**206g Deposition of $Wn_XC_Y$ Using Allylimido Complexes $CL_4(Rcn)W(Nc_3H_5)$: Effect of $Nh_3$ on Film Properties**

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## Abstract

Tungsten nitride carbide ($WN_xC_y$) is promising candidate for diffusion barrier application in copper metallization. Previously, it has been demonstrated that tungsten allylimido complexes $Cl_4(RCN)W(NC_3H_5)$ (**1a**, R = $CH_3$; **1b**, R = Ph) can be used as a single source precursor to deposit tungsten nitride carbide thin films. In this study, we have used a mixture of the tungsten allylimido complexes with ammonia as co-reactant to deposit tungsten nitride carbide films. The effect of ammonia on film composition, crystallinity, lattice parameter, grain size, film growth rate and resistivity was studied and compared with those for films deposited without ammonia. Thin films were deposited on Si (100) substrate in a CVD reactor. The lowest deposition temperature for **1a,b** and ammonia was 450 °C. Film composition was determined by Auger electron spectroscopy. Films deposited between 450 and 750 °C had a varying concentration of tungsten (36 at. % to 61 at. %), nitrogen (8 – 23 at. %), carbon (18 – 54 at. %) and oxygen (2 – 5 at. %). Films deposited with ammonia had significantly higher carbon and nitrogen content and substantially lower oxygen content as compared to films deposited without ammonia. No chlorine was detected in the XPS spectra over the entire deposition temperature range. The films deposited below 500 °C were amorphous whereas films deposited at or above 500 °C were polycrystalline. The peaks in the XRD spectra suggest that β-$WN_{0.5}$ and β-$WC_{0.6}$ coexist in the films. While films grown without ammonia showed an increase in film crystallinity with increasing deposition temperature, those grown with ammonia exhibited more complex behavior, with crystallinity peaking for growth at 600 °C. The lattice parameter of $WN_xC_y$ films decreased with increase in deposition temperature for depositions with ammonia, with the highest lattice parameter of 4.179 ± 0.002 Å observed at 450 °C deposition temperature and the lowest lattice parameter of 4.112 ± 0.002 Å observed at 750 °C deposition temperature. The film growth rate varied from 4 Å/min for film deposited at 450 °C to 17 Å/min for film deposited at 750 °C. The activation energy for the reaction of **1a,b** with ammonia is estimated to be 0.33 eV, which is significantly higher than the activation energy of 0.15 eV reported for film growth from **1a,b** without ammonia. Films deposited with ammonia have higher resistivity as compared to films deposited without ammonia because of a higher N and C concentration coupled with a lower W concentration. The lowest resistivity for films deposited with ammonia was the value of 1690 μΩ-cm obtained from growth at 550 °C.

From a diffusion barrier application standpoint, it has been demonstrated that ammonia can be used with **1a,b** to increase film N content of $WN_xC_y$ films. A corresponding increase in film resistivity is also seen and some optimization may be needed to strike a balance between higher N content and lower film resistivity. In situ deposition of copper on the barrier films to test their diffusion barrier properties is underway.