Ab initio study of electronic properties of graphene/MoS2 heterostructure under biaxial deformations

Conference Paper · January 2018

DOI: 10.1063/1.5079336

5 authors, including:

Anastasia Petrova
Kazan (Volga Region) Federal University
7 PUBLICATIONS **4** CITATIONS
SEE PROFILE

Oleg V Nedopekin
Kazan (Volga Region) Federal University
21 PUBLICATIONS **13** CITATIONS
SEE PROFILE

D. A. Tayurskii
Kazan (Volga Region) Federal University
122 PUBLICATIONS **362** CITATIONS
SEE PROFILE

Ab initio study of electronic properties of graphene/MoS_2 heterostructure under biaxial deformations

A. Valishina, R. Burganova, A. Petrova, O. Nedopekin, and D. Tayurskii

Citation: AIP Conference Proceedings **2041**, 020005 (2018); doi: 10.1063/1.5079336
View online: https://doi.org/10.1063/1.5079336
View Table of Contents: http://aip.scitation.org/toc/apc/2041/1
Published by the American Institute of Physics

Ab Initio Study of Electronic Properties of Graphene/MoS_2 Heterostructure under Biaxial Deformations

A. Valishina[1,a)], R. Burganova[1,2], A. Petrova[1], O. Nedopekin[1] and D. Tayurskii[1]

[1]*Institute of Physics, Kazan (Volga region) Federal University, Kremlyovskaya str, 18, 420008 Kazan, Russia*
[2]*Department of Physics and Earth Sciences, Parma University, Parco Area delle Scienze, 7/A, 43124 Parma PR, Italy*

[a)]Corresponding author: valishinalina@gmail.com

Abstract.
The electronic properties of strained graphene/molybdenum disulfide (Gr/MoS_2) heterostructure have been studied by using density functional theory. It is known that the linear band dispersion relation of graphene undergoes insignificant changes in the case of graphene adsorption on MoS_2 monolayer, when the in-plane lattice symmetry is broken, resulting in formation of a small band gap of 2 meV. At the present study, the equilibrium optimized state, corresponding to the maximal 14 meV band gap offset at 4% biaxial compression and 3.28 Å interlayer spacing, was found. It is established that the strain, applying to the Gr/MoS_2 interface along x,y - directions, leads to a change in the interlayer distance, which is crucial for the band gap value. Our results suggest that such xy-plane deformations can be considered as a tool for selectively controlling value of the band gap, and will be useful for the design of the materials with desirably induced properties.

INTRODUCTION

At the present time, the study of two-dimensional (2D) atomic crystals is one of the leading topics in condensed matter physics and materials science [1, 2, 3]. Graphene, the first representative of 2D atomic-layer-based materials, in the past decade has triggered enormous interest due to its remarkable properties and potential applications [4, 5]. In particular, the anomalous Quantum Hall effect, observed in graphene [6], the massless Dirac fermions as charge carriers [7], long spin-relaxation lengths and times [8], and its room-temperature ballistic transport [9] make it promising for development of new electronic nano-devices [10].

Since the presence of energy band gap is a crucial property in electronics and optics, and graphene is a semimetal with a zero band gap, the semiconducting layered transition metal dichalcogenides (TMDs) are the most promising [11]. This is a class of materials with the general formula MX_2, where M is a transition metal element and X is a chalcogen (S, Se or Te). The TMD monolayer consists of stacking X-M-X layers, so metal atoms are sandwiched between two chalcogen layers. There is strong covalent intralayer interaction, whereas the interlayer interaction is of the van der Waalse (vdW) type.

The 2D TMDs possess unique properties compared with their bulk counterparts. For example, molybdenum disulfide MoS_2, the most studied among MX_2 materials, demonstrates the dramatic change from an indirect gap of 1.2-1.3 eV in bilayer (BL) to a direct gap of 1.8-1.9 eV in monolayer (ML) [12, 13]. In addition, MoS_2 ML also demonstrates promising characteristics, regarding high charge carrier mobility (about 500 $cm^2\ V^{-1}\ s^{-1}$), up to 10^8 ON/OFF current ratio in the transistor element [14], and high mechanical strength [15, 16].

The possibility to combine graphene and related 2D materials in vertical stacks in a precisely chosen sequence has created a new class of vdW heterostructures, having potential application for various fields, including nanoelectronics, energy conversion and storage, nanooptics, and catalysis [17, 18, 19]. These hybrid systems demonstrate unusual properties that are not exhibited by individual layers, for example, the electron conductivity and electrochemical performance in Gr/MoS_2 heterostructure is higher than in MoS_2 ML [20]. Moreover, it has been reported in [21] that Youngs modulus of MoS_2 can be tripled by sandwiching it between two outer graphene layers.

The electronic properties of Gr/MoS_2 hybrid system undergo changes with the modification of interlayer orientation. The band structure of twisted Gr/MoS_2 BL, as in the case of nontwisted heterostructure, can be interpreted as

2D Systems of the Strong Correlated Electrons: From Fundamental Research to Practical Applications
AIP Conf. Proc. 2041, 020005-1–020005-4; https://doi.org/10.1063/1.5079336
Published by AIP Publishing. 978-0-7354-1767-0/$30.00

a superposition of its constituent states. According to the direct measurement of the electronic structure of twisted Gr/MoS_2 heterostructure [22], the contribution to the band dispersion, derived from the MoS_2 ML, is found to be twist-angle dependent, while the contribution from graphene layer is preserved with different twist angles. Predominantly for all twisted angles MoS_2 ML within the heterostructure becomes an indirect band-gap system. The first principle calculations results [23] show that the change, observed in electronic structures of twisted Gr/MoS_2 BL, with respect to rotational angles is a result of sensitive twist-angle dependence of the MoS_2 band structure on lattice strain, which is derived from layers commensurable condition for the supercell. In addition, the value of opened tiny band gap at Dirac cone behaves regardless of twist angle.

In this work, by using first-principles calculations, we study the electronic properties of vdW heterostructures, consisting of graphene and MoS_2 MLs, under biaxial deformations. Our focus concerns the influence of structural deformations, such as in-plane extension and compression, on the tiny band gap value at Dirac cone in the electronic structure of Gr/MoS_2 hybrid system.

The concept of strain engineering in 2D materials is a powerful technique for tuning their physical characteristics. The electronic and optical properties of graphene or single MoS_2 layer are significantly changed by applied uniaxial or biaxial strain along different crystallographic directions [24, 25, 26, 27]. Therefore, the study of the influence of the in-plane deformations in the Gr/MoS_2 heterostructure could be useful in the design of the materials with desirably adjusted properties.

COMPUTATIONAL DETAILS

The *ab initio* calculations were carried out within the density functional theory (DFT) [28, 29] on the basis of projector augmented wave (PAW) method [30] implemented in VASP package [31] – a part of the MedeA® software of Materials Design [32]. The exchange-correlation interaction was described by the local density approximation (LDA) [33]. For atomic relaxation and band structure calculation a Γ-centered $6 \times 6 \times 1$ grid and the plane wave energy cutoff of 400 eV was adopted. The structural optimization was carried out until the forces on each atom were less than 0.02 eV/ Å. The electronic convergence tolerance was set to 10^{-5} eV.

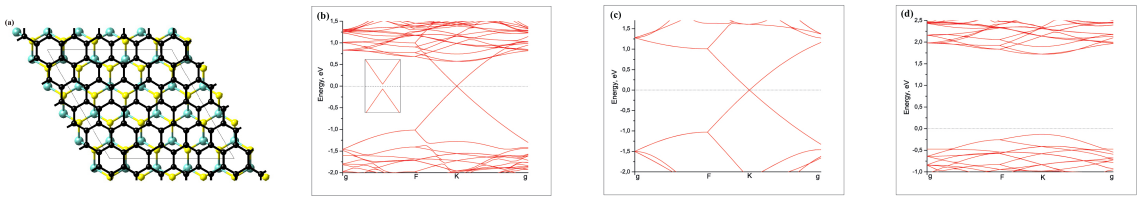

FIGURE 1. (Top view (a) of Gr/MoS_2 heterostructure. The black, blue, yellow balls represent C, Mo, S atoms, respectively. Electronic structures of the (b) Gr/MoS_2 BL, (c) isolated graphene, (d) MoS_2 ML. The horizontal lines in (b)-(d) represent the Fermi level. The insert in (b) is magnification of the area near the linear dispersion band at the *K*-point.

The interface of Gr/MoS_2 hybrid system, represented as a supercell, is illustrated in Fig.1(a). The BL structure contained 5×5 lateral periodicity of the graphene and 4×4 lateral periodicity of the MoS_2 ML for implementation a commensurable condition between layers. This led to a small lattice mismatch (2%). The 20 Å vacuum region was added in the direction normal to the Gr/MoS_2 interface to avoid the interaction of the BL with its periodic copies.

The optimized in-plane lattice parameter for heterostructure was 12.33 Å. It corresponds to a slight stretching of graphene (less than 1%) and to the compression of MoS_2 ML (around 1%). The interlayer distance of 3.38 Å of the relaxed undeformed structure with a corresponding binding energy of −23.0 meV are very close to the first-principle predictions of 3.66 Å and −21.0 meV in [34], or 3.32 Å and −23.0 meV in [35].

The strain was applied in the zigzag direction of graphene and MoS_2 edges. Deformation effect was carried out by changing the lattice parameters along x and y direction, while keeping the z-direction stress free.

RESULTS AND DISCUSSION

The calculated electronic band structure of Gr/MoS_2 BL is illustrated in Fig.1(b). The electronic spectrum seems to be a simple sum of pristine graphene (Fig.1(c)) and MoS_2 ML (Fig.1(d)). As reported in [35], the charge redistribution

breaks the equivalents of the two graphene sublattice, and the small band gap of 2 meV opens around the Fermi level at the *K*-point of the Brillouin zone [insert of Fig.1(b)]. Thus it can be argued that the graphene is no longer possessing metallic properties with massless electrons, but acquiring a direct narrow fundamental energy gap.

It was established that biaxial stretching of Gr/MoS_2 BL by 1% leads to decreasing the band gap value to 1 meV, and the further deformations (by 2-5%) do not change this value (Fig.2(a)). It is well-known graphene and MoS_2 are highly elastic materials with strong covalent bonding, therefore expansion of the heterostructure alters atoms position in xy plane only. In addition, interlayer distance increases (Fig.2(b)), preserving the weak interaction between Gr/MoS_2 MLs.

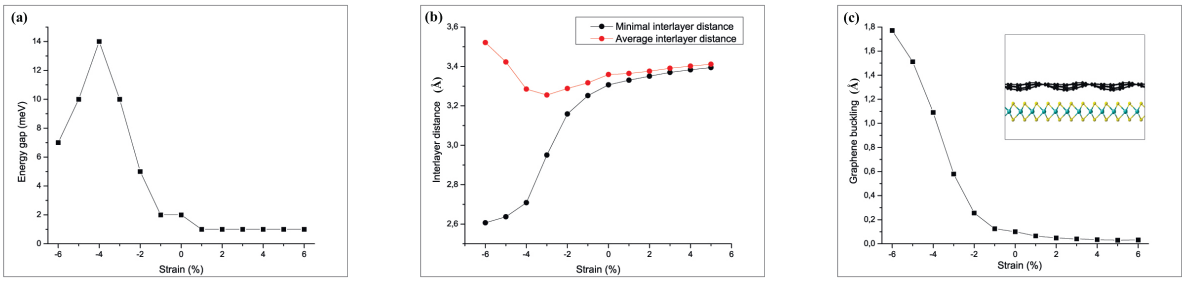

FIGURE 2. (a) - the variation in energy gap of Gr/MoS_2 heterostructure as a function of biaxial deformation. (b) - the functional dependencies of average and minimal distances on strain. (c) - graphene buckling as a function of strain, the insert illustrates the curvature of graphene surface due to in-plane compression.

A completely different situation was observed when the heterostructure is compressed. The band gap value sharply increases from 2 meV up to 14 meV at 1-4% compression, respectively, and decreases with further negative deformations (Fig.2(a)). It was found that graphene, absorbed on MoS_2 ML, exhibits small buckling of 0.10 Å, (which is in good agreement with the previous calculations of 0.08 Å [35]), and naturally increases up to 1.77 Å at the highest compression (insert in Fig.2(c)) and decreases during expansion (Fig.2(c)). The boundary conditions of the supercell probably affect to a period of the deformation waves, which are observed in compressed graphene. A detailed study of this assumption will be refined in subsequent investigations.

As notated in [35], the band gap value is extremely sensitive to interlayer spacing: decrease of interlayer distance leads to increase the band gap. Fig.2(b) demonstrates the variation of minimal and average interlayer distances between graphene and MoS_2 MLs as a function of strain. The optimization procedure ensures equilibrium states of the Gr/MoS_2 BL under biaxial deformation. It is seen that negative strain is the reason for the monotonic decrease in the minimum distance curve, whereas average interlayer distance slightly decreases up to 4% compression, resulting the maximal band gap opening (14 meV), and fast increases with the further compressing, causing decrease of the band gap value. Such result could arise from coupling of graphene buckling effect and variation of interlayer spacing, and detailed analysis is beyond the scope of this paper. Evidently, even weak interlayer interactions between graphene and MoS_2 MLs significantly influence the band gap offset of the heterostructure, as it was showed in [35], where by decreasing interlayer spacing the similar band gap value of 12 meV was reached at high-energy state, in contrast to our results, obtained at equilibrium.

CONCLUSIONS

The modern design of materials by highly accurate computer simulation methods opens the access to fine tuned materials properties, that could be verified by experiments. Our theoretical study presents one of the possible way to vary the electronic properties of Gr/MoS_2 heterostructure by the biaxial deformations. It is established that compression of the heterostructure in the xy-plane leads to a decrease of the interlayer distance, a significant curvature of the graphene surface, an energy band gap opening close to the Fermi level. The band gap value of 4% compressed hybrid system can be raised up to 14 meV compared to undeformed value. Biaxial expansions do not significantly change the band structure of Gr/MoS_2 BL. These findings can be important in the design of future nanoelectronic devices where high charge mobility, provided by graphene, and finite band gap are needed.

ACKNOWLEDGEMENTS

The work was supported by Russian Government Program of Competitive Growth of Kazan Federal University.The work of A.V. Petrova was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (project 3.9779.2017/8.9).

REFERENCES

[1] K. Novoselov, D. Jiang, F. Schedin, T. Booth, V. Khotkevich, S. Morozov, and A. Geim, Proceedings of the National Academy of Sciences **102**, 10451–10453 (2005).
[2] S. Lebegue and O. Eriksson, Physical Review B **79**, p. 115409 (2009).
[3] M. Xu, T. Liang, M. Shi, and H. Chen, Chemical reviews **113**, 3766–3798 (2013).
[4] A. C. Neto, F. Guinea, N. M. Peres, K. S. Novoselov, and A. K. Geim, Reviews of modern physics **81**, p. 109 (2009).
[5] K. S. Novoselov, V. Fal, L. Colombo, P. Gellert, M. Schwab, K. Kim, *et al.*, nature **490**, p. 192 (2012).
[6] Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, nature **438**, p. 201 (2005).
[7] K. S. Novoselov, A. K. Geim, S. Morozov, D. Jiang, M. Katsnelson, I. Grigorieva, S. Dubonos, Firsov, and AA, nature **438**, p. 197 (2005).
[8] M. Drogeler, C. Franzen, F. Volmer, T. Pohlmann, L. Banszerus, M. Wolter, K. Watanabe, T. Taniguchi, C. Stampfer, and B. Beschoten, Nano letters **16**, 3533–3539 (2016).
[9] A. S. Mayorov, R. V. Gorbachev, S. V. Morozov, L. Britnell, R. Jalil, L. A. Ponomarenko, P. Blake, K. S. Novoselov, K. Watanabe, T. Taniguchi, *et al.*, Nano letters **11**, 2396–2399 (2011).
[10] P. Chandrasekhar, in *Conducting Polymers, Fundamentals and Applications* (Springer, 2018), pp. 141–146.
[11] Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, Nature nanotechnology **7**, p. 699 (2012).
[12] E. S. Kadantsev and P. Hawrylak, Solid State Communications **152**, 909–913 (2012).
[13] T. Cheiwchanchamnangij and W. R. Lambrecht, Physical Review B **85**, p. 205302 (2012).
[14] X. Duan, C. Wang, A. Pan, R. Yu, and X. Duan, Chemical Society Reviews **44**, 8859–8876 (2015).
[15] S. Bertolazzi, J. Brivio, and A. Kis, ACS nano **5**, 9703–9709 (2011).
[16] R. C. Cooper, C. Lee, C. A. Marianetti, X. Wei, J. Hone, and J. W. Kysar, Physical Review B **87**, p. 035423 (2013).
[17] A. K. Geim and I. V. Grigorieva, Nature **499**, p. 419 (2013).
[18] K. Novoselov, A. Mishchenko, A. Carvalho, and A. C. Neto, Science **353**, p. aac9439 (2016).
[19] D. Deng, K. Novoselov, Q. Fu, N. Zheng, Z. Tian, and X. Bao, Nature nanotechnology **11**, p. 218 (2016).
[20] K. Chang and W. Chen, Chemical Communications **47**, 4252–4254 (2011).
[21] J.-W. Jiang and H. S. Park, Applied Physics Letters **105**, p. 033108 (2014).
[22] W. Jin, P.-C. Yeh, N. Zaki, D. Chenet, G. Arefe, Y. Hao, A. Sala, T. O. Mentes, J. I. Dadap, A. Locatelli, *et al.*, Physical Review B **92**, p. 201409 (2015).
[23] Z. Wang, Q. Chen, and J. Wang, The Journal of Physical Chemistry C **119**, 4752–4758 (2015).
[24] F. Guinea, M. Katsnelson, and A. Geim, Nature Physics **6**, p. 30 (2010).
[25] V. M. Pereira, A. C. Neto, and N. Peres, Physical Review B **80**, p. 045401 (2009).
[26] V. M. Pereira, R. Ribeiro, N. Peres, and A. C. Neto, EPL (Europhysics Letters) **92**, p. 67001 (2011).
[27] W. S. Yun, S. Han, S. C. Hong, I. G. Kim, and J. Lee, Physical Review B **85**, p. 033305 (2012).
[28] P. Hohenberg and W. Kohn, Physical review **136**, p. B864 (1964).
[29] W. Kohn and L. J. Sham, Physical review **140**, p. A1133 (1965).
[30] P. E. Blöchl, Physical review B **50**, p. 17953 (1994).
[31] G. Kresse and J. Furthmüller, Physical review B **54**, p. 11169 (1996).
[32] MedeA® - 2.16 Materials Design, Inc., Angel Fire, NM, USA 2015 .
[33] D. M. Ceperley and B. Alder, Physical Review Letters **45**, p. 566 (1980).
[34] R. H. Miwa and W. L. Scopel, Journal of Physics: Condensed Matter **25**, p. 445301 (2013).
[35] Y. Ma, Y. Dai, M. Guo, C. Niu, and B. Huang, Nanoscale **3**, 3883–3887 (2011).