

# Chemical vapour deposition of electrochromic tungsten oxide films employing volatile tungsten(VI) oxo alkoxide/ $\beta$ -diketonate complexes

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**Tungsten(VI) oxo alkoxides and tungsten(VI) oxo alkoxide/ $\beta$ -diketonate complexes are volatile precursors for the low-pressure chemical vapour deposition of tungsten oxide electrochromic films, which are characterized by SEM, XPS, XRD and cyclic voltammetry.**

Electrochromic materials find applications as smart windows, optical filters and display devices. Electrochromism may be based on organic or inorganic materials, and while both may enjoy certain advantages in specific applications, the potential for the use of inorganic oxides is particularly attractive with respect to angle independence, charge storage without drain, and stability to UV radiation. In particular, tungsten oxide glasses have been studied due to these materials high colouration efficiency.<sup>1</sup> We describe here the first report of the production of tungsten oxide electrochromic glasses by low-pressure chemical vapour deposition involving the use of tungsten(VI) oxo alkoxides and oxo alkoxide/ $\beta$ -diketonate complexes,  $[\text{WO}(\text{OR})_4]$  and  $[\text{WO}(\text{OR})_3\text{L}]$  [ $\text{R} = \text{Bu}^t, \text{Pr}^i, \text{CH}_2\text{Bu}^t, \text{Et}$ ;  $\text{L} = \text{acac}, \text{hfac}$  ( $\text{acac} = \text{MeCOCHCOMe}^-$ ,  $\text{hfac} = \text{CF}_3\text{COCHCOCF}_3^-$ )].

The  $[\text{WO}(\text{OR})_4]$  compounds were prepared by alcoholysis of  $[\text{WO}(\text{OBU}^t)_4]$  involving the appropriate alcohol ( $\text{R} = \text{Pr}^i, \text{CH}_2\text{Bu}^t, \text{Et}$ );<sup>2</sup>  $[\text{WO}(\text{OBU}^t)_4]$  was prepared by the metathesis reaction between  $[\text{WOCl}_4]$  and  $\text{NaOBU}^t$  (4 equiv.) in tetrahydrofuran.<sup>3</sup> The compounds were purified by sublimation under vacuum at *ca.*  $10^{-1}$  Torr ( $T = 60^\circ\text{C}$ ,  $\text{R} = \text{Bu}^t$ ;  $90^\circ\text{C}$ ,  $\text{R} = \text{Pr}^i$ ;  $100^\circ\text{C}$ ,  $\text{R} = \text{CH}_2\text{Bu}^t$ ;  $110^\circ\text{C}$ ,  $\text{R} = \text{Et}$ ). The  $\beta$ -diketonates were prepared by the addition of 1 equiv. of the free ligand Hacac or Hfac to a tetrahydrofuran solution of  $[\text{WO}(\text{OBU}^t)_4]$  or a pentane solution of  $[\text{WO}(\text{OPr}^i)_4]$ . Removal of the solvent under a dynamic vacuum gave  $[\text{WO}(\text{OR})_3\text{L}]$  compounds as pale yellow oils ( $\text{R} = \text{Bu}^t, \text{L} = \text{hfac}$ ;  $\text{R} = \text{Pr}^i, \text{L} = \text{acac}, \text{hfac}$ ) or as a waxy pale yellow solid [ $\text{R} = \text{Bu}^t, \text{L} = \text{acac}$ ] at room temp., 1 atm. These new compounds are formulated as pseudo-octahedral complexes of structure type **I** based on the NMR data (22–110  $^\circ\text{C}$ ) which reveal two types of OR groups in the ratio 2 : 1 (for  $\text{R} = \text{Pr}^i$  those of integral intensity 2 have diastereotopic Me groups) and two different Me or  $\text{CF}_3$  resonances for the  $\beta$ -diketonate ligand. The compounds are evidently stereochemically rigid on the NMR timescale and if the W–O bond *trans* to the oxo group breaks it does so reversibly without any accompanying rearrangements.<sup>†</sup> The new compounds of type **I** were volatile (60  $^\circ\text{C}$ ,  $10^{-1}$  Torr,  $\text{R} = \text{Bu}^t$  and 75  $^\circ\text{C}$ ,  $\text{R} = \text{Pr}^i$ ) and interestingly no significant differences in volatility were observed between the protio acac and the fluorinated hfac complexes.

Low-pressure chemical vapour depositions were carried out with a simple hot-walled reactor, (as described previously<sup>4</sup>) and films were deposited on quartz, Pyrex and ITO (indium tin

oxide coated Pyrex) with growth rates of *ca.*  $1 \mu\text{m h}^{-1}$  by SEM. The conditions pertaining to the sample temperature, the temperature of the substrate during decomposition and the appearance and adhesion (Scotch tape test<sup>5</sup>) of the films are summarized in Table 1. From this, it is seen that whereas  $[\text{WO}(\text{OBU}^t)_4]$  yields films at the lowest decomposition temperature of  $[\text{WO}(\text{OR})_4]$  compounds, these films were unsatisfactory with respect to adhesion. Those derived from other  $[\text{WO}(\text{OR})_4]$  compounds showed good adhesion and were found by SEM to be dense and generally featureless (no cracks, pinholes or ridges). With the exception of  $[\text{WO}(\text{OBU}^t)_3(\text{hfac})]$ , the  $\beta$ -diketonate complexes, **I**, also yielded good quality films with respect to adhesion and surface coverage. No surface selectivity (quartz, Pyrex, ITO) was observed in this study.

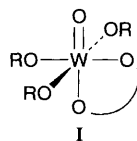
The majority of the films were pale blue (transparent) but those derived from  $[\text{WO}(\text{OBU}^t)_3\text{L}]$  ( $\text{L} = \text{acac}, \text{hfac}$ ) were pale yellow when initially formed but darkened to pale green–blue when exposed to air for a period of days. The films were examined by XPS and XRD. Only upon annealing were XRD patterns obtained and the initial state for the films may be defined as amorphous, or at least to contain microcrystalline domains too small to yield sharp X-ray diffraction lines. Annealing slowly at *ca.* 400  $^\circ\text{C}$  gave XRD patterns consistent with  $\text{WO}_3$  while heating to 1000  $^\circ\text{C}$  indicated the presence of both  $\text{WO}_3$  and  $\text{WO}_2$  with the latter being the thermodynamic end-product. XPS data revealed that the films derived from the alkoxides where  $\text{R} = \text{Pr}^i$  and  $\text{CH}_2\text{Bu}^t$  had low carbon content (< 2%) but significant nitrogen content (5–9 atom%). The latter presumably arises from activation of  $\text{N}_2$  in the background gas at a reactive W centre during film growth. Those derived from  $[\text{WO}(\text{OBU}^t)_4]$  had significant carbon content (5–8 atom%) but undetectable nitrogen content.

The films deposited on ITO were examined by cyclic voltammetry using  $\text{LiClO}_4$  and propylene carbonate electrolyte solution, typically 0.3 mol  $\text{dm}^{-3}$ . Upon application of a reduction potential, current was drawn at *ca.* 0.8 V vs. SCE, while application of positive potential shows a featureless oxidation current. The features of the reduction–oxidation process were analogous to those seen for tungsten oxide films grown by a sol–gel process, photochemical vapour deposition

**Table 1** Summary of low-pressure CVD of tungsten oxide films

Compound	$T_s^a/^\circ\text{C}$	$T_d^b/^\circ\text{C}$	Film appearance	Adhesion to substrate <sup>c</sup>
$[\text{WO}(\text{OBU}^t)_4]$	55–60	120	Blue	Fail
$[\text{WO}(\text{OPr}^i)_4]$	85–90	260	Blue	Pass
$[\text{WO}(\text{OEt})_4]$	110	390	Blue	Pass
$[\text{WO}(\text{OCH}_2\text{Bu}^t)_4]$	100	290	Blue	Pass
$[\text{WO}(\text{OBU}^t)_3(\text{acac})]$	60	170	Yellow	Pass
$[\text{WO}(\text{OBU}^t)_3(\text{hfac})]$	70	170	Yellow	Fail
$[\text{WO}(\text{OPr}^i)_3(\text{acac})]$	70	290	Blue	Pass
$[\text{WO}(\text{OPr}^i)_3(\text{hfac})]$	65	250	Blue	Pass

<sup>a</sup>  $T_s$  is the temperature of the sample during sublimation/distillation at  $10^{-2}$  Torr. <sup>b</sup>  $T_d$  is the temperature of the heated substrate in the hot-wall reactor and shows a variation of  $\pm 10^\circ\text{C}$  in the chamber. <sup>c</sup> Scotch tape test for films deposited on quartz, Pyrex and ITO coated Pyrex.



or electrodeposition.<sup>1</sup> Upon prolonged reduction at *ca.* 1.0 V vs. SCE the films turned dark blue. However, complete reoxidation to a clear transparent film was not complete because of surface effects. (The WO<sub>3</sub> formed on the surface is an insulator.) The same effect has been seen before for films of molybdenum and tungsten oxides. However, annealing in air does yield transparent films.

In summary, tungsten oxo alkoxides and tungsten oxo alkoxide/ $\beta$ -diketonates, **I**, are volatile precursors for the low-pressure chemical vapour deposition of tungsten oxide thin films and this preparative route warrants further investigation as an alternative to previous procedures. Further study of the chemical vapour deposition and thermal decomposition pathways of these precursors as well as continuing characterization of the ensuing tungsten oxide films is underway.

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#### Footnote

† Satisfactory elemental analyses and characterization data have been obtained. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 22 °C, 300 MHz) and <sup>19</sup>F (CDCl<sub>3</sub>, 22 °C, 360 MHz)

NMR of alkoxide  $\beta$ -diketonate complexes: [WO(OBu<sup>t</sup>)<sub>3</sub>(acac)],  $\delta$  1.46 (s, OBu<sup>t</sup>, 18 H), 1.54 (s, OBu<sup>t</sup>, 9 H), 1.65 (s, acac CH<sub>3</sub>, 3 H), 1.73 (s, acac CH<sub>3</sub>, 3 H), 5.16 (s, acac CH, 1 H); [WO(OBu<sup>t</sup>)<sub>3</sub>(hfac)], <sup>1</sup>H NMR,  $\delta$  1.30 (s, OBu<sup>t</sup>, 18 H), 1.36 (s, OBu<sup>t</sup>, 9 H), 6.25 (s, hfac CH, 1 H); <sup>19</sup>F NMR,  $\delta$  -77.96 (s, hfac CF<sub>3</sub>), -79.46 (s, hfac CF<sub>3</sub>); [WO(OPr<sup>i</sup>)<sub>3</sub>(acac)],  $\delta$  1.20 (d, OCHMe<sub>2</sub>, 6 H), 1.30 (d, OCHMe<sub>2</sub>, 6 H), 1.36 (dd, OCHMe<sub>2</sub>, 6 H), 1.64 (s, acac CH<sub>3</sub>, 3 H), 1.75 (s, acac CH<sub>3</sub>, 3 H), 5.14 (spt, OCHMe<sub>2</sub>, 2 H), 5.17 (s, acac CH, 1 H), 5.34 (spt, OCHMe<sub>2</sub>, 2 H); [WO(OPr<sup>i</sup>)<sub>3</sub>(hfac)], <sup>1</sup>H NMR,  $\delta$  1.07 (d, OCHMe<sub>2</sub>, 6 H), 1.17 (d, OCHMe<sub>2</sub>, 6 H), 1.21 (d, OCHMe<sub>2</sub>, 6 H), 4.97 (spt, OCHMe<sub>2</sub>, 2 H), 5.14 (spt, OCHMe<sub>2</sub>, 1 H), 6.23 (s, hfac CH, 1 H).

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