Chemical vapour deposition of chromium-doped tungsten disulphide thin films on glass and steel substrates from molecular precursors

DOI: 10.1039/c8tc01991f

Document Version
Accepted author manuscript

Link to publication record in Manchester Research Explorer

Citation for published version (APA):

Published in:
Journal of Materials Chemistry C

Citing this paper
Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights
Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy
If you believe that this document breaches copyright please refer to the University of Manchester’s Takedown Procedures [http://man.ac.uk/04Y6Bo] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.
Chemical vapour deposition of chromium-doped tungsten disulphide thin films on glass and steel substrate from molecular precursors

Ghulam Murtaza, a c Sai P. Venkateswaran, d Andrew G. Thomas, b Paul O’Brien* a b c and David J. Lewis.*b c

Polycrystalline thin films of chromium doped tungsten disulphide (WS2) have been deposited onto glass and steel substrates by Aerosol-Assisted Chemical Vapour Deposition (AACVD) using bis(diethyldithiocarbamato)disulfidothioxo tungsten(VI) (WS3L2) and tris(diethyldithiocarbamato) chromium(III) [Cr(S2CNEt2)3] complexes as precursors in different molar ratios at 450 °C. The deposited films were characterised by p-XRD, SEM, EDX, and Raman spectroscopies. Chromium doping of up to 15 mol% was achieved in WS2 thin films. The morphology of the doped films changed from lamellar for pure WS2 to florets in heavily doped material.

Introduction

Layered transition metal dichalcogenides (TMDs) such as tungsten disulfide (WS2) and molybdenum disulfide (MoS2) have attracted much attention due to several applications in photoelectrochemical (PEC) and photovoltaic (PV) cells, dry electrodes for batteries, gas sensors, and catalytic activity. 1-8 They are also often used as a dry lubricant in mechanical systems. 9-11 The excellent lubricating behavior is because of the layered crystal structure, in which a central layer atom is formed from tungsten between two layers of sulfur atoms. 12, 13 Weak non-covalent forces hold the layers together, so shearing of the crystal is easy in the lateral dimension. A number of deposition techniques have been used to grow tungsten disulfide (WS2) films which include atomic layer deposition (ALD), ion beam deposition, sputtering deposition and pulsed laser deposition and chemical vapour deposition. 14-17 We have used aerosol assisted chemical vapor deposition (AACVD) 18, 19 for the growth of MoS2 films onto glass substrates from single source precursors. 20 The stoichiometry of metal and ligand composition is easy to control using single source precursors. It is also easy to choose the decomposition temperature by informed precursor design and minimizes the use of toxic gases. 21 Yongfeng et al. have reported the deposition of tungsten disulfide films by atomic layer deposition (ALD) technique using W(CO)6 and H2S as precursors. 22 Zhu et al. deposited WS2 films on AISI 1045 steel by magnetron sputtering followed by ion sulfuration and was performed at low temperature to obtain a WS2 composite film which showed a superior hardness, elastic modulus and tribological properties compared to other samples prepared by the same method. 23 Zafer et al. reported the deposition of a WS2 film by an e-beam deposition method. They deposited the W film onto SiO2 substrate then annealed and finally sulfurization of W film was performed to get the WS2 film. They studied the etching behavior of the WS2 film into a series of triangular shaped pits while heating in the air. The triangular pits increase with the increase in the number of layers of tungsten disulfide film. 24 It has been demonstrated in previous studies that the doping of metallic elements such as Cr, Cu, Ag, Ti into WS2 films may improve the hardness, adhesion and wear resistance of the films. 25-29 The doping of non-metallic elements such as C or N also helps to improve wear resistance properties, hardness, and adhesion of the film. 30-33 Jhonattan et al. deposited titanium doped tungsten disulfide film onto AISI 304 stainless-steel substrates using the magnetron co-sputtering DC technique. 34 Petr et al. reported W-S-N coating deposited by d.c. reactive magnetron sputtering. They studied the effect of deposition conditions on chemical composition, morphology, tribological and mechanical properties. The hardness of the film deposited with a discharge pressure of 1.2 Pa increased with N content up to 7 GPa and the coatings deposited at lower pressure show hardness around 9 GPa. 35 Fredrik et al.
deposited W-S-C-Cr and W-S-C-Ti coatings by magnetron sputtering they examined both systems and indicated significant amounts of oxides in the form of a layer just underneath the crystalline WS₂ top layer. These coatings contained 40–50 at% C but there was no carbon present in the tribofilms. They also observed that the WS₂ basal plane is surrounded by Fe particles which show the chemical bonding between iron/steel and WS₂.36

Herein we report the deposition of Cr-doped tungsten disulfide (WS₂) thin films onto glass and steel substrates by AACVD from the bis(diethyldithiocarbamato)disulfido, thioxo, tungsten(VI) [WS₃(S₂CNEt₂)₂] (WS₃L₂) and tris(diethyldithiocarbamato)chromium(III) complexes as a single source precursor. Such films have not been deposited before by AACVD and this work is the first example of CVD of a series of heavily doped WS₂ films on glass and ferrous substrates.

**Experimental**

**Chemicals**

All reagents were purchased from Sigma-Aldrich and used without further purification, ammonium tetrathiotungstate [(NH₄)₂WS₄] (99.9%), sodium diethyldithiocarbamate trihydrate NaS₂CN(C₂H₅)₂.3H₂O (≥ 95%) and chromium trichloride hexahydrate (CrCl₃.6H₂O) (≥ 98%). Solvents were purchased from Sigma-Aldrich or Fisher acetone (99.0%), dichloromethane (≥ 99.8%), methanol (99.5%), Hydrochloric acid (HCl) (37%).

**Instrumentation**

Elemental analysis and thermogravimetric analysis (TGA) with a heating rate of 10 °C/min under nitrogen from 30 °C to 600 °C of the precursors were performed by the University of Manchester, School of Chemistry micro-analytical laboratory. Powder X-ray diffraction (XRD) was performed using Bruker D8 Advance diffractometer. All the samples were scanned between 10° to 80° using CuKα radiation (wavelength 1.5406Å) an increment of 0.02° and the dwell time was 3 seconds for every sample. Infrared spectra were recorded on a Specac single reflectance ATR instrument (4000–400 cm⁻¹, resolution 4 cm⁻¹). Scanning Electron Microscopy (SEM) was carried out using a Philips XL-30 FEG microscope. Energy-dispersive X-ray (EDX) spectroscopy was performed with a Philips EDAX DX4 X-ray micro-analyser SEM.

XPS measurements were carried out using a custom built Specs™ X-ray photoelectron spectrometer equipped with a microfocused monochromated Al kα X-ray source (hn=1486.6 eV) and 150 mm Phoibos hemispherical analyser. The base pressure in the analysis chamber was around 1 x 10⁻⁹ mbar during the measurements. WS₂ films were presented on glass and steel substrates. Spectra are aligned on the binding energy scale relative to the adventitious hydrocarbon C 1s signal at 284.8 eV.37 Peak fitting was performed using the CASA XPS software using a linear background subtraction and a 70:30 Gaussian:Lorentzian mixd peak shape.

**Synthesis of bis(diethyldithiocarbamato)disulfido, thioxo, tungsten(VI) [WS₃(S₂CNEt₂)₂] (WS₃L₂)**

WS₃L₂ was synthesised as previously reported,38 briefly, an aqueous solution (300 mL) of ammonium tetrathiotungstate (2.91 g, 8.3 mmol) and sodium diethyldithiocarbamate trihydrate (7.6 g, 33.8 mmol) was vigorously stirred with dropwise addition of 2 M HCl solution until a pH of 2 was obtained. Initially, yellow colored precipitates were produced which finally turns dark green with continued HCl addition. The mixture was stirred for 30 minutes. The precipitates were filtered by vacuum and washed with water (3 x 100 mL) and dried in a vacuum oven at room temperature for an hour. The crude product was dissolved in acetone (250 mL), filtered and the precipitates washed with acetone (3 x 40 mL) to give a dark green solution and an orange-brown powder. The green solution was stripped of its solvent by evaporation before drying in a vacuum oven to give WS₃L₂ as a dark green powder (2.53 g, 52.5 %). In addition, the orange-brown powder was dried in a high vacuum to give pure WS₃S₂L₂ (0.99 g, 1.25 mmol, 20.9 %). The unit cell of WS₂ and chemical structures of the precursors are shown in Fig. 1. FT-IR (solid), νmax/cm⁻¹: 1511 (C-N), 997 (C=S). Anal. calcd for C₁₀H₂₀N₂S₇W: C, 20.86; H, 3.50; N, 4.86; S, 38.86 %. Found: C, 21.00; H, 3.63; N, 4.78; S, 38.06.

**Fig. 1** (a) chemical structures of the precursors used in this study: [WS₃(S₂CNEt₂)₂] (1), and [Cr(S₂CNEt₂)₃] (2). (b) structure of WS₂ with the hexagonal unit cell marked (a= b = 3.1532Å, c = 12.232Å with α = β = 90°, γ = 120°), after Schutte.39 Gray atoms represent W and yellow atoms are S.
Synthesis of tris(diethylidithiocarbamato)chromium (III) [Cr(S$_2$CNEt$_2$)$_3$] (CrL$_3$)

The complex was synthesized by the literature method. Briefly, chromium trichloride hexahydrate (4.0 g, 18 mmol) was dissolved in water (250 mL). Concentrated hydrochloric acid was added to adjust the pH to 5. The acidic green solution of chromium trichloridehexahydrate was added dropwise to the aqueous solution of monosodium salt of diethyl dithiocarbamate (12.0 g, 54 mmol). The colour of the reaction mixture was changed to blue. These blue precipitates were removed by filtration and dried at room temperature in a vacuum oven. Column chromatography was used to purify the chromium complex. The bright blue band at the solvent front was collected. The solvent (dichloromethane) was removed under vacuum to obtain the pure product (1.2 g, 13%); mp, 260 − 261 °C.

FT-IR (solid) $\nu_{\text{max}}$/cm$^{-1}$: 2975 (w), 2930 (w), 1491 (m), 1460 (m), 1450 (m), 1433 (m), 1376 (m), 1356 (m), 1269 (m), 1208 (m), 1144 (m), 1098 (m), 1074 (m), 995 (m).

Anal. Calc for C$_{15}$H$_{30}$N$_3$S$_6$Cr: C, 36.27%; H, 6.09%; N, 8.46%. Found: C, 37.10%; H, 6.03%; N, 8.30%.

Aerosol-Assisted Chemical Vapor Deposition (AACVD)

The glass and X65 steel substrates were thoroughly washed with acetone to remove any contamination and used for the deposition of thin films. In a typical deposition, 0.2 g (0.35 mmol) of total precursors (WS$_3$L$_2$ and CrL$_3$) was dissolved in 25 ml of tetrahydrofuran (THF) in a two-necked 100 ml round-bottomed flask with a gas inlet. The solution was held over a piezoelectric humidifier and the aerosol thus created was carried by a stream of argon (180−200 cm$^3$ min$^{-1}$) into a quartz tube containing glass and steel substrates. The argon flow rate was controlled by a Platon flow gauge. The reactor tube was placed in a Carbolite furnace set at 450 °C. The deposition of metal chalcogenides onto glass and steel substrates was continued for 90-100 min in all experiments.

Results and discussion

Thermogravimetric Analysis

Thermogravimetric analyses (TGA) of the precursor CrL$_3$ shows single step decomposition while WS$_3$L$_2$ shows four step decomposition (Fig. 2), at 133.50, 197.08, 319.71 and 394.13 °C which correspond to weight loss of 10.7%, 16.7%, 7.79% and 7.84% respectively with a total weight loss of 43.0%. The theoretically calculated weight loss for the formation of pure WS$_2$ is 57.0%. Marks et al. have proposed that the small difference between calculated and theoretical weight loss is due to residue in the TGA analysis of transition metal dithiocarbamate complexes. The stepwise decomposition of dithiocarbamate complexes have been previously observed, with EtSH, EtNCS, CS$_2$, and H$_2$S expected as the volatile by-products.

Deposition of Cr-doped WS$_2$ thin films by AACVD

The temperature chosen for deposition of materials by AACVD was 450 °C as both precursors are completely decomposed to the metal chalcogenide products by inspection of the TGA trace (Fig. 2). Deposition of tungsten disulfide (WS$_2$) and Cr-doped WS$_2$ films was performed by AACVD. The molar ratio of precursor WS$_3$L$_2$ and CrL$_3$ was changed to give 5%, 10% and 15% at% feeds. The deposited films were characterised by powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM) and Raman and energy dispersive X-ray (EDX) spectroscopies.

Raman Spectroscopy of thin films

![Fig. 2 TGA of [WS$_3$(S$_2$CNEt$_2$)$_2$] (WS$_3$L$_2$) and [Cr(S$_2$CNEt$_2$)$_3$] (CrL$_3$) complexes](image-url)
Raman spectroscopy was used to study W_{1-x}Cr_xS_2 films deposited onto glass and steel substrates. The pure WS_2 film had two main bands observed at 418 cm\(^{-1}\) and 352 cm\(^{-1}\) corresponding to the A\(_{1g}\) and E\(_{12g}\) modes along with a small shift at 170 cm\(^{-1}\). The Raman spectra for the Cr-doped WS_2 films deposited onto glass are shown in Fig. 3. There was a significant change in Raman spectra observed with the increase of chromium in the films. The intensity of the band observed at 170 cm\(^{-1}\) increases with the increase of chromium. There was another shift appeared at 207 cm\(^{-1}\) which correspond to first-order longitudinal acoustic (LA) mode, was not present in pure WS_2 film. Upon increasing the amount of chromium in the films deposited on steel substrate, the intensity of the LA(M) longitudinal acoustic mode at 207 cm\(^{-1}\) was enhanced. The Raman spectra for the Cr-doped WS_2 films deposited onto steel are shown in Fig. 4. The Raman spectra for films deposited on steel substrate are same as films deposited on the glass substrate.

Powder X-ray Diffraction (p-XRD)

The p-XRD pattern of WS_2 films deposited onto glass substrates showed two main reflections at 2\(\theta\) = 14.2° for (002) plane and 2\(\theta\) = 33.5° which is assigned to the (101) (Fig. 5). Hence the tungsten disulfide thin films deposited onto the glass substrate by AACVD have preferred orientation in the (002) plane. The standard pattern is tungsten sulfide, WS_2 (ICDD No: 01-084-1398). p-XRD pattern (a) shows deposition of WS_2 without Cr-doping, (b) 5 at% Cr, (c) 10 at% Cr, (d) 15 at% and (e) 20 at% Cr-doped into WS_2.

The star (*) and hash (#) symbols represent the reflections from FeS and steel substrate respectively.
patterns of $W_{1-x}Cr_xS_2$ deposited onto glass substrate for the ratios 5, 10, 15 and 20 at% Cr show the reflection at $2\theta = 14.24^\circ$, $14.34^\circ$, $14.36^\circ$ and $14.36^\circ$ respectively which can be assigned to the (002) and $2\theta = 33.5^\circ$ which is assigned to the (101) plane become more intense with the increase in molar ratio of CrL$_3$ from 5 to 15 mole%. However, the p-XRD pattern of the thin film with 20 at% Cr shows comparatively weak reflection at $2\theta = 33.5^\circ$ for (101) which indicates the decrease in crystallinity with the increase in dopant. The graphical representations of the change in calculated d-spacing versus the amount of chromium found experimentally in the films show an almost linear dependence (Fig. 7). This suggests that the doping of chromium into the WS$_2$ structure contracted the structure in the z-direction, pulling the layers of WS$_2$ together. PXRD patterns of films grown on steel (Fig. 6) are markedly different in appearance compared to those grown on glass. We see the diffraction peaks from WS$_2$ and steel, but also the pattern of a troilite subphase (FeS). Marks et al have also observed this phenomenon when growing MoS$_2$ on steel, and it was attributed to an iron sulphide interphase between the steel substrate and the thin film, which leads to a seamless crystalline interface between thin film and substrate. This can also influence the morphology of the films produced (vide infra).

**SEM and Energy dispersive X-ray (EDX) Spectroscopy**

Energy dispersive X-ray (EDX) spectroscopy of the $W_{1-x}Cr_xS_2$ thin films deposited by AACVD at 450 °C using mixtures of WS$_3$L$_2$ and CrL$_3$ showed a linear relationship between the mol% of chromium in the feed solution and the mol% of chromium found in the alloyed thin films (Fig. 8). The target composition and elemental composition found by EDX spectroscopy is given in the table 1. W and S were found in films generated from the decomposition of WS$_3$L$_2$ alone, with ca. 33.38 at. % W found in the film, close to the theoretical value of 33 at. % W in WS$_2$. Other peaks observed include Si and O from glass substrates and Fe on steel substrates.

<table>
<thead>
<tr>
<th>Target Composition</th>
<th>Precursors Ratio (mmole)</th>
<th>EDX results (atomic %)</th>
<th>Alloy film Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS$_2$</td>
<td>W: 0.350 Cr: 0.000</td>
<td>W: 33</td>
<td>$W_{1.001}S_{1.999}$</td>
</tr>
<tr>
<td>W$<em>{0.95}Cr</em>{0.05}S_2$</td>
<td>W: 0.333 Cr: 0.017</td>
<td>W: 31</td>
<td>$W_{0.916}Cr_{0.084}S_{2.035}$</td>
</tr>
<tr>
<td>W$<em>{0.90}Cr</em>{0.10}S_2$</td>
<td>W: 0.315 Cr: 0.035</td>
<td>W: 33</td>
<td>$W_{0.898}Cr_{0.107}S_{2.015}$</td>
</tr>
<tr>
<td>W$<em>{0.80}Cr</em>{0.15}S_2$</td>
<td>W: 0.298 Cr: 0.052</td>
<td>W: 29</td>
<td>$W_{0.801}Cr_{0.199}S_2$</td>
</tr>
</tbody>
</table>

The morphologies of WS$_2$ and Cr-doped WS$_2$ thin films were imaged using secondary electron scanning electron microscopy (SE SEM). SE SEM images of the films deposited onto glass and steel substrate at 450 °C as a function of varying Mol% of Cr in the AACVD feed.

![Fig. 8 Plot of mol% Cr found by EDX spectroscopy in $W_{1-x}Cr_xS_2$ thin films deposited by AACVD at 450 °C as a function of varying Mol% of Cr in the AACVD feed.](image-url)
steel and films grown on glass are due to the substrate influencing the growth of the crystalline inorganic thin film and this is presumably caused by growth of the WS₂ phase over the FeS phase, as-observed in pXRD (vide supra).

EDX mapping of 15 at% chromium doped W₁₋ₓCrₓS₂ films deposited onto glass and steel substrate by AACVD at 450 ºC (Fig. 11) demonstrated that in both cases W, Cr and S are distributed uniformly throughout the film.

X-Ray Photoelectron Spectroscopy (XPS)
The survey spectra (Fig. 12) show the presence of W and S peaks for both films. Both samples show evidence of C and O contamination, most likely arising from adsorbed hydrocarbon contamination and adsorbed water/hydroxyl species. The glass mounted sample shows a significant amount of sodium contamination. The coated steel sample shows evidence of Cu. Neither sample has Cr peaks in the topmost 10 nm of the surface, suggesting tungsten oxide is formed at the surface, burying the Cr below.

Detailed scans of the W 4d and S 2p are shown in Fig.13 & 14. The Cu 2p spectrum indicates two Cu species with
Fig. 12 The XPS surveys spectra of Cr-doped WS2 thin films deposited onto glass and steel substrate at 450 °C by AACVD.

Cu 2p$_{3/2}$ peaks at binding energies of 932.6 and 935.0 eV. The strong and complex satellite centred around a binding energy of 942.6 eV indicates that these Cu species are in in the Cu(II) oxidation state. The Cu 2p$_{3/2}$ peak at the higher binding energy (B.E.) is consistent with Cu(II) hydroxide species 47, and is consistent with the presence of the O 1s peak observed in the survey spectrum. The lower energy peak has a binding energy, which could be due to CuO or CuS species.

The W 4d spectra show (Fig. 13) two sets of spin orbit doublets for the two films. The binding energies of the W 4d5/2 of 243.7 eV and 247.4 eV are consistent with WS$_2$ and WO$_3$ species respectively [refs], suggesting significant oxidation of the films in the topmost surface region and supporting the suggestion that the Cr remains buried in the film.

S 2p spectra (Fig. 14) can be fitted with three sets of spin orbit doublets in agreement with earlier work on WS$_2$ and MoS$_2$. These are consistent with the presence of sulfate (S 2p$_{3/2}$ B.E. = 168.3 eV) 48, and terminal S$^2-$ and/or S$^2-$ (S 2p$_{3/2}$ B.E. = 162.0 eV) and bridging S$^2-$ and/or apical S$^2-$ (S 2p$_{3/2}$ B.E. = 163.4 eV) in the WS$_2$ 49, 50.

Conclusions

WS$_2$ and Cr-doped W$_{1-x}$Cr$_x$S$_2$ thin films were deposited onto glass and steel substrates by AACVD using bis(diethylthiocarbamato)disulfido, thioxo, tungsten(VI) [WS$_3$(S$_2$CNEt$_2$)$_2$] and tris(diethylthiocarbamato)chromium (III) [Cr(S$_2$CNEt$_2$)$_3$] complexes as precursors. Scanning electron microscopy (SEM) indicated that the morphology and the microstructure of the deposited thin films significantly changes with the addition of chromium as a dopant. The EDX spectroscopy confirmed the presence and composition of the dopant.

The powder x-ray diffraction patterns confirmed the films grown onto the glass substrate were highly crystalline and
gave monophasic hexagonal WS$_2$ whereas the films deposited onto the steel substrate produced a mixture of hexagonal tungsten sulfide (WS$_2$) and hexagonal Iron sulfide which is due to strong adhesion or a chemical bonding between iron/steel and WS$_2$. The Raman spectroscopy also confirmed the presence of the chromium in W$_{1-X}$Cr$_X$S$_2$ films.

In summary, this method affords excellent control over dopant concentration by using dual pre-cursors in the feed. The work reported herein is a very simple and inexpensive route for the deposition of Cr-doped tungsten disulfide thin films which has the potential for scalability.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was enabled by the award of a grant to POB and DJL from the BP International Centre for Advanced Materials (BP-ICAM). We would like to thank Dr. Benjamin Dennis-Smither (BP) for useful comments regarding the manuscript.

Notes and references
42. N. Savjani, J. R. Brent and P. O’Brien, Chemical Vapor Deposition, 2015, 21, 71-77.