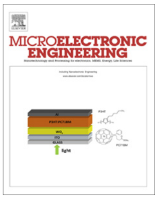

Electronic structure calculations of oxygen-doped diamond using DFT technique

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In this study, equilibrium geometry and band structure of oxygen-doped diamond have been investigated based on density function theory (DFT) using VASP code. These calculations have shown that the highest occupied molecular orbital is localized at the oxygen atom. Moreover, C_4—O bond lengths are equivalent to those of C—C bonds leading to no lattice distortions. Doping of oxygen into diamond seems to be thermodynamically favorable due to negative formation energy. Band structure calculations lead to the semiconducting behavior of oxygen-doped diamonds due to the creation of defects states inside the band gap extending to conduction band minimum. The spin projected density of states calculations illustrates significant contributions of O *2p* states at the Fermi level without the appearance of appreciable magnetic moments on oxygen or on carbon atoms (for all C_1–C_4) leading to its non-magnetic semi-conducting behavior with zero density of carriers at the Fermi level for both spin projections; $O{\downarrow}{\uparrow}(E_F) = 0$. Present DFT results verify our experimental findings that addition of oxygen into diamond lattice increases its conductivity so that oxygen-doped diamond films behave like a good semiconductor.

1. Introduction

Diamond is a kind of nonmetal material with unique physical and chemical properties. It is potentially useful for various applications in electronics, such as electron emitters, Schottky diodes [1,2]. It does not show any magnetism. However, various recent studies indicate that defects in carbon (diamond) lead to magnetization [3–7] that make it promising material in the field of spintronics [8,9]. In addition, its high thermal conductivity and possibility of appropriate doping can enhance its field of applications. Also the electronic quality of doped-diamond largely depends on the nature and number of its native defects and impurities. The p-type diamond thin films can easily be obtained by boron doping [10,11]. However, n-type diamond is more difficult to obtain [12,13] and its development is crucial for electronic applications. It is known that nitrogen as a simple substitutional defect forms deep level at 1.9 eV [14] below the conduction band edge while boron produces a shallower level at 0.365 eV above the valence band edge [15,16]. Moreover, none of such defects (B or N) create levels suitably located near the bulk band edges due to which diamond can show potential as an efficient electronic semiconductor. This is why properties of a variety of other chemical defects in diamond have also been investigated [17].

Such defect calculations on diamond [18] and many other materials [19] have shown that defect energy level is very much dependent upon the location of Fermi energy in the host material. Unlike the case for several semiconductors, a precise location of Fermi level in diamond is difficult to engineer. In type-IIb diamond, Fermi level is located near the valence band edge due to the presence of B so that it can be regarded as p-type. For type-I diamond, which contains N, Fermi level lies closer to the conduction band, but N as a simple point defect is quite deep so that it is not a feasible defect to use for n-type conductivity.

In the last decade a first-principles study has been carried out to evaluate the electronic and magnetic properties of diamond doped with halogens (F, Cl, Br, I) [20] based on density functional theory (DFT). They have shown that F defect acts as an acceptor in diamond, but other dopants Cl, Br and I show donor behavior in diamond. To achieve n-type diamond the dopant I, is considered the best donor. However, the research work on magnetic properties of oxygen doped diamond is quite few. Theoretical modeling of oxygen in diamond has remained a challenge for the computational field because of its chemical character.

Recently, we have studied electronic properties of transition metals (TMs) such as Cu, Cd, Hg and Zn doped diamond using DFT calculations [21], which show spin polarization of TMs

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dopants on substitution into diamond by the magnetization of *p* electrons of the four neighboring carbon atoms through *p–d* hybridization. This *p–d* hybridization is noticed to be very strong for Cu-doping as compared to other TMs dopants because Cu-doped diamond has shown higher magnetic moments. Moreover, this *p–d* hybridization prefers ferromagnetic (FM) coupling state among all dopants rather than that of antiferromagnetic (AFM) coupling. In our recent article on DFT calculations of B-doped diamond [22], we have shown that B-doping in diamond creates impurity states/bands at or near Fermi level leading to its semiconducting to metallic behavior. In continuation of our DFT calculations, theoretical modeling of oxygen in diamond has been performed to meet the challenge for the computational field.

In this research work, we shall investigate the electronic and magnetic properties of a simple substitutional oxygen atom in the diamond lattice using DFT based on the generalized-gradient-approximation (GGA) method. Moreover, using these DFT calculations, the lattice distortion and depth of donor levels of the oxygen-doped diamond will be studied and compared with those given in literature.

2. Computational methods and modeling

The structural, electronic and magnetic properties of oxygen (O)-doped nano-diamond films at concentrations of 1.56% are studied using super cell of 2 × 2 × 2 on substituting carbon atom by a neutral oxygen-atom in the second layer as C_4–O structure after optimization. Other types of defects associated with dopants are not considered because they are strongly unfavorable as compared to the substitution. Moreover, the most favorable position for oxygen atom on a (100) plane is the bridge (C–O–C) position as compared to that of on-top because its highest occupied level is significantly lower in energy than that of the same level in other situation throughout the Brillouin zone [23–25]. All calculations are carried out within plane–wave density functional theory by employing the Vienna *ab initio* simulation package (VASP) [26,27]. The generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) functional scheme is used for the exchange correlation potential. The projector augmented wave (PAW) potential is selected to represent the interaction between valance and core electrons in all these DFT calculations [28–30]. The convergence tests of total energy with respect to electron wavefunction expanded using plane–waves with a cut off energy of 400 eV have been examined. The ionic position, cell volume and lattice parameters of the system are fully relaxed with conjugate gradient method until Hellmann–Feynman forces are smaller than 0.02 eV/Å and energy convergence criteria is fulfilled at 1×10^{-5} eV. A popular scheme for *k*-point sampling is Monkhorst Pack (MP) [31,32]. The MP grid is chosen to be 6 × 6 × 6 for total energy and magnetic property calculations of oxygen-doped diamonds. All such calculations were performed for diamond structure incorporating oxygen atom not for pure diamond.

3. Structural optimization

A model structure of oxygen-doped diamond shown in Fig. 1 is constructed using a 64-atoms 2 × 2 × 2 supercell of diamond containing 1 O and 63 C atoms. Fig. 1 illustrates that dopant oxygen replaces C atom to form a substitutional defect. All atoms in the supercell are allowed to move freely and also to change the position of oxygen atom in the second as well as in the third layer in order to minimize the energy and hence to achieve a stable and the most probable configuration. Results presented here have been obtained for the optimized structure with minimum global. The optimized C—O bond lengths (1.54 Å) for substituted oxygen atom having bond angles of 109.47° are also shown in Fig. 1. It is also obvious from this figure that equilibrium lengths of all the C—O bonds are the same. It means equilibrium configuration of oxygen becomes C_4–O, which is slightly different from that illustrated by Zhou et al. [33]. In general it is known that the highest occupied molecular orbital is localized at the substituted atom; on the other hand, a node is usually created in the longer bond. Due to equivalent bond lengths, no such nodes are noticed and all C—O bonds are equally stronger. Moreover, it is noticed that the C_4—O bond lengths are almost the same as observed for C—C bond lengths in diamond lattice (1.54 Å [34]). As a result no lattice distortions are seen in the oxygen-doped diamond.

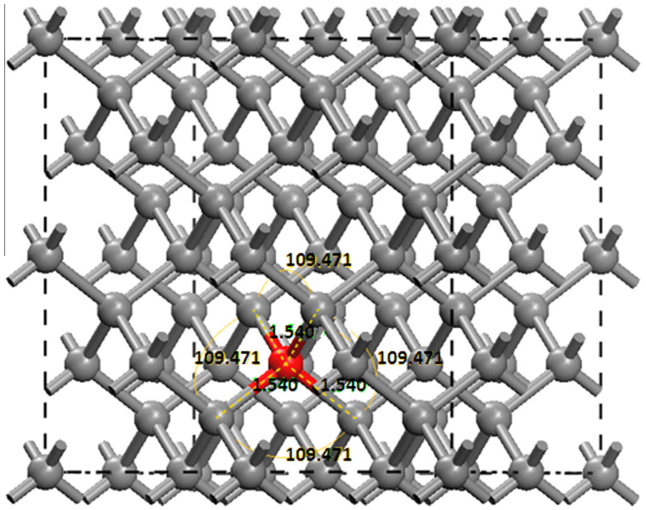

Fig. 1. Optimized structure of oxygen-doped diamond showing equilibrium geometry of carbon–oxygen bonds around the substituted atom (unit: Å).

3.1. Formation energy of oxygen defect

Energy required to form an oxygen substitutional site termed as formation energy ($\boldsymbol{E_f}$) in diamond is defined as [20]:

$$\boldsymbol{E_f} = \boldsymbol{E_{tot}} - \boldsymbol{E^{O}_{tot}} + \boldsymbol{n_{+}}\boldsymbol{\mu_C} - \boldsymbol{\mu_O} \qquad (1)$$

where $\boldsymbol{E_{tot}}$(−581 eV) is the total energy of diamond containing an oxygen defect, $\boldsymbol{E^{O}_{tot}}$(−572 eV), the total energy of diamond lattice, $\boldsymbol{n_{+}}$(=1), the number of oxygen atoms substituted into diamond lattice, $\boldsymbol{\mu_C}$(−156.22 eV [35]) and $\boldsymbol{\mu_O}$ are respective chemical potentials of diamond and oxygen ($\boldsymbol{\mu_O} = \frac{1}{2}\boldsymbol{\mu_{O_2}} = 0$) [20]. The oxygen-doping in diamond is found to be thermodynamically favorable because of the negative formation energy. This result is in good agreement with that of Riedel et al. [36]. A remarkable fact responsible for a shift in energy bands is the electronegativity which leads to polarization. Thus when diamond is doped by an impurity such as oxygen, $C^{\delta+}$–$O^{\delta-}$ dipole may be formed due to a difference of electronegativities [37] between C(2.55) and O(3.44) atoms. This causes polarization of C—O bond. Due to its higher electronegativity (3.44), oxygen atom carries negative charge received from C-atoms since electrons can easily transfer from C to O atoms [25]. This is why, the C—O bond is polarized towards O atom. This behavior causes a systematic shift in the energy bands, which is responsible for any change in the electronic properties of oxygen-doped diamond.

3.2. Band structure

Band structures (BSs) of oxygen-doped diamond films have been determined to elaborate their electronic properties. Fig. 2