MoS Enhanced T-Phase Stabilization and Tunability Through Alloying

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MoS$_2$ Enhanced T-Phase Stabilization and Tunability Through Allo"yng

Federico Raffone,$^*$ Can Ataca,$^*$‡ Jeffrey C. Grossman,$^‡$ and Giancarlo Cicero$^*$‡

†Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, Corso Duca degli Abruzzi 24, Torino 10129, Italy
‡Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Two-dimensional MoS$_2$ is a promising material for nanoelectronics and catalysis, but its potential is not fully exploited since proper control of its multiple phases (H, T, ZT) and electronic properties is lacking. In this theoretical study, alloying is proposed as a method to stabilize the MoS$_2$ T-phase. In particular, MoS$_2$ is alloyed with another material that is known to exist in a monolayer MX$_2$ T-structure, and we show that the formation energy difference among phases decreases even for low impurity concentrations in MoS$_2$, and a relationship between impurity concentration and alloy band gap is established. This method can be potentially applied to many two-dimensional materials to tune/enhance their electronic properties and stabilities in order to suit the desired application.

Among two-dimensional transition metal dichalcogenides (TMDs), MoS$_2$ has attracted the most attention due to its semiconducting characteristics and its direct band gap that make it suitable for a large number of applications. MoS$_2$ has been applied in electronics as a FET channel, in energy storage as lithium-ion battery anode or cathode, or in catalysis for CO$_2$ reduction. A small energy gap (theoretically predicted to be around 0.02 eV) is opened. Recently, much effort has been made to stabilize T phases over H with the aim of gaining enhanced electrical performance, such as lower contact resistance among phases decreases even for low impurity concentrations in MoS$_2$. In this theoretical work we propose a new route for the MoS$_2$ T-phase stabilization: alloying with an MX$_2$ (M: metal, X: chalcogen atom) material for which the T phase is the thermodynamically stable one. In particular, SnS$_2$ is found to be a suitable candidate for such a purpose, since it is known to exist in the T phase only. The advantage of alloying is that doping concentration is a direct way to tune MoS$_2$ properties, and a new degree of freedom would then be added to engineer devices based on this possibility. Unlike other techniques such as functionalization, alloying would not render TMDs susceptible to deterioration of organic bonds in air, although if desired the monolayer could still be chemically functionalized for further optimization.

The effects of substitutional impurities in MoS$_2$ have been studied both theoretically and experimentally. For example, Su et al. were able to dope single crystal H-MoS$_2$ with Nb up to 0.5% atomic percentage with the intention of realizing a p-type semiconductor. Concentrations up to 25% were experimentally reported in fullerene-like Nb$_x$Mo$_{1-x}$S$_2$ nanoparticles. Subsequently, Re impurities were successfully introduced both in Mo$_x$ fullerene-like nanoparticles and nanotubes. Modulation of the band gap was achieved by Se substitution in single layer MoS$_2$ and confirmed by photoluminescence experiments. An extensive theoretical work on a large variety of impurities has been performed by Dolui et al., who predicted Nb to be the most suitable p-type dopant due to its low formation energy and the induced shift of Fermi level into the valence band. By contrast, n-type dopants were found to generate deep donor levels in the MoS$_2$ band gap making electron promotion to the conduction band difficult.

In this study a combined density functional theory (DFT) and cluster expansion (CE) based approach is used to predict the structural and electronic properties of Mo$_x$Sn$_{1-x}$S$_2$ alloys with the aim of stabilizing the metallic MoS$_2$ phase. Cluster expansion has already been applied to MoS$_2$ to investigate how H-MoS$_2$ formation energy, lattice constant and band gap change when substituting Se and Te to S. Here, we exploit CE to compare the stability among MoS$_2$ phases, which also serves more broadly as an example for how the cluster expansion method has already been applied to MoS$_2$.
Moreover, even though the H-MoS2 total energy is known to be lowered by spin–orbit coupling, accounting for SOC in the cluster expansion does not alter the phase crossover point, indicating that SOC effects have a negligible impact on the stability analysis.

Before considering the alloying between MoS2 and SnS2, we calculate and discuss the properties of the pure phase as predicted by PBE-DFT. In Table 1, we list our calculated lattice parameters, bond distances, electronic band gaps, and relative formation energies. The MoS2 and SnS2 characteristics are well represented by the PBE functional and agree with previous results. The MoS2 phase stability ordering is also in good agreement with previous work, with H the most stable phase followed by ZT and T. H-MoS2 possesses a 1.58 eV band gap which is reduced to 0.06 eV in the ZT phase and disappears in the T phase. A small difference was found in terms of bond distances between H and T, while ZT distances vary greatly due to its puckered structure. In the case of tin, T-SnS2 is semiconducting with a PBE band gap of 1.57 eV. H-SnS2 is 0.87 eV higher in energy with respect to the T phase, and it has a band gap of 0.78 eV, although negative frequencies are found in the phonon dispersion spectrum, indicating a thermodynamically unstable structure.

### Table 1. MoS2 and SnS2 Monolayers Lattice Constants a and b, Metal–Sulfur Bond Distance d_{M-S}, Electronic Band Gap E_g, and Energy Difference ΔE Calculated with Respect to the Most Stable Phase for Each Material

<table>
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<tr>
<th>Material</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>d_{M-S} (Å)</th>
<th>E_g (eV)</th>
<th>ΔE (eV)</th>
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<tr>
<td>H-MoS2</td>
<td>3.19</td>
<td>3.19</td>
<td>2.41</td>
<td>1.58</td>
<td>0.00</td>
</tr>
<tr>
<td>T-MoS2</td>
<td>3.21</td>
<td>3.21</td>
<td>2.43</td>
<td>0.00</td>
<td>0.82</td>
</tr>
<tr>
<td>ZT-MoS2</td>
<td>6.51</td>
<td>3.19</td>
<td>2.39−2.46</td>
<td>0.06</td>
<td>0.59</td>
</tr>
<tr>
<td>H-SnS2</td>
<td>3.60</td>
<td>3.60</td>
<td>2.63</td>
<td>0.78</td>
<td>0.87</td>
</tr>
<tr>
<td>T-SnS2</td>
<td>3.69</td>
<td>3.69</td>
<td>2.59</td>
<td>1.57</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The CE of each phase (H, T, ZT) was computed separately, leading to three phase diagrams. Since SnS2 has no native ZT phase, SnS2 automatically recovered the T symmetry upon DFT relaxation when no Mo dopant was present. Results of cluster expansion performed on the three phases are plotted together in Figure 1, where the two reference energies are T−SnS2 total energy for concentration x = 0 and H-MoS2 total energy for x = 1. The H phase CE is plotted in blue, T phase in green, and ZT phase CE in red. The graph describes how the energy of each phase varies with respect to the most stable one. Figure 1a illustrates the energy of each DFT structure used in the expansion, whereas Figure 1b shows the related energy differences, i.e., the alloy configurational energies predicted by CE resulting from the DFT calculations. In both plots, the solid line represents the convex hull, which shows all the ground states throughout the phase diagram. DFT and fitted energies agree among each other, confirming the validity of the expansions. The large set of DFT calculations was needed to guarantee the correct identification of the ground state structures and to improve the accuracy of the expansion. The only difference between DFT and fitted energies is seen at x = 1 in the T phase. Pure T-MoS2 is unstable, so including this structure in the T phase CE would necessarily lead to inaccurate results. Therefore, for x = 1 only, the ZT-MoS2 DFT energy was taken as a reference point for the T phase CE (shown in Figure 1b), although T-MoS2 was left in Figure 1a for reference.
The reason for this is that Sn atoms introduce distortions and relaxation toward the more stable ZT phase. In ZT/T alloy in the MoS2 sheet that alter the initial T ordering and allow for substantial dissimilarity among structures arising from T and ZT phases. As seen in Figure 1, the only point in which the two phases differ is the elongation of the Mo−S bonds. Sn atoms are represented in red, and S atoms in yellow.

Moreover, the Sn−S bonds are reduced to 2.57 Å while bonds involving Mo are elongated to 2.49 Å from 2.43 Å in the pure T phase.

Beyond the phase stabilization itself, we next explore the question of whether the T and ZT MoS2 metallic behavior is conserved while alloying with Sn. Thanks to the large set of DFT calculations employed in the expansion fitting procedure, electronic properties can be effectively monitored throughout the phase diagram by extracting the electronic band gap of those calculated structures. Results are plotted in Figure 3a, which closely resembles the cluster expansion graph in Figure 1a. Each phase is represented by a different symbol (square for H, star for T and diamond for ZT), while the color indicates the band gap. In the 0.7−1 Mo concentration range both the T and ZT phase lowest energy structures are metallic, indicating that small amounts of Sn in MoS2 do not affect the metallic character of the compound.

Another important trend shown in Figure 3a is the appearance of semiconducting configurations in the mid Mo concentration range of the phase diagram. Although in the 0.35−0.65 concentration range there are many materials with negligible band gap, all of the most stable structures are indeed semiconducting. PBE band gaps extend from 0.2 to 0.9 eV. As a result, alloying not only stabilizes the T-phase but also gives the possibility of tuning electronic properties without causing a phase change.

A remarkable phenomenon occurs also within the most stable phases of both MoS2 and SnS2, respectively the H and T phases. As seen in Figure 3a, a slight doping causes a transition from semiconductor to metal. From the analysis of the densities of states (DOS) of the DFT calculated structures, we observe that in some cases a peak in energy close to either the valence or conduction band arises (structure labeled with II in Figure 3b), indicating that conduction for these cases is due to the doping effect of the impurities that generate defect states, respectively withdrawing or donating electrons from/to semiconductor bands. By contrast, the DOS of other configurations show broadened states across the Fermi level (structure labeled with I in Figure 3b), suggesting that band conduction takes place in these structures. The projected DOS and electronic densities at the Fermi level (Supporting Information) confirm this conclusion.

The semiconductor-metal transition observed in MoSn2−xS2−x by changing the alloy composition has many potential applications.

**Figure 1.** SnS2−MoS2 phase diagram showing the DFT calculated energies used for the CE fitting (a) and the resulting predicted energies from the CE (b). H, T, and ZT phases are respectively represented in blue, green, and red. In both plots, the reference energies are the DFT total energies of T-SnS2 for x = 0 and H-MoS2 for x = 1.

Energetically, the most stable phase of MoS2 is the H phase (Table 1 and right side of Figure 1). As tin is added within the MoS2 layer, the formation energy of the H phase increases, while formation energies of the T and ZT phases decrease until they become the most stable ones in the Mo-rich side of the plot, at around x = 0.6. Due to this simultaneous effect, even with a small amount of impurity atoms in MoS2, the energy difference among phases at fixed concentrations is reduced. Already at x = 0.8, the ZT/H formation energy is lowered by ~50% compared to the pure phases. Hence, alloying has a large impact on the MoS2 phase balance. The more Sn atoms, which would prefer to arrange in the T phase, the easier it is to turn H-MoS2 into the T/ZT phase. The opposite trend is seen in the Sn-rich portion of the phase diagram (left-hand side of Figure 1). However, due to the position of the phase crossover point at x = 0.6 arising from the higher energy difference of the pure SnS2 phases with respect to the MoS2 ones, the phase energy difference is slowly reduced as Mo is added.

Remarkably, the T and ZT phases coincide in the CE graph in Figure 1. The only point in which the two phases differ is the undoped case that, as stated before, does not exist. Inspection of the DFT structures used to interpolate the CE showed no substantial dissimilarity among structures arising from T and ZT expansions; all Mo-rich alloys showed the same puckered sulfur arrangement of ZT phase (an example is shown in Figure 2a). The reason for this is that Sn atoms introduce distortions in the MoS2 sheet that alter the initial T ordering and allow for relaxation toward the more stable ZT phase. In ZT/T alloy structures in the x ≥ 0.8 portion of the plot, a progressive elongation of the Mo−S bond is observed from the 2.39−2.46 Å range to the 2.40−2.49 Å range as more Sn is added. At the same time the Sn−S bond is reduced to 2.53−2.54 Å from the initial 2.59 Å. On the other hand, Sn-rich DFT structures (Figure 2b) show the typical T arrangement due to the higher Sn content. Sn−S bonds are reduced to 2.57 Å while bonds involving Mo are elongated to 2.49 Å from 2.43 Å in the pure T phase.

**Figure 2.** Side view of two examples of T-phase alloys for x = 0.8 (a) and x ≤ 0.2 (b). Mo atoms are represented in blue, Sn atoms in red, and S atoms in yellow.
268 applications. For instance, it allows for the design of metal−
269 semiconductor (MS) junctions for optical and photovoltaic
270 purposes simply by joining two alloy sheets in the same phase
271 at different concentrations. The feasibility of such structures has
272 already been proven for other TMDs (see ref 32). A sample
273 junction is here analyzed to show how this method can be
274 potentially applied. Pure H-MoS2 was interfaced in plane with a
275 metallic H−Mo0.75Sn0.25S2 forming a monolayer MS junction as
276 shown in Figure 4. For the above-mentioned applications the
277 junction must have a highly electron-blocking or hole-blocking
278 Schottky barrier (SB) in order to separate photogenerated
279 charge carriers. The SB is de
280 fined as the di
281 ff
282 ference between
283 Fermi level and valence band maximum (for holes) or
284 conduction band minimum (for electrons) of the semi-
285 conductor. One detrimental phenomenon that may occur
286 when interfacing a metal with a semiconductor is so-called
287 Fermi level pinning, which causes the Fermi level to move to
288 the center of the semiconductor band gap. As a result, electron
289 SB matches hole SB and carriers are not effectively dissociated.
290 Charge redistribution, new bond formation, and interface states
291 are often regarded as the source of the Fermi level pinning
292 effect.33 All these features were analyzed to gauge their impact
293 on the H-MoS2/Mo0.75Sn0.25S2 SB height. Since both metal and
294 semiconductor share the same lattice, no bond is broken when
295 the two materials are brought together. This can be seen by
296 analyzing the DOS of the H-MoS2 and H-Mo0.75Sn0.25S2 part of
297 the heterojunction reported in Figure S5, before and after
298 joining them into the MS junction. Both structures present gap
299 states arising from dangling bonds at the edge of the slabs. Such
300 states are completely removed when the slabs are joined to
301 form the heterostructure of Figure 4 because all bonds become
302 saturated. Bader charge analysis predicts a very small electron
303 transfer toward the semiconductor per interface unit length
304 (~0.01 e−/Å), affecting only the two rows of atoms that are
305 closest to the interface. As a consequence, limited Fermi level
306 pinning is expected for this junction. To measure the SBs, the
307 band structure and projected DOS of the MS interface were
308 plotted (Figure 5). Since metal states overlap with semi-
309 conductor bands, the identification of the H-MoS2 valence band
310 maximum and conduction band minimum is obtained,307 projecting the electronic states of the semiconductor innermost
311 Mo atoms (shown in blue in Figure 5). As seen in Figure 5, the
312 electron SB was calculated to be 1.26 eV, while hole SB was
313 0.32 eV. These results indicate that a H-MoS2/Mo0.75Sn0.25S2
314 junction would be suitable for photovoltaic applications. Once
315

Figure 3. (a) Electronic band gap energies of the DFT structures plotted in Figure 1 for the three phases. H phase is marked with squares, T with stars, and ZT with diamonds. The colormap indicating the band gap was truncated to 0.6 eV to highlight differences between metallic and semiconducting systems. (b) Examples of DOS representative of both band (I dashed circles of panel a) and doping (II circle) conduction.

Figure 4. H-MoS2/Mo0.75Sn0.25S2 metal−semiconductor junction structure, side (a) and top (b) view. Molybdenum atoms are represented in blue, tin atoms in red, and sulfur in yellow.

Figure 5. H-MoS2/Mo0.75Sn0.25S2 metal−semiconductor junction projected band structure and projected density of states. The total DOS lines are plotted in gray, while the ones referring to the semiconductor-side innermost molybdenum atoms are shown in blue. Resulting Schottky barriers for electrons and holes are respectively indicated as e-SB and h-SB.
313 electron–hole pairs are photogenerated in H-MoS2 holes can
314 easily diffuse into the metal due to band bending at the interface for a n-doped semiconductor. Electrons, by contrast,
315 are blocked by the 1.26 eV Schottky barrier so that a net photocurrent can flow through the device. Doping H-MoS2
316 with the opposite polarity could lead to interesting optical devices for light detection. In this case it is the 0.32 eV h-SB
317 process:34,35 when photons with energy between h-SB and the MoS2 band gap impinge on the junction, holes from the metal side jump above the barrier and are injected into the semiconductor giving rise to a net photocurrent. Due to the small barrier height, such a device could detect light down to the infrared range. Even assuming a gradual change in doping concentration of the H–Mo$_x$Sn$_{1−x}$S$_2$ side, the junction will still result in a metal–semiconductor interface since for low substitutional concentrations of Sn in H-MoS2 the alloy behaves as a metal (see Figure 3a). Thanks to the large concentration range of metallic alloys, there is no need for precise doping to achieve a MS junction.

333 To conclude, a new technique for MoS2 T-phase stabilization was proposed based on alloying with another metal dichalcogenide with stable T phase in order to induce a phase switch from H to T. A combined cluster expansion and DFT approach was exploited to theoretically predict the phase diagram. Our results show that the addition of impurities efficiently lowers the energetic cost of the T-phase, and that alloying is an effective way to tune the TMD electronic properties. The reported intraphase metal–semiconductor transition occurring for a slightly doped material could be useful for multiple applications. Toward this end, we examined a MS junction between H-MoS2 and H-Mo$_x$Sn$_{1−x}$S$_2$ and found that due to the electron and hole SB heights, the junction could be suitable for photovoltaic and photodetection applications.

## ASSOCIATED CONTENT

338 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b00794.

342 MoS$_2$ and SnS$_2$ spin–orbit coupling effect, phonon spectra, impurity–impurity interaction, ECI coefficients in Cluster Expansion, band conduction in T/ZT alloys in CE and metal–semiconductor junction characterization. (PDF)

## AUTHOR INFORMATION

Corresponding Authors

*E-mail: ataca@mit.edu.

*E-mail: giancarlo.cicero@polito.it.

Notes

The authors decline any competing financial interest.

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