Tungsten Amides and Imides as Precursors to Tungsten Nitride and Carbonitride Thin Films via Chemical Vapour Deposition

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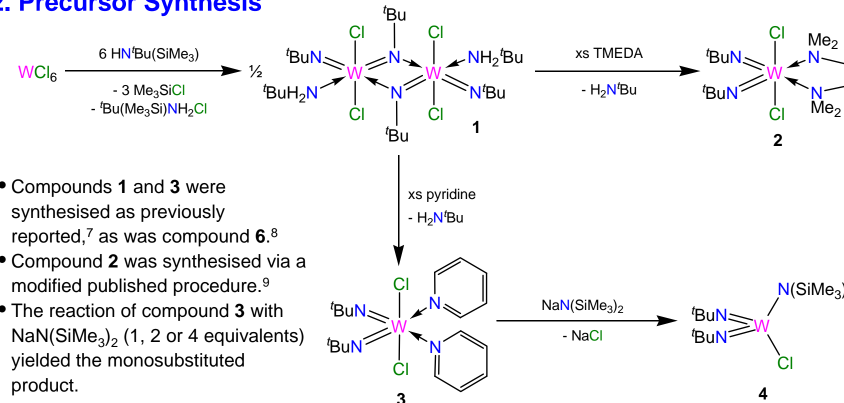
1. Introduction

- Transition metal nitrides are known for their hardness and semiconducting properties.[1]
- These properties have lead to their use as barrier layers, which prevent the diffusion of copper into silicon in gate electrodes.[2]
- TiN and ZrN are currently the materials of choice for interconnects containing aluminium, but WN_x is more suited to copper and is more effective at higher temperatures.[3,4]
- Chemical vapour deposition (CVD) and atomic layer deposition (ALD) of transition metal nitrides and carbonitrides at low temperatures (200-600 °C), using imido and amido complexes as precursors, has been reported.[5-7]
- This work has concentrated on tungsten imides and amides as precursors to their respective nitrides and carbonitrides via low pressure (LP-) and aerosol-assisted (AA-) CVD.

2. Precursor Synthesis



- Compounds **1** and **3** were synthesised as previously reported,[7] as was compound **6**.[8]
- Compound **2** was synthesised via a modified published procedure.[9]
- The reaction of compound **3** with $NaN(SiMe_3)_2$ (1, 2 or 4 equivalents) yielded the monosubstituted product.

Scheme 2.1: Synthesis of tungsten precursors.

3. Precursor Analysis

- Vapour pressure studies were carried out on compounds **1-3**.
- These were compared to industry standards:
  - $[Hf(NMe_2)_4]$, a high pressure standard.
  - $[Ta(NMe_2)_5]$, a low pressure standard.

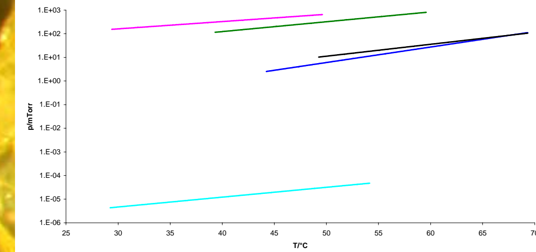
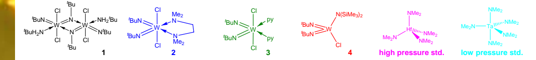
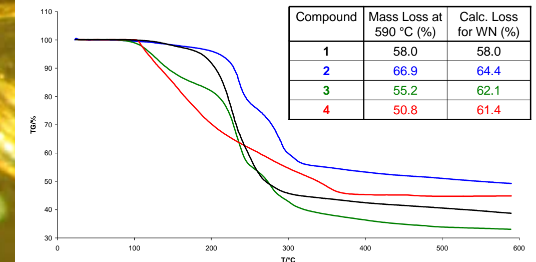


Figure 3.1: Vapour pressure plots of the tungsten complexes.



- Thermogravimetric analysis (TGA) provides a good indication as to how a precursor might decompose when heated.



Compound	Mass Loss at 590 °C (%)	Calc. Loss for WN (%)
1	58.0	58.0
2	66.9	64.4
3	55.2	62.1
4	50.8	61.4

Figure 3.2: TGA plots of the tungsten complexes.

4. Low Pressure CVD

Conditions

- Deposited on glass microscope slides at 550 °C, 0.25 Torr, from 250 mg precursor
- Nominal flow rates: N_2, 5 cm^3 min^{-1}; NH_3, 7.5 cm^3 min^{-1}

Adhesion & Scratch Tests

- Tissue and Scotch tape did not remove the films from the substrate.
- Brass and steel styluses left no marks.

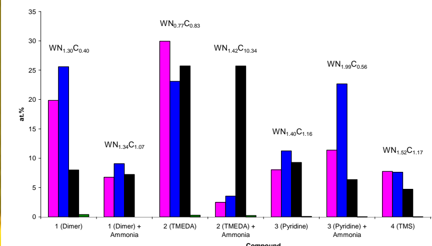


Figure 4.1: Composition of films by WDX.

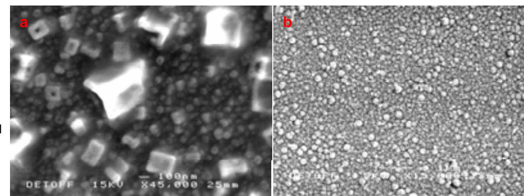


Figure 4.2: SEM images of films deposited by (a) compound **1** and ammonia, and (b) compound **3** and nitrogen.

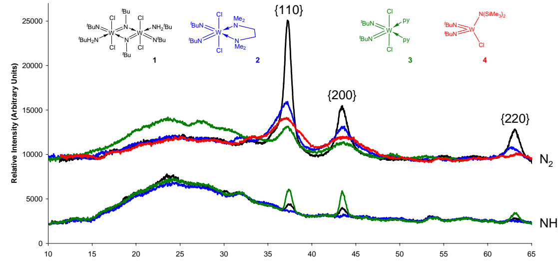


Figure 4.3: XRD patterns of the films deposited with nitrogen (top) and ammonia (bottom).

5. Aerosol-Assisted CVD

Conditions

- Deposited on silica-coated glass at 550 °C
- 500 mg precursor in 20 cm^3 toluene
- N_2 flow rate: 1 L min^{-1}

Composition

- Grey/gold
- Amorphous
- Island growth
- W:N = 1:0.51 (W_2N)

Adhesion & Scratch Tests

- Tissue and Scotch tape did not remove the films from the substrate.
- Brass and steel styluses left no marks.

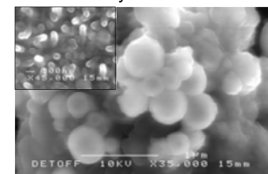


Figure 5.1: SEM image of the top plate film formed from compound 1. Inset: bottom plate.

6. Summary

- Tungsten imido and amido complexes **1-4** deposited adhesive, polycrystalline tungsten carbonitride films via LPCVD with a nitrogen bleed.
- Substituting nitrogen for ammonia gave films that were more nitrogen rich in the WN_xC_y lattice, according to XRD patterns.
- AACVD of compound **1** in toluene gave amorphous tungsten carbonitride films.
- The chlorine content of the films was notably low (<1at.%).

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