

Electronic Properties of Reduced Molybdenum Oxides

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

The electronic properties of MoO₃ and reduced molybdenum oxide phases are studied by density functional theory (DFT) alongside characterization of mixed phase MoO_x films. Molybdenum oxide is utilized in compositions ranging from MoO₃ to MoO₂ with several intermediary phases. With increasing degree of reduction, the lattice collapses and the layered MoO₃ structure is lost. This affects the electronic and optical properties, which range from the wide band gap semiconductor MoO₃ to metallic MoO₂. DFT is used to determine the stability of the most relevant molybdenum oxide phases, in comparison to oxygen vacancies in the layered MoO₃ lattice. The non-layered phases are more stable than the layered MoO₃ structure for all oxygen stoichiometries of MoO_x studied where 2 ≤ x < 3. Reduction and lattice collapse leads to strong changes in the electronic density of states, especially the filling of the Mo 4d states. The DFT predictions are compared to experimental studies of molybdenum oxide films within the same range of oxygen stoichiometry. We find that whilst MoO₂ is easily distinguished from MoO₃, intermediate phases and phases mixtures have similar electronic structures. The effect of the differing band structures is seen in the electrical conductivity and optical transmittance of the films. Insight into the oxide phase stability ranges and mixtures is not only important for understanding molybdenum oxide films for optoelectronic applications, but is also relevant to other transition metal oxides such as WO₃ which exist in analogous forms.

1 Introduction

In order to utilize molybdenum oxide films, it is important to understand how optical and electrical properties change with stoichiometry and crystal structure. Molybdenum oxide has applications in numerous optical and electronic devices, including organic light emitting diodes, photodetectors, gas sensors, photovoltaics, batteries and multi-chromic coatings.^{1–9} The layered structure of MoO₃ has proved useful in creating many highly oriented nanostructures, such as two-dimensional flakes and belts, as well as nanorods, nanowires and nanoparticles.^{3,10–18} These architectures are often seen in the morphology of thin films, where they can be exploited for their novel properties.^{14,16–24} For such wide-ranging applications, there exist many combinations of stoichiometry, crystallinity and morphology.^{6,25–29} In addition, phase mixtures of compositions MoO_x for 2 < x < 3 can be present in films and devices.^{30–34} Many reported devices rely on sub-stoichiometric MoO₃, with mid-gap states necessary for device operation.^{1,26,27,31,33,35–38} However it is unlikely that oxygen vacancies remain as point defects, as ordering of oxygen vacancies has been observed at very low concentrations.³⁹

The crystal structures of molybdenum oxide phases can be

split into three groups: those based on the layered MoO₃ structure, those based on the distorted ReO₃ structure, and MoO₂ which exists in the distorted rutile structure. The stable, orthorhombic polymorph of MoO₃ is built up of distorted MoO₆ octahedra which are edge and corner sharing in two directions, forming bilayers which are held together by dispersed interactions. The separation of the layers is known as the van der Waals gap. There are oxygen ions on three symmetrically inequivalent positions – O1, singly coordinated and pointing towards the van der Waals gap, O2, corner-sharing and O3, edge-sharing. Metastable structures based on crystallographic shear of MoO₃ have been observed in the reduction of MoO₃.^{40–43} These fall into the series Mo_nO_{3n-m+1}, in which only Mo₁₈O₅₂ has been produced in pure form.⁴⁴ Upon further reduction, the lattice collapses into ReO₃ type structures with crystallographic shear planes. These are described by the Magnéli series Mo_nO_{3n-1}, for which Mo₉O₂₆ and Mo₈O₂₃ are known to exist.^{45,46} Early calculations based on a cluster model found that oxygen vacancy formation is more favourable when accompanied by crystallographic shear, in both molybdenum oxide and rhenium oxides.⁴⁷ In addition, the Mo₁₇O₄₇ and Mo₅O₁₄ phases are based on pentagonal bipyramids within the ReO₃ structure.^{48,49} Mo₄O₁₁, most stable in the orthorhombic form, can also be described by the ordered emission of oxygen from the ReO₃ lattice.^{49,50} In this work, the ReO₃ based structures are described as non-layered due to the loss of the van der Waals gap. A recent study has been done to develop a thermodynamic description of the Mo–O system using the CALPHAD (CALculation of PHase Diagrams) method.⁵¹ To complete the phase diagram, a lack of reliable

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DOI: 10.1039/x0xx00000x

thermochemistry data prompted the use of first principles density functional theory (DFT) calculations.

The electronic structure of MoO₃ has been modelled by Scanlon *et al.* in good agreement with X-ray photoemission spectra.⁵² MoO₃ is a semiconductor with a band gap of 3.2 eV in a thin film.^{11,53} Other studies have investigated the electronic details of oxygen vacancies in MoO₃, such as the localisation of electrons on surface vacancies.^{54,55} Electrons donated from oxygen vacancies fill Mo 4*d* states which then lie in the band gap as gap states.^{54,56} The stabilization of shear structures of oxygen deficient MoO₃ and ReO₃ has been ascribed to filling of Mo 4*d* states in the formation of Mo-Mo bonds.⁴⁷ Thus, oxygen vacancies provide n-type doping which enables alignment of band levels with metals, oxides and organic molecules, via band bending and charge transfer doping.^{36,56} The high work function of MoO₃ means that its role in organic electronic devices is as a hole conductor, despite its n-type nature.³⁶ Distortion of the MoO₃ lattice and electron doping has been shown to reduce the band gap.⁵⁷ Furthermore, amorphous MoO_x films have exhibited a metallic band structure, due to states at the Fermi level attributed to Mo⁴⁺ ions.³⁷ A transition to correlated metal conduction was demonstrated for MoO_x close to *x* = 2.6, although the lattice structure was not determined.²⁸ It is known that MoO₂ is metallic based on the Mo-Mo bonding in the distorted rutile structure, and Scanlon *et al.* found that the Fermi energy lies in a trough in the density of states.^{52,58} Although Mo₄O₁₁ is the next most stable oxide phase, it has not been extensively studied with respect to electronic structure, but is predicted to be metallic.¹⁰

In order to elucidate the structure-property relations of the reduced molybdenum oxides, we use density functional theory to predict the electronic structure of a representative sample of MoO₃ and ReO₃ lattice types. We find the stabilities relative to MoO₂ and MoO₃, and include a comparison with oxygen vacancies as point defects in various concentrations. The theoretical predictions are compared to X-ray photoelectron spectra and measured optical properties of molybdenum oxide films with a range of oxygen stoichiometries.

2 Methods

Computational details

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) with the projector augmented wave (PAW) pseudopotentials Mo_sv ($4s^2 4p^6 5s^1 4d^5$) and O_h ($2s^2 2p^4$) supplied with VASP.⁵⁹⁻⁶² Based on previous testing of exchange functionals used with vdW-DF, the functional vdW-DF2 was used for optimization of MoO₃.⁶³ The DFT + U approach of Dudarev *et al.* was applied to the Mo 4*d* to better match the lattice parameters and band structures.⁶⁴ A U correction of 5 eV was used, based on the value previously determined by comparison of the position of band gap states with experimental results.⁶³ Supercells of MoO₃ were used to replicate three different finite concentrations of oxygen vacancies. Cell sizes 1x1x1, 2x1x2 and 3x1x3 were each used

with a single oxygen vacancy, corresponding to O/Mo ratios of 2.75, 2.9375 and 2.972 respectively. The calculations were repeated for vacancies on each of the three oxygen lattice positions.

Structural optimization was also done on selected molybdenum oxide phases. The most experimentally stable structure from each of the series and structure types was chosen, thus the oxides examined were Mo₁₈O₅₂, monoclinic Mo₉O₂₆, Mo₁₇O₄₇, orthorhombic Mo₄O₁₁ and MoO₂. The vdW-DF approach did not perform well with the non-layered structures. Instead, GGA, PBEsol and LDA were tested for optimization of these structures (Table 1). GGA predicted larger and LDA predicted smaller lattice parameters than experimental values, whilst the PBEsol functional gave values in between. This is in agreement with calculations in another study of the Mo-O system which found PBEsol to give excellent agreement with experiment.⁵¹ In addition, the MoO₃ structure was optimized with PBEsol in order to compute relative enthalpies. A U value of 5 eV was applied to Mo 4*d* in keeping with the treatment of electron correlation in MoO₃. However, electron correlation is known to vary with oxidation state and the best choice of U will not be the same for MoO₂. To overcome this for electronic structure calculations, a non-self-consistent calculation with the hybrid functional HSEsol was done to determine the density of states after pre-convergence of eigenvalues with PBEsol.⁶⁵

Convergence was reached for an energy cut-off for the plane-wave basis set of 810 eV. For a unit cell of MoO₃ a 6x2x6 Gamma centered k-point grid was used for Brillouin zone integration, with equivalent k-point density used for other unit cells. All considered structures were fully optimized until the residual forces on the ions were less than 0.05 eV·Å⁻¹. For the hybrid calculations, an energy cut-off of 400 eV was used with (PAW) pseudopotentials Mo_sv and standard O.⁵⁹⁻⁶² For metallic structures the Methfessel Paxton sampling scheme was used, in which case the contribution of the electronic entropy was less than 0.1 meV·atom⁻¹ and considered negligible. The zero-point energy was not taken into account.

Experimental details

Films of molybdenum oxide were synthesised by pulsed laser deposition. A KrF excimer laser (Lambda Physics COMPex Pro 110, 248 nm, 20 ns) was operated at 10 Hz to ablate a MoO₃ target (Testbourne Ltd., 99.95% pure). Before each deposition, the target was pre-ablated by 3000 pulses to regulate the target condition. The films were deposited on Si (100) and quartz substrates which were prepared by degreasing with ethanol and acetone. The target to substrate distance was 4 cm for all films, and 18,000 pulses were used for the depositions. Deposition temperatures were 500 and 570 °C. The chamber base pressure was $\leq 1.3 \times 10^{-5}$ Pa with O₂ gas flow in the range of 55 to 70 sccm, resulting in a corresponding background pressure of 2.4 and 4.5 Pa, respectively. The films are denoted by their deposition conditions [°C]/[Pa]: 500/4.5, 500/2.4 and 570/2.4. These had the corresponding growth rates 2.97, 2.17 and 0.94 Å sec⁻¹.

Table 1 Reference experimental lattice parameters and calculated lattice parameters for MoO₂, MoO₃ and Mo₁₈O₅₂, calculated with GGA, LDA, PBEsol and vdW-DF2, with U = 0 or 5 eV. Percentage deviation from experimental values is given in brackets below

		U	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	
		(eV)	(Δ (%))	(Δ (%))	(Δ (%))	(Δ (%))	(Δ (%))	(Δ (%))	
MoO ₂	Experimental ⁶⁶		5.537	4.859	5.607		119.37		
	GGA	0	5.594 (1.0)	4.890 (0.6)	5.654 (0.8)		120.86 (1.2)		
	LDA	0	5.506 (-0.6)	4.826 (-0.7)	5.555 (-0.9)		120.86 (1.2)		
	PBEsol	0	5.513 (-0.4)	4.842 (-0.4)	5.563 (-0.8)		120.89 (1.3)		
	PBEsol	5	5.515 (-0.4)	4.914 (1.1)	5.591 (-0.3)		121.22 (1.5)		
	vdW-DF2	0	5.738 (3.6)	4.957 (2.0)	5.748 (2.5)		121.14 (1.5)		
	vdW-DF2	5	5.769 (4.2)	5.022 (3.4)	5.814 (3.7)		121.60 (1.9)		
	MoO ₃	Experimental ⁶⁷		3.963	13.855	3.696			
MoO ₃	GGA	0	3.927 (-0.9)	14.191 (2.4)	3.687 (-0.2)				
	LDA	0	3.799 (-4.1)	13.005 (-6.1)	3.669 (-0.7)				
	PBEsol	0	3.852 (-2.8)	13.556 (-2.2)	3.677 (-0.5)				
	PBEsol	5	3.809 (-3.9)	13.490 (-2.6)	3.735 (1.1)				
	vdW-DF2	0	3.976 (0.3)	13.876 (0.1)	3.743 (1.3)				
	vdW-DF2	5	3.914 (-1.2)	13.900 (0.3)	3.801 (2.8)				
	Mo ₁₈ O ₅₂	Experimental ⁴⁴		8.15	11.89	21.23	102.67	67.82	109.97
		vdW-DF2	5	8.191 (0.6)	12.108 (1.8)	21.435 (1.0)	102.61 (-0.1)	67.91 (0.1)	109.71 (-0.2)
PBEsol		5	8.031 (-1.4)	11.890 (0.0)	20.912 (-1.5)	102.67 (0.0)	67.80 (0.0)	109.68 (-0.3)	

Determination of the phase composition of the films was done by X-ray diffraction (XRD) using a Bruker AXS D8 Focus with Solid state LynxEye™ detector. CuKα radiation source was used in Bragg-Bretano geometry (0.01° step size, 1.5 s step time and 10° to 60° 2θ). XRD was carried out on films on Si substrates in order to eliminate the amorphous background of quartz substrates. Scanning electron microscopy (SEM, Hitachi S-5500, 30 kV) was performed on film cross-sections to investigate film thickness and morphology. The root mean square roughness of film surfaces was determined by atomic force microscopy (AFM, Veeco Multimode V, Nanoscope software) with Peak Force Tapping™ in ScanAsyst mode over a 1 μm x 1 μm area.

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation states present and their relative content was used to infer the oxygen stoichiometry. This was obtained with a Kratos Axis Ultra with monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV, 15 mA, 15 kV, with lowest energy resolution 150 meV). The binding energies (Eb) were corrected

by Eb equal to 284.8 eV of adventitious C1s. XPS survey scans were performed within 2 min for surface elemental analysis. The Mo 3p and Mo 3d core levels were measured for the Eb range 385–427 eV and 219–242 eV, respectively. Measurements were carried out with a pass energy of 20 eV. Background modelling and subtraction, peak fitting and quantification of the components were processed using CasaXPS software (version 2.3.16). Prior to peak fitting, an offset Shirley background was subtracted from the spectrum. The offset Shirley background was calculated from a blend of a Shirley and linear backgrounds $OS(E;\lambda) = S(E)(1 - \lambda) + L(E)\lambda$, where the Shirley and the linear background are represented by $\lambda = 0$, and $\lambda = 1$, respectively. In the curve fitting models, $\lambda = 0.3$ is used for all the components. Mo 3p and Mo 3d peaks were symmetrical and a Lorentzian line shape was used. A Gaussian is also convoluted to consider the Gaussian instrumental broadening in addition to the Lorentzian energy distribution of the electrons.

The sheet resistivity of the films was determined using a Singatone four point probe and a Keithley 2449 5A SourceMeter for films on quartz substrates. The radius of the tips was 0.125 mm and the spacing between them 1 mm. A UV/Vis/NIR spectrophotometer (OLIS 14) was used to measure the transmittance of the films over the range 250 – 2100 nm.

3 Results and discussion

Density functional theory calculations

Oxygen vacancies in layered MoO₃. The layered structure of orthorhombic MoO₃ is well described by the exchange functional with vdW-DF, vdW-DF2, as discussed in a previous study considering the dilute limit of oxygen vacancies in MoO₃.⁶³ Here, finite concentrations of oxygen vacancies are considered. Oxygen vacancies on the O1, O2 and O3 positions were modelled individually inside three supercells, (1x1x1 = 16 atoms, 2x1x2 = 64 atoms, 3x1x3 = 144 atoms) and the ion positions and cell volume were allowed to relax. These correspond to stoichiometries of MoO_{2.75}, MoO_{2.9375} and MoO_{2.972} respectively. The ground state lattice parameters and MoO₃ unit cell volumes with supercell size are shown in Figure 1. As expected, the perfect structure shows negligible change with supercell size, within 0.01 Å of atomic positions. In the case of the 1x1x1 cell, the vacancies have a large effect on different cell parameters. The O1 vacancy yields a smaller *a* parameter whilst increasing *c*, with relatively unchanged *b* parameter across the van der Waals gap. The O2 vacancy gives the same trends but with smaller deviation from the stoichiometric lattice. The O3 vacancy, however, shows a large increase in *b* with decreased *a* and *c*. These contributions result in a similar unit cell volume for all three vacancies, which is smaller than the stoichiometric volume by 1.2-1.3 Å³. The large effect on the 1x1x1

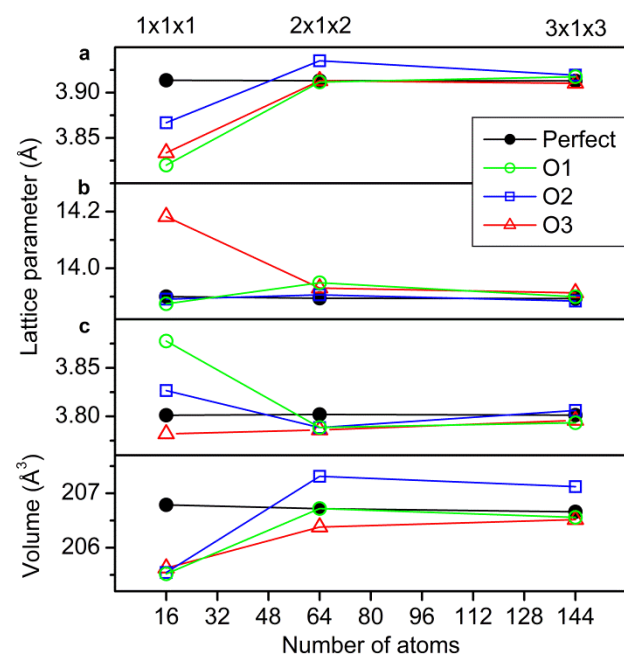


Figure 1 Lattice parameters and unit cell volume of MoO₃ supercells with vacancies on O1, O2 and O3 positions.

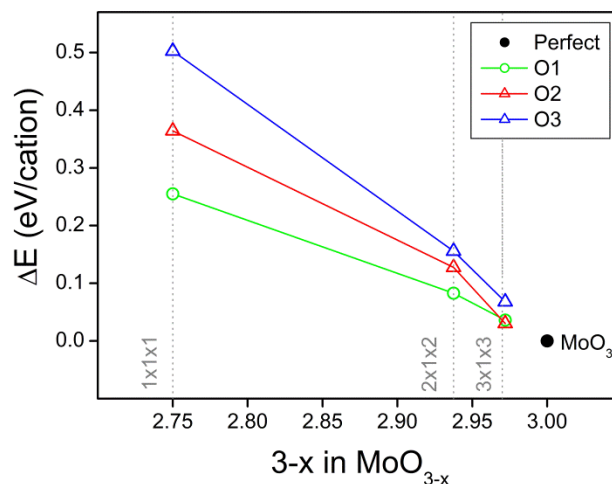


Figure 2 Energy difference per cation versus stoichiometry, for MoO₃ supercells with vacancies on O1, O2 and O3 positions, compared to stoichiometric MoO₃. Values are corrected for mass balance by the chemical potential of oxygen in the MoO₃-MoO₂ regime.

cell is a result of the high vacancy concentration, and with a lower vacancy concentration there are lesser effects on the lattice cell parameters. The 2x1x2 cell has lattice parameters converged within 0.05 Å and the 3x1x3 cell within 0.02 Å with respect to the stoichiometric structure. The volume changes are within 0.6 Å³ and 0.5 Å³ for the 2x1x2 and 3x1x3 cells respectively. This shows that the larger cell size effectively screens the elastic interactions between the point defects.

The energy cost of oxygen vacancies decreases with decreasing vacancy concentration, approaching the stoichiometric composition. The energy difference per MoO₃ formula unit with the three vacancy concentrations is given in Figure 2. For all concentrations, the O1 vacancy has lowest energy difference, except the 3x1x3 cell where the O2 vacancy position is equivalent to O1 within 6 meV. It can be expected that the O1 vacancy position is the most energetically favourable as it breaks only one Mo–O bond. This is in agreement with a previous theoretical study of surface oxygen vacancies in MoO₃.⁵⁵

Locally, the charge compensating electrons act to distort the vacancy containing octahedra. The bond lengths of the octahedron containing the O1 vacancy in the three supercells are shown in Figure 3. In the 1x1x1 case, the Mo ion is shifted away from the vacancy and displaced in the direction of the asymmetrically bridging, corner-sharing oxygens, shortening four out of five of the bonds. Baur's distortion index⁶⁸ is decreased in this case, from 0.093 for the stoichiometric octahedron to 0.024 for the square pyramid of the O1 vacancy in the 1x1x1 cell. This is reflected in the density of states, shown in Figure 4, in which there is smearing of the filled Mo 4*d* states across the entire band gap, to the extent that the DOS is metallic. The 2x1x2 and 3x1x3 cells exhibit a different distortion in which the Mo ion is shifted towards the vacancy. This allows an overall lengthening of the bonds in order to accommodate the charge compensating electrons. There is an increase in the distortion indices to 0.139 for both the 2x1x2 and 3x1x3 supercells. The DOS shows a narrow band of Mo 4*d*

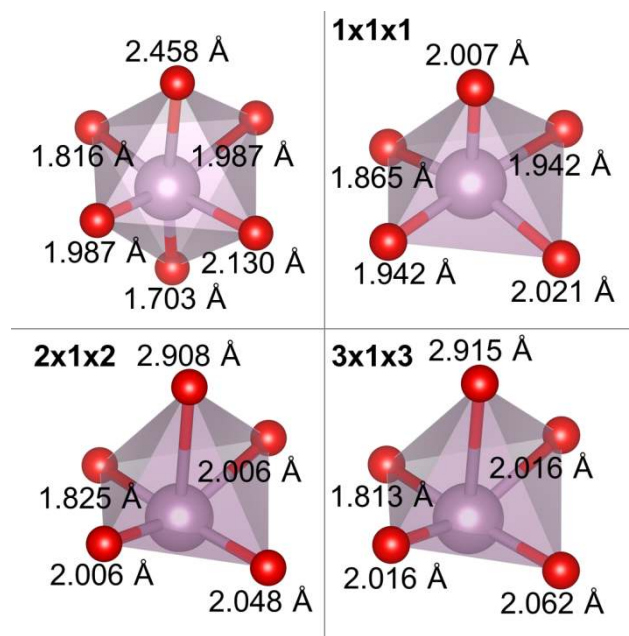


Figure 3 Mo–O bond lengths of an octahedron in stoichiometric MoO₃, and the bond lengths of distorted polyhedrons adjacent to an apical O1 vacancy in 1x1x1, 2x1x2 and 3x1x3 supercells.

states within the band gap. Compared to the calculated band gap of the perfect structure, 1.56 eV, the 3x1x3 and 2x1x2 supercells with an O1 vacancy have band gaps of 1.50 and 1.32 eV, respectively. The reduced band gap of the 2x1x2 supercell is due to the higher dispersion with the increase in concentration of charge compensating electrons. The similarity in the octahedral distortion and DOSes between the vacancies in 2x1x2 and 3x1x3 supercells further demonstrates that the point defect interaction is already well screened in the 2x1x2 supercell.

Reduced molybdenum oxides. MoO₃ and the reduced molybdenum oxide phases are compared by using the PBEsol functional. The lattice parameters given by the PBEsol functional are given in Table 2, and the crystal structures and unit cells are shown in Figure 5. As the dispersed interactions of the layered MoO₃ and Mo₁₈O₅₂ structure are not well described by PBEsol, there is a larger deviation from the experimental lattice parameters than with vdW-DF2 (Table 1), and the lattice parameters across the van der Waals gap are underestimated. There is reasonable agreement in the lattice parameters of Mo₉O₂₆ and Mo₁₇O₄₇. The deviations may also stem from the uncertainty in experimental determination of these structures.^{44,45,48} Mo₄O₁₁ and MoO₂ are better matched, within -1.2 Å of experimental parameters.

The enthalpy of formation for the four intermediate Mo–O phases and three finite O1 vacancy concentrations relative to MoO₂ and MoO₃ was calculated at T = 0 K by the relation,

$$\Delta H = E_0(\text{MoO}_{3-x}) - E_0(\text{MoO}_3) + x \cdot (E_0(\text{MoO}_3) - E_0(\text{MoO}_2))$$

where E₀ is the ground state energy given by DFT, which provides an approximation to the energy of the closed isothermal and isobaric system. ΔH per cation is shown with oxygen stoichiometry in Figure 6, in which the solid line indicates the convex hull formed by the most stable DFT

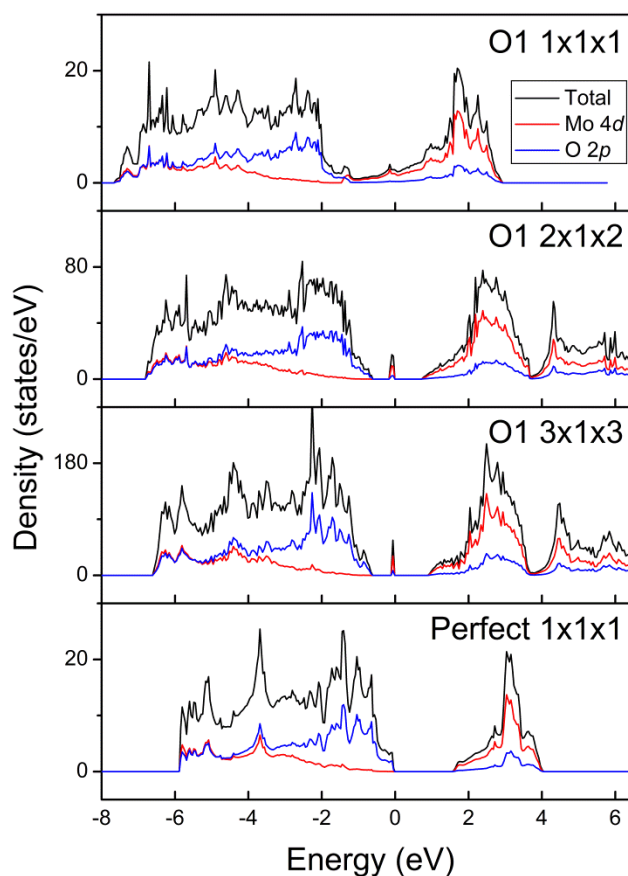


Figure 4 Total and orbital resolved density of states for an O1 vacancy in 1x1x1, 2x1x2 and 3x1x3 supercells, compared to a perfect lattice. The Fermi energy is set at 0 eV.

ground state structures for a given stoichiometry.⁷⁰ The convex hull connects the phases that are stable against decomposition into the other phases, and consists of MoO₂, Mo₁₇O₄₇, Mo₉O₂₆ and MoO₃. Any phase lying above the convex hull but with negative ΔH is favourable to form from the primary oxides, but is thermodynamically unfavourable relative to the ground state. All intermediate phases have a negative ΔH, which means that they are stable relative to the end phases. For the two stoichiometrically equivalent phases Mo₉O₂₆ and Mo₁₈O₅₂, Mo₉O₂₆ is a vertex of the convex hull whereas Mo₁₈O₅₂ lies 220 meV above it. Thus, the non-layered Mo₉O₂₆ was calculated to be more thermodynamically stable than the layered Mo₁₈O₅₂. Mo₄O₁₁ lies above the convex plot, 108 meV higher than the similarly reduced Mo₁₇O₄₇. This result is contrary to experimentally determined phase diagrams, from which Mo₄O₁₁ is known to be the most stable intermediate phase.^{51,71} This discrepancy can be related to the difference in comparing 0 K ground state structures to finite temperature experimental data, and effects of entropy as well as errors innate to the DFT method can be considered. Firstly, there is a lack of data on the low temperature stabilities of molybdenum oxides. The thermodynamics-based CALPHAD method has provided data which is well matched to experimental data, suggesting that thermodynamic considerations are at least partly at fault, however, it was noted that the compositional homogeneity range of the intermediate oxide phases is small, suggesting that configurational entropy may not play a large

role.⁵¹ Alternatively, DFT could be used to evaluate the true ground state at finite temperatures by calculation of phonon spectra, which would indicate the effect of vibrational entropy. In contrast to the CALPHAD data, DFT calculations of formation enthalpies were shown to be strongly dependent on method. In particular, the choice of U value may be a source of discrepancy amongst the various phases, as the electron correlation varies across the reduction degree as well as with crystal structure. The difference in formation enthalpy between Mo₄O₁₁ and Mo₁₇O₄₇ is a similar magnitude to that of two polymorphs of MoO₃ where the discrepancy of DFT calculated relative stability with experimental data was attributed to a U value that could not adequately describe both phases.⁵¹ However, it is hard to quantify the error from these DFT calculations as, to our knowledge, there is no experimental data available on the formation enthalpy of Mo₁₇O₄₇.

The three O1 vacancy concentrations each have a positive ΔH . This suggests that the intermediate phases are energetically favourable compared to any finite concentration of oxygen vacancies in MoO₃. This corroborates with previous observations that vacancy ordering occurs at very low oxygen vacancy concentrations.⁷² The oxygen vacancies which distort the lattice come at an energy cost, and non-stoichiometry is better accommodated by annihilation of vacant anion sites by crystallographic shear planes. Furthermore, it is believed that the oxomolybdenum cations, (Mo=O)⁴⁺, stabilize the layered structure of MoO₃.⁷³ It follows that the sheared Mo₁₈O₅₂ structure, which no longer has one (Mo=O)⁴⁺ bond per cation, is destabilized relative to the non-layered structure of Mo₉O₂₆. This could also be a reason why all known phases with a smaller O/Mo ratio are non-layered, i.e. they do not exhibit a van der Waals gap.

MoO₃, Mo₉O₂₆, Mo₄O₁₁ and MoO₂ are the most studied molybdenum oxides, and their density of states are shown in Figure 7. The HSEsol functional gives an improved treatment of unoccupied bands compared to the DFT+U method. The band gap of MoO₃ is calculated as 2.84 eV, which is within the range of experimentally determined values of 2.7–3.4 eV.^{31,53} The valence band is composed mainly of O 2p states, and the width increases from MoO₃ to Mo₉O₂₆ and Mo₄O₁₁ as there is smearing of O 2p states into the band gap. The other effect of decreasing O/Mo ratio is that Mo 4d states are filled and lowered in energy, narrowing the band gap, and the Fermi level therefore lies in the conduction band. This results in a metallic character of Mo₉O₂₆, Mo₄O₁₁ and MoO₂. This differs from the gap states in the DOS of oxygen vacancies in MoO₃, in which the Mo 4d states are separated from the conduction band, due to the filling of Mo 4d states by charge compensating electrons. In the non-layered structures however, the Mo 4d states are filled due to the formation of Mo–Mo bonds, which are not strong enough to split the band off from the rest of the unoccupied conduction band. MoO₂ has a higher density of occupied Mo 4d states per cation, characterized by two narrow peaks. The higher intensity of these peaks is attributed to the Mo–Mo bonding which is present for every cation in MoO₂, but is confined to fewer cations in the Mo₄O₁₁ and Mo₉O₂₆ structures (Figure 5). This corroborates with conductivity measurements, which show the metallic nature MoO₂ and increased resistivity in Mo₄O₁₁ and Mo₉O₂₆.^{46,69,74}

Table 2 Calculated lattice parameters for molybdenum oxides calculated with PBEsol and U = 5 eV, with percentage deviation from experimental values, and reference experimental lattice parameters given in brackets.

	a	Δ	b	Δ	c	Δ	α	Δ	β	Δ	γ	Δ	Ref.
	(Å)	(%)	(Å)	(%)	(Å)	(%)	(°)	(%)	(°)	(%)	(°)	(%)	
MoO ₃	3.809 (3.963)	-3.9	13.490 (13.855)	-2.6	3.735 (3.696)	1.1							67
Mo ₁₈ O ₅₂	8.031 (8.15)	-1.4	11.890 (11.89)	0.0	20.912 (21.23)	-1.5	102.67 (102.67)	0.0	67.80 (67.82)	0.0	109.68 (109.97)	-0.3	44
Mo ₉ O ₂₆	17.015 (16.74)	1.6	3.861 (4.019)	-3.9	14.750 (14.53)	1.5			94.98 (95.75)	-0.8			45
Mo ₁₇ O ₄₇	21.928 (21.615)	1.4	19.776 (19.632)	0.7	3.775 (3.952)	-4.5							69
Mo ₄ O ₁₁	24.397 (24.40)	0.0	6.675 (6.723)	-0.7	5.385 (5.45)	-1.2							50
MoO ₂	5.515 (5.537)	-0.4	4.914 (4.859)	1.1	5.591 (5.607)	-0.3			121.22 (119.37)	1.5			66

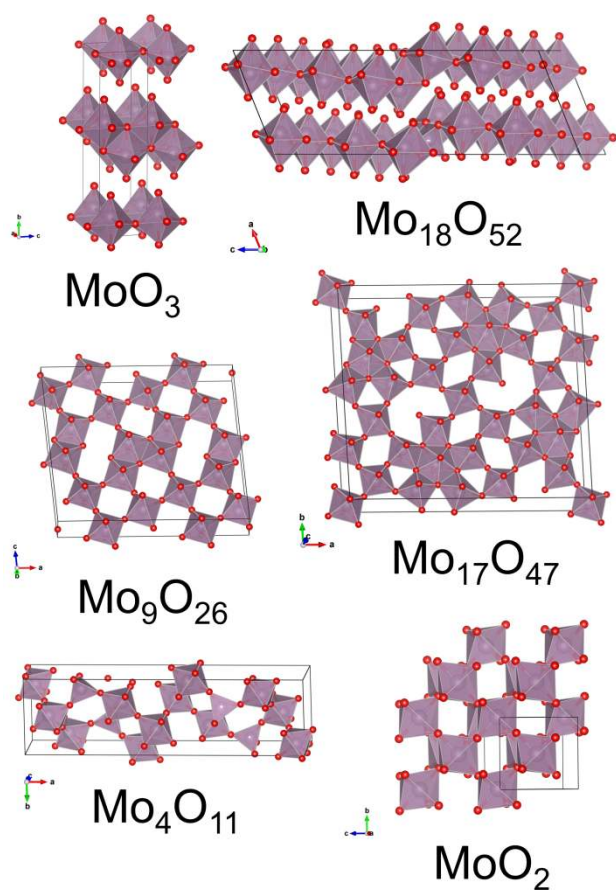


Figure 5 The crystal structures of the modelled molybdenum oxides, with their respective single unit cells shown.

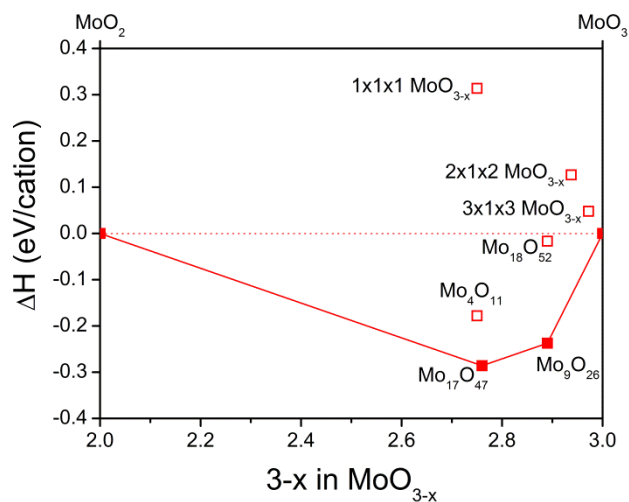


Figure 6 Enthalpy of formation (ΔH) relative to the end members MoO_3 and MoO_2 , for four Mo-O phases and three finite oxygen vacancy concentrations in MoO_{3-x} . The solid line represents the convex hull which connects the phases that are most thermodynamically stable against decomposition into other phases or the end members.

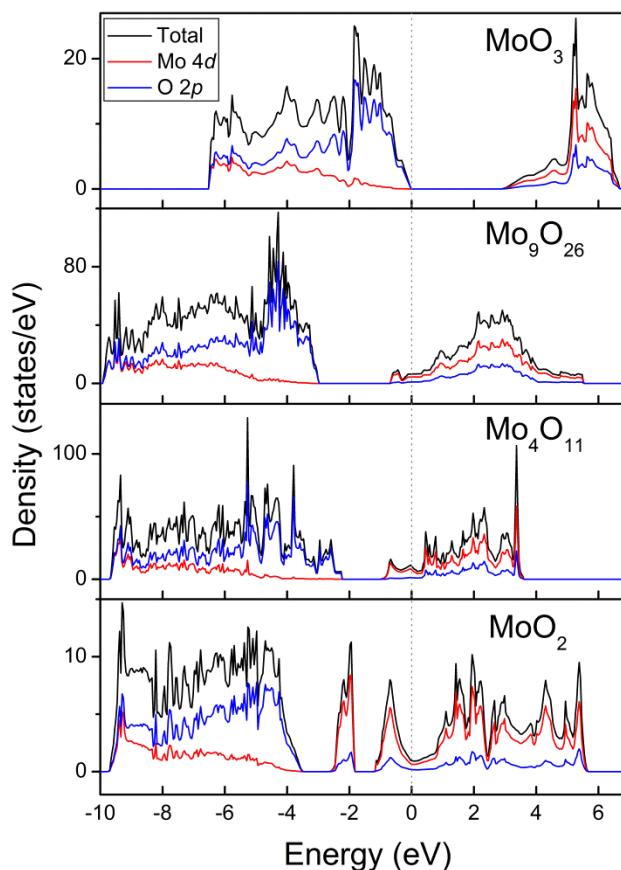


Figure 7 Total and orbital resolved density of states of molybdenum oxides MoO_3 , Mo_9O_{26} , Mo_4O_{11} and MoO_2 . DOSes were calculated in a non-self-consistent electronic calculation with HSEsol, from eigenvalues pre-converged with PBEsol. The DOSes are aligned with the Fermi energy set to 0 eV.

Structure and properties of thin films

The deposition parameters of temperature and oxygen partial pressure affect the composition of the film by creating more reducing or more oxidising conditions. The lower temperature of 500 °C and higher pressure of 4.5 Pa allows orthorhombic MoO_3 to form. This is shown in the XRD pattern of 500/4.5 in Figure 8, which matches the MoO_3 reference pattern, but also shows some reflections of the Mo_4O_{11} phase. For a lower deposition pressure, the 500/2.4 film has reflections of Mo_4O_{11} and MoO_2 . The most reduced is the 570/2.4 film, which shows strong MoO_2 reflections and faint reflections of Mo_4O_{11} . In addition, the 500/4.5 and 570/2.4 films exhibit a broad reflection at low values of 2θ , whereas the 500/2.4 film does not. This broad reflection can indicate the presence of an amorphous phase.

The morphology of the films differs with deposition conditions, as evident from cross-sections of the three deposited films in the SEM micrographs in Figure 9. The 500/4.5 film consists of columnar grains in a dense, forest-like structure. Film 500/2.4 consists of highly oriented rods. There is an apparent difference in crystallinity between these films that can explain the amorphous background of the more oxidized film. The sharp peaks of the Mo_4O_{11} phase in the XRD pattern suggest that the highly crystalline rods are Mo_4O_{11} . In

addition, there is a dense layer adjacent to the substrate, approximately one third of the thickness of the entire film. This has a similar morphology to the 570/2.4 film, so the MoO₂ content is likely confined to the bottom third of the 500/2.4 film. The 570/2.4 film is considerably thinner and less oriented, and appears to have an overall higher density. This is reflected in the RMS roughness values which is lowest for the 570/2.4 film. The film thicknesses and RMS roughness are given in Table 3, as well as the measured resistivity. The sheet resistivity, ρ_{\square} , was calculated by $\rho_{\square} = \frac{\pi V}{\ln(2) I}$

and the bulk resistivity, ρ , by $\rho = t \frac{\pi V}{\ln(2) I}$

where V is the voltage, I is the current and t is the film thickness. The 500/4.5 film had a high resistivity that could not be measured with our experimental setup. The resistivity measurements are consistent with the calculated band

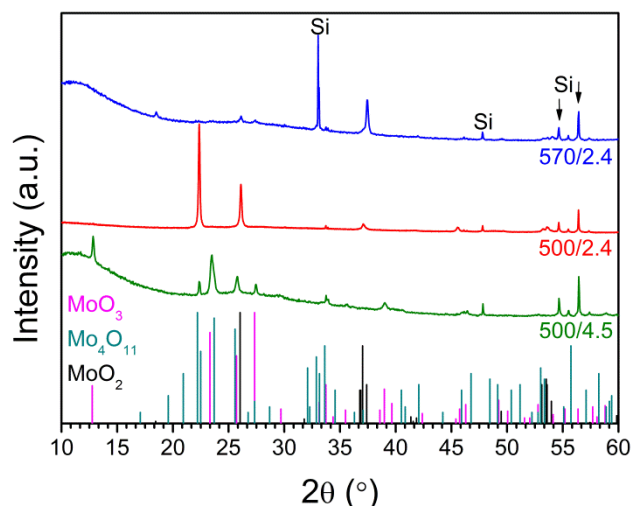


Figure 8 XRD patterns of the molybdenum oxide films, with the reference diffraction patterns MoO₃ (PDF 00-005-0508), Mo₄O₁₁ (PDF 00-005-0337) and MoO₂ (00-032-0671). Reflections from the silicon substrate are labelled with Si.

Table 3 Film properties: root mean square roughness, Rq, measured over a 1 μm x 1 μm area; thickness measured by SEM cross-section; sheet resistivity, ρ_{\square} , and bulk resistivity ρ .

[T]/[P] (°C)/(Pa)	Rq (nm)	Thickness (nm)	ρ_{\square} ($\Omega \square^{-1}$)	ρ ($\Omega \cdot \text{cm}$)
500/4.5	25.9	570 ± 80 nm	-	-
500/2.4	37.5	400 ± 40 nm	227.2	9.09 × 10 ⁻³
570/2.4	13.1	175 ± 25 nm	949.9	16.62 × 10 ⁻³

structure, showing the metallic nature of Mo₄O₁₁ and MoO₂, and insulating nature of MoO₃. Resistivity depends strongly on stoichiometry, and these results are close to values reported for films with stoichiometry MoO_{2.3}.²⁸ Furthermore, the morphology of the 500/4.5 film is rod-like throughout, which will also impact the conductivity severely. The 500/2.4 and 570/2.4 films have a continuous layer, facilitating the carrier transport. The lower resistivity of the 500/2.4 film compared

to the 570/2.4 film could be due to the high crystallinity seen by SEM.

The composition and stoichiometry of the films can be further elucidated by XPS analysis. Deconvolution of the spectra is displayed in Figure 10, with fitting parameters given in Table 4. The phase segregation and difference in crystallinity between phases that is clearly seen in the microstructure of the films influences both the XRD and XPS results. Knowledge of this morphology allows a consistent interpretation of both techniques. The 500/4.5 film mainly contains Mo⁶⁺, with 14 % Mo⁵⁺. This corresponds to the XRD analysis that the film is

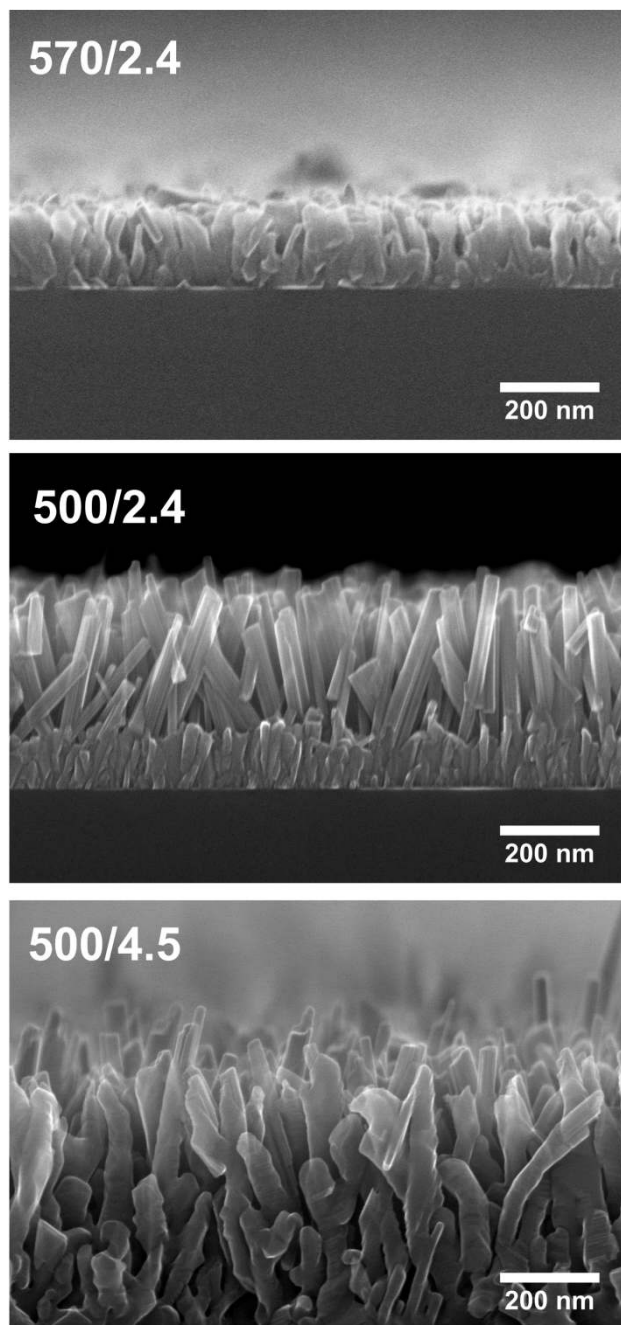


Figure 9 SEM micrographs of the molybdenum oxide film cross sections deposited at [T]/[P] of 570/2.4, 500/2.4 and 500/4.5.

mainly MoO_3 with some Mo_4O_{11} , which contains both Mo^{6+} and Mo^{5+} oxidation states. The proportions of cation oxidation states lead to an estimated film composition of 75 % MoO_3 , 25 % Mo_4O_{11} . However, the Mo^{5+} could be partly due to surface reduction of MoO_3 or oxygen vacancies in the bulk, and the amorphous phase likely comprises both Mo^{5+} and Mo^{6+} . The 500/2.4 film has approximately equal proportions of Mo^{6+} and Mo^{5+} . This is in keeping with the distribution of Mo^{5+} and Mo^{6+} in Mo_4O_{11} . In addition, there is a small amount of Mo^{4+} . This gives an estimated film composition of 97 % Mo_4O_{11} , 3 % MoO_2 , in agreement with the phases indicated by XRD. Yet, the XRD reflections of Mo_4O_{11} and MoO_2 are of the same order of magnitude, which suggests a higher content of MoO_2 than 3 %. This underestimation of Mo^{4+} is most likely due to the film morphology; assuming from SEM that MoO_2 is confined to the

bottom of the film, it is beyond the sampling depth of XPS. For the 570/2.4 film, the $\text{Mo } 3d$ spectrum shows a well-resolved, narrow peak at the binding energy of Mo^{4+} (229.82 eV). However, due to complications with the number of components in $\text{Mo } 3d$, including screened and unscreened peaks of the intrinsic Mo^{4+} spectrum, it is preferable to fit the components of the three oxidation states to the $\text{Mo } 3p$ peaks.⁵² The large Mo^{4+} content (39.5 %) shows that the film is mainly MoO_2 . This Mo^{4+} content is likely even higher, due to atmospheric oxidation of the surface. This conclusion is consistent with the XRD result that showed that sample has mainly MoO_2 reflections. The remainder is equal amounts of Mo^{6+} and Mo^{5+} , which can be partly attributed to the Mo_4O_{11} content and partly related to surface oxides. Considering XPS alone gives a film composition of 60 % Mo_4O_{11} , 40 % MoO_2 ,

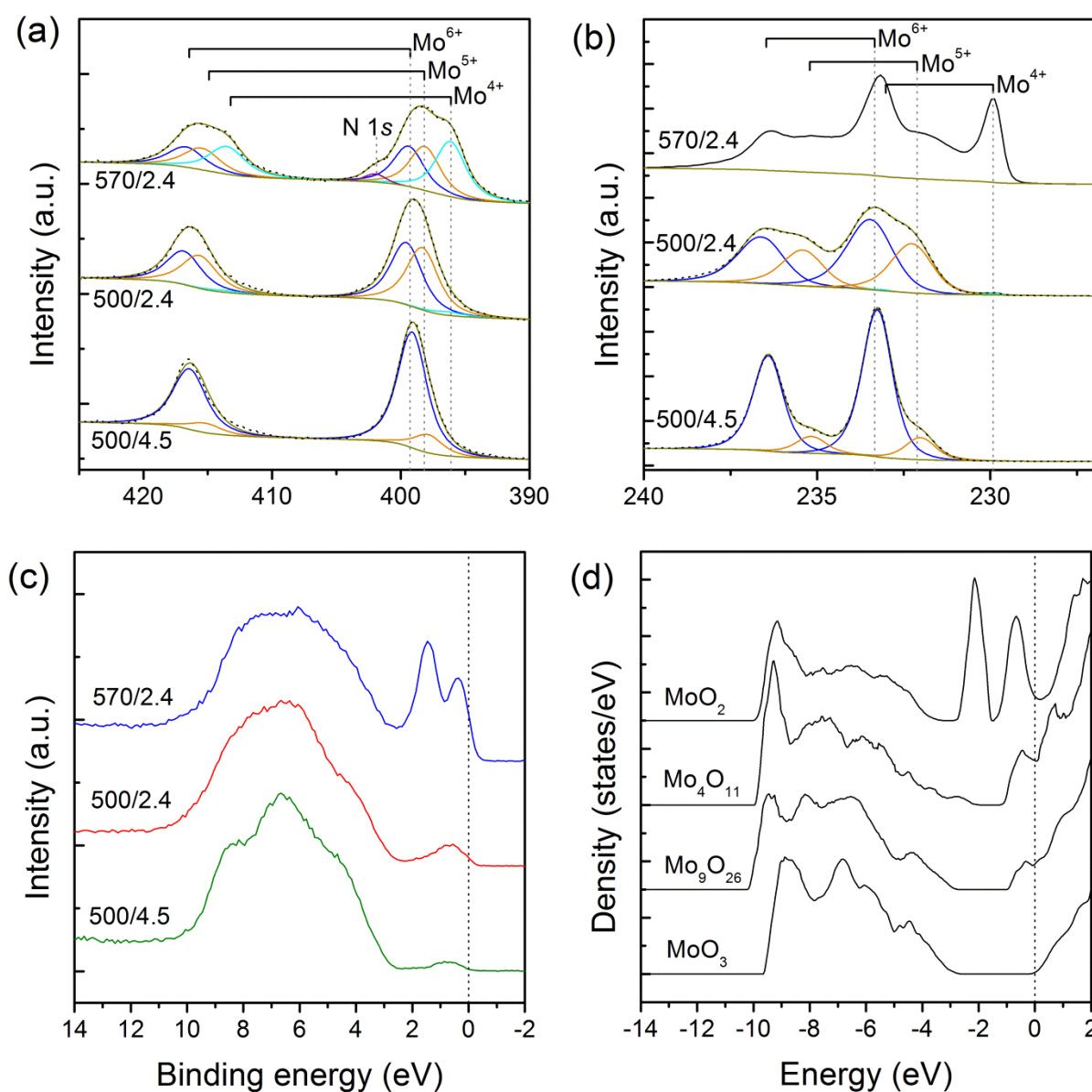


Figure 10 XPS spectra of the molybdenum oxide films, a) Mo $3p$ peaks; b) Mo $3d$ peaks; c) the valence band region. d) Calculated DOSes of molybdenum oxides weighted to the ionization cross-sections of Mo $4d$ and Mo O $2p$. The DOS of MoO_3 is aligned to 0 eV at the CBM, and data has been smoothed by 15 point adjacent averaging.

but the XRD pattern indicates that the film is partially amorphous and shows only weak Mo₄O₁₁ reflections. Thus, some of the Mo⁵⁺ and Mo⁶⁺ is likely to be contained in the amorphous phase. There is also small amount of nitrogen impurity incorporated in the 570/2.4 film, revealed in the N 1s peak in the Mo 3p spectra. Nitrogen impurities are thought to promote the formation of oxygen vacancies in MoO₃, and nitridation improves the electrical conductivity of both MoO₃ and MoO₂ by the formation of molybdenum oxynitrides and molybdenum nitride.^{75–77}

The valence band spectra in Figure 10c have been calibrated to the Fermi level of a metal contact, determined by a step function. The Fermi level is aligned to 0 eV. In order to compare the spectra to the calculated DOSes, the intensities of the Mo 4d and O 2p partial DOSes are shown in Figure 10d weighted to the one-electron ionization cross-sections of 0.92 kb and 0.06 kb respectively.⁵² The valence band region is made up of mainly O 2p states in the 10 – 3 eV range, and Mo 4d states adjacent to the Fermi level. The valence band has a similar energy range and width in the calculated DOS. There are prominent shoulders on the O 2p states of the 500/4.5 film, which reflects the anisotropy of Mo–O bonding of MoO₃ and can also be recognized in the MoO₃ weighted DOS.⁷⁸ The Mo 4d states are filled with progressing reduction, and show a broad signal at approximately 1 eV below the Fermi level for the 500/4.5 and 500/2.4 films. The 570/2.4 film exhibits two peaks below the Fermi energy that are distinctive of MoO₂. It is possible that there are other components contributing, as there is a continuum of states between the top of the valence band and the Mo 4d states which is not seen in the calculated DOS. This could be due to the amorphous content of the film. Despite the presence of Mo⁴⁺ in the 500/2.4 film, the gap states are broad, weak and without two distinct peaks. This

can be related back to the microstructure of the films, where the phase segregation means that most of the MoO₂ content is not within the XPS sampling depth. At 0 eV, the 570/2.4 film has metallic behaviour, while the valence band maximum for the other two samples are slightly shifted with respect to the Fermi level. The 500/2.4 film is also showing metallic behaviour as some filled states coincide with the Fermi level position. For the 500/4.5 film, the signal is too weak to determine if there is a gap between the Fermi level and the gap states.

In comparison with the calculated DOS, the Mo 4d peaks of the 500/4.5 and 500/2.4 films could be attributed to either MoO₃ with oxygen vacancies, Mo₄O₁₁, or Mo₉O₂₆. Despite the low stability of the point defects compared to the reduced phases, there are likely point defects still present in the MoO₃ due to the role of kinetics and entropy contribution above 0 K. There is certainly a contribution from the Mo₄O₁₁ phase, and despite the weak XPS signal at the Fermi level, from the calculated DOS we can expect metallic behaviour with Mo₄O₁₁ being present. The possibility of Mo₉O₂₆ being present can also be considered, as small quantities may not be detected by XRD. Because of the calculated stability of Mo₉O₂₆ between MoO₃ and Mo₄O₁₁, the presence of the Mo₉O₂₆ phase is not unlikely in the 500/4.5 film.

The 500/4.5 film has a transmittance of 50% in the visible range (Figure 11a). This is lower than the reported transmittance of MoO₃ films due to the Mo₄O₁₁ content.⁷⁹ The optical band gap of the films, E_g, can be estimated by utilizing the relation, $(\alpha h\nu)^n = A(h\nu - E_g)$ where α is the absorption coefficient, h is the Planck constant, ν is the frequency of light and A is the band edge parameter. The Tauc plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) is shown in the inset in Figure 11.

Table 4 Spectral fitting of Mo 3p and Mo 3d peaks: Mo 3d_{5/2} and Mo 3p_{3/2} binding energy (eV), FWHM value (eV), and the relative content of 4+, 5+ and 6+ oxidation states of Mo (%). The distribution of oxidation states is found from deconvolution of both Mo 3d_{5/2} and Mo 3d_{3/2} for Mo 3d, and from both Mo 3p_{3/2} and Mo 3p_{1/2} for Mo 3p.

	Mo 3p _{3/2}			Mo 3d _{5/2}		
	Mo ⁴⁺ BE (eV), FWHM (eV) Content (%)	Mo ⁵⁺ BE (eV), FWHM (eV) Content (%)	Mo ⁶⁺ BE (eV), FWHM (eV) Content (%)	Mo ⁴⁺ BE (eV), FWHM (eV) Content (%)	Mo ⁵⁺ BE (eV), FWHM (eV) Content (%)	Mo ⁶⁺ BE (eV), FWHM (eV) Content (%)
500/4.5	0	397.87 2.68 13.6 %	399.12 2.68 86.4 %	0	232.01 1.01 13.8 %	233.25 1.01 86.2 %
500/2.4	396.31 2.90 2.7 %	398.31 2.90 48.5 %	399.56 2.90 48.8 %	229.82 0.36 0.5 %	232.22 1.36 39.4 %	233.42 1.51 60.1 %
570/2.4	396.13 2.78 39.5 %	398.13 2.78 31.6 %	399.38 2.78 28.9 %	-	-	-

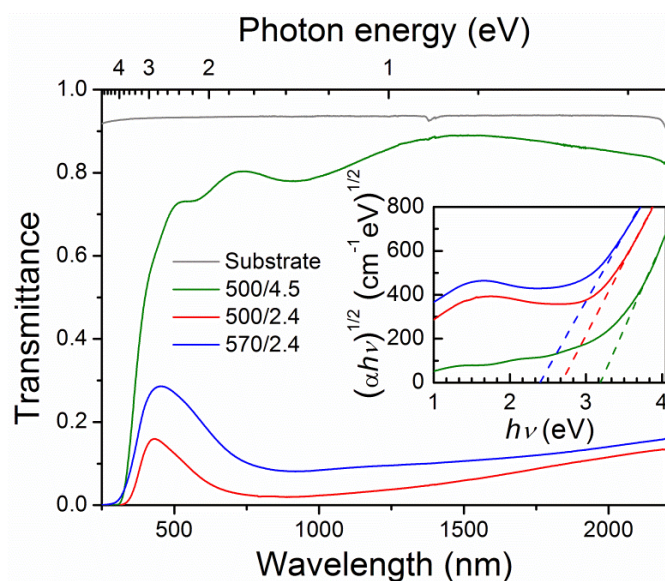


Figure 11 Transmittance spectra for the three molybdenum oxide films and the quartz substrate. Inset, the corresponding Tauc plot of $(\alpha h\nu)^{0.5}$ of the samples, for indirect transitions.

The exponent n is set as 0.5 for allowed indirect transitions. α is defined by transmittance $T = e^{-\alpha z}$ where z is the optical path length which is taken as the film thickness. Direct transitions ($n = 2$) are often used to describe crystalline MoO_3 films, with reported optical band gaps in the range 2.8 to 3.5 eV.^{17,23,79–81} However, when allowed direct transitions are plotted for amorphous films, a larger band gap is generally predicted, up to 4 eV, due to the wider absorption edge.^{79,82} Instead, when indirect transitions are considered for amorphous MoO_3 films band gaps of 2.7 to 3.5 eV are estimated.^{6,32,34,83} Indirect transitions are commonly used for amorphous materials, such as in the initial development of the model by Tauc *et al.*⁸⁴ Relating this to the thin films of MoO_3 characterized here, it follows that $n = \frac{1}{2}$ is appropriate for these films which are not completely crystalline, and indeed this gives a better approximation to linear behaviour. Plotting this, the linear region of the 500/2.4 film is extrapolated to give a band gap 3.2 eV, which matches with reports for MoO_3 thin films.^{11,53} The more reduced films have a drastically reduced transmittance compared to the 500/4.5 (Figure 11). As the more reduced films are thinner, this lower transmittance is directly related to the change in composition. The difference between the transmittance of the 500/2.4 and 570/2.4 films, however, can be related to the change in film thickness. The optical band gaps of the 500/2.4 and 570/2.4 films are also lower at 2.7 eV and 2.4 eV respectively. This and the wider absorption edge are a result of the higher proportion of reduced phases due to the position of their absorption bands, for example Mo_4O_{11} (1.3 eV, 2.13 eV and 2.42 eV) and Mo_9O_{26} (2.12 eV), or MoO_2 (2.48 eV).⁸⁵

Conclusions

The crystal structures, electronic structures and electrical and optical properties of molybdenum oxide thin films were

investigated with change in O/Mo ratio. Modelling of oxygen vacancy concentrations in MoO_3 showed that the cost of removing the oxygen pointing towards the van der Waals gap is lowest. Modelling of the possible structures in the stoichiometry range MoO_2 to MoO_3 has shown that the layered van der Waals structure $\text{Mo}_{18}\text{O}_{52}$ is destabilized by loss of oxygen from the lattice, and enables restructuring to the ReO_3 based structure Mo_9O_{26} . Furthermore, point defects are less energetically favourable than shear structures at all vacancy concentrations investigated. Density of states calculations showed a similar metallic DOS for Mo_4O_{11} and Mo_9O_{26} phases, compared to the distinctive two peaks of the MoO_2 DOS, and the wide gap MoO_3 . The metallic DOSes differed from the gap states modelled for point defects in MoO_3 . In synthesised films, MoO_2 , Mo_4O_{11} and MoO_3 phases were detected in varying ratios in three films. The phase composition affected the electronic and optical properties, with Mo_4O_{11} and MoO_2 content lowering the resistivity, transmittance and band gap. The valence band region measured by XPS was compared to the calculated DOS; MoO_2 could be discerned by its two peaks, whereas Mo_4O_{11} , Mo_9O_{26} and oxygen vacancies in MoO_3 could all contribute to the peak from 0 to 2 eV.

Acknowledgements

This work was performed within The Norwegian Research Centre for Solar Cell Technology project number 193829, a Centre for Environmentally-friendly Energy Research co-sponsored by the Norwegian Research Council and research and industry partners in Norway. Computational resources were provided by NOTUR, The Norwegian Metacentre for Computational Science, through the project nn9264k. NTNU NanoLab is acknowledged for support and subsidized use of their facilities.

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