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Electronic structure and STM images simulation of defects on hBN/black-phosphorene heterostructures: A theoretical study

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ABSTRACT

By first principles calculations which include van der Waals interactions, we studied the electronic structure of hexagonal boron-nitride/black-phosphorene heterostructures (hBN/BP). In particular the role of several kind of defects on the electronic properties of black-phosphorene monolayer and hBN/BP heterostructure was analyzed. The defects under consideration were single and double vacancies, as well Stone-Wale type defects, all of them present in the phosphorene layer. In this way, we found that the electronic structure of the hBN/BP is modified according the type of defect that is introduced. As a remarkable feature, our results show occupied states at the Fermi Level introduced by a single vacancy in the energy gap of the hBN/BP heterostructure. Additionally, we performed simulations of scanning tunneling microscopy images. These simulations show that is possible to discriminate the kind of defect even when the black-phosphorene monolayer is part of the heterostructure hBN/BP. Our results may help to discriminate among several kind of defects during experimental characterization of these novel materials.

1. Introduction

Among two-dimensional (2D) materials, the most widely studied to date has been graphene [1], a stable monolayer of graphite. However, another atomically thin materials have started to attract scientific interest. Monolayer of transition metal dichalcogenides (TMDC) [2] and hexagonal boron nitride (hBN) [3] are good examples of this tendency, while the recently discoveries of silicene [4], stanene [5], and phosphorene [6], have enlarged the family of 2D materials and widening the scientific and technological interest on them. An exciting and common feature for all the 2D materials is that they can be bonded together by van der Waals (vdW) forces [7]. This feature allows building heterostructures, which are stacks of different 2D materials, and has opened the way for innovative technological applications [8–10], particularly in the field of electronics [11,12]. For example, heterostructures formed by graphene and hBN have shown remarkable electrical properties [13–15], while $MoSe_2/WS_2$ heterostructures have been proposed to enable novel approaches to energy harvesting and optical conversion [16].

In this context the heterostructures based on phosphorene have shown interesting technological projections [17,18]. For example, Cai et al. [17] have shown that a graphene or a hBN layer can be used to protect phosphorene from structural and mechanical degradation without modifying its direct band gap and high carrier mobility [19]. In the same way, Sun et al. [18] have reported that a sandwiched phosphorene-graphene hybrid material shows high specific capacity and extended cycle life as an anode material in sodium-ion batteries. More recently, Wang et al. [20] have investigated the effect of different vacancies on hBN layer of hBN/ black-phosphorene (hBN/BP) heterostructures, showing that the intrinsic defect boron monovacancy in the hBN sheet can magnetize the system. Nevertheless, to advance to practical implementations it is also necessary to understand the role played by defects in such heterostructures, specially because defects are easily created in phosphorene, while some of them can introduce important modifications to the corresponding electronic structure [21].

These facts have motivated us to apply ab-initio methods to obtain the electronic structure for hBN/BP heterostructures presenting defects in the black-phosphorene layer. With this aim, we have organized this paper as follows: in Section 2 we introduce the heterostructure and the defects under study, as well the details of the theoretical calculations. The results for the electronic structure corresponding to different defects are given in Section 3, while Section 4 is devoted to present and analyze

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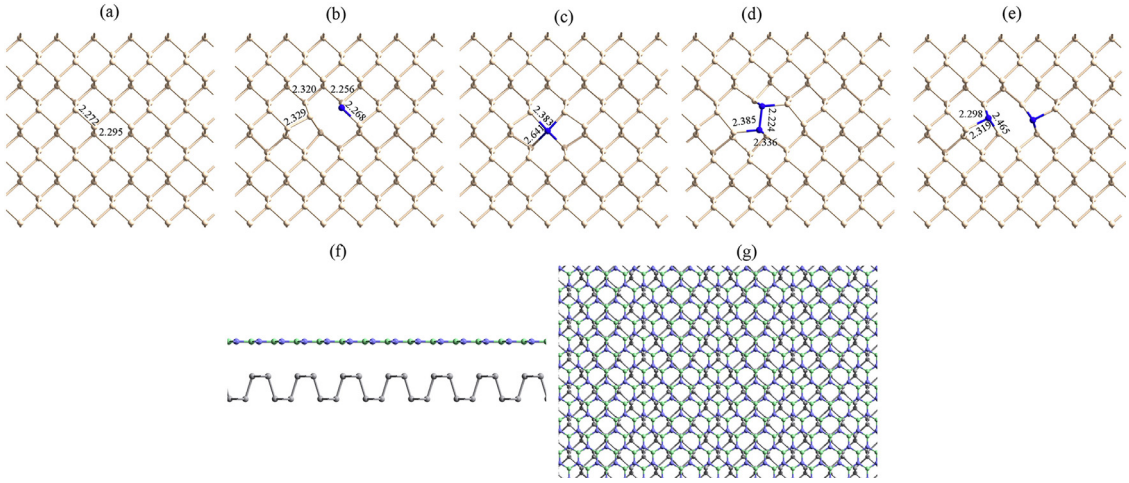

Fig. 1. Geometric structure of pristine phosphorene (a) and phosphorene presenting defects of type: (b) SV-(5|9), (c) SV-(55|66), (d) SW-2 and (e) DV-(5|8|5)-1. Geometric structure of the hBN/BP heterostructure: lateral (f) and upper (g) views. Interatomic distances after relaxation are indicated (in Å) for some selected bonds. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

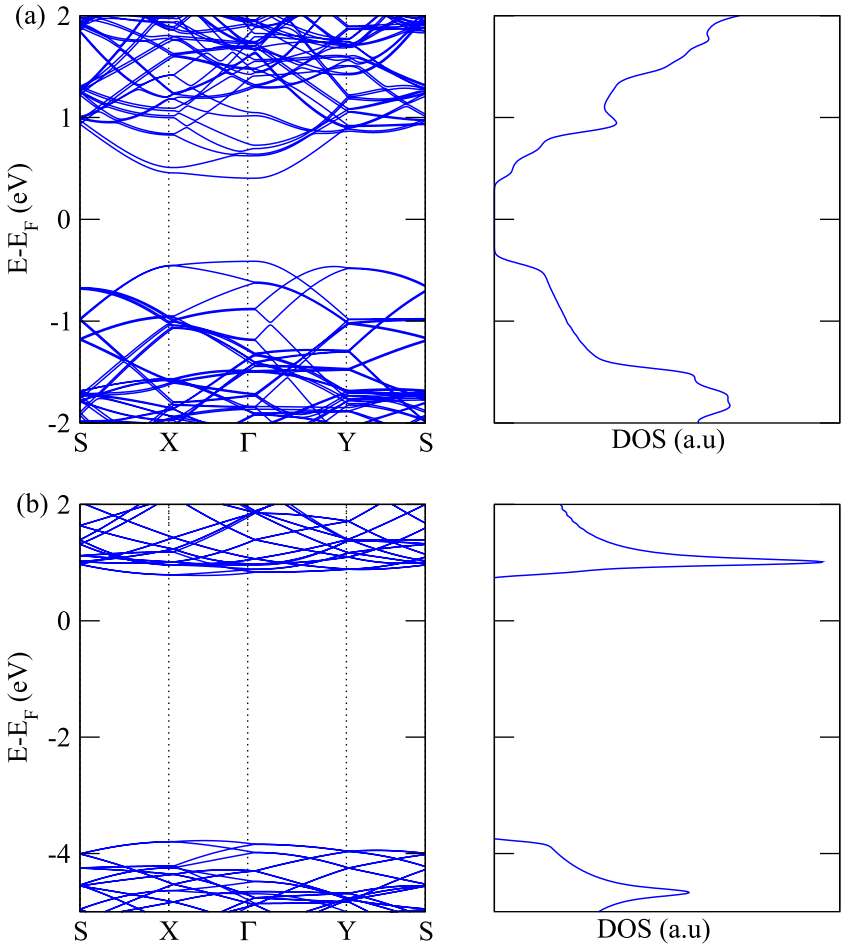

Fig. 2. Electronic band structure and density of states for (a) pristine phosphorene and (b) pristine hBN supercells. Fermi Level is set to 0 eV.

theoretical scanning tunneling microscope (STM) images of different defects on hBN/BP. Finally, Section 5 contains the main conclusions and comments.

2. Calculation method

To present the general geometry of the main system under study, the hBN/BP heterostructure, it is illustrative to introduce a pristine black-phosphorene monolayer, which is formed by phosphorus atoms arranged in two planes [6]. Fig. 1(a) presents an upper view of a black-phosphorene monolayer, which can be bonded with a flat hexagonal boron nitride (hBN) layer by vdW interactions to form the hNB/BP heterostructure [see Fig. 1(f) and (g)].

We have focused in defects introduced in the black-phosphorene monolayer of the hBN/BP heterostructure. In this context, it was possi-