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Chemical Vapour Deposition of Rhenium Disulfide and Rhenium-Doped Molybdenum Disulfide Thin Films Using Single-Source Precursors

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Abstract
Polycrystalline thin films of the alloy Mo1-xRexS2 (0 ≤ x ≤ 0.06) have been deposited by aerosol-assisted chemical vapour deposition (AA-CVD) using [Re(µ(SiPr)3(SiPr)6] (1) and [Mo(S2CNEt2)4] (2) in different molar ratios at 475 °C. The deposited films were characterised by p-XRD, SEM, ICP-OE, Raman, and EDX spectroscopies. The p-XRD patterns of the films deposited from (1) correspond to ReS2 and those deposited from (2) matched to MoS2 (x = 0). Re-doping of up to 6% was achieved in MoS2 thin films by using different concentrations of precursor (1), the morphology of the doped films changed from lamellar for pure MoS2 to clusters at 6 mol% alloying with rhenium. The films are promising candidates as models for the incorporation of technetium into transition metal dichalcogenides as a means of immobilisation in nuclear waste processing. Exfoliation of these films is also a potential route towards modification of the optoelectronic properties of 2D molybdenite.

Introduction
Two-dimensional transition metal dichalcogenides (TMDCs), which have the general formula MX2, include molybdenum disulfide (MoS2), tungsten disulfide (WS2), and tungsten diselenide (WSe2) have attracted interest because of their optoelectronic properties in monolayer form1-3 with useful carrier mobilities and mechanical flexibility.4-9 MoS2, in particular, has attracted considerable attention because of its potential applications in hydrogen storage, solid lubricants, capacitors, and electrochemical devices.10-14 MoS2 can also be used as a catalyst (e.g. in hydrogen evolution reactions) due to its high-energy crystal edges.15 The structure of bulk MoS2 is akin to that of graphite in terms of a repeating layer structure,16 held together by non-covalent interactions. 2H-MoS2 bulk shows a change from an indirect bandgap to a direct bandgap as the 1H-MoS2 monolayer form is approached,15 as per MoSe2, WSe2, and WS2.17,18 MoS2 thin films have been synthesised by aerosol assisted chemical vapour deposition (AA-CVD) using metal dithiocarbamate-based precursors.19 Thin films of MoS2 doped with Re have been previously synthesised by using spray pyrolysis.20 We and others have recently developed a general approach to doping MoS2 with transition metal cations such as chromium based on AA-CVD.21,22

Rhenium disulfide (ReS2) has has a direct bandgap which remains as such in the monolayer form unlike most other TMDCs. Few, if any, changes are observed in the Raman spectrum of monolayer ReS2 compared to bulk and few-layer variants.23 Transition metal doped ReS2 has been reported.24 Single crystals of Mo-doped ReSe2 have been synthesised by chemical vapour transport method with bromine as a transport agent.25 The growth of ReS2 monolayers has been achieved using CVD at 450 °C, the as-deposited ReS2 is an n-type semiconductor.26 Colloidal ReS2 nanoparticles have also been prepared with average size of 5.5 nm.27 Two-dimensional nanosheets of ReS2 have been prepared by lithium intercalation, and have unique photocatalytic properties which are superior to other two-dimensional materials.28 Large area deposition of ReS2 sheets with good crystallinity has been achieved using
simple CVD, from ReO$_3$ treated with elemental sulfur vapour at 500 °C.$^{29}$

Rhenium-doped MoS$_2$ can potentially be used as a model for immobilization of radioactive technetium-99 ($^{99m}$Tc).$^{30}$ Technetium-99 is very mobile in water; hence there is concern about its release into the environment. In 2008 the production of $^{99m}$Tc was close to 290 metric tonnes worldwide.$^{31}$ Technetium ($^{99}$Tc) is produced from uranium fission, and is present in nature at a very low level.$^{32}$ The isotope $^{99}$Tc has a long half-life (ca. 2 × 10$^5$ years), and it forms about 6% of the fission product from uranium.$^{33,34}$ The relatively short-lived isotope $^{99m}$Tc is a widely used radionuclide in nuclear medicine.$^{35}$

The above illustration suggests that the Fajans constant of each Re atom is $0.79$ Å, which is lower than most transition metal dichalcogenides which are comparable to metal dichalcogenides. A simple model is that the $d^5$ ion bonding to Re is $2.35$ Å, which is similar to the ionic radius of Re in the +4 oxidation state. Significantly, this makes Re(doped MoS$_2$)$_x$ a potentially useful model system for understanding the thermodynamic stability of $^{99}$Tc in a host molybdenum disulfide lattice which will be of particular interest in nuclear chemistry for storage capability. (Re ion bonding to Re, 63.65; Cl, 36.65. Found (%): Re, 61.63; Cl, 36.57. Anal. calc. for ReCl$_3$: Re, 63.65; Cl, 36.65. Found (%): Re, 61.63; Cl, 36.57. Anal. calc. for ReCl$_3$: Re, 62.38; Cl, 37.62. Found (%): Re, 62.38; Cl, 37.62.)

In this paper we report the deposition of Mo$_3$, Re$_2$, S$_x$ (0 ≤ x ≤ 0.65) alloyed thin films using AA-CVD from Mo and Re source precursors. Molybdenum exists usually as the 2H stacked (ABA) polytype (P6$_3$mc).$^{39,40}$ Rhenium disulfide has a different layered structure that is classified in the P6$_3$ space group,$^{41}$ of much lower symmetry than most transition metal dichalcogenides which seems to be driven by the participation of each $d^5$-Re ion bonding to three other in the same layer which results in the formation of Re$_2$ parallelograms, with vertices linked in a linear fashion throughout the sheet. The Re-based parallelograms dictate the relative displacements of the sulfur atoms in the hexagonal close packed arrays, and due to this, the sulfur atoms in the layer are rippled on the sheet surface, in contrast to MoS$_2$, where the sulfur layers appear smooth. At low levels of rhenium incorporation we find that the parent molybdenite structure holds due to the aforementioned similarities in crystal radii and the thermodynamic similarities in their +4 oxidation state. Significantly, this makes Re-doped MoS$_2$ a potentially useful model system for understanding the thermodynamic stability of $^{99}$Tc in a host molybdenum disulfide lattice which will be of particular interest in nuclear chemistry for storage capability-building using inert materials that do not leak radioactive material. This is the first example of single source precursors being used to produce such materials.

**Experimental Section**

All reactions were carried out under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were purchased from Sigma-Aldrich or Fisher and used without further purification. Reagents were purchased from Sigma-Aldrich.

**Synthesis of rhenium nonachloride (Re$_6$Cl$_9$)**

The apparatus was dried by heat gun in a stream of dry nitrogen, and then the apparatus moved with the stopcock closed into a glove bag. Rhenium pentachloride (ReCl$_5$, 2.35 g) was added into the tube and moved from the glove bag and clamped in a vertical way, with a moderate stream of N$_2$. The tube was heated in a slow Bunsen burner flame, after that the ReCl$_5$ started to melt and the vapour was under reflux. Brown fumes were observed to be liberated. Heating was stopped during the reaction at regular intervals to harvest the crystals which were formed on the wall of tube. This process was repeated until no more brown fumes were liberated and only solid remained.$^{42}$

The apparatus was allowed to cool, and the tube sealed off and moved to a nitrogen filled glove bag to transfer the product, black-red solid, into an ampoule. Yield: 72%. Anal. Calc. for Re$_5$Cl$_9$ (%): Re, 63.65; Cl, 36.65. Found (%): Re, 61.63; Cl, 36.57.

**Synthesis of rhenium iso-propylylthiolate Re$_6$Cl$_9$µ-S(µ-SPr)$_3$ (1)**

Re$_6$Cl$_9$µ-S(µ-SPr)$_3$ was prepared as previously reported.$^{43}$ Re$_5$Cl$_9$ (2.3 g, 2.6 mmol) was placed into a thimble in the Soxhlet, then Re$_5$Cl$_9$ was extracted from a Soxhlet thimble by refluxing with THF (40 mL) under nitrogen over 48 h or more until the solvent passing through the thimble became colorless. The THF solvent was evaporated and then dark purple solid were collected and washed with diethyl ether (2 × 20 mL). Traces of solvent were removed in vacuo to furnish the title product. Yield: 58%. IR (v$_{max}$/cm$^{-1}$): 2956 (w) 1418 (w), 1412 (w), 1336 (w), 1042 (w), 1014(m), 917 (w), 839 (s), 686 (w).

**Synthesis of rhenium iso-propylthiolate Re$_6$µ-S(µ-SPr)$_3$(SPr)$_3$ (1)**

This compound was prepared using the method of Cohen and co-workers.$^{44}$ Briefly, Re$_5$Cl$_9$µ-S(µ-SPr)$_3$ (1.7 g, 1.5 mmol) was dissolved in THF (140 mL). Sodium isopropylthiolate (1.7 g, 17.8 mmol) was added to the red solution of Re$_5$Cl$_9$µ-S(µ-SPr)$_3$. This mixture was refluxed for 48 h after which the THF was removed under reduced pressure. The resulting solid was then extracted by dissolving in hexane five portions of 20 mL; the combined organic phase was filtered through Celite, the solvent was removed by reduced pressure then dried by vacuum oven overnight. Yield: 55%. Anal. calc. for Re$_5$S$_6$C$_2$H$_{41}$ (%): C, 26.28; H, 5.14; Found (%): C, 25.82; H, 5.77. $^1$H

**Instrumentation:**

Elemental analysis was performed by the University of Manchester micro-analytical laboratory. A Seiko SSC/S200 model was used for TGA measurements with a heating rate of 10 °C min$^{-1}$ under nitrogen. Scanning electron microscopy (SEM) was performed in secondary electron mode with a Zeiss Ultra55 microscope with an accelerating voltage of 10 kV. Energy-dispersive X-ray (EDX) spectroscopy was performed on the same system at an accelerating voltage of 30 kV using an Oxford Instruments INCA pentaFETx3 detector. A Bruker D8 AXE diffractometer was used to record p-XRD patterns, equipped with a Cu-K$_\alpha$ source (1.5406 Å). Thin films were scanned between 10 and 80° with step size 0.02° and a dwell time of 3 s.
NMR (CDCl₃, 400 MHz) δ/ ppm: 1.18 (d, J=6.81 Hz, 3 H, SCHMe₂), 1.21 (d, J=6.81 Hz, 3 H, SCHMe₂), 1.23 (d, J=6.56 Hz, 3 H, SCHMe₂), 1.27 (d, J=6.81 Hz, 3 H, SCHMe₂), 1.37 (d, J=6.81 Hz, 4 H, SCHMe₂), 1.42 (d, J=6.81 Hz, 4 H, SCHMe₂), 1.58 (d, J=6.81 Hz, 4 H, SCHMe₂), 1.70 (d, J=4.29 Hz, 3 H, SCHMe₂), 1.71 (d, J=4.29 Hz, 3 H, SCHMe₂), 2.84 - 2.96 (septet, 1 H, SCHMe₂), 3.40 - 3.53 (septet, 1 H, SCHMe₂), 3.55 - 3.67 (septet, 1 H, SCHMe₂), 3.99 - 4.12 (septet, 1 H, SCHMe₂), 4.19 - 4.32 (septet, 1 H), 4.34 - 4.45 (septet, 1 H, SCHMe₂), 13C NMR {1H} (CDCl₃, 101 MHz) δ/ ppm: 22.61 (s, 5 C), 25.40 (s, 2 C), 25.71 (s, 2 C), 26.46 (s, 2 C), 27.21 (s, 2 C) 27.78 (s, 2 C), 28.07 (s, 2 C), 28.21 (d, J=2.21 Hz, 5 C), 28.50 (s, 2 C), 30.95 (s, 2 C), 32.23 (s, 1 C), 37.32 (s, 1 C), 37.78 (s, 1 C), 41.46 (s, 2 C), 44.02 (d, J=7.37 Hz, 3 C), 44.05 - 44.28 (m, 2 C), 46.89 (s, 1 C).

Fig. 1. TGA of (a) Re(µ-SPr₃)(SPr₃)₄ (1) and (b) [Mo(S₂CNEt₂)₄] (2) complexes.

Synthesis of tetrakis(diethylaminodithiocarbomato)molybdate(IV) ([Mo(S₂CNEt₂)₄], (2).

A mixture of Mo(CO)₆ (10g, 37.8 mmol) and bis(diethylthiocarbamoyl)disulfide (22.4 g, 75.6 mmol) was dissolved in degassed acetone (400 mL) and heated under reflux at a temperature range of 55-60 °C for 2 h. The mixture was cooled to room temperature, which prompted violet crystals to appear which were filtered and washed with pentane and dried in vacuo. All characterisation data showing four decomposition steps in the range 0–600 °C with a final residue (29 %) close to that of MoS₂ (calc. 24%).

Fig. 2. Powder X-ray diffraction pattern for rhenium disulfide (ReS₂) deposited by AA-CVD using precursor (1) at 475 °C. The black sticks refer to the powder pattern of ReS₂ as reported by Wildervanck et al. A simulated powder pattern is also available in the Supporting Information. The amorphous background is from the glass substrate.

Deposition and Characterization of ReS₂ Thin Films. Deposition of ReS₂ films was performed using AA-CVD. The reactor temperature for deposition of ReS₂, MoS₂, and Re-doped MoS₂ was chosen based on thermogravimetric analysis results (TGA, vide supra). Varying molar ratios of precursor (1) and (2) were used in a THF aerosol to achieve doped thin films which were deposited at 475 °C. The films were studied by inductively coupled plasma atomic emission spectroscopy (ICP-AES), powder X-ray diffraction...
(p-XRD), scanning electron microscopy (SEM) and Raman and energy dispersive X-ray (EDX) spectroscopies. The p-XRD pattern of rhenium disulfide thin films deposited at 475 °C (Figure 2) revealed two major reflections at $2\theta = 14.37^\circ$, which is assigned to the (001) plane of 1T-ReS$_2$, and at $2\theta = 27.89^\circ$ corresponding to the (111) plane. Thus the ReS$_2$ produced by AACVD has an apparent preferred orientation in the (001) plane.

**Fig. 3.** The Raman spectrum of as-deposited ReS$_2$ thin films produced by AA-CVD at 475 °C. The profile is consistent with the Raman spectrum of ReS$_2$ previously reported.$^{28,29}$

Raman spectroscopy of the films revealed three identifiable vibrational modes that can be linked to ReS$_2$ films. $E_g$ modes, in-plane vibrations of Re atoms in ReS$_2$, an $A_g$ modes at low frequency, corresponding to the out-of-plane vibrations of Re atoms(Figure 3). The morphological features of thin films of rhenium sulfide were investigated by scanning electron microscopy (SEM), which revealed particles with teardrop morphology (Figure 4a and 4b). Bright field transmission electron microscopy (TEM) reveals that this material is flake-like in appearance at the nanoscale (Figure 4c – 4g), which is consistent with the layered structure of ReS$_2$. Selected area electron diffraction (SAED) patterns taken from these flakes show that they are highly crystalline (Figure 4h).

**Fig 4.** Electron microscopy of rhenium disulfide (ReS$_2$) thin films. (a) – (b) Secondary electron SEM images (10 kV) of thin films deposited by AA-CVD at 475 °C. Scale bars represent: (a) 2 µm; (b) 5 µm. (c) – (g) Bright field TEM images of ReS$_2$ thin films (200 kV). (h) Selected area electron diffraction pattern of an ReS$_2$ flake.

Elemental analysis of the rhenium sulfide thin films by energy dispersive X-ray (EDX) spectroscopy. Thin films of ReS$_2$ grown from Re(µ-SiPr)$_3$(SiPr)$_6$ at 475 °C analysed as follows: Re 30%, S 70% giving a composition of ReS$_{2.3}$. Molybdenum Sulfide was also grown under the same conditions.$^{19}$ SEM and EDX and Raman spectroscopies were consistent with that previously reported for this material (Supporting Information).

**Deposition and Characterization of Mo-doped ReS$_2$ Thin Films.** Rhenium-alloyed thin films of molybdenum disulfide (Mo$_{1-x}$Re$_x$S$_2$ where $0 \leq x \leq 0.06$) were synthesised by AA-CVD at 475 °C. EDX spectroscopy and ICP-OES confirmed that the rhenium dopant was successfully entrained into MoS$_2$ thin films (Figure 5). In all cases, the incorporation of Re into MoS$_2$ is inefficient and the amount of Re found by EDX and ICP-OES in the films is only ca 10% of that available Re in the aerosol feed.
The p-XRD patterns of Mo<sub>1-x</sub>Re<sub>x</sub>S<sub>2</sub> (0 ≤ x ≤ 0.06) show four reflections at 2θ = 14.3, 33.2, 39.5, and 58.7° which can be assigned to the (002), (100), (103), and (110) reflections respectively. There was no significant change with the incorporation of 1.79 and 1.80 mol% of Re on the pXRD patterns. However, on increasing the level of Re to more than 1.80 mol%, a significant change in the appearance of the powder patterns was observed. The (002) reflection became weak and broadened (Figure 6). These changes in the powder pattern can be attributed to increasing Re mol%, which affects the stacking layers of the S-MoS<sub>2</sub> layers in the basal plane, which has previously been observed for Cr-doped MoS<sub>2</sub>.<sup>21</sup> Bright field TEM of the doped thin films (Supporting Information) reveal that increasing the level of Re in the films does indeed cause a shift to material with a more amorphous appearance. This could potentially be caused by the formation of interlayer Re-Re bonds that locally disrupt the structure by S displacement (<i>vide supra</i>). The d-spacing for the (002) plane of the MoS<sub>2</sub> film was 6.23 Å which is larger than that reported by Schoenfeld et al.<sup>40</sup> Indeed, in our other reports of MoS<sub>2</sub> synthesised by AACVD from dithiocarbamato molybdenum(IV) precursors the observed spacings of 6.25 and 6.20 Å,<sup>19,21</sup> suggest that MoS<sub>2</sub> produced by AA-CVD is lattice expanded in the [002] direction as compared to bulk material. The rhenium doped MoS<sub>2</sub> displays a monotonic increase in the d-spacing that is linear with doping, suggesting that doping of Re affords a linear lattice expansion in the [002] direction of the crystal. If the literature value of d(002) for bulk molybdenite is used,<sup>46</sup> the trend becomes linear. We tentatively suggest that the effect of doping is pseudo-Vegardian.

Raman spectroscopy was used to study Mo<sub>1-x</sub>Re<sub>x</sub>S<sub>2</sub> (0 ≤ x ≤ 0.06) films. The MoS<sub>2</sub> film had two main bands observed at 407.6 cm<sup>-1</sup> and 380.6 cm<sup>-1</sup> corresponding to the A<sub>1g</sub> and E<sub>2g</sub> optical phonon modes (Supporting Information). The Raman spectra for the Re-doped MoS<sub>2</sub> films are shown in Figure 7a. Significant changes in Raman spectra occurred at 3.6 mol% Re with the appearance of a band which could correspond to the A<sub>1g</sub> mode for ReS<sub>2</sub>. Dependence of the Raman shift of the E<sub>2g</sub> and A<sub>1g</sub> optical modes of Mo<sub>1-x</sub>Re<sub>x</sub>S<sub>2</sub> on the amount of Re.
dopant is shown in Figure 7b. The difference in the magnitude of the shifts observed for both bands gives insight into the manner of doping.48 The A1g mode, which consists of the vibrational displacement of sulfur atoms only is only slightly shifted from ca. 407 cm\(^{-1}\) to ca. 406 cm\(^{-1}\). On the other hand, the E'2g mode, which involves the vibration of metal and sulfur atoms in a layer is significantly shifted from ca. 382 cm\(^{-1}\) to ca. 376 cm\(^{-1}\). This is consistent with the substitutional doping of the heavier Re atoms into the Mo layer.

Fig. 7. (i) Raman spectra of Mo\(_{1-x}\)Re\(_x\)S\(_2\) (0 \(\leq x \leq 0.06\)) thin films deposited at 475 °C by AA-CVD. (a) MoS\(_2\), (b) 1.79 mol \% Re, (c) 1.80 mol \% Re, (d) 3.60 mol \% Re, (e) 6.25 mol \% Re, and (f) ReS\(_2\); thin films were synthesized by using AA-CVD at 475 °C. EDX spectrum maps (30 kV) of (g) Mo L\(_\alpha\) and (h) Re K\(_\alpha\) emission in 1.8 mol\% Re-doped MoS\(_2\) films. All scale bars represent 5 \(\mu\)m.

The surface morphology of the Mo\(_{1-x}\)Re\(_x\)S\(_2\) (0 \(\leq x \leq 0.06\)) films deposited by AA-CVD at 475 °C were investigated by SEM. Different morphologies were observed on changing the amount of rhenium; MoS\(_2\) had a lamellar morphology, but Re-doped MoS\(_2\) 1.79 \% gave clusters. Increasing the Re to 3.60\% gave feather-like crystals which were also observed for material with 6.25\% Re (Figure 8). Representative elemental mapping of the Re-doped MoS\(_2\) thin film at 1.80\% revealed that rhenium is evenly distributed in the film (Figure 8). This was found in all alloyed films, suggesting that the isovalent substitution of Re(IV) for Mo(IV) was homogeneous under the conditions employed in this study.

Fig 8. Secondary electron SEM images (10 kV) of Mo\(_{1-x}\)Re\(_x\)S\(_2\) (0 \(\leq x \leq 0.06\)) thin films deposited at 475 °C by AA-CVD. (a) 0 mol\% Re, (b) 1.79 mol \% Re, (c) 1.80 mol \% Re, (d) 3.60 mol \% Re, (e) 6.25 mol \% Re, and (f) ReS\(_2\); thin films were synthesized by using AA-CVD at 475 °C. EDX spectrum maps (30 kV) of (g) Mo L\(_\alpha\) and (h) Re K\(_\alpha\) emission in 1.8 mol\% Re-doped MoS\(_2\) films. All scale bars represent 5 \(\mu\)m.
Conclusions

Thin films of Mo$_x$Re$_2$S$_2$ (0 ≤ x ≤ 0.06) were deposited by AA-CVD from the single-source precursors Re$_x$S$_y$Pr$_y$S$_z$(S$_t$)$_r$_t(1) and Mo$_x$S$_y$C$_z$N$_d$E$_e$$_f$(2). The Re-doped MoS$_2$ thin films were deposited by using different molar ratios of (1) and (2). The morphology of thin films as investigated by SEM changes as the doping of MoS$_2$ with rhenium is increased. The p-XRD patterns for the Re-doped MoS$_2$ shows systematic variations in the peak shape, intensity, and the position of the (002) planes as the rhenium content varies. The d(002) spacing in the alloys increases in a pseudo-Vegardian manner. EDX mapping of films demonstrated the spatial homogeneity of the doping. The MoS$_2$ alloy with Re is a promising model system for the stability of $^{99}$Tc in the host molybdenum disulfide crystal due to crystal radii and thermodynamic similarities between Re(VI) and Tc(VI). The materials could also be exfoliated either by liquid or mechanical means to make novel 2D materials; we are currently investigating this possibility.

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