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First principles study of the 2D Mo(S_{1-x}Te_x)\_2 TMD alloy adsorbed on an Al-terminated sapphire (0001)-substrate

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Abstract
A first principles study, performed for a 2D, three atom thick monolayer of the Transition Metal Dichalcogenide (TMD) alloy Mo(S_{1-x}Te_x)\_2 adsorbed on an Al-terminated (0001)-sapphire surface. Bulk composition dependent binding energies and band-gaps, and a partial phase diagram, were calculated, using the cluster expansion method. Although the 3D Mo(S_{1-x}Te_x)\_2 alloy system has a phase diagram that is dominated by S-rich/Te-rich phase separation, the 2D system adsorbed on sapphire is dominated by S:Te-ordering. Five ground-state phases are predicted; all have P1 symmetry, and all disorder via continuous (2’nd order) transitions. These results indicate that synthesis on the substrate is favorable for band-gap engineering, in which a continuous single phase solid solution allows continuous band-gap tuning, as a function of bulk composition. Whereas, bulk TMD-synthesis followed by exfoliation favors the formation of two-phase mixtures.

1. Introduction
There is great interest in two-dimensional (2D) transition metal dichalcogenide (TMD) materials such as MoS\_2, MoSe\_2 and MoTe\_2, their solid solutions, and related 2D materials [1, 2]. Traditionally, MoS\_2 has been used as a dry lubricant [3] that is stable up to 623 K. Currently, interest is focused on applications as: band-gap engineering materials [4, 5]; nano-electronic devices [2, 6–8]; photovoltaic devices [9, 10]; valleytronics applications [11, 12]; 2D building blocks for electronic heterostructures [13]; and as sensor materials [14].

Previous studies performed first principles phase diagram (FPPD) calculations for: (1) 2D TMD alloys in vacuum [4]; (2) bulk 3D Mo(S_{1-x}Te_x)\_2 alloys [15]; and (3) W(S_{1-x}Te_x)\_2 alloys [16]. Predicted phase diagrams for all these systems are dominated by phase separation of S-rich and Te-rich phases. This study considers a 2D Mo(S_{1-x}Te_x)\_2 alloy adsorbed on an Al-terminated (0001) face of sapphire. The thermodynamics of the adsorbed layer system favors S:Te-ordering, predicting five ordered ground-state (GS) phases. Little if any phase separation is predicted below the critical temperatures for ordering (T_c \geq 1250 K) of the various GS-phases. Thus, synthesis of 2D TMD-alloys as adsorbed layers on a substrate is more favorable for band-gap engineering than synthesis in bulk followed by exfoliation: because ordering with little or no phase separation implies homogenous samples that exhibit unimodal band-gaps; whereas phase-separated samples are likely to exhibit a mixture of bi- or multimodal band-gaps.

2. Methodology
2.1. Formation Energies
Total structure energies, \Delta E_{\text{Str}}, were calculated for 196 147-atom-supercells with bulk stoichiometries; Mo_9S_{18}; Mo_9Te_{18}; and, Mo_{9}S_{18-m}Te_{m} (m = 0, 1, \ldots, 18), figure 1. Molar formation energies, \Delta E_f (equation (1)) were obtained from the \Delta E_{\text{Str}} (first RHS term in equation (1)) by subtracting bulk composition weighted linear combinations of the MoS_{2} and MoTe_{2} structure energies, and normalizing.
The Vienna *ab initio* simulation program (VASP, version 5.3.3 [17]) with projector augmented waves (PAW) and a generalized gradient approximation (GGA) for exchange energies, was used for all total energy calculations. Electronic degrees of freedom were optimized with a conjugate gradient algorithm. Valence electron configurations were: Al$_{sv}$ 2$p^1$; O$_{sv}$ 2$p^4$; Mo$_{sv}$ 4$s^2$5$p^5$6$d^1$; S 2$p^4$; Te 2$p^4$. Van der Waals interactions that bond the three-atom thick 2D TMD-layers to the sapphire substrate were modeled with the non-local correlation functional of Klimes *et al* [18]. Reported structure energies are for constrained optimizations in which the 2D alloy plus the top six layers (3 Al- + 3 O-layers) are fully relaxed, and the remaining Al- and O-layers are fixed as they would be in fully relaxed bulk Al$_2$O$_3$. Structure energies were for a 3,3,1 Monkhorst-Pack k-point mesh, and a 600 eV cutoff-energy, in the 'high precision' mode, which converges absolute energies to within a few meV mol$^{-1}$ (a few tenths of a kJ mole$^{-1}$) of exchangeable S- and Te-anions. Precision is at least an order of magnitude better. Residual forces of order 0.02 eV or less were typical.

Formation energies ($\Delta E_f$) for 196 Mo$_9$S$_{18-m}$Te$_m$ ($m = 0, 1, 2, \ldots 18$) supercells are plotted in figure 2, in which values for $\Delta E_f$ are normalized per mole of exchangeable anions, S and Te:

$$\Delta E_f = [\text{Mo}_9\text{S}_{18-m}\text{Te}_m - (18 - m)\text{E}_{\text{Mo}_9\text{S}_{18}} - m\text{E}_{\text{Mo}_9\text{Te}_{18}}]/18 \quad (m = 0, 1, \ldots 18)$$  \hspace{1cm} (1)

Negative $\Delta E_f$ indicate that ordered phases are predicted. In particular five ordered intermediate GS-structures are predicted. In each GS except structure-43, an ordered arrangement of S and Te occupies the (S,Te)-layer closest to the sapphire substrate, and Te makes more relatively short van der Waals bonds to the substrate than S, figures 3.

### 2.2. The cluster expansion hamiltonian

A cluster expansion Hamiltonian (CEH) [19], for the quasibinary system was fit to the set of 196 formation energies, $\Delta E_{VASP}$, solid dots (green online) in figure 2 with a cross validation score of CV = 0.0499. Fitting of the CEH was performed with the Alloy Theoretic Automated Toolkit (ATAT) [20–22] (see footnote 1) which automates most of the tasks associated with CEH construction. A complete description of the algorithms underlying the code can be found in [21]. Large open squares in figure 2 (red online) indicate values of the 196 $\Delta E_{\text{fit}}$ that were calculated with the CEH. Smaller open squares ($\Delta E_{\text{GS}}$ blue online) indicate the results of a

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1. cf. http://tph.tuwien.ac.at/vasp/guide/vasp.html.
2. Reference to specific software packages does not imply a NIST endorsement.
ground-state analysis in which the CE was used to calculate formation energies for all ordered supercell configurations with 18 or fewer anion sites, 87,424 structures.

3. Results and discussion

3.1. Binding energies

Binding energies are the stabilizations of supercell products relative to MoS$_2$, MoTe$_2$, and Al$_2$O$_3$ reactants. Excess binding energies have an ideal mixing term subtracted out; i.e. binding energy is to excess binding energy as structure energy is to formation energy. Binding energies were not cluster expanded, rather they were calculated for each supercell that has lowest energy at its bulk composition. They exhibit an approximately linear trend from $-11.6$ eV mol$^{-1}$, in the MoS$_2$-on-sapphire system, to $-5.6$ eV mol$^{-1}$ in the MoTe$_2$-on-sapphire system, figure 4. Evidently, S:Te-ordering has little effect on binding energies.

Figure 2. Comparison of formation energies, $\Delta E_f$, for the 196 VASP, Density Functional Theory (DFT) calculations (solid circles, green online) to Cluster Expansion (CE) formation energies: $\Delta E_{f,CE}$ (large open squares, red online) is the CE-fit to the DFT set; $\Delta E_{f,GS}$ (smaller open squares, blue online) are the CE-based ground-state analysis; Most $\Delta E_f < 0$ implies that ordered ground-states are predicted; specifically, at $X = 2/9, 1/2, 11/18, 7/9, and 17/18$ (small black circles). CV is the cross validation score.

Figure 3. Predicted ground-state configurations for the TMD-ground-states, plus the sapphire surfact to which they are adsorbed: (a) Structure 43, $X = 2/9$; (c) Structure 68958, $X = 1/2$; (d) Structure 63863, $X = 11/18$; (e) Structure 761608, $X = 7/9$; (f) Structure 3, $X = 17/18$;

3 Details of the DFT calculations are available on the NIST First Principles Phase Stability (FPPS) Files DSpace Repository: https://materials.registry.nist.gov/pid/rest/local/cdcs/T8UQC8ID2CWRRS7A8PT.
3.2. Band gaps

Band gaps were calculated for a set of 112 supercells, including the lowest energy calculations at each bulk composition figure 5. A perl script from VTSTscripts\(^23\) was used to obtain band-gaps from converged VASP calculations. The results were cluster expanded and the solid line indicates composition dependence of band-gaps for a disordered and ordered solid solutions at \( T = 1000 \) K. Clearly, ordering correlates with larger band-gaps.

Curiously, calculated band-gaps for adsorbed TMD-monolayers on Al-terminated sapphire, are roughly an order of magnitude less than those from the bulk systems: MoS\(_2\), 0.003 eV versus 0.016 eV; and MoTe\(_2\), 0.005 eV versus 0.110 eV. Also, they are roughly an order of magnitude smaller than those calculated for the TMD-monolayer alloy sandwiched between two graphene layers. (to be published separately). Possible explanations include: DFT underestimations of band-gaps; the anomalous quantum confinement effect\(^24\); or a combination of both.

3.3. Phase diagram

A first principles phase diagram (FPPD) calculation was attempted, but owing to the continuous (classically 2’nd order) characters of predicted phase transitions, the FPPD calculation was only partially successful figure 6. All predicted ordered structures have P1 symmetry, and disorder via continuous (2’d order) transitions; all of which exhibit substantial order-parameter fluctuations as functions of temperature in the Monte Carlo (MC) simulation. Order-parameter fluctuations obscure the kink that occurs at the transition point. Hence critical temperature determinations are highly uncertain (i.e. as much as \( T \pm 50 \) K; see figure 7, appendix).

When two continuous transitions intersect, one expects a two-phase field below the birectical point at which they intersect. However attempts to locate such fields via brute force grand-canonical MC simulations, and by using the phb-thermodynamic integration program (ATAT package\(^20\–22\)) detected no measurable two phase fields. Evidently, the expected two-phase fields are sufficiently narrow, that they defy resolution.

Kang et al\(^4\) performed first principles phase diagram calculations for four 2D TMD systems in vacuum: Mo(S\(_{1-x}\)Te\(_{x}\))\(_2\); W(S\(_{1-x}\)Te\(_{x}\))\(_2\); Mo(Se\(_{1-x}\)Te\(_x\))\(_2\); W(Se\(_{1-x}\)Te\(_x\))\(_2\); Mo(S\(_{1-x}\)Se\(_x\))\(_2\); and W(S\(_{1-x}\)Se\(_x\))\(_2\). In these
calculations, van der Waals interactions do not apply. Their CEs were fit to about 40 structures per system (maybe too few), and all systems were predicted to have miscibility gaps.

A FPPD calculation for the 3D bulk system that includes van der Waals interactions between $\text{Mo}(\text{S}, \text{Te})_2$-layers, predicts extensive miscibility gaps, plus narrow single phase fields for incommensurate phases, both at $X \approx 0.46$ [15].

In the 2D system adsorbed on an Al-terminated (0001) sapphire substrate, S:Te-ordering with five GS-phases is predicted; and no two-phase fields were detected.

Figure 5. Calculated band-gaps as a function of bulk composition. Unconnected symbols are $T = 0$ K values for specific supercells. Small, solid, connected circles are for $T = 1000$ K.

Figure 6. Partially calculated phase diagram indicating that ordered phases persist up to about $T = 1250$ K.
4. Conclusions

First principles studies of the Mo(S$_{1-x}$Te$_x$)$_2$ alloy indicate that: (1) in the 2D-alloy in vacuum [4], phase separation is favored; (2) in a bulk 3D system, the thermodynamics mostly favor phase separation; (3) Adsorbed on Al-terminated sapphire, the thermodynamics favor S:Te-ordering, below about $T = 1250$ K, with little if any phase separation. Similarly, calculations for an Mo(S$_{1-x}$Te$_x$)$_2$ alloy sandwiched between two graphene layers, or on a graphene substrate (to be published elsewhere), also predict S:Te-ordering with little if any phase separation. Hence, synthesis in contact with a substrate is more likely to yield a homogenous sample with a unimodal band-gap, than a sample that is grown in bulk and then exfoliated. It seems likely that the correlation between S:Te-ordering and van der Waals bonding to a substrate and/or suprastrate is more general than these few systems. Irregularities of the fits between substrate and adsorbates inevitably creates sites that favor one adsorbate atom over the other and ordering is therefore favored.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

Appendix

![Figure 7. Typically noisy order-parameter vs temperature curve illustrating the uncertainty in estimates of critical temperatures for S:Te-ordering.](image-url)
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