Nonstoichiometric Phases of Two-Dimensional Transition-Metal Dichalcogenides: From Chalcogen Vacancies to Pure Metal Membranes

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ABSTRACT: Two-dimensional (2D) membranes consisting of a single layer of Mo atoms were recently manufactured [Adv. Mater. 2018, 30, 1707281] from MoSe₂ sheets by sputtering Se atoms using an electron beam in a transmission electron microscope. This is an unexpected result as formation of Mo clusters should energetically be more favorable. To get microscopic insights into the energetics of realistic Mo membranes and nonstoichiometric phases of transition-metal dichalcogenides (TMDs) MₓXᵧ, where M = Mo and W and X = S, Se, and Te, we carry out first-principles calculations and demonstrate that the membranes, which can be referred to as metallic quantum dots embedded into a semiconducting matrix, can be stabilized by charge transfer. We also show that an ideal neutral 2D Mo or W sheet is not flat but a corrugated structure, with a square lattice being the lowest-energy configuration. We further demonstrate that several intermediate nonstoichiometric phases of TMDs are possible as they have lower formation energies than pure metal membranes. Among them, the orthorhombic metallic 2D MₓXᵧ phase is particularly stable. Finally, we study the properties of this phase in detail and discuss how it can be manufactured by the top-down approaches.

Recent progress in the mechanical and liquid exfoliation of two-dimensional (2D) systems from layered bulk solids bonded by weak van der Waals (vdW) forces, as well as their direct synthesis by chemical methods, made it possible to manufacture dozens of 2D materials with unique and diverse characteristics. In addition to tailoring their properties for particular applications, the investigations of 2D systems gave rise to a fundamental question: Is it possible to synthesize free-standing 2D counterparts of solids, which normally have bulk isotropic, but not layered, structure? Recent experiments indicated that this is indeed possible as hematene layers were indicated that this is indeed possible. In that context, a lot of attention has also been paid to free-standing 2D metals. Specifically, patches of 2D iron were reported to appear inside of graphene nanopores in the transmission electron microscopy (TEM) experiments. Likewise, suspended one-atom-thick Mo membranes were recently fabricated from monolayer MoSe₂ sheets via complete sputtering of Se atoms in a scanning TEM. As for the theoretical efforts, the trends in the stability and properties of perfectly flat 2D metals have been studied using first-principles calculations, along with the energetics of small 2D metallic patches embedded in graphene and stabilized by the strong covalent bonds at the metal–graphene interface. It should be pointed out, though, that the experimental observations of 2D systems, which were interpreted as pure metal membranes, could also be explained through the formation of mixed 2D phases, e.g., carbides or oxides, as reported for gold, iron, or copper, which hints that mixed phases may also be present in the case of 2D Mo embedded into MoSe₂ sheets.

Specifically, taking into account that Mo sheets were produced by the electron beam by removal of Se atoms from 2D MoSe₂, there are several contradictions or points that should be clarified. The membranes were reported to have a hexagonal structure, but the calculated and experimentally measured bond lengths did not match. This may be due to the mechanical strain present in the system, but, as we show below,
a hexagonal lattice does not correspond to the lowest-energy 2D configuration of Mo. Besides, as Se atoms were gradually (over a time of a few minutes) removed by the electron beam, similar to other experiments on the exposure of TMDs to electron-beam irradiation, a natural question is why other phases with intermediate stoichiometry were not observed, contrary to, e.g., tin dichalcogenides. This problem is not only of fundamental importance but also directly relevant to the electron-beam engineering of 2D materials.

In this work, we use extensive first-principles calculations to study the structure and energetics of 2D metals and nonstoichiometric phases of MoSe₂ and some other most common 2D transition-metal dichalcogenides (TMDs). The 2D phases were assumed to appear by the formation and aggregation of vacancies in the pristine system. The energetics of the 2D materials with different stoichiometries is analyzed for a wide range of chemical potentials. We further calculate the electronic structure of the most stable nonstoichiometric phase. Specifically, we employed density functional theory (DFT) as implemented in the VASP code, with the PBE exchange and correlation functional. A plane-wave cutoff of 600 eV was used in all of the calculations. The geometry optimization was carried out based on minimization of the forces acting on the atoms in the structure, with the force tolerance being set to 0.01 eV Å⁻¹. The Brillouin zone of the primitive cells of the materials was sampled with a 12 × 12 × 1 Monkhorst-Pack k-mesh. We also carried out test calculations using GPAW code and got similar results.

We simulated both finite metallic patches inside of a sheet of the parent TMD and infinite nonstoichiometric sheets assuming that they are also embedded into the 2D TMDs. In the latter case, we used two approaches: “manual” search for the metastable nonstoichiometric phases and “automatic” search using the evolutionary algorithm USPEX, which is a powerful tool for predicting stable compounds of various dimensionalities of given elements. USPEX was successfully extended to 2D materials. First, the variable-composition search for stable 2D-MoₓSeᵧ was performed using the algorithm described in ref. There were two searches with the initial thickness of the layer equal to 3 and 5 Å because MoₓSeᵧ may prefer nonplanar structures. Both calculations showed similar results. There were three stable structures predicted, namely, Mo₅Se₂, MoSe, and MoSe₂. After that, for each stable composition, the fixed-composition search was performed in order to predict the most thermodynamically stable structure of each composition. Computational search for free-standing two-dimensional MoₓSeᵧ and MoSe layers was performed with 2, 3, 4, 8, and 12 formula units in the considered unit cell. The first generation of 160 structures was created using a plane group symmetry generator, while all subsequent generations contained 20% random structures, and 80% were created using heredity, soft mutation, and trans-mutation variation operators. The newly produced structures were all relaxed, and the energies were used for selecting structures as parents for the new generation of structures. Structure relaxations were performed with the same DFT method with the exception that the plane-wave kinetic energy cutoff was set to 500 eV and the Brillouin zone was samples by Γ-centered k-point meshes with a resolution of $2\pi \times 0.05$ ā⁻¹. The phonon density of states of predicted MoSe was calculated...
using the finite displacement method as implemented in the PHONOPY code.

The annular dark field scanning TEM (ADF-STEM) image simulations were carried out with the Dr. Probe code assuming an aberration-free probe and $5 \text{ Å}$ source size to give a focus spread of $3.0 \text{ nm}$. The STEM simulations were performed at $80 \text{kV}$ with a $30 \text{ mrad}$ illumination half-angle and $20 \text{ mrad}$ outer detection angle.

We studied first the energetics of the periodic 2D phases of transition metals, which are present in the most common TMDs: Mo and W. To assess the stability of 2D metals, the atomic structure of various 2D infinite periodic systems was fully optimized without any constraints, and cohesive energy $E_{\text{cohesive}}$ was calculated. It was defined as usual as $E_{\text{cohesive}} = E_{\text{atom}} - \frac{E(N)}{N}$, where $E_{\text{atom}}$ is the energy of an isolated atom, $E$ is the energy of the structure, and $N$ the total number of atoms in the unit cell. Note that $E_{\text{cohesive}}$ is positive, and larger values indicate a higher stability of the system.

The atomic structures of transition metal membranes and the associated cohesive energies are presented in Figure 1. Contrary to the simulation setup employed in ref 8, where perfectly flat structures were studied to get insights into the trends in the geometry and bonding, we allowed out-of-plane relaxation. Our results for flat structures proved to be in good agreement with those presented in ref 8, and the hexagonal (flat) phase was found to have the highest cohesive energy for both Mo and W. However, our simulations indicate that when out-of-plane relaxation is allowed the most energetically favorable phase is the square one. This stresses the importance of the out-of-plane degrees of freedom for the realistic 2D materials in the three-dimensional space.

However, a Mo hexagonal lattice was observed in the experiment, contrary to the most energetically favorable square lattice. The experimental bond length was found to be $2.7 \text{ Å}$. From our simulations, the apparent separation between the atoms (projected into the plane) in the corrugated hexagonal lattice and the planar hexagonal lattice is $2.47$ and $2.57 \text{ Å}$, respectively, in the case of Mo. Because the Mo domains are formed by sputtering of Se atoms from MoSe$_2$, the islands may be subjected to tensile strain, but to match the experiment, strain must be rather high, nearly $10\%$. Moreover, careful analysis of the STEM images shown in Figures 1 – 3 in ref 7 using the scale bar of $5 \text{ Å}$ indicates that many bonds are much longer, nearly $3 \text{ Å}$. The same conclusion also can be drawn from the analysis of the atomically perfect interface between MoSe$_2$ and the new phase, which suggests close lattice constants of both phases. The tensile strain of $20\%$ is unrealistically high, especially with account for migration of Mo atoms into the membrane areas, as observed in the experiment, and in general, it is unclear why hexagonal lattice is preferred.

To understand the reason for large separations between the atoms, we considered possible charging of Mo membranes. A Mo island in a MoSe$_2$ sheet is essentially a quantum dot embedded into a semiconductor matrix. If the sample is n-type doped, it may give rise to negative charge accumulation. The additional charge may also come from other defects created in MoSe$_2$ by the electron beam or adsorption of impurities on these defects, which gives rise to the occupied or partially occupied defect-induced states in the gap.

Simulations for the neutral and charged systems were conducted, and the results are presented in Figure 2. In the neutral system considered, a small cluster of metal atoms is formed, and the cluster moves then to one of the edges. The behavior of the charged system is different. As evident from Figure 2c, the extra charge is localized in the membrane area, giving rise to longer bonds between the metal atoms. From the radial distribution function shown in Figure 2d, it is clear that charging of the system improves the agreement between theory and experiment. With a charge of $0.2 \text{ e}$, the bond length of the structure matches well the experimental value of $2.7 \text{ Å}$, with some distortions at the edges of the interface to MoSe$_2$. Moreover, calculations for infinite free-standing metals showed...
that the hexagonal phase is energetically preferable over the square lattice when an additional charge is added.

As an alternative scenario, we also investigated the changes in the atomic structure of the membrane when extra Mo atoms are added to the system, Figure 2b. Extra atoms do stabilize the membrane, but interatomic distances are smaller than those in the experiment, as follows from Figure 2b and the analysis of the radial distribution function. On the basis of these results, it appears that accumulation of the extra charge is the main reason for the stabilization of the membrane and rather a long separation between the Mo atoms.

As in the experiment, Se atoms were gradually (over a time of a few minutes) sputtered by the electron beam before patches of pure metals were produced; we also studied phases with intermediate stoichiometry, which hypothetically can also appear in the chalcogen-deficient material. We considered various nonstoichiometric binary compounds \( M_xX_{2(a-b)} \), where \( M = \text{Mo and W} \) and \( X = \text{S, Se, and Te} \). Mimicking the experimental situation, the phases were created by adding vacancies to the pristine structure and optimizing the geometry. Some of the structures that we studied are shown in Figure 3. The stability of these phases, which should naturally depend on the chemical potentials of the atoms, was evaluated by calculating the formation energies of the structures. Assuming that the nonstoichiometric phase is embedded into the pristine stoichiometric phase, the formation energy \( E_f \) per formula unit of the phase \( M_xX_{a-b} \) consisting of \( a \) transition metal atoms and \( b \) chalcogen atoms was calculated as a function of chalcogen atom chemical potential \( \mu_X \) as

\[
E_f = \frac{E(MX_b)}{a} - E(MX_a) + \frac{2a - b}{a} \mu_X
\]

where \( E(MX_b) \) and \( E(MX_a) \) are the total energies of the primitive cells of the nonstoichiometric and stoichiometric phases, respectively. Correspondingly, for any value of \( \mu_X \), the formation energy \( E_f \) of the \( MX_2 \) phase is zero. Equation 1 is essentially the formation energy of a defect in the pristine material normalized to the defect area. We stress that in these calculations we do not take into account the actual structure of the interface between the stoichiometric and nonstoichiometric phases, assuming that the structure is large enough, so that the interfaces can be neglected. It can also be used to assess the energy loss for removing all chalcogen atoms from the system and forming a pure metal membrane. As the phase is embedded into the stoichiometric phase, it is assumed that for any stoichiometry

\[
\mu_M + 2\mu_X = \mu_{MX}
\]

where the value of \( \mu_M \) and \( \mu_X \) are limited by the lowest-energy phases.

The formation energies for nonstoichiometric phases and for pure metal membranes are shown in Figure 4. It is seen that there are nonstoichiometric phases that are more stable than...
pure 2D metals. The most stable nonstoichiometric phase from the simulation is M4X4, with the energy difference between the hexagonal metal phase and M4X4 being over 1 eV. As evident from Figure 4, the energy difference between this and the stoichiometric phase is 0.3−0.6 eV in the metal-rich limit, which indicates that the phase can potentially be synthesized or manufactured using an electron beam by sputtering chalcogen atoms, e.g., by using moderate heating during irradiation. Another nonstoichiometric phase of interest is M5X2, which, unlike M4X4, has a hexagonal lattice with a formation energy comparable to the lowest-energy M4X4 at the metal-rich end. The phase can be referred to as a corrugated Mo sheet with attached chalcogen atoms, and it is a likely candidate for forming domains when chalcogen atoms are sputtered away by the electron beam.

Although we considered single-layer structures, the vdW interaction is known to affect the cohesive energies of nonlayered materials by up to 0.3 eV per atom, especially when defects are present (for an overview, see ref 40). To address this issue, we repeated the calculations of the total energies and geometries of all of the phases of the MoSe system that we considered with the Tkatchenko−Scheffler vdW exchange and correlation functional.41 The primitive cell size of every phase was carefully optimized. The account for the vdW interaction decreased the energy difference between the nonstoichiometric phases and MoSe by 0.1−0.3 eV but did not change the qualitative picture. The geometry of the systems remained the same, and the Mo membrane was still corrugated.
To further facilitate a comparison with the experimental results, we simulated STEM images of the phases with the lowest energies, along with those for a pure Mo membrane and pristine MoSe₂. Figure 5 presents the simulated STEM images of the Mo₄Se₄ and Mo₅Se₂ phases in comparison to a pure Mo membrane and MoSe₂. The intensity scale is the same for all of the images. Interestingly, the Mo₄Se₄ has a slightly distorted hexagonal lattice with a lattice constant of ∼2.7 Å, close to the experimental result reported in ref 7. On the other hand, the simulated metallic Mo membrane has a lattice constant of only 2.57 Å. Thus, some areas in the irradiated MoSe₂ sheets may not be a purely metallic phase but one of the mixed phases.

Independently, we also carried out a global minimum search of nonstoichiometric 2D structures by the evolutionary algorithm. The simulation yielded the same 2D molybdenum monoselenide with a distorted puckered honeycomb lattice of orthorhombic symmetry, Figures 3 and 5c. Such a phase has lattice parameters a = 5.455 Å and b = 4.449 Å (Pbcm space group) with one Mo atom (0.402, 0.250, 0.477) and one Se atom (−0.016, 0.250, 0.425). The dynamical stability of a predicted monolayer was studied by the phonon calculations, shown in Figure 6a. One can see no imaginary phonon modes, Figure 6a, so that even the free-standing structure should be stable. The presence of a substrate will further stabilize this phase. The elastic constants of the Mo₄Se₄ phase were found to be C₁₁ = 87.1 N/m, C₂₂ = 204.7 N/m, C₁₂ = 46.4 N/m, and C₆₆ = 53.7 N/m. One elastic constant of uniaxial deformation (C₃₃) is almost 2 times larger than the corresponding value for MoSe₂ (110.5 N/m), whereas another constant (C₁₁) is slightly lower.

We further calculated the electronic structure of Mo₄Se₄ phase. The PBE band structure of Mo₄Se₄ is shown in Figure 6b. It is evident that the phase is metallic. We obtained similar results for other M₄X₄ systems. The metallic nature of these compounds was also confirmed by the GGA calculations.

To sum up, using first-principles calculations, we demonstrated that the lowest-energy configuration of a neutral 2D membrane composed of Mo atoms only is not the hexagonal one, as previously assumed, but the square lattice. The structure is not flat but develops out-of-plane corrugation. However, when a finite-size Mo membrane embedded into a semiconducting MoSe₂ material is negatively charged, the lowest-energy configuration corresponds to the hexagonal lattice, which has experimentally been observed, provided that indeed no other chemical element (e.g., carbon, oxygen) is present, as confirmed by EELS. We further showed that the extra charge also gives rise to increased separations between the atoms, which may explain the apparent contradiction between the bond lengths obtained in the calculations and those experimentally measured in Mo membranes derived from MoSe₂ sheets by sputtering Se atoms using the electron beam in the scanning TEM. We also provide evidence that other nonstoichiometric 2D phases of MoSe₂ and other TMDs MX₂(M = Mo, W; X = S, Se, Te) with low formation energies can exist. Among these 2D phases, the 2D M₄X₄ and M₅X₂ phases are particularly stable, especially in the Mo-rich limit, which corresponds to the conditions in the TEM experiments. This indicates that, although the formation of the pure Mo/W phase may be related to the dynamical effects and preferential sputtering of chalcogen atoms, it should in principle be possible to quench the system into this configuration by, e.g., moderate heating of the sample during exposure to the electron beam. The lowest-energy M₄X₄ phase is metallic, contrary to the original material, which is a semiconductor. This potentially opens new avenues for patterning and atomic-scale engineering of the properties of 2D TMDs with high miniaturization and integration. As exposure to chalcogen atoms combined with annealing will likely lead to the restoration of the original structure, the system can be used in rewritable electronics.

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ACKNOWLEDGMENTS

We thank J. Nevalaita, P. Koskinen, and A. Oganov for discussions. We acknowledge funding from the German Research Foundation (DFG), Projects KR 48661/1 and KR 48661/2, and the Academy of Finland under Project No. 286279. We also acknowledge the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST "MISiS" (No. K2-2019-016) and a Grant of President of Russian Federation for government support of young DSc (MD-1046.2019.2). Study of the Mo₄Se₄ monolayer was supported by the Russian Science Foundation (Project Identifier: 17-72-20223). We further thank CSC Finland.
PRACE (HLRS, Stuttgart, Germany), and TUD (Taurus cluster) for generous grants of CPU time.

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