586g Decomposition of Aryl- and Alkylimido Precursors for the Cvd of Tungsten Nitride: a Combined Density Functional Theory and Experimental Study

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Successful MOCVD growth of tungsten nitride (WNx) and tungsten carbonitride (WNxCy) thin films has been reported using three similar single-source precursors: the phenylimido complex Cl4(CH3CN)W(NPh) (1), the isopropylimido complex Cl4(CH3CN)W(NiPr) (2), and the allylimido complex Cl4(CH3CN)W(NC3H5) (3). In order to evaluate the design strategy of these precursors, determine the impact of the imido substituent on properties of the deposited film, and elucidate gas phase homogeneous decompositions of precursor molecules in the earlier stage of growth, computational chemistry based on density functional theory (DFT) was employed. Plots of calculated Gibbs energy vs. temperature verified that dissociation of the acetonitrile ligand (CH3CN) should be facile for 1-3 in the temperature range of 0 - 100 oC. A computational search for transition states for chlorine removal by H2 was consistent with W-Cl cleavage via homogeneous sigma-bond metathesis with hydrogen. Natural bonding orbital (NBO) analysis and bond energy calculations indicated that 1 has the strongest N-C bond in the imido ligand and a slightly weaker W-N bond, consistent with W-N cleavage and concomitant low nitrogen content in films deposited from 1. Moreover, it was also shown that 2 and 3 have relatively stronger W-N bonds than 1, matching with the results of positive ion electron-impact (EI) and negative ion electron-capture chemical ionization (NCI) processes and corresponding to the increased nitrogen content in the films from 2 and 3.