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Full Length Article

Alkali (Li, K and Na) and alkali-earth (Be, Ca and Mg) adatoms on SiC single layer

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ABSTRACT

First-principles calculations within the density functional theory (DFT) have been addressed to study the energetic stability, and electronic properties of alkali and alkali-earth atoms adsorbed on a silicon carbide (SiC) single layer. We observe that all atoms are most stable (higher binding energy) on the top of a Si atom, which moves out of the plane (in the opposite direction to the adsorbed atom). Alkali atoms adsorbed give raise to two spin unpaired electronic levels inside the band gap leading the SiC single layer to exhibit n-type semiconductor properties. For alkaline atoms adsorbed there is a deep occupied spin paired electronic level inside the band gap. These finding suggest that the adsorption of alkaline and alkali-earth atoms on SiC layer is a powerful feature to functionalize two dimensional SiC structures, which can be used to produce new electronic, magnetic and optical devices as well for hydrogen and oxygen evolution reaction (HER and OER, respectively). Furthermore, we observe that the adsorption of H_2 is ruled by dispersive forces (van der Waals interactions) while the O_2 molecule is strongly adsorbed on the functionalized system.

1. Introduction

When silicon and carbon are arranged in the 1:1 stoichiometry they form silicon carbide (SiC). It compound crystalizes in many different phases: α hexagonal (2H-SiC, 4H-SiC and 6H-SiC), β cubic (3C-SiC), etc. In all the phases it is a stable and large band gap semiconductor (2.4–3.2 eV) and the cubic phase show many stable surface reconstructions [1,2], being appropriate to be used as substrate to grow graphene [3–5]. Due to the difference in the electronegativity between Si and C charges, SiC is an ionic semiconductor (charges are transferred from Si to C) and the Si—C bonds are strong with a mixture between ionic and covalent character. SiC exhibits interesting properties like low weight, extreme hardness, stable in high temperature and power. These properties leads SiC an useful material to be used in the manufacture of devices working at high temperature, high voltage and high frequency [5–7]. The hydrogenation of a C-rich SiC surface induces the presence of stable tubular (nanotunnels) in the surface [8].

Carbon and others group IV elements like Si, Ge and Sn can be arranged in a hexagonal honeycomb lattice and form one and two-dimensional (2D) structures. The combination of C and Si in the 1:1 stoichiometry maximizes the number of Si—C bonds leading SiC to form one and two-dimensional structures very similar to carbon nanotubes and graphene where the sp^2 hybridization predominates [9–12]. These SiC structures are nonmagnetic semiconductors with large band gap being appropriate for nanodevices in harsh environment.

Doped nanostructures can exhibit different properties compared to their pristine forms. Chemical doping by adsorption of atoms and molecules is a powerful feature to modify the 2D structures, leading the doped nanostructures with new electronic, optical and magnetic properties. The doped process opens the possibility of using the functionalized planar structure in many applications, such as charge transport, gas sensor, spintronics and hydrogen storage. The adsorption of alkaline and earth-alkaline metal atoms in planar structures such as graphene, silicene, germanene, stanene, phosphorene, and boron nitride has been recently studied [13–21]. It was observed that these planar structures exhibit new electronic properties after the metal adsorption.

In order to investigate the stability (binding energies), electronic, optical and magnetic properties when alkaline and earth-alkaline metal atoms adsorb on a SiC single layer, we use first principles calculations within the spin polarized density functional theory (SP-DFT) to analyze the interaction between these atoms and a planar SiC nanostructure. Our results show that these atoms strongly and preferentially adsorb on top of a silicon atom, which

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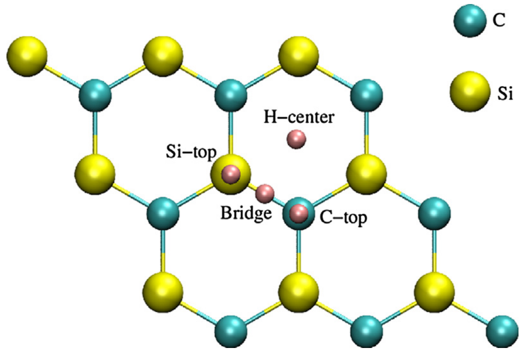

Fig. 1. The supercell used to simulate the adsorption of a metal atom (small pink ball) on the SiC monolayer. The C and Si atoms are illustrated with small (cyan) and big (yellow) spheres. In the supercell are illustrated the four possible sites (h-center, Si-top, C-top and bridge) for the metal atom adsorption (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

moves out of the SiC plane. For all the functionalized structures, there are new electronic levels inside the band gap. In addition, we investigate the possibility to use the functionalized SiC single layers for water splitting by calculated the free energy diagrams and HER and OER evolution process. We observe that the O_2 molecule strong bonds with the doped system while the H_2 molecule interacts through dispersive forces (van der Waals interactions).

2. Methodology

DFT calculations are performed with the Vienna *ab initio* simulation package (VASP) [22,23] within generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof (PBE) [24] to modulate the exchange-correlation functional (ε_{xc}). It is well known that due to the self-interaction problem present in a local or semilocal approximation for the ε_{xc}, the empty states are not correctly describe and for semiconductors systems the band gap present a difference (smaller absolute value) when compared to the experimental one. To improve the band gap description and calculate the electronic band structure a hybrid functional proposed by Heyd, Scuderia and Erzenrhof (HSE06 functional) [25,26] was successful implemented in the VASP code [27,28]. This functional use results from Hartree-Fock calculations to modulate the exchange term and use the PBE approach for the correlation term part. The strong core-valence electrons interactions are described by the projector augmented-wave (PAW) method [29], which is the state of art in DFT calculations within plane waves.

The basis set is constructed using plane waves with kinetic energy cutoff of 400 eV. To calculate the periodic functions, the *k*-points in the Brillouin zone (BZ) are generate using the Monkhorst-Pack (MP) scheme. The BZ is sample through a 5 × 5 × 1 grid. To obtain the energetic stability of the pristine and functionalized structures the conjugated gradient (CG) method is used and the forces on the atoms are calculated using the Hellmann-Feynman procedure. In our calculation no constraint are imposed, all atoms in the supercell are allowed to relax (until the forces are smaller than 0.04 eV/Å) without imposing any symmetry. In the HER and OER process intermediate compounds are adsorbed on the functionalized structures. To calculate the point zero energy and vibrational frequencies for the intermediates adsorbed, a molecular dynamics study is necessary. In the calculations, the equilibrium geometry for these intermediaries on the doped SiC layer is obtained by CG calculations, then we use molecular dynamics to obtain the vibrational frequencies by keeping the doped SiC layers in their equilibrium position.

We use the supercell approach. The supercell consists of three basic unit cells (3 × 3 × 1 supercell), as illustrated in Fig. 1. The calculated equilibrium lattice parameter of the enlarged hexagonal supercell is 9.27 Å and no buckling is observed, in accordance with others similar calculations [30]. To ensure negligible interactions between SiC layers images, a vacuum region of 15.0 Å perpendiculars to the SiC plane (C axis) is used.

The stability of the doped system is analyzed through binding energies (E_b), which is calculated as the energy difference between the total energy of the metal doped structure and the total energies of the respective isolated systems (the SiC single layer and the adsorbed metal atom):

$$E_b[M] = \left\{ E_T[\text{pristine}] + E_{\text{at}}[M] - E_T[M + \text{pristine}] \right\}. \tag{1}$$

In Eq. (1), $E_T[M + \text{pristine}]$ is the total energy of the supercell with a M atom adsorbed (M = Li, K, Na, Be, Mg or Ca) on the SiC monolayer, $E_T[\text{pristine}]$ is the total energy of the SiC monolayer, and $E_{at}[M]$ is the total energy of the isolated (M) metal atom. Positive values of $E_b[M]$ indicate that the M atom is readily adsorbed (an exothermic process).

After obtain the main properties when a single metal adsorbs on the SiC single layer we check whether the functionalized material can be used to adsorbed important molecules like H_2 and O_2. It is well known that these molecules interact with the 2D materials through dispersive forces (van der Waals interactions). The standard DFT within the semilocal approximation (like the GGA) for the ε_{xc} term fail to describe the dispersive forces (physical interactions). To improve the results when dispersive forces are present the Grimme's dispersion potential [31] implemented in the VASP-code [32] is used in the calculations.

3. Results and discussion

Initially, we analyze the stability of the SiC single layer and calculate the electronic band structure for the pristine systems. The SiC single layer is a metastable structure with a cohesive energy smaller by 7% as compared to the β-bulk system. The calculated electronic band structure and the density of states are shown in Fig. 2(a) and (b), respectively. As can be seen, SiC single layer is an indirect band gap semiconductor. The calculated band gap is 3.37 (2.55) eV when the HSE06 (PBE) functional is used to modulate the exchange-correlation interactions. Due to the folder of the Brillouin Zone, the valence band maximum (VBM) localizes in the Γ point while the conduction band minimum (CBM) localizes in the M point. It is worth to point that the VBM in the 3 × 3 × 1 unit cell correspond to the K-point of the basic unit cell (1 × 1 × 1) while the (M-point) is the same one for the 3 × 3 × 1 and 1 × 1 × 1 unit cells, respectively. The difference between the indirect and direct band gap is only 0.065 (0.035) eV using HSE06 and PBE functional, respectively. These small differences between the indirect and direct band gap is because the CBM is almost no dispersive state along the BZ. The states that form the VBM come mainly from the C (2p) orbitals while the Si (3p) orbitals give the greater contribution to the CBM. Our results for the (indirect and direct) band gap using the PAW method is in accordance with the calculations performed by Lü et al [33] using the more accurate FPLAPW method within the WIEN2k code [34].

To analyze the optical properties we use the same procedure to investigate the optical properties for BNC nanostructures (tubes and layers) [35,36]. We calculate the absorption cross section as function of the energy [$\alpha(E)$] for incident photons by the following equation:

$$\alpha(E) = \frac{4\pi e}{hc} \left\{ \frac{\left[\varepsilon_1^2 + \varepsilon_2^2\right]^{1/2} - \varepsilon_1}{2} \right\}^{1/2}, \tag{2}$$