Tunable MoS2 bandgap in MoS2-graphene heterostructures
Abbas Ebnonnasir, Badri Narayanan, Suneel Kodambaka, and Cristian V. Ciobanu

Citation: Applied Physics Letters 105, 031603 (2014); doi: 10.1063/1.4891430
View online: http://dx.doi.org/10.1063/1.4891430
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/105/3?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Toward epitaxially grown two-dimensional crystal hetero-structures: Single and double MoS2/graphene heterostructures by chemical vapor depositions

Mechanical properties of MoS2/graphene heterostructures

Density functional theory study of chemical sensing on surfaces of single-layer MoS2 and graphene
J. Appl. Phys. 115, 164302 (2014); 10.1063/1.4871687

Strain-induced magnetism in MoS2 monolayer with defects

Theoretical study on strain induced variations in electronic properties of 2H-MoS2 bilayer sheets
Tunable MoS2 bandgap in MoS2-graphene heterostructures

Abbas Ebnonna,1,2 Badri Narayanan,1 Suneel Kodambaka,2,a) and Cristian V. Ciobanu1,a)

1Department of Mechanical Engineering and Materials Science Program, Colorado School of Mines, Golden, Colorado 80401, USA
2Department of Materials Science and Engineering, University of California Los Angeles, Los Angeles, California 90095, USA

(Received 10 April 2014; accepted 15 July 2014; published online 25 July 2014)

Using density functional theory calculations with van der Waals corrections, we investigated how the interlayer orientation affects the structure and electronic properties of MoS2-graphene bilayer heterostructures. Changing the orientation of graphene with respect to MoS2 strongly influences the type and the value of the electronic bandgap in MoS2, while not significantly altering the binding energy between the layers or the interlayer spacing. We show that the physical origin of this tunable bandgap arises from variations in the S–S interplanar distance (MoS2 thickness) with the interlayer orientation, variations which are caused by electron transfer away from the Mo–S bonds.

Two-dimensional (2-D) materials can vary in terms of their electronic properties (e.g., graphene is metallic, hexagonal-BN (hBN) is insulating, and MoS2 is semiconducting) and, hence, are attractive, often in combinations, for technological applications. Among this class of materials, many studies have focused on molybdenum disulfide, which exhibits a number of interesting properties such as bandgap variation with the number of layers,1,2 high carrier mobility,3,4 high Seebeck coefficient,5 photoconductivity,6,7 large excitonic effects,8 environmental sensitivity,9,10 and high mechanical strength,11—properties which make this material promising for next-generation optoelectronic and nanoelectronic devices.12,13 Recent efforts have focused on taking advantage of the individual properties of different 2-D materials by fabricating heterostructures,14 which are vertical stacks of 2-D layers of dissimilar materials held together by van der Waals (vdW) forces. Such heterostructures not only can lead to opening of a bandgap in graphene (e.g., in graphene-hBN bilayers)15 without impairing its electronic mobility but can also develop direct bandgaps in multilayer heterostructures16 or improve the on/off current ratios drastically (∼103 in graphene-MoS2).12,17,18

Motivation for the present study stems from the fact that interlayer orientation can affect the electronic properties of monolayers on their growth substrate,19,20 as well in multi-layered structures of the same material.21 In this Letter, we investigate the use of interlayer orientation between two different 2-D materials as a tuning parameter for the electronic properties of the bilayer heterostructure. We present results from vdW-corrected density functional theory (DFT) calculations on the effect of interlayer orientation on the electronic structure of the MoS2-graphene bilayers. We find that the relative orientation of graphene with respect to the MoS2 layer strongly influences the value and type of the bandgap in MoS2, while having little effect on both the interlayer spacing and the binding energy. The physical origin of this strong orientation dependence stems from particular atomic

registrations in which carbon atoms of graphene can effectively weaken a significant number the MoS2 bonds, thus changing both the thickness and the bandstructure of MoS2. Using a tight-binding approach to rationalize the results of DFT calculations, we show that it is valence band edge at the Γ point that is the most sensitive to the variations in MoS2 thickness, sensitivity which gives rise to the computed changes in MoS2 bandgap with graphene orientation. These results are relevant for heterostructures as potential photovoltaic devices in which exciton pairs could be created in MoS2 and collected by graphene electrodes,22 and furthermore, provide perspective on previous related works23–25 showing the tunability of the bandgap in single-layer MoS2 via tensile strain.

To study the effect that graphene has on the electronic structure of the MoS2 monolayer, we constructed commensurate moiré patterns of graphene on MoS2 for two interlayer orientations with large spatial periodicities (refer to Fig. 1). The DFT calculations were performed using the SIESTA Package26 with Troullier-Martins pseudopotentials,27 vdW exchange-correlation functional of Klimes et al. (optB88-vdW version),28 and double-ζ basis set with polarization functions. This basis set is sufficient, since the use of larger sets did not lead to significant changes in the structural and electronic properties.28 We have validated our computational approach by reproducing the structural and electronic properties of MoS2 single-layers and bulk crystals; the validation for graphene was performed in our earlier works26,28,30 on epitaxial graphene. We have ensured commensurability of the graphene and MoS2 layers by applying small biaxial strains to graphene while keeping the lattice constant of MoS2 at the relaxed equilibrium value of 3.204 Å. This value for single-layer MoS2 is close to those reported from X-ray diffraction experiments,31,32 and consistent with values from other DFT approaches.33,34 Our use of the equilibrium value for the lattice constant of MoS2 ensures that we do not introduce spurious strains that might obfuscate the effects of interlayer orientation that we seek to reveal. For atomic relaxations and bandstructure calculations, we used Monkhorst-Pack Γ-centered 10 × 10 × 1 and 24 × 24 × 1 grids, respectively. The structural optimization was carried

a)Authors to whom correspondence should be addressed. Electronic addresses: cciobanu@mines.edu and kodambaka@ucla.edu

© 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4891430]
out until the residual forces fell below 0.01 eV/Å. The electronic convergence tolerance was set to 10⁻⁶ eV. For all calculations, an energy cutoff of 250 Ry was chosen for the integration mesh.

Our results on interlayer binding energies and structural properties of the heterostructures shown in Fig. 1 are summarized in Table I. The strains in graphene are sufficiently small that they do not unduly influence our conclusions regarding the electronic properties of the MoS₂ layer. The binding energies and interlayer distance, measured between graphene and the closest S atomic plane, do not change significantly with the graphene orientation. The atomic-scale corrugations of MoS₂ and graphene are practically inexistent. Large 2-D crystals undergo the formation of spontaneous corrugations, whose effect on the bandstructure is negligible with the graphene orientation. At a given interlayer orientation in a large-period moiré pattern, the in-plane sliding of the layers does not change their binding or the electronic properties.

Figure 2 shows the bandstructures and orbital-decomposed densities of states for the structures studied (Fig. 1). Graphene retains its semi-metallic character, as there is no distinguishable bandgap in the p_z states. However, the bandgap in MoS₂ varies: 1.674 eV for the 4:5z supercell, and 1.561 eV for 4:3a. As seen in Fig. 2, the nature of the bandgap is different for the two systems (Fig. 1): the gap is direct at the K point for the 4:5z structure, and indirect (from K to Γ) for 4:3a. Although the assignment of a bandgap type (direct versus indirect) when using supercells that consist of multiple primitive cells is affected by the well-known Brillouin zone folding effect, the variations in bandgap values and type are physically significant for cells of the same size (4:5z and 4:3a) for which the folding across the Brillouin zone is identical. Next, we will focus on understanding why the orientation of graphene affects the bandstructure of MoS₂.

Table I shows that the MoS₂ bandgap is direct for the 4:5z configuration, but indirect for 4:3a. Since both systems have the same 4 × 4 MoS₂ cell, we focus on the Table I information pertaining to MoS₂ that can be influenced by the proximity of graphene. This key information is the MoS₂ thickness t, which changes from 3.227 Å to 3.174 Å. To understand how the thickness of MoS₂ can affect its bandstructure, we first study the bandgap as a function of thickness using 1 × 1 unit cells—which ensures the removal of zone folding artifacts. Our results for MoS₂ 1 × 1 are shown in Figs. 3(a) and 3(b): in these calculations, the atomic positions are kept fixed, and the bandgap is computed for different values of t. At equilibrium (t = 3.21 Å), the bandgap is direct, while a slight decrease in the thickness makes the bandgap indirect. As seen in Fig. 3(b), the bandgap can be tuned over a span of ~0.6 eV by varying the MoS₂ thickness over a span of only ~0.2 Å—which is consistent with other reports. The reason for this high

Table I: Calculated properties of the MoS₂-graphene systems: binding energy, corrugation of graphene, average spacing between graphene and MoS₂, strain imposed for commensurability, thickness, and corrugation of MoS₂.

<table>
<thead>
<tr>
<th>System</th>
<th>Binding Energy eV/Å²</th>
<th>Graphene Corrugation Å</th>
<th>Interlayer Distance Å</th>
<th>Strain %</th>
<th>MoS₂ Thickness Å</th>
<th>Correlation Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:5z</td>
<td>0.051</td>
<td>0.086</td>
<td>3.110</td>
<td>0.0</td>
<td>3.227</td>
<td>0.001</td>
</tr>
<tr>
<td>4:3a</td>
<td>0.051</td>
<td>0.014</td>
<td>3.131</td>
<td>−0.7</td>
<td>3.174</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Fig. 1. Surface unit cells of the MoS₂-graphene bilayer heterostructures considered in this work: (a) 4:5z, denoting a 4 × 4 MoS₂ cell and a 5 × 5 graphene cell, oriented so as the [2 1 1 0] crystallographic directions of the two layers in the heterostructure are parallel to one another, and (b) 4:3a, denoting a 4 × 4 MoS₂ cell matched to a 3√3 × 3√3 graphene unit cell, in which the armchair graphene direction is parallel to MoS₂ [2 1 1 0] axis.
sensitivity of the bandgap is that the small variations in $t$ (e.g., 0.05 Å) amount to changing the length of the Mo–S bonds by $\sim$1%: Since these bonds are strong and covalent, a bondlength variation of $\sim$1% will significantly affect the bandstructure.23,24

Fig. 3(a) shows that a small decrease in the thickness $t$ results in a large increase in energy of the valence band at $\Gamma$, while the energy values of both the valence and conduction band maxima at $\Gamma$ and $K$ causes the direct-indirect band gap transition in the MoS$_2$ layer [Fig. 3]. To understand the physical origin of such a disparity, we turn to a tight-binding (TB) model that describes the band structure of MoS$_2$ in terms of electronic hopping processes associated with the 4$d$ Mo and 3$p$ S orbitals.44,45 In this description, the energy of the valence edge $E_v^i (j = \Gamma, K)$ at $\Gamma$ or $K$ points is expressed as:

$$E_v^i = \left( \frac{h_1^i + h_2^i}{2} \right) + \sqrt{\left( \frac{h_1^i - h_2^i}{2} \right)^2 + 2 \left( h_1^i \right)^2},$$

where $h_1^i$ are hopping terms related to different types of atom-pairs. The terms $h_1^i$ and $h_2^i$ describe electronic Mo–Mo hopping and S–S hopping, respectively, while $h_3^i$ is associated with Mo–S nearest-neighbor pairs.

In general, hopping terms $h_j^i$ ($i = 1, 2, 3; j = \Gamma, K$) in Eq. (1) are influenced by the variation in the distances between relevant atom pairs.44 However, in the range of thickness values considered here (i.e., 3 Å–3.3 Å), the $h_1$ and $h_2$ parameters should not be affected by $t$. This is because they depend primarily only on the in-plane S–S and Mo–Mo distances, which do not change. Therefore, the variations in band edges at $K$ and $\Gamma$ (Eq. (1)) are mostly governed by changes in $h_1^K$ and $h_1^\Gamma$, respectively, which do vary significantly with $t$ because the Mo–S bonds are directly affected by thickness variations. Figures 4(a) and 4(b) show the thickness-dependence of the $h_1^K$ and the corresponding valence band edges at $K$ and $\Gamma$. The calculations were performed using the parameters in Ref. 45. As seen in Fig. 4, the variations of $h_1^K$ and $E^K$ are more pronounced than their counterparts at the $K$ point, which leads to significant thickness-dependence of the valence band energy at $\Gamma$ and to the direct-to-indirect bandgap transition upon decreasing layer thickness below its equilibrium value.

Last, we discuss the reason why the in-plane rotation of graphene affects the MoS$_2$ thickness, which, as we have seen, leads to changes in the bandgap (Fig. 3). To this end, we have determined the electronic transfer that occurs when the two layers (graphene and MoS$_2$) are brought together. For the larger supercells, 4:5z and 4:3a, this electron transfer is shown in Figs. 5(a) and 5(b). Focusing on Fig. 5(a), we note that nine out of the 48 Mo–S bonds on the graphene side (the three-lobed areas identified for clarity in Fig. 5(a)), lose electronic density, meaning that they become weaker and slightly longer (by 0.25%). In turn, the thickness $t$ increases beyond the equilibrium value of 3.22 Å and the bandgap becomes smaller and indirect. Consequently, there is no electronic loss in the Mo–S bonds. Instead, we find a weak and directional increase in the charge associated with these bonds, which makes them slightly shorter; consequently, the S–S interlayer spacing $t$ becomes smaller than its equilibrium value, and the bandgap becomes smaller and indirect.
In conclusion, we have shown that the orientation of graphene in MoS$_2$ heterostructures affects the bandgap of MoS$_2$, and have traced the physical origin of this result to the highly sensitive dependence of the bandgap value on the thickness of the MoS$_2$ layer. Changes in registry between graphene and MoS$_2$ are accompanied by interfacial electronic transfer, which affects the Mo–S bond lengths and hence the bandstructure. This suggests that graphene-MoS$_2$ heterostructures are suitable for photovoltaic devices, in which the exciton pair could be created in MoS$_2$ and collected at graphene layers situated on either side of the MoS$_2$ layer. Furthermore, our results provide another perspective on previous works which showed tunability of the bandgap via tensile strain in the MoS$_2$ layer, and contributes to an increasing body of work that exploits different stacking registries for discovering useful electronic properties (e.g., Ref. [46]).

The authors thank Dr. E. Cappelluti for discussions regarding the tight-binding parametrization published in Ref. [45]. The authors gratefully acknowledge funding from National Science Foundation (A.E., B.N., and C.V.C.) through Grant No. CMMI-0846858, and from the Office of Naval Research (A.E. and S.K.), ONR Award No. N00014-12-1-0518 (Dr. Chagaan Baatar). Supercomputer time for this project was provided by the Golden Energy Computing Organization at Colorado School of Mines.


$^{13}$W. J. Yu, Z. Li, H. Zhou, Y. Chen, Y. Wang, Y. Huang, and X. Duan, Nat. Mater. 12, 246 (2012).


$^{24}$W. J. Yu, S. W. Han, S. C. Hong, I. G. Kim, and J. D. Lee, Phys. Rev. B 85, 033305 (2012).


$^{35}$See supplementary material at http://dx.doi.org/10.1063/1.4891430 for the atomic coordinates associated with each structure shown in Fig. 1, and for a detailed description of the tight-binding calculations.


