Effect of point defects and functionalization on structural stability and electron properties of borophene as investigated by means of density functional theory

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Abstract. The discovery of a new two dimensional material is a new trend emerged after the discovery of graphene in 2004. Hundreds of new materials have been predicted, designed and investigated during last decade. Many of them have outstanding properties for potential application in new technologies. One of those materials is so-called borophene, being isolated atomically thin boron. This material can show different electronic properties, including semiconducting, semi-metallic, and metallic states due to its unique structure. Borophene demonstrates unusually high in-plane elasticity and strength. The crucial point for application of borophene is its low structural stability at room temperature. A possible way to solve this problem is the functionalization of its surface by external atoms like hydrogen and fluorine. This work presents a study on the effect of O dopants and the presence of vacancy defects on electronic properties of borophene by using first-principles calculations. It was revealed that unlike other 2D materials, the band structure of borophene is stable by respect to the above-mentioned factors. However, the doping by O atoms is found as an effective way to increase the stability of the borophene sheet.

1. Introduction
The active development of studies on new two dimensional materials emerged by the discovery of graphene in 2004 has been inspired by an outstanding set of properties, explained by their reduced dimension. Unusual features are revealed both in the mechanical behavior [1–7], physical properties [5,8–13] and in the nonlinear dynamics [14–16] of such materials. Recently, a two-dimensional boron named borophene has been obtained upon deposition of boron atoms on (111) Ag substrate. This material has attracted great interest due to its unique properties [17,18]. The possibility of the existence of various phases depending on the processing conditions, such as the deposition rate and processing temperature, indicates a large polymorphism of borophene. It was predicted that borophene has anisotropic metallic properties [7,19]. In addition, borophene exhibits extraordinary mechanical properties, for example, its Young's modulus (398 GPa·nm) exceeds that for most known two-dimensional materials [17]. All these features characterize borophene as a promising material for use in nanoelectronics.

The main obstacle in the study of borophene is its low structural stability. It was proposed to solve this problem by functionalizing the surface of borophene, which allows one to stabilize its structure and
also contributes to a change in its electronic properties [17]. For example, it was predicted that the structure of borophene can be stabilized by hydrogen atoms [20]. However, detailed studies of the functionalization of the surface of a two-dimensional borophene sheet by oxygen atoms were not mentioned in literature reviews.

In addition, it is well known that the structural persistence and electronic properties of two-dimensional materials significantly depend on the presence of vacancies in them. For example, lattice defects can easily arise instability of atomically thin two-dimensional materials [6]. Although there is a fairly large number of studies on defects in various two-dimensional materials, defects in borophene have not yet been considered.

Considering the abovementioned facts, the purpose of the present work was to estimate the influence of oxygen functionalization (O-functionalization) and point defects on the structural stability and electronic properties of borophene.

2. Simulation details

The studies were carried out by means of the density functional theory. First-principle calculations were performed using the VASP software package [21]. The exchange – correlation interaction was specified by the generalized GGA gradient approximation using the Perdew–Burke–Ernzerhof (PBE) function [22]. Summation over the Brillouin zone using a 10×10×1 wave vector lattice was performed for structure relaxation and calculation of the electronic structure of the borophene sheet. The maximum effect of functionalization while maintaining the stability of the structure, corresponded to the 50% concentration of O atoms. Periodic boundary conditions were applied in two transverse directions in the plane of the borophene nanosheet under investigation, and free boundary conditions were applied along the direction perpendicular to the plane of the 2D structure by creating a vacuum space of 15 Å.

3. Results

3.1. Structure and electronic properties of pure and O-functionalized borophene

In figure 1a, b optimized structures of pure and O-functionalized borophene sheets are shown, respectively. For a pure borophene sheet, the optimized lattice parameters are \(a = 1.618\) Å and \(b = 2.864\) Å, which is in good correspondence with previously published results [19]. For O-functionalized borophene, the optimized Γ lattice parameters were found to be \(a = 3.324\) Å and \(b = 5.558\) Å respectively.

Figure 1c,d shows the electronic structure of pure and O-functionalized borophene sheets, respectively. According to figure 1c, borophene bands cross the Fermi level along the Γ–X and S–Y directions, which indicate the metallic nature of pure borophene. These results are in good agreement with previous studies [19]. For O-functionalized borophene (figure 1d), there is no gap in the phonon spectrum, thus, O-functionalized borophene retains its metallic nature.

Next, we examined the structural stability of pure (equation (1)) and O-functionalized (equation (2)) borophene by calculating the average binding energy \(E_b\)

\[
E_b = (n_B E_B - E_{tot})/n, \quad (1)
\]

\[
E_b = (n_B E_B + n_O E_O - E_{tot})/n, \quad (2)
\]

where \(E_{tot}\) is the total energy of the system, \(E_B\) is the energy of one boron atom, \(E_X\) is the energy of one oxygen atom, \(n_B\) is the total number of boron atoms, \(n_O\) is the total number of oxygen atoms, and \(n\) is the total number of atoms in the system. The calculated \(E_b\) values for pure and O-functionalized borophene are 5.86 and 5.32 eV, respectively. Therefore, the functionalization of borophene by oxygen enhances its structural stability.
Figure 1. Atomic configurations of (a) pure and (b) O-functionalized borophene sheet; electronic structure of (c) pure and (d) O-functionalized borophene sheet. The black dashed line corresponds to the Fermi level. The red lines indicate the oxygen induced bands.

The work functions of all the considered structures were calculated as the difference between the electrostatic potential and the Fermi energy [14, 15]. Figure 2e shows the work function of pure and O-functionalized borophene sheets in comparison with that of other materials. From the presented results it follows that the work function of a pure borophene sheet (-5.31 eV) is higher than that of graphene (-4.50 eV) [16]. It is also important to note that the O-functionalization of the borophene surface contributes to a significant decrease in the work function up to -9.46 eV. Thus, the O-functionalization of borophene sheet is an effective way to change the work function of borophene allowing to control its contact resistance.

3.2. The effect of vacancy defects on the electronic structure of borophene
An important point is the estimation of the effect of vacancy defects on the electronic structure of two-dimensional materials and, in particular, borophene. In this paper, various vacancy defects in borophene were considered: monovacancy (figure 2b) and two possible bivacancies (figure 2c, d). An analysis of electronic structure of borophene sheets containing vacancy defects revealed a significant overlap and cross of the Fermi level, mainly due to pz orbitals of boron atoms. Thus, the electronic structure of borophene practically does not change both with the appearance of vacancy defects on its surface and with its O-functionalization, which is a hallmark of borophene compared to other two-dimensional materials [13].

Figure 2. Atomic structures of (a) pure, containing (b) monovacancy, (c) bivacancy (100) and (d) bivacancy (110) of borophene sheets; graph comparing the work functions of various materials. Black markers indicate the work function of pure and O-functionalized borophene sheets, while red markers indicate the work function of other materials (values taken from [23]).

4. Discussion of results and conclusions
The first-principle calculations were used to study the effect of surface O-functionalization and presence of point defects of a borophene sheet on its properties, such as structural stability, electronic structure, and work function. It was found that, unlike many other two-dimensional materials, borophene is inert to the influence of impurity atoms and vacancies and retain metallic type of conduction. Nevertheless, O-functionalization of the borophene surface sheet can be used as an effective way to control the work
function of borophene, which is significantly reduced from -5.31 eV (for the pure borophene sheet) to -9.46 eV (for O-functionalized borophene). Thus, the present work contributes significantly to understanding of the effect of O-functionalization and vacancies on the stability and electronic structure of borophene.

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