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Layered heterostructures based on graphene, hexagonal zinc oxide and molybdenum disulfide: Modeling of geometry and electronic properties

Alexander G. Kvashnin [a,b,c], Pavel B. Sorokin [b,d,e], Leonid A. Chernozatonskii [b,*]

[a] Skolkovo Institute of Science and Technology, Skolkovo Innovation Center, 3 Nobel Street, Moscow 143026, Russian Federation
[b] Emanuel Institute of Biochemical Physics of RAS, 4 Kosygin Street, Moscow 119334, Russian Federation
[c] Moscow Institute of Physics and Technology, 9 Institutsky lane, Dolgoprudny 141700, Russian Federation
[d] Technological Institute for Superhard and Novel Carbon Materials, 7a Centralnaya Street, Troitsk, Moscow 108840, Russian Federation
[e] National University of Science and Technology, MISIS, 4 Leninsky Avenue, Moscow 119049, Russian Federation

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ABSTRACT

Here we present a comprehensive investigation of novel composite layered structures based on graphene, molybdenum disulfide (MoS_2) monolayers and hexagonal zinc oxide (ZnO), which display promising optical and electronic properties for photovoltaic applications. Theoretical study of the atomic structure, optical and electronic properties of proposed ZnO/MoS_2 and G/MoS_2/ZnO/G nanostructures were carried out. We show that making the G/MoS_2/ZnO/G heterostructure leads to high doping ratio of graphene layers and zero band gap which allows a conclusion of the possibility of using such structures in photovoltaic applications, due to broad energetic region of high electronic density of states.

1. Introduction

Nowadays a great interest of the scientists is directed to investigations of new composite materials and heterostructures with new physical properties. Such interest is often linked with the van der Waals heterostructures [1]. The possibility to build quasi-two-dimensional material with new properties just by placing one material on another opens a new way of synthesis of 2D materials of different compounds.

In recent work made by Claeyssens et al. [2] a new hexagonal phase of 2D-ZnO was observed. Later Freeman et al. [3] theoretically analyzed polar materials with favorable zinc blende structures (with dominant covalent-ionic bonding) which tend to split into layered structures in the case of two-dimensionality. The prediction was confirmed in a number of experimental works [2,4–6] where the graphitic-like thin ZnO, AlN and SiC films were fabricated by different experimental techniques. Ionic materials with rocksalt crystal structure (with dominant ionic bonding) also can reveal transformation to a new graphitic phase to reduce the huge stress of the polar surface as was shown in Refs. [7–10].

In very recent work made by Quang et al. [11] the free-standing graphene-like mono- and bilayer ZnO membranes were observed. Graphene-like phase of ZnO has a wide direct band gap of 3.37 eV, which makes such material suitable for application in semiconducting electronics. The larger band gap gives devices the ability to work at higher temperatures and allows to switch larger voltages [12]. There are several theoretical and experimental works that predict and observe the controlling of electronic and optoelectronic properties of bilayered structures based on graphene, transition metal dichalcogenides, ZnO, silicene, etc. [13–18].

Here we considered heterostructures based on ZnO, MoS_2 and graphene monolayers. We considered atomic structure of moiré patterns made of MoS_2, ZnO and graphene (G) monolayers and studied their electronic properties. The optical properties of ZnO/MoS_2 heterostructure were studied by calculating the real and imaginary parts of dielectric functions, which are the essential parameters for optical application. Then we considered more complex structure based on MoS_2 and ZnO monolayers placed between two graphene layers caused by potential applications in photovoltaics as solar cell elements.

* Corresponding author.
E-mail address: cherno@sky.ras.chph.ru (L.A. Chernozatonskii).

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2. Computational methods

Electronic properties of two-dimensional planar structures based on MoS_2 monolayers, graphene-like ZnO and graphene were performed using density functional theory (DFT) [19,20] in the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional [21], as implemented in the VASP [22–24] package. The plane–wave energy cutoff was set to 500 eV. Atomic structure optimization was carried out until the maximum interatomic force less than 0.01 eV/Å. For geometry relaxation the Brillouin zone was sampled using Monkhorst–Pack grid [25] of 8×8×1, ensuring the convergence of total energies better than 10^{-6} eV/atom, while for calculations of optical properties much denser mesh of 16×16×1 was used. The total number of bands for calculations of dielectric matrix was set to 512, while for the geometry relaxation number of bands varies from 8 to 24, depending on the system. The considered unit cell of MoS_2/ZnO heterostructure consists of the 5 atoms (2 atoms in the ZnO unit cell and 3 atoms for MoS_2 layer), unit cell of G/MoS_2/ZnO/G structure consists of the 109 atoms: 4×4 supercell of graphene layers (32 atoms per each layer) and 3×3 supercell for MoS_2 and ZnO structures (27 and 18 atoms, respectively). To avoid interaction between the neighboring planar structures in calculated scheme with periodic boundary condition the translation vector along *c*-axis of the supercells was set to be greater than 20 Å. To evaluate the accuracy of calculated interlayer forces (i.e. correct interlayer distances) of considered heterostructures the calculations of atomic structure were provided with van der Waals corrections within the method of Tkatchenko and Scheffler [26]. Using this method after the relaxation the calculated distance between graphene and ZnO layer was equaled to 3.32 Å. The atom projections on the band structure were carried out with aid of the pymatgen Python library for materials analysis [27].

For the calculations of optical properties, the Random Phase Approximation (RPA) approach was used as implemented in VASP package, where the local field effects are included at Hartree level. Here only the interband transitions were taken into account. Thus, inaccuracy in dielectric function only at low energies could be observed. The Fourier transform of the frequency dependent symmetric dielectric function in the RPA is given by [28]:

$$\varepsilon_{G,G'}(q,\omega) = \delta_{G,G'}(q,\omega) - \frac{4\pi e^2}{|G+q||G'+q|} X^0_{G,G'}(q,\omega) \quad (1)$$

where G and G' are reciprocal lattice vectors, q is the Bloch vector of incident wave. The matrix χ_0 is the irreducible polarizability matrix, which was derived by Adler and Wiser [29,30] for independent particle in the self-consistent field approach.

After the electronic ground state had been determined by VASP, the calculations of frequency dependent dielectric matrix were provided. The imaginary part is determined by a summation over empty states using the equation:

$$\varepsilon''_{\alpha\beta}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q\to 0} \frac{1}{q} \sum_{c,v,k} 2\omega_k \delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega) u_{ck+e_\alpha q} | u_{vk} u_{ck+e_\alpha q} | u_{vk} \quad (2)$$

where vectors e_α are the unit vectors along three directions, c and v refer to conduction and valence band states respectively, ε_{ck} refers to energy of conduction band and ε_{vk} refers to energy of valence band and u_{ck} is the cell periodic part of the orbitals at the k-point k. The real part of the dielectric tensor can be obtained by the Kramers- Kronig transformation:

$$\varepsilon'_{\alpha\beta}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''_{\alpha\beta}(\omega')\omega'}{\omega'^2 - \omega^2 + i\eta} d\omega', \quad (3)$$

where P is principal value. More details about the applying approach could be found in Ref. [28].

3. Results and discussion

First we studied the atomic structure and electronic properties of bilayers based on the MoS_2 monolayer and two-dimensional graphene-like layers of ZnO. To study their properties in details the band structures of each constituent part were calculated as shown in Fig. 1a and b.

The band structure of MoS_2 monolayer with direct band gap of 1.5 eV (systematic underestimation should be taken into account; the experimentally observed band gap is 1.9 eV [31]) along with the density of states is shown in Fig. 1a. Atomic geometry and band structure with DOS for two-dimensional ZnO are shown in Fig. 1b. Monolayer of hexagonal graphene-like ZnO has direct band gap of 1.6 eV. These values agree well with ones in reference data [14,32]. We believe that combination of these two layers in one bilayered structure will lead to more interesting and promising features with broader permission transitions in its spectra for photovoltaic properties than each separated layer.

Good match between lattice parameters of MoS_2 and ZnO (3.17 and 3.24 Å, respectively, mismatch is 3%) makes it possible to create a layered structure with minimal mechanical in-plane stresses in the structure. After placing ZnO on the top of the MoS_2 layer, different possible positions of ZnO could be considered. For example, the case when Zn atoms locate above the S atoms of the MoS_2 layer in MoS_2/ZnO composite structure.

Here we considered three possible positions of ZnO monolayer on the top of the MoS_2, where (1) Zn atoms locate directly above the sulfur atoms (MoS_2/ZnO(Zn) structure), (2) oxygen atoms locate above the sulfur atoms (MoS_2/ZnO(O) structure) and (3) the sulfur atoms locate beneath the center of ZnO hexagon (MoS_2/ZnO structure). These three cases could be obtained by shifting of ZnO layer with respect to MoS_2 layer. In order to obtain the most stable structure we calculated the energy barrier of shifting process of one layer with respect to another as shown in Fig. 1c, where the top-viewes of considered cases are shown in the bottom panel. One can note that MoS_2/ZnO(Zn) structure has lower energy compared to others. The energy difference between MoS_2/ZnO(Zn) and MoS_2/ZnO(O) positions equals about 0.1 eV, while the MoS_2/ZnO structure is almost equals to the energy of MoS_2/ZnO(Zn) (difference is 0.02 eV). However, the phonon calculations were performed for all studied MoS_2/ZnO heterostructures, which indicate their dynamical stability (see Fig. S1 in Supporting information).

The binding energies of two types of MoS_2/ZnO were calculated to indicate the energetic preference of one structure compared to another. The binding energy of MoS_2/ZnO(O) hybrid structure is positive and equals to 77 meV. Calculated binding energy of MoS_2/ZnO structure is less than 0.5 meV, while binding energy of MoS_2/ZnO(Zn) structure is −23.2 meV which agrees well with energy of van der Waals interaction in graphite [33]. Positive binding energy indicates instability and inability of formation of MoS_2/ZnO(O), which proves the formation of only MoS_2/ZnO(Zn) heterostructure.

We studied electronic properties of 1×1 supercell (due to good correspondence between lattice parameters) which is shown in Fig. 1d–f. The atom projections on the band structure were carried out to determine the contribution of each atom type or each constituent part to the band structure of hybrid bilayered structure. Contribution from ZnO is highlighted by red color while the contribution from MoS_2 is highlighted by blue. One can see from Fig. 1d that resulting band structure can be characterized as a superposition of the bands of its constituent parts. However, there are several changes in the band structure caused by the electron transfer to the MoS_2 monolayer from the ZnO one. This led to n-doping of MoS_2 layer and shifting the conduction bands towards