MOCVD OF TUNGSTEN NITRIDE THIN FILMS FROM THE IMIDO COMPLEX $Cl_4(CH_3CN)W(N^iPr)$: EFFECT OF NH_3 ON FILM PROPERTIES

Omar J. Bchir[1], Timothy J. Anderson[1,*], Benjamin C. Brooks[2], Lisa McElwee-White[2,*]

[1]Department of Chemical Engineering, University of Florida, Gainesville, FL 32611 USA
[2]Department of Chemistry, University of Florida, Gainesville, FL 32611 USA

The semiconductor industry is transitioning from aluminum to copper as the interconnect material for integrated circuits. Diffusion barriers are essential for prevention of copper migration into silicon in the resulting integrated circuits. Tungsten nitride (WN_x) films grown by metal-organic chemical vapor deposition (MOCVD) are promising diffusion barriers for copper metallization schemes. In this study, the tungsten imido complex $Cl_4(CH_3CN)W(N^iPr)$ was synthesized and used as a single source precursor for growth of tungsten nitride thin films in a custom CVD reactor [1]. Films deposited below 500 °C exhibited an amorphous structure, while those deposited at and above 500 °C were polycrystalline. Film composition studies indicated that carbon contamination increased with deposition temperature, and that the films were low in nitrogen, with a maximum nitrogen content of 11 at. % at 500 °C. The activation energy for film growth from the precursor was determined to be 0.84 eV, with growth rates ranging from 10 to 27 Å/min throughout the deposition temperature range 450 to 700 °C. In addition, film resistivity ranged from 750 to 15000 μΩ-cm, with the lowest value of resistivity observed in material deposited at 450 °C.

Tungsten nitride thin films were then deposited from $Cl_4(CH_3CN)W(N^iPr)$ in the presence of ammonia (NH_3) as a co-reactant gas. The impact of the NH_3 co-reactant on film structure and composition was analyzed by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) for comparison with analogous studies previously performed with material grown in the absence of NH_3. Films grown in the presence of NH_3 exhibited increased nitrogen levels and decreased carbon and oxygen levels over the entire deposition temperature range (450 to 700 °C) relative to films grown without NH_3 (Figure 1). Moreover, films deposited with the NH_3 co-reactant at higher temperature (≥ 600 °C) exhibited higher crystallinity. Binding energies determined from XPS studies were consistent with the formation of WN_x and WO_3 in the films [2-6], regardless of whether the NH_3 co-reactant was present during deposition.

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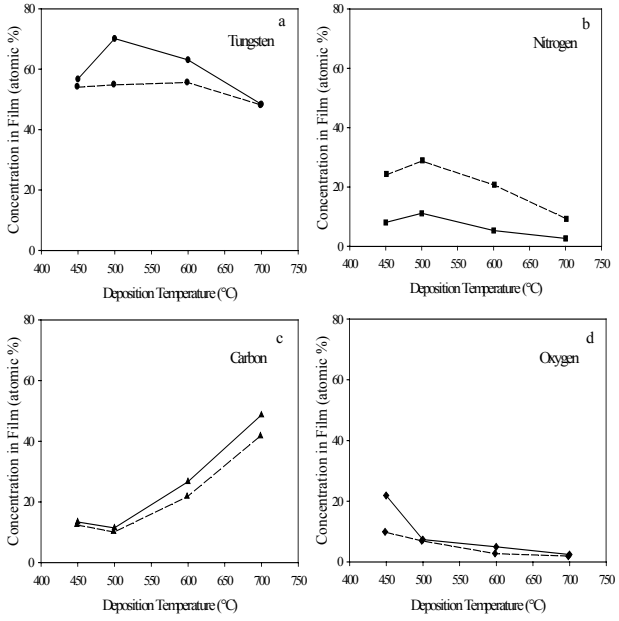

Figure 1. Variation of a) tungsten b) nitrogen c) carbon and d) oxygen content in the WN_x films with deposition temperature. Dashed lines are for growths with NH_3. Data are estimated from AES spectra taken after 2 min sputter time.