Electronic Transport along Hybrid MoS$_2$ Monolayers

Ganesh Sivaraman, Fábio A. L. de Souza, Rodrigo G. Amorim, Wanderlã L. Scopel, Maria Fyta, and Ralph H. Scheicher

†Institute for Computational Physics, Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany
‡Departamento de Física, Universidade Federal do Espírito Santo-UFES, Vitória, Espírito Santo, Brazil
§Department of Physics and Astronomy, Materials Theory, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden
¶Departamento de Física, ICEx, Universidade Federal Fluminense - UFF, Volta Redonda, Rio de Janeiro, Brazil

ABSTRACT: Molybdenum disulfide (MoS$_2$) is a two-dimensional material in which a semiconducting and a metallic phase can coexist. In this work, we investigate the electronic and transport properties of a hybrid MoS$_2$ monolayer composed of a metallic strip embedded in the semiconducting MoS$_2$ phase. Using quantum mechanical calculations within the density functional theory scheme together with the non-equilibrium Greens functions approach, we study in detail the structural and electronic properties of this hybrid material and its metal–semiconductor interface. A single point-defect analysis is performed in order to assess the stability of the hybrid system. Focus is given to the electronic transport properties of the hybrid MoS$_2$ monolayer extracted from the electronic transmission spectra. These are linked to the local current across the monolayer. A clear asymmetry of the current flowing across the hybrid monolayer was found and was attributed to the atomistic characteristics of the material’s interfaces. The results suggest strong potential for the application of hybrid MoS$_2$ in the next generation biosensing devices.

INTRODUCTION

Two-dimensional (2D) materials have attracted high interest in recent years. Starting with graphene and its numerous potential applications, the research of 2D nanomaterials was followed by intense investigations on 2D transition metal dichalcogenides (TMDs). TMDs (MX$_2$, with M = V, Mo, W, etc., and X = S, Se, etc.) are quasi two-dimensional layered materials with strong interlayer ionic–covalent bonding. 2D TMDs can be found in two phases, semiconducting (2H) and metallic (1T). Liquid-phase exfoliation is the typical method to produce the monolayer TMDs from their layered counterparts. It was shown that the transition from the 2H to the 1T phase of MoS$_2$, MoSe$_2$, WS$_2$, and WSe$_2$ during their chemical exfoliation depends on the MX$_2$ composition of these materials.

The most famous member of the 2D TMD family is MoS$_2$, which has been used as a dry lubricant for many decades in its bulk form. In the earlier studies, focus was given on MoS$_2$-based nanoparticles, such as MoS$_2$ nested inorganic fullerenes, nanotubes, and MoS$_2$ nanoclusters used as catalysts. The investigations then turned to MoS$_2$ surfaces and their ability to adsorb hydrogen. The research on MoS$_2$ has shown a 4-fold increase since the year 2010 when the direct band gap in the single-layered structure was discovered. The coexistence of a metallic and semiconducting phase has been reported in MoS$_2$ in the past in several studies. This represents a distinct polymorphism in terms of structural and electronic properties, a marked deviation from graphene. The coexistence of the semiconducting (2H) and metallic (1T) phase in MoS$_2$ monolayers has been characterized. In principle, gliding only one S plane of MoS$_2$ to the center of the hexagonal rings of the semiconducting 2H phase will gradually transform the structure to the metallic 1T phase. During this transformation, while the size of the 1T part increases, three different boundaries—α, β, and γ—emerge. The α boundary is related to the Mo–Mo distance shrinking, the β boundary involves the Mo + S gliding, and the γ boundary is based on the S gliding. The recent development of controlled techniques to induce 2H to 1T phase transition opens up promising routes for an atomically precise fabrication of single-layered chemically homogeneous electronic devices. Lately, another important achievement in the field was the formation of nanopores in MoS$_2$. These nanopores are formed using an electrochemical reaction method, and it has been demonstrated that DNA can be translocated through them within a salt solution. These nanopores are efficient in discriminating among DNA nucleotides and can lead to a novel sequencing technique.

In this study, we focus on hybrid monolayers of MoS$_2$. The term “hybrid” refers to the combination of the two different phases (2H and 1T) composing the monolayer. It accounts for the polymorphism of MoS$_2$ linking to materials with tunable functionalities. The combination of different phases in

Received: August 5, 2016
Revised: September 19, 2016
constructing the hybrid structures offers additional pathways to electrons and is expected to enhance the electronic transport properties along the hybrid monolayers. This would be relevant to electronics applications and also for sequencing DNA using a hybrid MoS$_2$ in which a nanopore can be opened. Within a similar context, the capability of MoS$_2$ monolayers to act as highly sensitive and selective gas sensors has also been explored experimentally. The electronic current confinement on the entrenched 1T MoS$_2$ nanoribbon could make a hybrid MoS$_2$ device more sensitive to the electronic characteristics of possibly adsorbed biomolecules than the single-phase MoS$_2$ devices. This article is organized as follows: we first present the methodology used and then proceed to the results on the structural, electronic, and transport properties of hybrid MoS$_2$ monolayers. Our results also include a point-defect analysis, which reveals the stability characteristics of the hybrid monolayers. In the end, we discuss the implications of our results on novel nanobiotechnological applications of hybrid MoS$_2$ 2D materials.

**METHODOLOGY**

Density functional theory (DFT) based simulations as implemented in the code SIESTA were carried out. We used the generalized gradient approximation of Perdew–Burke–Erzernhof (PBE-GGA) and the norm-conserving Troullier–Martins pseudopotentials. For expanding the Kohn–Sham states, we considered a double-$\zeta$ with polarization basis set (DZP). An energy shift of 0.01 Ry with a real space sampling grid (mesh cutoff) of 200 Ry and 10 $\times$ 12 k-points within the Monkhorst–Pack scheme were used. This mesh was found suitable for the smallest unit in Figure 1a. The geometry relaxations were performed until the net forces of each atomic component became smaller than 0.01 eV/Å. The electronic transport calculations were performed using DFT combined with the non-equilibrium Green’s functions (NEGF) formalism, as implemented in TranSIESTA.

We first carried out benchmark calculations separately on both the pristine metallic and the semiconducting phases of MoS$_2$. For the pristine 1T phase, the lattice parameter of 3.23 Å and the Mo–S bond length of 2.47 Å were found. Because the pristine free-standing 1T phase is not very stable, there are no experimental data for comparison. We also find that 2H MoS$_2$ is a semiconductor with a direct band gap, a lattice constant, and a Mo–S bond length of 1.64 eV, 3.23 Å, and 2.45 Å, respectively. These values are in very good agreement with previous theoretical results.

In this work, we study a monolayer hybrid MoS$_2$ structure, which combines both the 1T (metallic) and the 2H (semiconducting) phase of MoS$_2$. More specifically, a 1T phase is embedded in the 2H phase as evident from Figure 1e. To investigate the electronic properties of the hybrid MoS$_2$ system, we consider different supercell sizes. The different unit cells used to generate these supercells are shown in Figure 1a–d. These correspond to 36, 48, 60, and 66 atoms per unit cell, respectively. By going from the 36 up to the 66 atom unit cell system, the width of the embedded 1T nanoribbon is increased from 4.7 to 20.5 Å. A k-grid of 60 $\times$ 1 $\times$ 90 is used for the Monkhorst–Pack sampling of the density of states.

The setup for the transport calculations across the hybrid MoS$_2$ monolayer is shown in Figure 1e. The hybrid MoS$_2$ device is composed of the two electrodes (left and right) and the scattering region (device). Both parts, the leads and the scattering region, are hybrid, meaning that these are composed of both the 1T and the 2H phases. With this setup, the electronic transport occurs along the 1T ribbon. The structure shown in Figure 1d was relaxed further up to a force tolerance of 0.001 eV/Å. The resulting relaxed structure formed the lead for the transport setup. The device region was generated by replicating four units of the leads along the z-direction. The electronic transport occurs along the z-direction. The S atoms are shown in brown and the Mo atoms in cyan. The same color coding will be used throughout this work.
transport calculations, finite structures rather than periodic supercells were considered.

■ RESULTS AND DISCUSSION

Structural Characteristics and Defect Analysis. We initially considered a hybrid structure with zigzag edges along the interface. In this case, the fully relaxed atomic structure led to buckling, in agreement with previous results. This buckling did not lead to any significant induced curvature outward from or inward towards the hybrid structure. Theoretical studies have shown that neither the armchair nor the zigzag interfaces in hybrid MoS₂ show out-of-plane distortion. Nevertheless, our findings demonstrate that the armchair interface does not show inflection, but it is the most stable against buckling. Accordingly, the armchair interface will be the one considered herein. Thus, we begin our analysis with the structural details of the hybrid MoS₂ monolayers. Representative fully relaxed structures with varying 1T regions are shown in Figure 2. Inspection of the side view of these reveals a planar system in which distorted bonds due to the interface are evident. From a structural point of view, it is clearly visible from the top views in Figure 2 that the interfaces are armchair-like and not symmetric.

Hence, we chose a nonsymmetric interface, which did not lead to buckling consistent with the experimentally stable structures. To generate this interface, the β- and γ-phases of the interface were shifted by one unit cell in the bottom interface with respect to the top one (“bottom” and “top” refer to the interfaces clearly seen in Figure 1). From Figure 2, it is verified that the 2H phase does not change, whereas the 1T phase presents a structural distortion induced by the interface. Each of the 1T phases contains a Mo–Mo trimer unit. In the pristine 1T phase, all of the Mo–Mo distances are equal to the lattice constant. In our hybrid model, the observed distortion in the 1T region (for all 1T sizes modeled here) can be quantified by the Mo–Mo distance shortening along two of the Mo–Mo distances. These distances are in the range of 2.75–2.85 Å. The third Mo–Mo distance remains undistorted, and its values are close to the lattice parameter (3.15 Å). Similar experimental results have been reported for a Mo–Mo distance of 2.9 Å. Such a partial distortion in the Mo–Mo trimer unit of 1T remains as the number of 1T units increases. This can be confirmed also for the smallest unit cell taken (36 atoms/unit cell in Figure 1a) in which the 1T region is very thin and is equal to about 4.7 Å. Further inspection of this in Figure 2 reveals the atomically sharp interface in conjunction with the experiments. No atom loss or affluence was observed in our hybrid monolayers, in accordance with previous theoretical investigation.

To study the energetic stability of the hybrid system model, we have calculated the formation energy of single sulfur vacancies. Aiming to identify the regions which are energetically more favorable to form vacancies, we move along a sulfur line across the armchair interface of the monolayer as shown in Figure 3 and remove one sulfur atom (labeled and pointed by the arrows in the figure) leaving the monolayer with a single vacancy. The stability is cast in the form of the formation energy of the single point sulfur defect in the monolayer. The calculation of the formation energy, \( E_{\text{form}} \), for a single sulfur vacancy in hybrid MoS₂ is based on the comparison of the total energies of the monolayers with and without the vacancy on the chemical potential of a single sulfur atom as calculated through our simulations. Accordingly, the formation energy is given through

![Figure 2](image1.png)

**Figure 2.** Relaxed structures of the hybrid MoS₂ monolayer for the smallest and largest unit cells from Figure 1a, d. The upper panels show top views, while the lower panels show a side view of the relaxed structures. The gray rectangular regions in the top panel indicate the three periodic unit cells in the structures.

![Figure 3](image2.png)

**Figure 3.** Single vacancy formation energies (\( E_{\text{form}} \)) of sulfur sites located along a vertical line crossing the 66 atom unit cell system. Each bar in the graph gives the formation energy of a single S defect for the corresponding S atoms from the string of encircled atoms below the graph, as denoted by the respective arrow.
The precise fabrication of electronic devices built from hybrid materials such as the 1T/2H MoS₂ monolayer considered here requires a deep understanding of how the electronic structure could be affected by changing the size, as well as the shape, of the 2H and 1T domains in the MoS₂ heterostructure. We have therefore investigated the influence of the width of the embedded 1T-MoS₂ on the electronic properties of the hybrid monolayer. Through the analysis of the electronic density of states (DOS) (shown only for the largest width, see Figure 4), we find that for all the different widths of the 1T ribbon considered here, the hybrid monolayer shows a metallic behavior.

The total electronic DOS of the largest hybrid MoS₂ considered here (see Figure 2b) is depicted in Figure 4a. Results are shown only for this structure, as the relevant properties for the smaller structures are qualitatively similar. The top and bottom panels of this graph display the projected and partial DOS (PDOS) of the same system. From Figure 4a, it can be seen that in the vicinity of the Fermi level the largest contribution comes from the 1T phase. In addition, a comparison of the Mo and S contributions reveals that in both phases, the largest contribution originates from the Mo rather than the S atoms. Regarding the different orbital contributions to the electronic structure, it is known from the literature that in 2H MoS₂ both valence and conducting bands are mainly dominated by the 4d states of Mo with a slight contribution from the 3p states of S. For the single-phase metallic 1T-MoS₂, the 4d states of Mo and the 3p states of S contribute to the electronic states in the vicinity of the Fermi level. The projected DOS decomposition with respect to the 3p and 4d orbitals of the S and Mo atoms in the upper graph of Figure 4a corroborate with previous observations. Indeed, around the Fermi level (from -0.5 to +0.5 eV), the 4d orbitals of Mo and the 3p orbitals of S from the 1T part of the monolayer dominate. The respective orbitals of the 2H phase become more important further away from the Fermi level and are connected to the band gap edges of this phase.

An additional important feature is related to the interface. As mentioned previously, by construction, the interfaces between the 2H and 1T phases in our hybrid MoS₂ model are not symmetric. This asymmetry prompted us to investigate the partial DOS and the contributions of the Mo and S atoms of the 1T and 2H phases close to both interfaces. The different atoms/regions included in the analysis are shown in Figure 4b. The hybrid structure is divided into three regions, the 2H phase, the top 1T, and the bottom 1T phase. The PDOS of the Mo and S atoms in the different parts of the hybrid monolayer

\[
E_{\text{form}} = E_{\text{defect}} + \mu_s - E_{\text{pristine}}
\]
on both sides of the two interfaces are given in the lower panel of Figure 4a. It becomes clear that atoms from the top and down part of the 1T ribbon make different contributions to the total DOS. From this figure, we note that the down part of the 1T region contributes more to the total DOS than the top part of 1T close to the Fermi level, a clear confirmation of the interface asymmetry. The contributions of the Mo atoms in all parts of the system are higher than those from S, as expected. It is also clear that more states are associated with both Mo and S atoms of the down 1T part than in the case of the top 1T part. In view of the transport properties, which we will discuss next, this feature would relate to additional electronic pathways for the movement of electrons along the down interface of the material compared to the top interface.

**Electronic Transport.** We next turn to the calculation of the electronic transport along the hybrid MoS$_2$ monolayer. Previous theoretical studies only considered the coexistence of the 1T and 2H phases within the same monolayer.$^{19,21}$ The studies did not investigate a single 1T ribbon embedded in the 2H phase which more closely resembles the situation in experimental studies$^{17}$ that aim for the realization of electronic transport devices. In fact, the periodic boundary conditions used in the DFT calculations induce a potential repeating across the periodic images of the hybrid MoS$_2$ structure. Within the transport simulations, no such periodicity is assumed. Accordingly, the DOS from the transport calculations reveals a small gap unlike the results from the periodic DFT simulations.

For the structure in Figure 1e, the calculated electronic transmission curves are drawn in Figure 5a. No transmission of typical hybrid MoS$_2$ electronic device. Overall, the transmission profile close to the Fermi level is well structured, having many peaks denoting a large transmission at the respective energies. In the inset of Figure 5a, the transmission curves for the single-phase MoS$_2$, both the 1T and the 2H, are given for comparison. A clear metallic behavior for the 1T phase is shown, while the 2H phase shows zero transmission between roughly −1.0 and 1.0 eV. The transmission function of the hybrid MoS$_2$ shows a stepwise behavior indicating a ballistic transport. Although the transmission of single-phase MoS$_2$ shows a smoother behavior, the system is also ballistic. In the simulations, increasing the number of k-points perpendicular to the transport direction leads to a decrease of the transmission steps until reaching the limit of the smooth curve. The length of the scattering region along the transport direction for the systems studied here is much smaller ($\approx 22 \, \text{Å}$) than the electron mean free path in MoS$_2$. Accordingly, one might expect a ballistic transport for these systems. A similar behavior would be expected even if the device length was increased by several factors. Note that the gap in the hybrid case is much smaller than that in the 2H case. Similar to the small DOS discrepancy between the periodic and the finite structures in Figure 4 and Figure 5b, this might indicate that in the limit of a large width of the 1T phase, the gap in the transport $T(E)$ might close.

To understand the transmission curves in Figure 5a and to unveil the microscopic mechanism behind them, the local currents transmitted across the hybrid system are visualized for the energy values $-0.64$ eV (Figure 6a) and $-0.22$ eV (Figure 6b). The local currents at zero bias essentially map the transmittance projection between two sites and can be obtained from the non-equilibrium Greens functions and the transmission using a Keldysh formalism. Details on the full derivation of the local currents are described elsewhere.$^{29,50}$ Comparison of the two energy values reveals a qualitative difference in the electronic transmission across the hybrid MoS$_2$. The energy value of $-0.64$ eV corresponds to a higher transmission than at $-0.22$ eV (referring to the dotted lines in Figure 5a). The corresponding local currents for these two energies also show different characteristics. Interestingly,
current is not flowing along the whole 1T region as was expected. The local currents are rather associated with specific parts in the 1T ribbon. Figure 6a shows a significant current across the top interface and the top half of the 1T region. The amount of local currents is less on the lower part of the 1T phase. This is confirmed by the zero bias scattering state eigenchannel wave functions (EWFs) (not shown). These wave functions are not equally spread across the metallic region along the transport direction. At this energy, the different signs of the EWFs on the bottom 1T part cancel out, so that there is only a small amount of local current in this region. At −0.64 eV, there is current flowing across a different part of the metallic phase in the hybrid system compared to the case at −0.22 eV. There is more current flowing across the upper half of the metallic region and less current in the lower part at −0.64 eV. At −0.22 eV (Figure 6b), the EWFs are spread out across the lower part of the 1T material and the bottom interface supporting the finding that local currents are found at the bottom interface. The results indicate that at both energies, both Mo and S atoms are involved in promoting the flow of the electrons and that electron motion is indeed associated mainly with the metallic region and the interface, while the 2H phase virtually does not participate. We have chosen two energy values which link the electronic properties shown in Figure 4 to the asymmetry in the structure and transport properties in Figure 6 and the EWFs. Other energies should lead to different contributions to these properties.

One can observe that by construction the bottom and the top interfaces are not symmetric to each other (see Figures 1, 4b) as mentioned in the Structural Characteristics and Defect Analysis section on the structural characteristics of the hybrid MoS₂. Accordingly, depending on the energy, only one of the two interfaces is strongly related to the transport. Across that interface, a layer of Mo and S atoms from the 2H region is involved in the transport. This is evident from the local currents. Nevertheless, we have observed that the energy (or gating voltage) controls which parts of the metallic regions are involved in the transmission. As a way to unveil the mechanism which leads to a transmission along part of the metallic region, we turn again to the partial DOS in the lower graph of Figure 4a. Because of the asymmetry of the interface, the down part of the 1T ribbon has shown a larger contribution to the PDOS close to the Fermi level than the top 1T part (green and orange lines in the lower graph in Figure 4a). This observation can explain the non-homogeneous current flow through the 1T ribbon. In addition, the higher DOS at −0.64 eV compared to −0.22 eV justifies why the currents are localized in the upper 1T part in the former case and the lower 1T part in the latter case as visualized in Figure 6. Nevertheless, on the interface at each energy value, a current accumulation due to interface states has been observed. This analysis shows the strong dependence of the electron transport along the hybrid MoS₂ monolayer on its PDOS and the available electronic states at different parts of the material. Accordingly, these results suggest that a careful design of the hybrid interface would selectively tune the electronic transport along the hybrid monolayer and would control which part of the embedded ribbon is involved in the transmission. Such a design would link to the exact experimental gating voltages leading to the desired transmission pattern.

**SUMMARY**

In this work, we have probed the structural, electronic, and transport properties, as well as the stability of hybrid MoS₂ monolayers. These hybrid systems are composed of a 1T metallic ribbon embedded in the 2H MoS₂ phase forming an interface with armchair edges. We have varied the size of the embedded metallic ribbon in order to assess its influence on the properties of the hybrid system and have obtained converged properties. We have observed the formation of a stable, planar interface which includes atomic sites of different stabilities. Following a single sulfur vacancy analysis along the heterostructure, we have identified the unstable regions of the hybrid system, which are located at the armchair interface. The electronic properties of the hybrid monolayer showed a clear metallic character, as the 1T part of the heterostructure introduces states in the electronic band gap of the 2H region. Clear electronic transmission signals across the structure, which become negligible very close to the Fermi energy, have been observed and are attributed to the finite structures in the calculations. Extrapolation to a large periodic hybrid MoS₂ is expected to promote electron transmission also close to the Fermi level. Visualization of the local currents at different energies clearly manifests the flow of electrons across the metallic part and the interface of the material. The exact features vary with the exact energy value and the asymmetry of the interface. The local currents have verified the strong influence of interface states on the transmission spectra.

Interpretation of our results in view of the current high interest in 2D MoS₂ and in general on TMD structures would lead to 2D materials with tunable properties. This would be a special feature of 2D TMDs as opposed to graphene. Specifically, the variable properties of hybrid MoS₂ would allow for a selective design of electronic devices as controlling the interface between the semiconducting and the embedded metallic phase would lead to a modulation of the transmitted current. Tuning the interface would control not only the amount of current flowing along a device but also the part of the device that is conducting. A further thorough investigation of this polymorphism, as proposed through our work, would lead to new materials and novel applications in nanoelectronics well beyond those based on graphene. Specifically, our point defect investigation is highly relevant to the nanopore formation using an electrochemical reaction process in MoS₂ nanopores and the subsequent detection of translocating DNA.26 Within this concept, our analysis provides a deeper understanding on the earliest stages of the nanopore formation process and a qualitative insight into the direction of pore growth. The results denote that in order to begin a pore-opening process in a hybrid MoS₂ monolayer, first a sulfur atom at the interface needs to be missing. Using then an electrochemical reaction process, the pore opening can be initiated in the neighborhood of the single point defect. We conclude that on the basis of our results, the pore growth is therefore likely to start at the interface and to move favorably in the direction of the 1T phase/interface rather than toward the 2H phase. Accordingly, our work provides important insights regarding the pathways for selectively opening a nanopore in hybrid MoS₂ leading to properties superior to those of single-phase MoS₂. These results are expected to have a large impact on the fabrication of novel nanopores, biosensors, and tunable electronic devices.
Author Contributions

Equally contributing authors.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

G. S. and M. F. acknowledge financial support from the collaborative network SFB 716 “Dynamic simulations of systems with large particle numbers” funded by the German Funding Agency (Deutsche Forschungsgemeinschaft-DFG). The initial benchmarks calculations were performed on the computational resource ForHLR Phase I funded by the Ministry of Science, Research, and the Arts Baden-Württemberg (MWK) and German funding agency (Deutsche Forschungsgemeinschaft-DFG). This research was supported in part by the bwHPC initiative and the bwHPC-C5 project (http://www.bwhpc-c5.de) funded by the MWK and DFG and provided through associated computer services of the JUSTUS HPC facility at the University of Ulm. R. G. A. acknowledges financial support from Carl Tryggers Stiftelse and R. H. S. thanks the Swedish Research Council. W. L. S acknowledges Brazilian agency FAPES. F. A. L. S. thanks the CAPES Foundation (Ministry of Education of Brazil, Brasilia-DF 70040-020) for a scholarship (Process No. 1640/14-3).

REFERENCES

(40) Johari, P.; Shenoy, V. B. Tuning the Electronic Properties of Semiconducting Transition Metal Dichalcogenides by Applying Mechanical Stains. ACS Nano 2012, 6, 5449−5456.