DFT Study on the Gas Phase Decomposition of Tungsten Imido Guanidinate Complex W(N*i*Pr)Cl₃[*i*PrNC(NMe₂)N*i*Pr] for Chemical Vapor Deposition of Tungsten Carbonitride Films

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Tungsten nitride (WN$_x$) and tungsten carbonitrides (WN$_x$C$_y$) are one of the promising barrier materials to prevent copper migration into the adjacent oxide layer of integrated circuits (ICs).[1] Hitherto, a series of single source precursors for the growth of WN$_x$C$_y$ thin films by metal-organic chemical vapor deposition (MOCVD) has been reported: the imido precursors[2-4] such as Cl₄(CH₃CN)W(N*i*Pr), Cl₄(CH₃CN)W(NPh), Cl₄(CH₃CN)W(NC₃H₅) and W(N*i*Pr)Cl₃[*i*PrNC(NMe₂)N*i*Pr] (guanidinato),[5,6] and the hydrazido precursors[7,8] such as Cl₄(CH₃CN)W(NNMe₂) and Cl₄(CH₃CN)W(N-pip). As well as their CVD experiments, mechanistic approaches employing density functional theory (DFT) calculations were accompanied to analyze the effects of the decomposition pathways of the organometallic complexes and the implications for the choice of carrier gas on the constitutions of deposited films.[9-11] In the present study, we report the most probable decomposition pathway of the tungsten
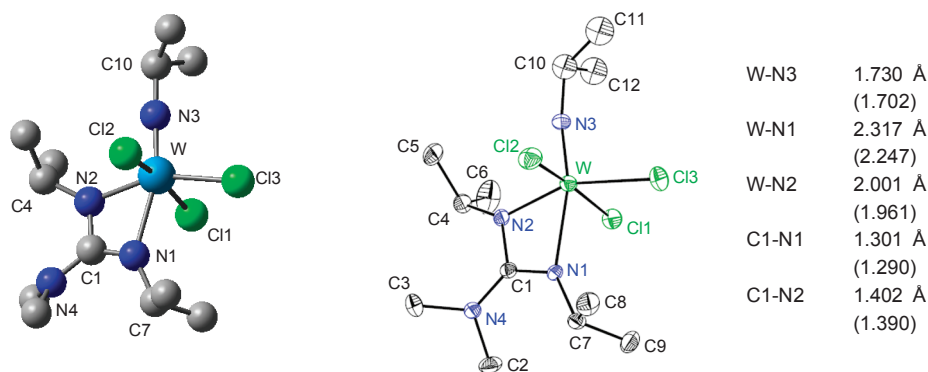
imido guanidinate precursor, W(N*i*Pr)Cl₃[*i*PrNC(NMe₂)N*i*Pr], to explain its CVD results.

The guanidinate and amidinate derivatives were synthesized to produce WN$_x$C$_y$ films of much higher nitrogen content with possible *bis*-imido intermediates under CVD conditions,[12] compared to the single imido precursors.[2-4] The possible decomposition pathway of the guanidinate and amidinate ligands to generate a second imido ligand was illustrated as Scheme 1.[12]

For a qualitative analysis of the tungsten guanidinate imido precursor, W(N*i*Pr)Cl₃[*i*PrNC(NMe₂)N*i*Pr], its geometry was computationally optimized as shown in Figure 1. The calculated bond lengths are overestimated as a whole compared to their corresponding solid X-ray crystallographic data.[12] The W-N1 bond is apparently elongated too much for the single bond. To obtain the bonding information of the guanidinate ligand more precisely, the natural bonding orbital (NBO) analysis was performed.[13] Table 1 summarizes the atomic charges of atoms calculated from natural population analysis (NPA) and the Wiberg bond indices (WBIs) for bonds. The small WBI of the W-N1 bond reflects its coordination covalent characteristic. The electron back donation from N1 to W builds the stable octahedral geometry around the tungsten at the center as did the acetonitrile in Cl₄(CH₃CN)W(N*i*Pr).[2-4] The C1-N2 bond is apparently weaker than the C1-N1 bond according to their WBIs. Although the W-N2 bond is inferior to the C1-N2 bond in terms of WBI, the larger difference of atomic charges renders the W-N2 bond stronger to compensate for its inferiority in WBI.
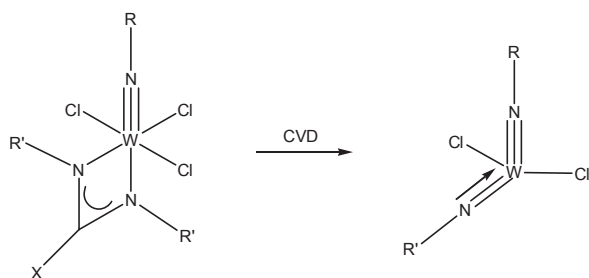
Scheme 1. Possible *bis*-imido intermediates in the precursor decomposition under CVD conditions

W-N3	1.730 Å (1.702)
W-N1	2.317 Å (2.247)
W-N2	2.001 Å (1.961)
C1-N1	1.301 Å (1.290)
C1-N2	1.402 Å (1.390)

Figure 1. The optimized geometry (left) of the tungsten imido guanidinato precursor, W(N*i*Pr)Cl₃[*i*PrNC(NMe₂)N*i*Pr]. Hydrogens are omitted for clarity. The calculated bond lengths are compared to their corresponding solid X-ray crystallographic data[12] in parenthesis.
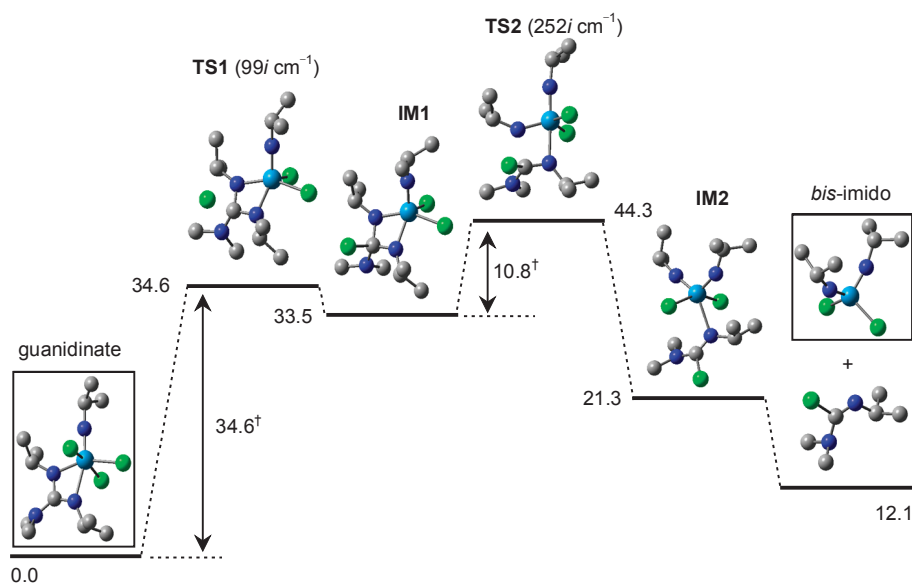
Figure 2. Energetics for the most probable unimolecular decomposition pathway of the tungsten imido guanidinate precursor, W(N*i*Pr)Cl$_3$ [*i*PrNC(NMe$_2$)N*i*Pr], to generate a *bis*-imido intermediate. Electronic energy values (ΔH°_{298}) have the unit of kcal/mol.

Table 1. The atomic charges and WBIs from NBO analysis for the tungsten guanidinate imido precursor and the intermediate, **IM1** (see Figure 2).

Bonds	guanidinate → **IM1**		
	Atomic charge	WBI	Atomic charge
W-N3		2.00 → 1.91	N3 (−0.41 → −0.52)
W-N1	W (1.23 → 1.45)	0.30 → 0.68	N1 (−0.58 → −0.74)
W-N2		0.82 → 0.94	N2 (−0.59 → −0.64)
C1-N1	C1 (0.69 → 0.62)	1.57 → 1.06	N1 (−0.58 → −0.74)
C1-N2	C1 (0.69 → 0.62)	1.09 → 0.95	N2 (−0.59 → −0.64)

The reaction pathway suggested in Scheme 1 was computationally constructed in Figure 2, and the optimized geometries of all concerned species were presented in the Supporting Material. The pathway has two transition states (**TS1** and **TS2**), one ($v = 99i$ cm^{-1}) for the chlorine transfer to C1 and the other ($v = 252i$ cm^{-1}) for the generation of *bis*-imido species and C(N*i*Pr)Cl(NMe$_2$). The WBI of the W-N1 bond of the intermediate (**IM1**) indicates the change of its bonding characteristic from coordination covalent to nominal covalent after chlorine migration, while the C1-N1 bond changes from double to single. Then, the C1-N2 bond dissociates in **TS2** and the W-N1 bond restores to the back donated coordination covalent bond in the other intermediate, **IM2**. The bond length of the W-N1 bond changes in accordance; 2.317 Å (guanidinate) → 2.074 Å (**TS1**) → 2.047 Å (**IM1**) → 2.211 Å (**TS2**) → 2.462 Å (**IM2**). Although the other transition state for the dissociation of the coordination covalent W-N1 bond in **IM2** may exist, the activation energy for this simple bond dissociation would not much larger than the reaction energy.[17,18] The activation energies for **TS1** and **TS2** were calculated as 34.6 and 10.8 kcal/mol, respectively. Considering the range of the activation energies (35 ~ 45 kcal/mol) reported for σ-bond metathesis and transamination

exchange of imido precursors,[9,10] the decomposition pathway suggested in Figure 2 would be viable under CVD conditions (400 ~ 750 $^{\circ}$C). The expected increase of N content in the deposited films probably because of the *bis*-imido intermediate was confirmed by CVD experiments.[11]

In summary, a computational study based on DFT calculations was successfully able to suggest the decomposition pathway of the tungsten imido guanidinate precursor, W(N*i*Pr)Cl$_3$ [*i*PrNC(NMe$_2$)N*i*Pr], to generate *bis*-imido intermediate. The W-N1 bonding characteristic changes from coordination covalent to nominal covalent, and restores to coordination covalent during the decomposition, as supported by NBO analysis. The DFT calculations are very useful to investigate possible decomposition pathways of metalorganic precursors to explain corresponding experimental results.

Computational Details

All calculations were performed with *GAUSSIAN 03*, using the B3LYP DFT method and split basis sets (LanL2DZ for tungsten and 6-311G(d) for other elements).[14-16] Full geometry optimization was carried out for all species. The transition states (TSs) were obtained using the Berny algorithm as implemented in *GAUSSIAN 03*. Harmonic vibrational frequencies were calculated for each structure, and used to compute enthalpy. GuassView was used for the visualization of the results.

References

1. Kaloyeros, A. E.; Eisenbraun, E. *Annu. Rev. Mater. Sci.* **2000**, *30*, 363.
2. Bchir, O. J.; Green, K. M.; Hlad, M. S.; Anderson, T. J.; Brooks, B. C.; Wilder, C. B.; Powell, D. H.; McElwee-White, L. *J. Organomet. Chem.* **2003**, *684*, 338.
3. Bchir, O. J.; Johnston, S. W.; Cuadra, A. C.; Anderson, T. J.; Ortiz,

C. G.; Brooks, B. C.; Powell, D. H.; McElwee-White, L. *J. Cryst. Growth* **2003**, *249*, 262.

4. Bchir, O. J.; Green, K. M.; Ajmera, H. M.; Zapp, E. A.; Anderson, T. J.; Brooks, B. C.; Reitfort, L. L.; Powell, D. H.; Abboud, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **2005**, *127*, 7825.

5. Ajmera, H. M.; Heitsch, A. T.; Anderson, T. J.; Wilder, C. B.; Reitfort, L. L.; McElwee-White, L.; Norton, D. P. *J. Vac. Sci. Technol. B* **2008**, *26*, 1800.

6. Wilder, C. B.; Reitfort, L. L.; Abboud, K. A.; McElwee-White, L. *Inorg. Chem.* **2006**, *45*, 263.

7. Ajmera, H. M.; Anderson, T. J.; Koller, J.; McElwee-White, L.; Norton, D. P. *Thin Solid Films* **2009**, *517*, 6038.

8. Kim, D.; Kim, O. H.; Anderson, T. J.; Koller, J.; McElwee-White, L.; Leu, L. C.; Tsai, J. M.; Norton, D. P. *J. Vac. Sci. Technol.* **2009**, *27*, 943.

9. Won, Y. S.; Kim, Y. S.; Anderson, T. J.; Reitfort, L. L.; Ghiviriga, I.; McElwee-White, L. *J. Am. Chem. Soc.* **2006**, *128*, 13781.

10. Won, Y. S.; Kim, Y. S.; Anderson, T. J.; McElwee-White, L. *Chem. Mater.* **2008**, *20*, 7246.

11. Ajmera, H. M.; Heitsch, A. T.; Bchir, O. J.; Anderson, T. J.; Reitfort, L. L.; McElwee-White, L. *J. Electrochem. Soc.* **2008**, *155*, H829.

12. Wilder, C. B. Study of Tungsten (IV) and Tungsten (VI) Imido Complexes: Synthesis, Structural Analysis and Reactivity. Ph.D. Dissertation, University of Florida, Gainesville, 2005.

13. Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

14. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.

15. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

16. Ditchfield, R.; Herhe, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.

17. Okamoto, Y. *J. Cryst. Growth* **1998**, *191*, 405.

18. Timoshkin, A. Y.; Bettinger, H. F.; Schaefer, H. F., III. *Inorg. Chem.* **2002**, *41*, 738.