Thermal Decomposition of Tungsten Nitrido Precursors for Low Temperature MOCVD of WNₓCy

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Tungsten nitrido complexes of the type WN(NR₂)₃ have been demonstrated to serve as single-source precursors for metal organic chemical vapor deposition (MOCVD) of WNₓCy barrier layers. To elucidate the thermal decomposition mechanisms for WN(NMe₂)₃ and to optimize conditions for deposition of WNₓCy films, in-situ Raman spectroscopy experiments were carried out in an up-flow, cold-wall MOCVD reactor. In this study, Raman spectra were detected at temperatures from 159 °C to 474 °C. Density Functional Theory (DFT) calculations were also performed to assess possible steps in the mechanistic pathway.

Introduction

Integrated circuits adopting Cu interconnects require more effective barrier layers due to the high diffusivity of Cu in Si and its deleterious effect on devices. Among various candidates, W-based nitrides are considered to be promising barrier layers due to their low resistivity, good thermal stability, the possibility of one-step CMP with Cu slurry, and the simplicity of processing a single layer material as opposed to the commercial TaN/Ta bilayer (1-4). The performance of W-based nitride diffusion barriers is enhanced when alloyed with carbide to make ternary WNₓCy, which creates amorphous films due to the carbon residing at grain boundaries. These ternary films also have lower resistivities than WNₓ systems (5, 6). Early deposition systems utilized homoleptic organometallic precursors such as WF₆ and W(CO)₆ with NH₃ as a coreactant (7). Use of WF₆ and NH₃ to deposit WNₓ promotes undesirable byproducts that produce impurities in the deposited films and induce undesired crystallization (7, 8). To mitigate these unwanted effects, single source precursors with N-coordinated ligands such as amide (1, 9, 10), imido (6, 11), or hydrazido (12-14) have been introduced for growth of WNₓCy thin films (15). Recent work has focused on designing precursors that decompose at low temperatures. Previous studies with the imido precursors Cl₄(CH₃CN)W=NR (1a, R = iPr; 1b, R = Ph; 1c, R = allyl) [Figure 1] demonstrated that the bond dissociation energies (BDE) of the N-C bonds correlate with the apparent activation energies for the rate determining step for deposition of the WNₓCy films. The precursor design was modified to lower the deposition temperature by replacing the N-C bond in the imido substituent of 1a with an N-N bond, due to the lower BDE of the N-N bond [typical BDE values are N-C 69 kcal/mole, N-N 38 kcal/mole (16)]. Replacement of the isopropyl group of 1a with a dimethylamido substituent leads to the hydrazido complex Cl₄(CH₃CN)W=NN(CH₃)₂ (2) (13) as a target precursor. This modification dropped the minimum film growth temperature from 450 °C with 1a (6, 11) to 300 °C with 2 (12, 17). Further reduction of the decomposition temperature was
possible by eliminating the rate determining bond cleavage step for the imido and hydrazido complexes with the tungsten nitrido complex WN(NMe₂)₃ (3), which bears a terminal nitrido moiety (W≡N) as its W-N multiply bonded ligand in lieu of the imido or hydrazido group (18, 19). In addition, the W-Cl bonds of 1a-c and 2 have been replaced with W-N(amide) bonds, eliminating the possibility of formation of the corrosive byproduct HCl, which had been detected by mass spectrometry during depositions from 1a (6). Films can be grown from nitrido complex 3 at a deposition temperature of 125 °C, which was unprecedented for deposition of WNₓCᵧ from single source precursors. To examine the gas phase thermal decomposition mechanism of WN(NMe₂)₃ under MOCVD conditions, in-situ Raman spectroscopy studies were performed.

Figure 1. Structures of 1a, 2, and 3.

Experimental and Theoretical Methods

The thermal decomposition experiments were carried out in a custom designed up-flow, cold-wall MOCVD reactor interfaced with an in-situ Raman spectroscopy system. The Raman system consists of a 532 nm Nd:YVO₄ solid state laser (Verdi G2, Coherent) as the light source and a double additive monochromator (Ramanor U-1000, Horiba), which has two diffraction gratings of 1800 grooves/mm. A schematic of the MOCVD reactor used for this study is shown in Figure 2 (20). The reactor body is made of four flat quartz panels, which form a square shape, allowing the laser beam to pass through the reactor with minimized position-dependent scattering variations. A cylindrical quartz tube with 4 vertical slits is located inside the optically flat quartz shell, which allows the laser beam to access the centerline of the reactor and the scattered light to be detected. The reactor is an up-flow inverted design with the gas inlet positioned below the heated susceptor. The susceptor consists of a high temperature resistive heater positioned inside an evacuated flat closed-one-end quartz tube, which is in contact with the reactive gas. A K-type control thermocouple is inserted into the heater assembly contacting the inside face of the quartz tube. The system design allows a stable 2-D laminar flow that simplifies the reactor model used to extract rate parameters and avoids wall deposition caused by parasitic reactions or turbulent flows. The system is also designed to be translated three-dimensionally, which allows the laser to independently sample position in the reactor (~30x30x300 μm³). The reactor inlet is a set of 3 concentric center, annular, and sweep tubes. The center tube is used to introduce the reactants and carrier gas, while the annular tube to allows a second reactant stream to be introduced. The outer tube includes the slits for laser probing and sampling as well flowing a sweep gas to prevent reactants from reaching the optically flat quartz outer walls. Glass beads (3 mm diameter) are
packed below the inlet of each of the three concentric inlet tubes, which establish a parallel flow inlet boundary condition. In this study precursor 3 was introduced through the center tube only.

For Raman experiments, aerosol-assisted CVD (AACVD) was utilized due to the relatively low volatility of 3 (21). Solutions of 3 in pyridine (0.051 M) were injected at 1 mL/h from a syringe into a nebulizer, which has a piezoelectric material vibrating at 1.44 MHz frequency. The aerosol generated on the surface of this piezoelectric material was transported by N₂ carrier gas (99.999 %, Airgas) through the center tube into the reactor at a flow rate of 2.5 cm/s. All experiments were conducted at the heater set temperature of 650 °C. Previous experiments using CH₄ as tracer verified that the flow pattern was laminar and validated the 3-D reactor model used to extract kinetic data. In addition, previous scattering experiments of the reactor operating with the aerosol delivery system revealed the aerosol transport and reactant delivery system functioned well (20).

Figure 2. Schematic drawing of the MOCVD reactor interfaced with in-situ Raman spectroscopy.

There is a temperature gradient in the reactor, with the temperature decreasing as the distance from the susceptor increases. To determine the actual temperature range at which the decomposition reactions are taking place, the temperature profile in the MOCVD reactor was measured. Temperature can be calculated from the rotational band distribution of gas molecules with an accuracy within 7 % uncertainty in the temperature range of 20 to 2230 °C (22). In this study, the N₂ rotational band was used. This method of measurement allows for the temperature to be measured without modifying the gas flow inside the reactor. Figure 3 plots the measured temperature profile along the centerline of the reactor with respect to the distance from the susceptor, as measured by the distribution of N₂ rotational bands.
After sufficient time for the gas flow to be stable and steady-state conditions to be established, Raman experiments were performed. A Nd:YVO₄ solid state laser line with power of 1.5 W was used to excite molecules in the sample, which subsequently scatter the light.

Infrared spectra were measured on a Perkin-Elmer Spectrum One FTIR Spectrometer using the Universal ATR sampling accessory.

Results and Discussion

In-situ Raman spectroscopy

Initial liquid phase experiments were carried out to obtain spectral data on an authentic sample of 3 before decomposition occurs. The vibrational Raman bands were scanned from 80 to 4000 cm⁻¹ at 0.1 W of laser power at room temperature (20 °C). Solid 3 was dissolved in pyridine, which is the same solvent used in the gas phase experiments but the concentration of 3 was doubled to 0.1 M to enhance the signal. The Raman bands of solutions of 3 were compared to those of neat pyridine as shown in Figure 4. Peaks at 572, 1068, 1150 and 1268 cm⁻¹ were assigned to W-N (23), W≡N (24), and two N-C (25, 26) stretching modes, respectively, by comparison to literature data for related compounds and the FTIR spectrum of 3 (Figure 5). Note that the signal for the N-C stretch at 1150 cm⁻¹ coincides with a pyridine band (Figure 4c) but it can be unambiguously located in the FTIR spectrum of neat 3, where no solvent interference is possible. To differentiate the overlapped signals at around 1068 cm⁻¹ from the pyridine signal, the peaks were deconvoluted.
Figure 4. Liquid phase signals from pyridine solutions of 3 observed by in-situ Raman spectroscopy. The solid line is from 0.1 M 3 in pyridine and the dashed line is from neat pyridine in (a), (b), and (c). (a) W-N, (b) N-C, (c) W≡N (1068) and N-C (1155), respectively. (d) and (e) are deconvolutions of peaks of (c) by Gaussian-Lorentzian peak shape routine as incorporated in the software package PeakFIT 4.12.
by the commercial software package PeakFIT 4.12 (Seasolve Software Inc. Framingham MA) using the Gaussian-Lorentzian peak shape routine. These liquid phase signals from the authentic sample of 3 were used in the gas phase experiments to identify the starting material in the presence of product signals.

Corroboration of the assignment of the Raman peaks of 3 was obtained from the FTIR spectrum of 3 (Figure 5). The Raman band at 1068 cm\(^{-1}\) assigned to W≡N stretching was also IR active and was found at 1064 cm\(^{-1}\), within the error bars for locating the peak positions in the two spectra. Likewise, the Raman peaks at 1150 and 1268 cm\(^{-1}\) assigned to N-C stretching are also found in the IR spectrum, although the latter peak appears at a higher frequency in the Raman spectrum due to solvent effects and the difficulty that exists in locating the peak maximum in a broad shoulder peak with significant noise.

Gas phase Raman experiments were subsequently performed to observe the decomposition products in situ. Figure 7 shows the peaks detected when nitrido complex 3 is decomposed at temperatures from 159 to 474 °C. A new peak consistent with a W≡N stretching vibration was detected at around 1035 cm\(^{-1}\) (24). The peak observed at 1640 cm\(^{-1}\) was assigned to the N=C double bond stretch in CH\(_3\)N=CH\(_2\) (4) on the basis of literature IR data (27) and characteristic Raman frequencies (28). Imine 4 was previously detected as a decomposition product from dimethylhydrazido complex 2 by in situ Raman spectroscopy during depositions and attributed to disproportionation of dimethylaminyl radical (12). In contrast to the chemistry of 2, DFT calculations on the decomposition mechanisms for 3 located a relatively low energy pathway via TS1-A to the intermediate INT1-A, which bears dimethylamine and 4 as ligands (19) (Scheme 1). Dissociation of the imine ligand of INT1-A is consistent with observation of imine 4 upon thermolysis of 3 in the reactor.
Scheme 1. Possible mechanistic pathway for formation of imine 4 upon thermal decomposition of 3.

In the higher frequency range, a broad signal centered at approximately 2850 cm\(^{-1}\) is consistent with a complex set of vibrational modes for stretching of sp\(^3\) C-H bonds. A signal observed at 3429 cm\(^{-1}\) is in the region for N-H stretching modes (12) but dimethylamine can be ruled out as the source of this signal, as its Raman active N-H stretch has been reported at 3377 cm\(^{-1}\) (29). The frequency of the signal is consistent with previously observed N-H stretches in W(VI) compounds with imido (NH) and amido (NH\(_2\)) ligands (30). Although the exact pathway leading to an imido group during decomposition of 3 has not yet been elucidated, protonation of Group 6 nitrido complexes to afford their imido derivatives has been described during experimental and computational studies of conversion of nitrogen containing ligands to ammonia (31-34). A decomposition pathway for 3 involving intra- or intermolecular proton transfer to the nucleophilic nitrido lone pair would provide a route to an imido complex.

Because the low concentrations of 3 and its decomposition products in the reactor lead to low intensity signals, a second nitrido derivative, WN(N'Pr\(_2\))\(_2\)(NMe\(_2\)) (5), was studied to provide corroboration for the observed signals from 3. Analogous signals for W≡N, N=C (35), and N-H bonds were observed upon decomposition of 5 (Figure 8), providing evidence that both compounds undergo similar decomposition pathways.

Figure 6. Structure of compound 5.
Figure 7. Peaks observed by in-situ Raman spectroscopy when 3 is decomposed at temperatures from 159 to 474 °C. The heater temperature was set at 650 °C. The N$_2$ Raman band at 2331 cm$^{-1}$ (36) was chosen as a standard in this study.

Figure 8. Peaks observed by in-situ Raman spectroscopy when 5 is decomposed at temperatures from 159 to 355 °C. The heater temperature was set at 650 °C.
Conclusion

The decomposition pathways of tungsten nitrido precursors were studied under film deposition conditions using in-situ Raman spectroscopy. Spectra from WN(NMe$_2$)$_3$ (3) were compared to those from WN(N$'$Pr$_2$)(NMe$_2$) to corroborate the peak assignments. Raman peaks of decomposition products were obtained by an AACVD reactor customized for the in-situ observation of gas phase species during deposition. Evidence was found for formation of an imine and for N-H bonds consistent with a pathway involving proton transfer to the nitrido lone pair. Further gas phase Raman studies are underway.

Acknowledgments

We would like to thank the National Science Foundation for support under NSF Grant CHE-0911640.

References