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# Oxygen-doped c-BN(110) surface: DFT calculations

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**Abstract.** Density functional theory calculations have been performed to investigate the structural and electronic properties for both unrelaxed and relaxed cases of oxygen-doped c-BN(110) surface. Oxygen atom has been substituted in a neutral charge state on both the B site ($O_B$) and the N site ($O_N$). Defect formation energies, [unrelaxed ($E_f^o$) and relaxed ($E_f$)], and relaxation energies, $E_r$, have been calculated. It has been found that substitution $O_N$ is more probable, moreover the $O_N$ causes an inward relaxation of the first neighbor surface B atom.

## 1. Introduction

In recent years, the physical and chemical property of boron nitride (BN), as one of the III-V nitride compounds, have been studied both theoretically and experimentally [1-14]. This is mainly because of its attracting properties, such as its extreme hardness, high melting point, low dielectric constant. In general, wide-band-gap semiconductors can be doped either n-type or p-type, but not both. However, as one of the widest band-gap III-V compound, c-BN can be easily doped to obtain both n-type and p-type conductivities [15-16]. The cubic phase of BN (c-BN) is similar to diamond with outstanding physical and chemical properties. It can be used for metalworking tools and other wear applications due to its inertness. In addition, its high thermal conductivity and the possibility of appropriate doping make it a potential material for applications. Silva et al. have shown that an isolated Mn substitutional impurity in a c-BN matrix may be used as a memory storage media [17].

A real semiconductor invariably has either some defects due to heat treatment or impurities during the crystal growth process. The electronic quality of a semiconductor is largely determined by the nature and number of its native defects and impurities. In the last decade a significant amount of carbon and oxygen impurities have been detected in c-BN thin films by X-ray photoelectron spectroscopy [18] showing that the two impurities are common contaminants. The theoretical modeling of oxygen in semiconductor materials has remained a challenge for the computational field because of its chemical character. The oxygen atom (O) is a common substitutional impurity in both AlN and GaN crystals [19]. Ab initio study of oxygen point defects in GaAs, GaN and AlN is reported that the calculations demonstrate a qualitatively different behavior of oxygen impurities in these materials [20]. Silva et al. [21] have investigated the electronic and structural properties of oxygen-doped BN nanotubes. The energetics of carbon and oxygen impurities and their interaction with vacancies in c-BN were studied by Orellana et al. [22]. Using DFT method, the atomic and electronic of single-walled BN nanotubes containing N vacancies as well as C and O substituted of N atoms are studied by Zhukovskii et al. [23].

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In this paper, we report the results of theoretical studies on the influence of O impurity on the surface structure and energetics of c-BN(110) surface by using DFT calculations.

## 2. Method of Calculation

The cubic boron nitride (110) surface is stoichiometric, with one B atom for every N atom. The c-BN(110) surface is generated from a bulk-like termination. The experimental bulk lattice parameter value (3.615 Å [24]) has been used as starting geometry. The odd number of atomic planes in the (110) slab is considered to take advantage of the reflection symmetry about the central plane. 9-layer thick of the 2×2 slab of the c-BN(110) surface contains 8 atoms per plane, four B atoms and four N atoms to give 72 atoms in the working cell of the slab.

The calculations are performed by using CRYSTAL03 package program [25], in which density-functional theory (DFT) type of calculation is implemented. CRYSTAL03 uses localized Gaussian-type basis sets: 6-21$G^*$ basis set has been used for B, N atoms, 8-411d11 [26] has been used for O atom. CRYSTAL03 computes the matrix elements of the coulomb and exchange terms by direct summation of infinite periodic lattice. The reciprocal space integration has been performed by sampling the Brillouin zone of the unit cell with the 4×4×1 the Monkhorst-Pack net [27] that provides, the balanced summation in direct and reciprocal space [28]. The calculations have been realized by using the B3LYP exchange–correlation hybrid functional and 4×8×1 grid of 25 k-points. The numerical thresholds used to ensure the numerical convergence of the self-consistent-field procedure are set to $10^{-9}$ a.u. for one electron eigenvalues and $10^{-7}$ a.u. for the total energy.

In the present work, we investigate the energetics and structural properties of substitutional single oxygen atom impurity in a neutral charge state on both the B site ($O_B$) and N site ($O_N$) of c-BN(110) surface by using DFT calculations. In particular, we calculate the formation [unrelaxed ($E_f^o$), and relaxed ($E_f$)] and the relaxation ($E_r$) energies of a single defect X ( $O_B$ or $O_N$ substitutes) on the (110) surface of c-BN. Cation and anion formation energies, $E_f(X)$, have been calculated using the equation

$$E_f(X) = E_d + E(B\ or\ N) - E_p - E(X) \tag{1}$$

where $E_d$ is the energy of the defective system, $E_p$ is the energy of the perfect system and $E(B)$ or $E(N)$ is the energy of the isolated boron or nitrogen atom, whereas E(X) is the total energy for an isolated defect. The relaxation energies ($E_r$) for $O_B$ and $O_N$ have been calculated. All calculations in the present work have been performed on 72-atom supercells. The total energy of the defective supercell has been optimized with respect to the position of the impurity atom and of its first neighbors. The relaxation of farther neighbors has not been considered here.

## 3. Results and Discussion

The obtained structural data are compared with the available theoretical values [29-33] in Table 1. For neutral $O_N$, it has been found an inward relaxation of the first-neighbor surface B atom of about 2.70% with respect to the unrelaxed positions. It has been also calculated that, for $O_B$, the distance from the impurity to its first-neighbor (N) atom is found to be 10.86% larger than in the unrelaxed system.

The formation energies $E_f$ and $E_f^o$ for both $O_N$ and $O_B$ impurities, are given in Table 2. The formation energies are relatively higher in the $O_B$ replacement with respect to $O_N$, indicating a greater probability for the oxygen to replace the nitrogen atom than the boron atom. The higher values of formation energies in the $O_B$ substitution also indicates the low probability of finding neutral B defects on the c-BN(110) surface. The relaxation energies, $E_r$, for $O_N$ and $O_B$ impurities have been also calculated from the difference between the relaxed and the unrelaxed systems, which are presented in Table 2. We hope that the present results will be useful for the

researchers working in this field.

**Table 1.** Comparison of interatomic distances (in Å ) on the relaxed c-BN (110) surface. Bulk lattice constant ($a_0$), B-N bond length in bulk ($d_b$), B-N bond length in surface layer ($d_s$), and bond length between surface B atom and subsurface N atom ($d_{BN}$). Last four lines give the bond lengths $d(C_X)$, $d(O_X)$ of subtituted $C_B$, $C_N$ and $O_B$, $O_N$ atoms.

| Quantity | Ref[29] | Ref[30] | Ref[31] | Ref[32] | Ref[33] | This work |
|---|---|---|---|---|---|---|
| $a_0$ | 3.605 | 3.600 | 3.623 | 3.615 | — | — |
| $d_b$ | 1.561 | 1.560 | 1.569 | 1.565 | — | — |
| $d_s$ | 1.545 | 1.440 | 1.455 | 1.457 | — | — |
| $d_s/d_b$ | 0.990 | 0.920 | 0.920 | 0.930 | — | — |
| $d_{BN}$ | — | — | 1.561 | 1.515 | — | — |
| $d(C_B)$ | — | — | — | — | 1.437 | — |
| $d(C_N)$ | — | — | — | — | 1.510 | — |
| $d(O_B)$ | — | — | — | — | — | 1.522 |
| $d(O_N)$ | — | — | — | — | — | 1.735 |

**Table 2.** Defect formation (relaxed $E_f$, un-relaxed $E_f^o$) and relaxation ($E_r$) energies (in eV) of c-BN(110) surface.

| $Defect$ | $E_f$ | $E_f^o$ | $E_r$ |
|---|---|---|---|
| $O_N$ | 5.262 | -1.670 | 2.386 |
| $O_B$ | 19.641 | 12.220 | 1.899 |

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