THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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J. Phys. Chem. C, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpcc.5b10904 • Publication Date (Web): 02 Feb 2016

Phase Transition of MoS_2 Bilayer Structures

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Abstract

In the present study, using density functional calculations we have investigated a possible mechanism for the structural phase transition of the semiconducting bilayer 2H-MoS_2 via lithiation. The results indicate that the addition of lithium to the bilayer 2H-MoS_2 transforms the bilayer to a heterostructure of the 2H and 1T structures instead of a complete conversion to the 1T bilayer structure. Therefore, we propose that the desired synthesis of the 1T-MoS_2 from the bulk 2H-MoS_2 takes place through the hybrid 2H-1T structure. Our finding gives physical insight to the experimentally described microscopic mechanism of the phase transition in MoS_2 and enrich the atomic scale understanding of the interaction of MoS_2 with the alkali ions and also other transition metal dichalcogenides manifesting similar phase transition.

Keywords: Heterostructure, density functional theory, bilayer, phase transition, lithiation

Introduction

In the past decade low dimensional materials have drawn much attention due to their unique chemical and physical properties in comparison to their bulk counterparts. The dimensionality reduction may lead to zero-dimensional structure like quantum dots, one dimensional-structures like nanotubes or two-dimensional (2D) structures like graphene. The 2D stuctures have attracted significant attention due to the advent of graphene and other 2D materials like monolayer or few layers of the MoS_2. One of the decisive factor for a significant change in the electronic properties of a few layer and the monolayer structure of the layered compounds like MoS_2 is the interlayer coupling. Although, the coupling is weak but it has dramatic effects on the electronic properties of the layered materials.[1] For example, monolayer MoS_2 is a direct bandgap semiconductor whereas the nature of the bandgap changes from direct to indirect if the number of layers is increased to two or more.[2] In the recent years, monolayer MoS_2 has been explored for a wide gamut of applications, for example, in flexible transistors and sensors,[3–6] photoluminescence,,[7–9] batteries[10] and photodetectors.[11]

The naturally occuring bulk structure of the MoS_2 known as '2H' structure has a trigonal prismatic structure.[12] In the monolayer form it has also been synthesized in a different structure known as '1T' structure which has an octahedral symmetry.[12] The undistorted 1T structure is metallic in nature[8,13,14] whereas it has been found that the 1T-MoS_2 structure shows distortions which gives rise to interesting electronic properties.[15,16] Recently Qian *et. al* have proposed the existence of the Quantum Spin Hall (QSH) effect in the distorted 1T-MoS_2 and it has also been explored for hydrogen evolution reaction (HER)..[12,16] On the other hand, 1T-MoS_2 despite having useful properties does not exist naturally and has to be derived from the 2H-MoS_2.

Different methods have been explored to derive 1T-MoS_2 from the bulk 2H-MoS_2.[17–20] One of the most widely used method involves the intercalation of alkali metal ions in the interlayer spacing of the multilayer structure. Subsequently, the hydration of the alkali ions increases the distance between the layers thus leading to exfoliation of the 1T-MoS_2.[21–24] Unlike mechanical exfoliation to isolated monolayers from the bulk structure, the intercalation method can also be used to tune the crystal structure of the MoS_2. For example, tuning the crystal structure of MoS_2 in the intercalation method using lithium as an intercalant involves the inclusion of the lithium to the MoS_2 crystal which changes in *d*-electron count via electron transfer from the valence *s*-orbital of the lithium to the lowest lying unoccupied energy levels of the transition metal center. In order to accommodate the additional charge a local rearrangement of the atomic structure takes place accompanied by the metal-metal bond distortions[25] which eventually leads to the transformation of the 2H structure of MoS_2 to the 1T structure.

However, despite the large body of work done on the phase transition of the monolayer 2H-MoS_2 to 1T structure, we lack a detailed understanding of the phase transition involving multilayers. Since, the synthesis 1T-MoS_2 in the monolayer form takes place by intercalating the bulk 2H-MoS_2, having an understanding of the phase transition in multilayers will give a more realistic picture of the mechanism involved in the synthesis of the monolayer 1T-

MoS_2. Therefore, in the present work we study the phase transition of the bilayer 2H-MoS_2. Our findings suggest that the lithiation process in the bilayer involves a combination of intercalation and adsorption of lithium. Additionally, we find that instead of complete transformation of both the layers of the 2H structure to the 1T structure, the transformation leads to a heterostructure of the 2H and 1T phases. Based on energetics we find that the 1T side of the heterostructure originates from the 2H layer which has adsorbed and intercalated lithium and not from the 2H layer which has only intercalated lithium. Therefore, based on thermodynamic arguments we suggest that the transformation of the 2H-MoS_2 to 1T-MoS_2 starts from the surface and permeates to the bulk. 1 (a) shows the top and side view of the 2H structure, (b) shows the bilayer of 1T structure and (c) corresponds to a heterostructure of the 2H and 1T phase.

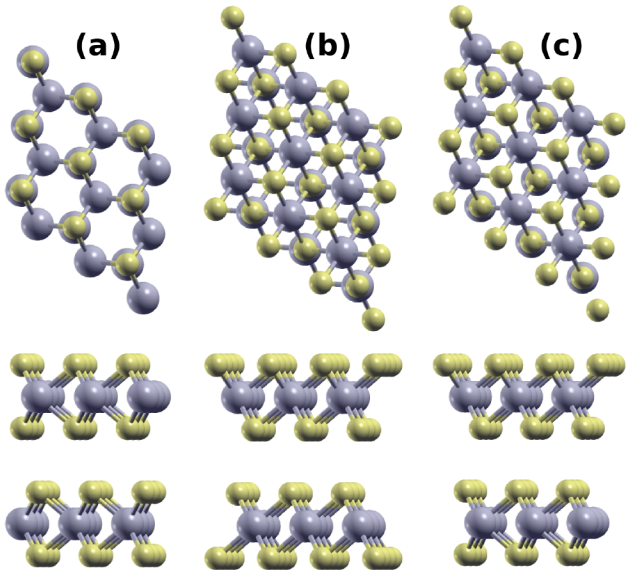

Figure 1: (a) The top and side view of the bilayer of the 2H structure. (b) Similar as (a) for the 1T structure. (c) The heterostructure comprising of monolayer of each of the 2H and 1T structure.

Computational Methodology

All the calculations have been performed using the density functional theory as implemented in Quantum Espresso.[26] Throughout the work the generalized gradient approximation was employed using PW91 functional.[27] The ionic cores have been described by the ultrasoft pseudopotentials taken from the publicly available repository of the Quantum Espresso distribution. Brillouin zone sampling was performed with Monkhorst-Pack scheme[28] and the k-point grid of 4×4×1 has been chosen for all the calculations. The wavefunctions were expanded with a plane wave basis set with a kinetic energy cutoff of 30 Ryd. Electronic occupancies were allowed by using an energy smearing of 0.01 Ryd of Marzari-Vanderbilt scheme. The bilayer MoS_2 surfaces in the present study were represented as two-dimensional slabs in a 3D periodic cell with a periodic 2×2×1 unit cell with 15 Å vacuum to avoid any spurious interactions. Additionaly, to account for van der Waals interactions dispersion corrections were employed. We use 'DFT-D2' treatment of Grimme, which gives a fairly accurate treatment of London dispersion interactions at relatively low computational cost.[29] Structural optimizations were performed until the forces on each atom become less than 10^{-3} eV $Å^{-1}$. For the calculation of the activation barriers climbing image nudged elastic band method (CI-NEB) was used.[30] In order to make sure that the transition takes place via the translation of the sulfur planes as suggested by experiments,[31] few intermediate images with translated sulfur planes are provided for the NEB calculation.

Results and Discussion

In most of the previous experiments the 2H phase of MoS_2 bulk in powder form has been used as a precursor to obtain the 1T phase. On the other hand, recent theoretical studies on the 2H to 1T transformation has been carried out for monolayers. Phase transition involving only the monolayers will be a plausible route when the 2H precursor itself is in the monolayer form. However, most of the lithiation mediated solution phase synthesis of

the 1T structure has been performed with the bulk MoS_2 in the 2H phase. Therefore, it is possible that the synthetic route of the 1T structure with the bulk MoS_2 precursor requires more than one layer of MoS_2. In the current work we explore one such possibility of the phase transition of the 2H to 1T structure in bilayer form via commonly used lithiation process. We emphasize that approximating a multilayer structure by a bilayer structure will not significantly affect the energetics. The effect of hybridization (direct to indirect band gap transition) is already captured in going from the monolayer to bilayer regime. Additionally, the interlayer spacing in the bilayer structure is very close to the interlayer spacing in the bulk. Therefore, approximating a multilayer structure by a bilayer structure is justified for the purpose of the energetics.

As pointed out earlier, the charging (lithiation) of the 2H phase induces an instability in the structure. Eventually, the instability leads to distortions driving the transition from the semiconducting 2H phase to the metallic 1T phase above a threshold charging i.e. above a certain concentration of lithium. Since the 2H and 1T structure differ from each other by a translation of the sulfur plane as shown in the, therefore, a process which eases the translation will drive the transition. Additionally, apart from favoring the distortion, lithiation also weakens the sulfur-metal bonds thus assisting the translation of the sulfur atoms.

In the initial stage of Li addition to the 2H-MoS_2, the following reaction takes place $x\mathrm{Li} + MoS_2 \rightarrow \mathrm{Li}_x MoS_2$ without any substantial change in the atomic structure. This phenomenon has been demonstrated previously in a high resolution scanning transmission electron microscope (STEM)[31] imaging where a heterojunction of the 2H and 1T phase has been observed within the intermediate range of x. In the above mentioned experiment, upon gradual addition of Li atom to the host lattice, a critical range of x is reached where the complete phase transition from the 2H to 1T phase is observed. Additionally, it was also observed that excess addition of the Li atoms, i.e. under deep lithiation 1T-$LiMoS_2$ transforms into Li_2S and Mo cluster. Since the whole process depends solely on the Li atom stoichiometry x, it is vital to get the clear understanding of critical concentration of Li that

stabilizes a particular phase along with a possible mechanism of the phase transition of the 2H to 1T.

In order to have a microscopic understanding of the possible mechanism of the lithiation driven phase transition of the MoS_2 bulk we explore different structures of the MoS_2 bilayer as a model system. The addition of Li atoms in the bilayer structure may result to following possibilities (1) 2H-2H bilayer (2H-2H) (2) 1T-1T bilayer (1T-1T) (3) A heterostructure consist of the 2H and 1T monolayers generating 2H-1T bilayer (2H-1T). These possibilities have also been observed in previous experiments[8,32–34] thus suggesting the transition via multilayer structures a plausible route. Using bilayer as a representative system for the multilayer structure we assess the thermodynamic stability of the bilayers upon Li intercalation/adsorption we calculate the binding energy E_b as,

$$E_b = E^{Li_xMoS_2} - xE_{Li} - E_{MoS_2} \quad (1)$$

where $E^{Li_xMoS_2}$, E_{Li} and E_{MoS_2} are the total energies of the lithiated MoS_2, bulk lithium and the pure MoS_2 host bilayer respectively and x indicates the number of Li atoms in $E^{Li_xMoS_2}$.

In lithiation of the bilayers, the Li atoms can either be intercalated or adsorbed on the surface; hence lithiation in bilayers is different from the monolayer structure where the lithium atoms can only be in an adsorbed state. This difference might give rise to different energetics in the monolayer and the bilayer structure. Therefore, in order to study the thermodynamics of lithiation in the bilayers we systematically adsorb and intercalate lithium atoms and choose the configuration with lowest energy. As a result, we find that the lithiation proceeds via combination of intercalation and adsorption in the following order; intercalation → intercalation → adsorption → intercalation → adsorption. Binding energies of Li are found to be negative for all concentrations, however, it is clear from 2 (a) that binding of Li is more favourable with 1T-MoS_2 than to 2H-MoS_2. The stronger Li binding with the 1T polytype can be justified with the help of crystal field theory.[35,36] For 2H-MoS_2,

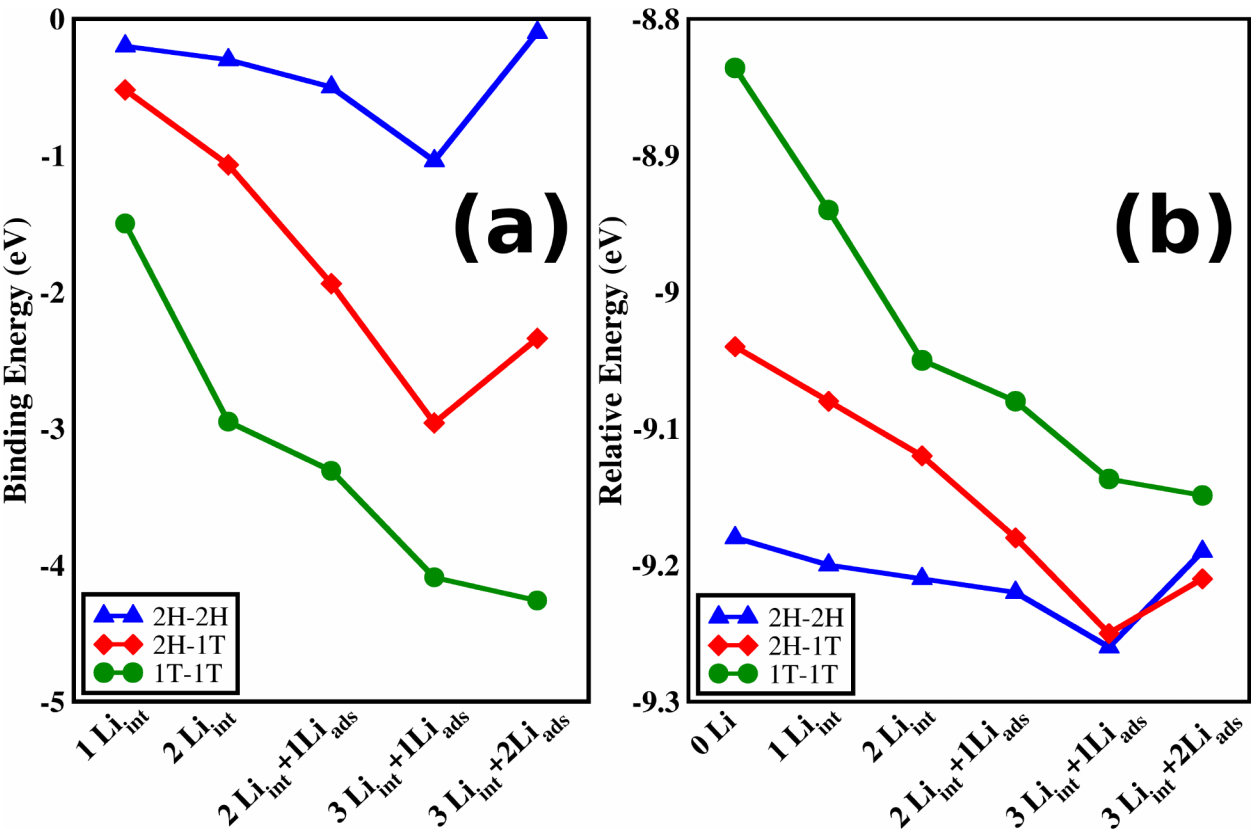

Figure 2: (a) Binding energy per Li atom for 2H-2H, 2H-1T and 1T-1T bilayer of Li_xMoS_2 as a function of Li concentration. Li_{int} and Li_{ads} correspond to intercalated and adsorbed lithium, respectively. (b) Relative energy of 2H-2H, 2H-1T and 1T-1T bilayers as a function of Li concentration.

the lowest energy orbital, Mo $- 4d_{z^2}$ is fully occupied, hence an electron from donor Li has to take in the higher energy orbitals, $4d_{xy}$ and $4d_{x^2-y^2}$. On the other hand, for the 1T-MoS_2, the lowest energy orbitals ($4d_{xy}$, $4d_{yz}$ and $4d_{xz}$) are degenerate and partially occupied; hence, readily accommodate the electrons from Li which leads to a larger negative binding energy.

In order to find out the critical concentration of Li atoms which initiates the phase transition of the 2H-2H bilayer, the relative energies of Li incorporated (2H-1T) and (1T-1T) bilayers have been computed with respect to 2H-2H bilayer. The relative energies are shown in 2 (b). As evident from 2 (b), 2H-2H bilayer is the most stable phase over the concentration range of four Li atoms. However, addition of the fifth Li atom makes the 2H-1T bilayer more stable than 2H-2H one indicating greater thermodynamic stability of the 2H-1T bilayer. The addition of electron donors (Li) in large concentrations causes a mutation of Mo-*d* orbitals stabilising the octahedral coordination of Mo in 1T phase leading to a junction of two different domain boundaries, 2H and 1T layers.[37] The highest energy of 1T-1T phase throughout the lithiation process suggests that there is no probable formation of 1T-1T phase as an intermediate during the transition. It can be concluded from the above observations that the transformation of the bulk 2H-MoS_2 to the bulk 1T-MoS_2 is a dynamical process which takes place layer by layer.

Based on the above thermodynamic analyses we explore the kinetics of one possible pathway for the phase transition. The pathway explored involves the gliding of the sulfur plane which breaks the mirror plane symmetry of the 2H monolayer and converts it to a 1T monolayer. The suggested route for the phase transition is qualitatively similar to the recent experiments exploring the mechanism of phase transition involves gliding of the sulfur atomic plane which occurs in two stages, namely nucleation of the 1T phase and growth of the 1T phase via migration of the two domain boundaries.[31] The suggested pathway is shown in the 3. The kinetic barriers are calculated with and without the lithiation and are shown in the 1. The table clearly shows that the lithiation significantly reduces the barrier and it has the minimum value for the 2H-2H $\rightarrow$ 2H-1T transition. Additionally, the final

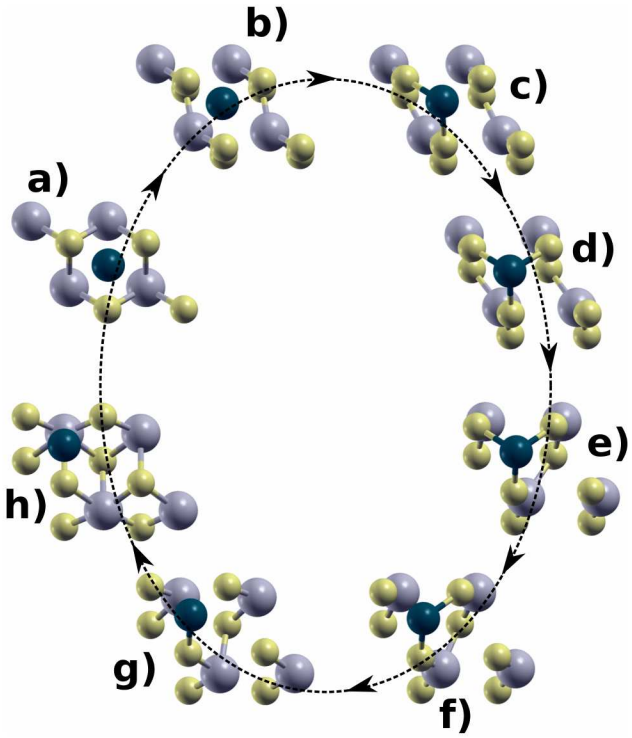

Figure 3: Top view of few steps involved in the proposed pathway for the transtion of the 2H structure to the 1T structure via lithiation. (a) represents the starting 2H phase whereas (h) represents end product of the transition i.e. the 1T phase and the remaining sub-figures show intermediate structures. Grey, yellow and dark cyan spheres represent molybdenum, sulfur and lithium atoms respectively.

step being de-lithiation in the process of solution phase synthesis, the back transition of the 2H-1T bilayer is prevented due to significantly large barrier for the transtion of the 1T structure to the 2H structure in the absence of lithium.

Table 1: Kinetic barriers for the phase transition. 'BL' denotes bilayer whereas 'ML' denotes monolayer. All the barriers are in eV

Structure	Lithiation	Barrier (eV)
2H-2H (BL) $\rightarrow$ 2H-1T (BL)	yes	0.70
2H (ML) $\rightarrow$ 1T (ML)	yes	0.95
1T (ML) $\rightarrow$ 2H (ML)	yes	0.43
2H (ML) $\rightarrow$ 1T (ML)	no	1.72
1T (ML) $\rightarrow$ 2H (ML)	no	0.95

Conclusion

In the current study we explore the thermodynamics of lithiation driven transition of the bilayer 2H-MoS2 to the bilayer of 1T structure and a heterostructure containing the 2H and 1T monolayers. The study of the bilayer is expected to represent the phase transition of the bulk MoS2. The results show that the lithiation occurs in a combination of intercalation and adsorption thus favoring the transition initiating from the surface layer and permeating to the bulk. Additionally, the calculated kinetic barrier for different pathways indicate that the inclusion of lithium significantly decreases the barrier in all the cases. The agreement of our model systems and results and few recent experiments makes our approach potentially useful for other metal dichalcogenides existing in the 2H and 1T structure and their phase transition. The findings of this study help in identifying possible transition pathways and guides towards the synthesis of the different phases of transition metal dichalcogenides.

Acknowledgments

PB acknowledges the CSIR for a research fellowship. SKP acknowledges research support from the CSIR and DST, Government of India.

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