Synthesis of Tungsten Nitrene Complexes as Precursors to Tungsten Nitride

Lisa McElwee-White

Department of Chemistry
University of Florida
Gainesville, FL 32611

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

Approved for public release; distribution unlimited.

Chemical vapor deposition using organometallic precursors (MOCVD) provides a method for the preparation of thin films. Low valent tungsten nitrene complexes were synthesized as potential precursors to tungsten nitride (WNₓ), a material used in diffusion barriers for Si or GaAs semiconductor devices. The original target precursors for MOCVD of WNₓ were the carbonyl-containing complexes (CO)₅₋₃n(PR₃)ₓW=NR, where R is an alkyl or aryl group. Later synthetic work involved the tungsten(IV) imido (or nitrene) complexes (CO)₂IxLW=NPh, which were prepared by oxidation of the zwitterionic species (CO)₂xWNPhNPh(C(OMe)Ph) with one equivalent of I₂ followed by addition of a coordinating species L [L= THF, pyridine, PMe₃, P(OMe)₃].
1. ARO PROPOSAL NUMBER: 33087-CH

2. PERIOD COVERED BY REPORT: 15 May 1994 - 14 November 1994

3. TITLE OF PROPOSAL: Synthesis of Tungsten Nitrene Complexes as Precursors to Tungsten Nitride

4. GRANT NUMBER: DAAH04-94-G-0096

5. NAME OF INSTITUTION: University of Florida

6. AUTHOR OF REPORT: Lisa McElwee-White

7. STATEMENT OF PROBLEM:

Chemical vapor deposition using organometallic precursors (MOCVD) provides a method for the preparation of thin films. We are developing syntheses of low valent tungsten nitrene complexes as precursors to tungsten nitride (WNₓ), a material used in diffusion barriers for Si or GaAs semiconductor devices. Our target precursors for MOCVD of WNₓ are the carbonyl-containing complexes (CO)₅₋ₓ(PR₃)ₓW=NR, where R is an alkyl or aryl group. Upon heating at a surface, these compounds should lose the five ancillary ligands and undergo fragmentation of the NR group to deposit a film of WNₓ.

8. SUMMARY OF MOST IMPORTANT RESULTS:

We have recently begun to explore the chemistry of tungsten (IV) imido complexes bearing CO ligands. The new target complexes were molecules of the type (CO)₁₂L₂W=NPh. These species maintain the CO ligands that should be good leaving groups during MOCVD of tungsten nitride but the higher oxidation state renders the metal nitrene (or imido) moiety much more stable than in the zero-valent nitrene complexes studied in the earlier stages of the project. We had previously reported that the zwitterionic complex (CO)₅WNPhNPhC(OMe)Ph decomposes upon thermolysis or photolysis to yield (CO)₅W=NPh. We have now demonstrated that this species is also a precursor to the tungsten (IV) imido complexes since the zwitterion can serve as a protected imido functionality during oxidation of the metal center. Treatment of the zwitterionic complex (CO)₅WNPhNPhC(OMe)Ph with one equivalent of I₂ leads to the formation of highly unusual iodo-bridged tungsten (IV) imido dimer [(CO)₁₂I₂W=NPh]₂ and phonic(OMe)Ph (Scheme 1). Cleavage of the dimer with coordinating species leads to formation of the monomeric compounds (CO)₁₂I₂L₂W=NPh [L = pyridine, amines, phosphines, or phosphites] These complexes are now being explored as MOCVD precursors in collaboration with Professor Timothy J. Anderson, Department of Chemical Engineering, University of Florida.
Scheme 1

9. LIST OF PUBLICATIONS:


10. PARTICIPATING SCIENTIFIC PERSONNEL:

Graduate Students: Scott T. Massey
                 Man Lung Kwan

Undergraduates:  Kacy Gapinski
                 Joel Weber

Postdoctorals: Dr. Patrick C. McGowan
               Dr. Nicholas D.R. Barnett

Graduate Students and Postdoctorals received stipends, undergraduates received only research supplies.