Supporting Information

The Influence of Precursor on Rhenium Incorporation into Re-doped MoS_2 ($Mo_{1-x}Re_xS_2$) Thin Films by Aerosol-Assisted Chemical Vapour Deposition (AACVD).

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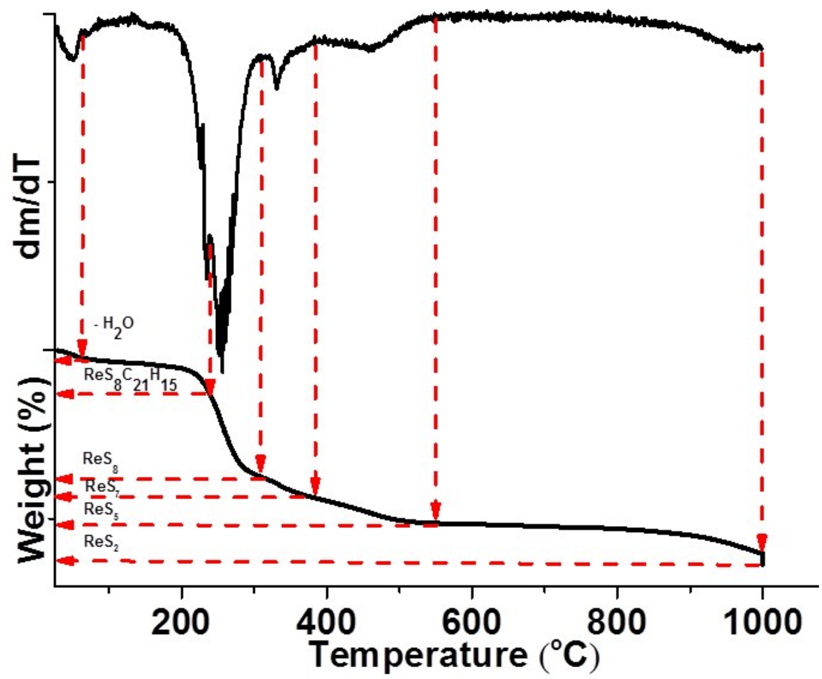

Figure S1 1st derivative of the TGA profile overlayed on TGA profile of $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$, (**2**).

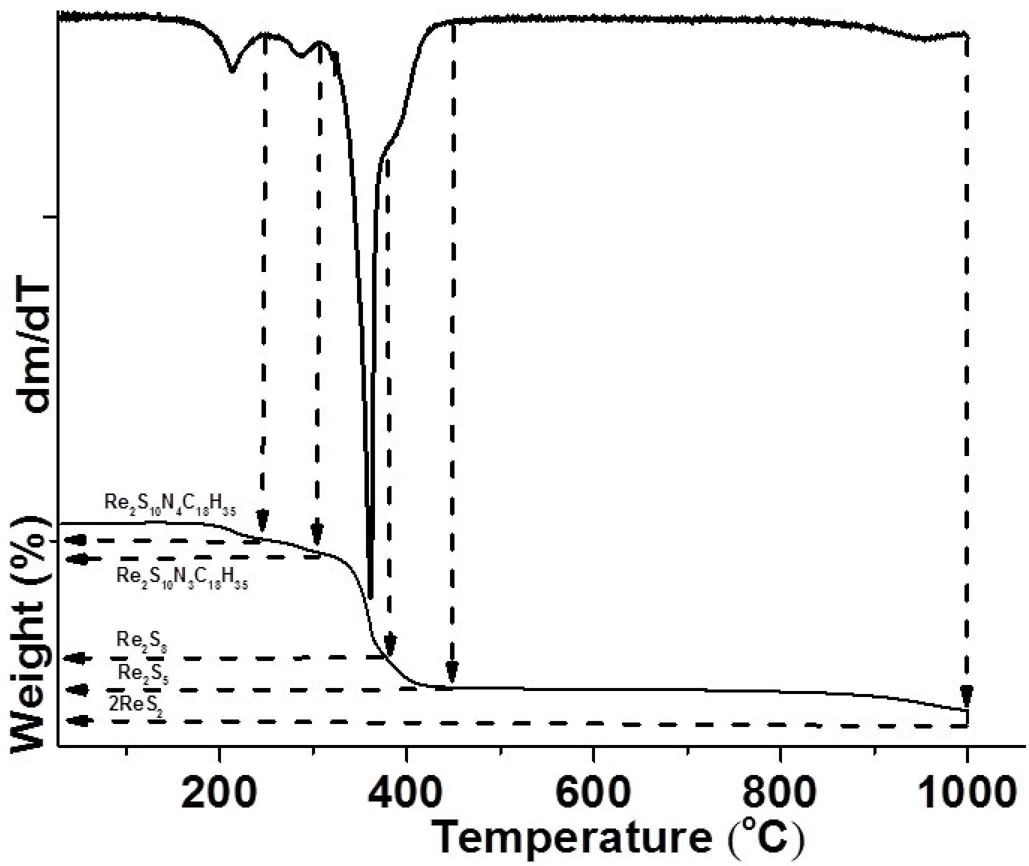

Figure S2 1st derivative of TGA profile overlayed onto the TGA profile of $[Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4]$ (**3**).

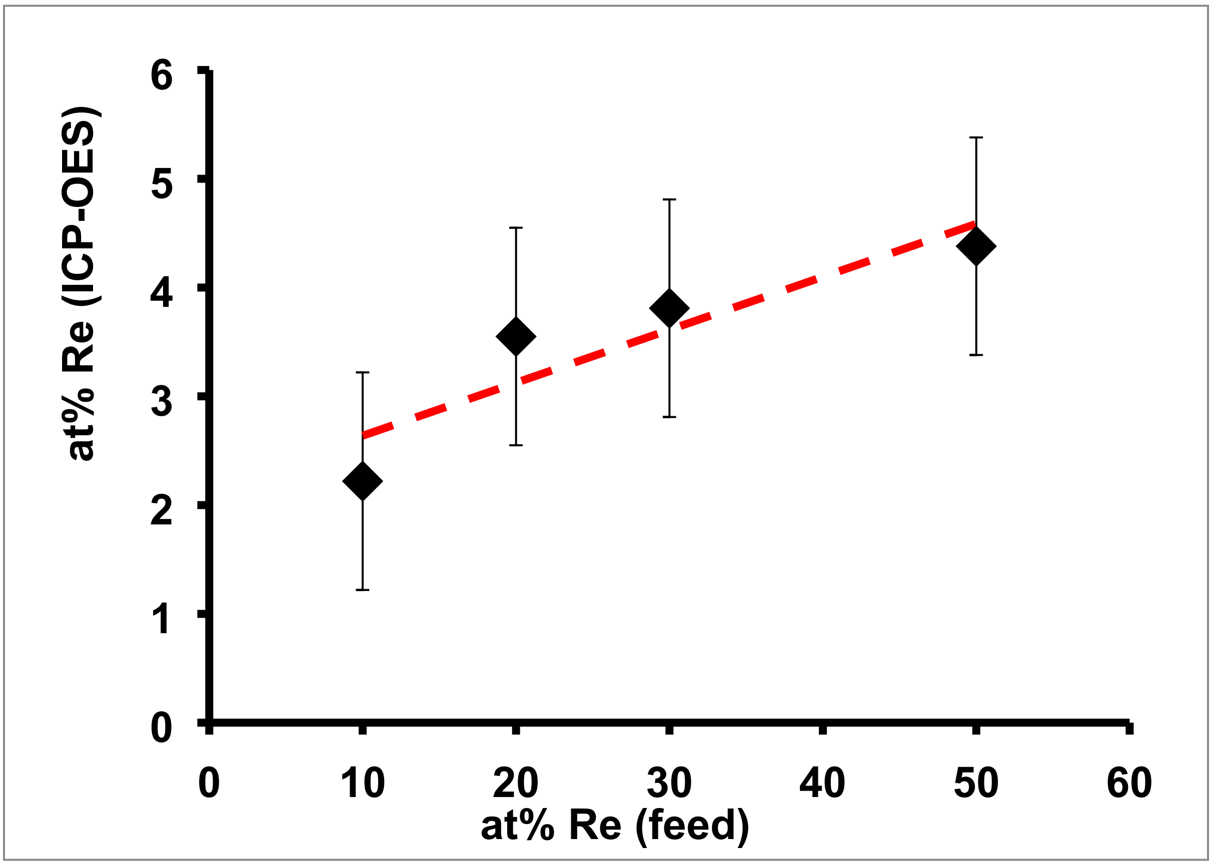

Fig. S3. The at% of Re that found using elemental analysis of thin films produced by AACVD using (**1**) and (2) at 550 °C by ICP-OE spectroscopies with varying Re mol% in the AACVD feed .

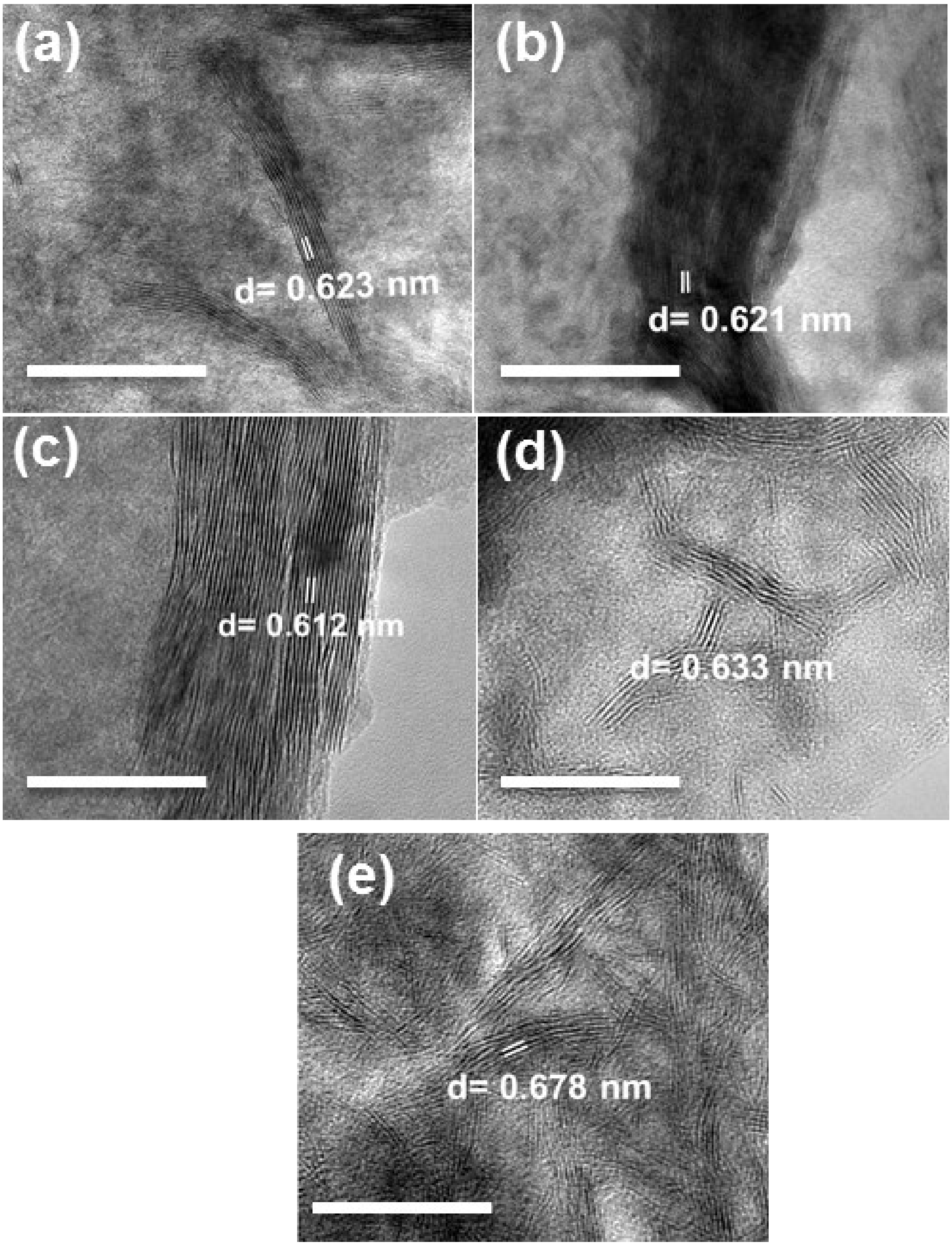

Fig. S4. Bright field TEM of undoped MoS_2 and doped MoS_2 thin films using (**1**) and (**2**) at 550 °C: **(a)** MoS_2, **(b)** 2.2% Re, **(c)** 3.5 % Re, **(d)** 3.8% Re, **(e)** 4.4% Re. The scale bars represent 20 nm.

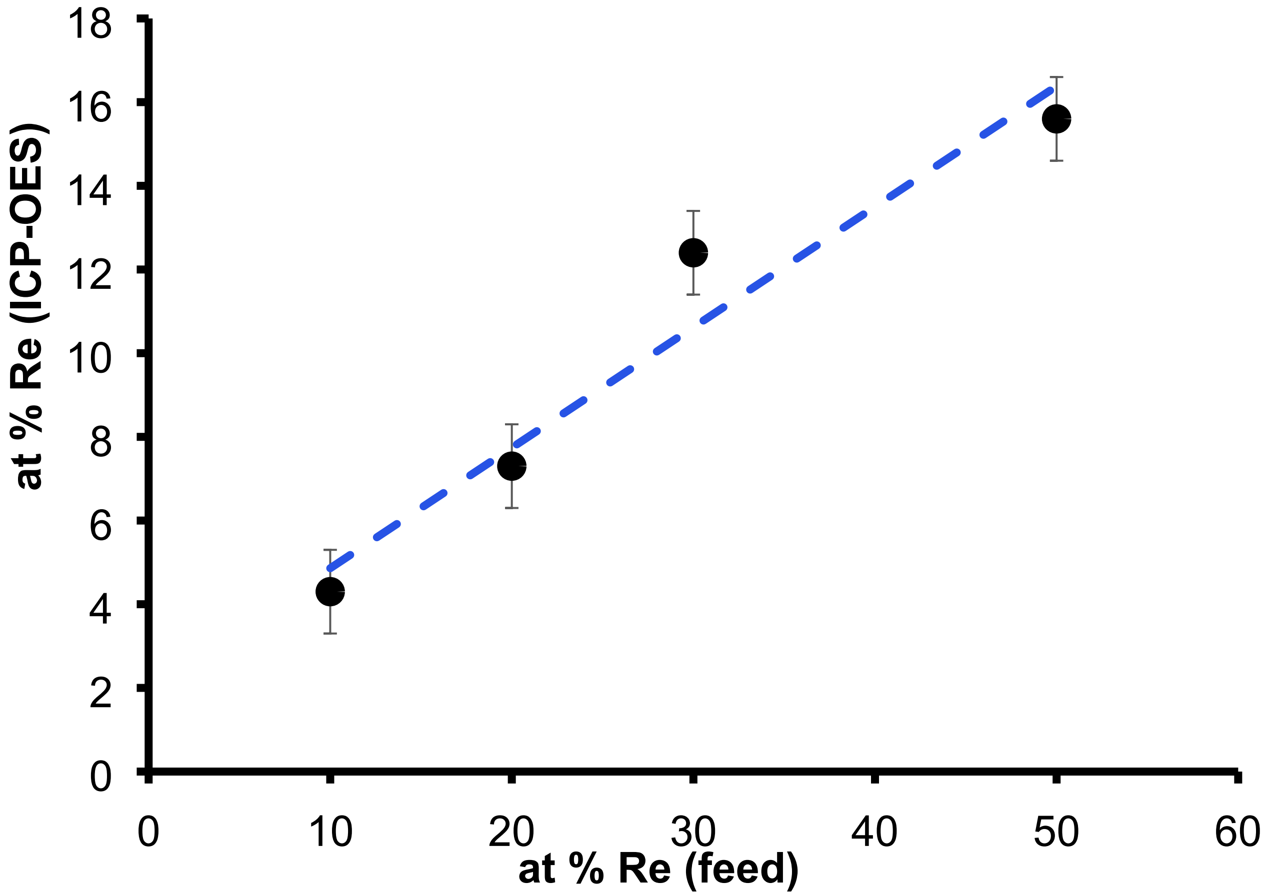

Fig. S5. Plot of mol% Re found in elemental analysis of thin films produced by AACVD using (**1**) and (**3**) at 550°C by ICP-OES. as a function of the mol% of Re in the AACVD feed.

Deposition of ReS_2 thin films using (3) as feed in AACVD

In previous work, we found it was possible to use (2) as a molecular precursor to produce ReS_2 thin films by AACVD.[1] We showed that p-XRD patterns of thin films deposited at 550 °C by AACVD onto glass substrates using precursor (**2**) correspond to 1*T*-ReS_2 with a preferred orientation in the (001) plane. This is also the case when homobimetallic complex (**3**) is used as the molecular precursor in AACVD (Fig 3a), with an intense reflection centred at 2θ = 14.47°, which we again assign to the (001) plane and gives an interlayer spacing d_{001} = 6.110 Å from the Braggs' law. This value is close to the reported (001) plane of 1*T*-ReS_2 (6.068 Å).[2]

Raman spectroscopy of the films revealed three identifiable vibrational modes that can be attributed to the successful production of ReS_2 films. E_g-like modes corresponding to the in-plane vibrations of Re atoms in ReS_2, and A_g-like modes observed at low frequency, corresponding to the out-of-plane vibrations of Re atoms (Fig. 3b). Secondary electron scanning electron microscopy (SEM) imaging reveals that these thin films of ReS_2 are uniform and comprised of small granular crystallites, interestingly without lamellar appearance, which is generally expected. Elemental analysis of the rhenium sulfide films was carried out by energy dispersive X-ray (EDX) spectroscopy and shows the grown thin films are comprised of (at%, found (calc.)): Re 37.4 (33); and S 62.6 (66). The sulfur deficiency can be attributed to the high temperatures used for thin film deposition which can, in certain cases volatilise the chalcogen component.[3]

It was possible to directly measure the *d*-spacing of the (001) plane in ReS_2, by TEM of crystallites removed from the substrate. A value of 6.06 Å was found. The likely discrepancy between the p-XRD and TEM lattice-resolution images potentially lies in the statistical relevance difference between techniques.

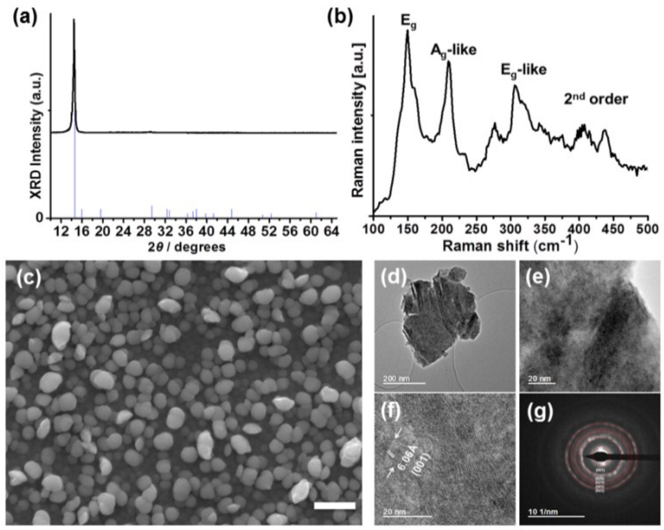

Fig S6: Characterization of ReS_2 films deposited on glass substrates by AACVD at 550 °C using $[Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4]$ (**3**) as precursor. (a) Powder X-ray diffraction pattern. The blue sticks represent the standard reference pattern of ReS_2.[31] (b) Raman spectrum with assignments. (c) Representative secondary electron SEM image of ReS_2 thin film in plan view, scale is 1µm. (d) – (f) Bright field TEM images of a polycrystalline ReS_2 flake cleaved from the thin film. (g) Selected area electron diffraction SAED pattern associated with the same ReS_2 flake as imaged in (d).

References

1. N. Al-Dulaimi, E. A. Lewis, D. J. Lewis, S. K. Howell, S. J. Haigh and P. O'Brien, *Chem. Commun.*, 2016, **52**, 7878-7881.
2. J. Wildervanck and F. Jellinek, *J. Alloys Compd.* , 1971, **24**, 73-81.
3. M. Afzaal, M. A. Malik and P. O'Brien, *J. Mater. Chem.* , 2010, **20**, 4031-4040.