MOCVD of tungsten nitride (WN\textsubscript{x}) thin films from the imido complex Cl\textsubscript{4}(CH\textsubscript{3}CN)W(N\textsubscript{i}Pr)

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Abstract

Thin films of tungsten nitride (WN\textsubscript{x}) were deposited by MOCVD from the single-source precursor Cl\textsubscript{4}(CH\textsubscript{3}CN)W(N\textsubscript{i}Pr). Films were analyzed by X-ray diffraction (XRD), Auger electron spectroscopy (AES) and cross-section scanning electron microscopy (X-SEM), while the film resistivity was determined by four-point probe. Film growth rates ranged from 10 to 27 \textmu m/min within a temperature range of 450–700 °C. The apparent activation energy for film growth in the kinetically controlled regime was 0.84 eV. Films grown at temperatures below 500 °C were amorphous, with minimum film resistivity and sheet resistance of 750 \textmu Ω cm and 47 Ω/□, respectively, occurring for deposition at 450 °C.

Keywords: A3. Metalorganic chemical vapor deposition; A3. Thin films; B1. Nitrides; B2. Diffusion barrier

1. Introduction

The performance and functionality of integrated circuits (ICs) have continuously increased over the last three decades, due in large part to higher levels of device integration. In addition to larger chip sizes, the device packing density has significantly increased through a reduction in the physical sizes of features. To further this trend, copper is increasingly being used as a replacement for aluminum and its alloys in interconnects. This is due to copper’s lower bulk resistivity (1.67 vs. 2.65 \textmu Ω cm for standard Al contacts), higher resistance to electromigration, and smaller contact resistance to many materials [1]. This is expected to produce a reduction in the RC time constant and a roughly 15% increase in overall microprocessor speed [2].

Despite these advantages, copper is highly mobile in Si and is very reactive with Si and SiO\textsubscript{2}.

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Cu diffusion can result in an increase in contact resistance, change in the barrier height, leaky pn junctions, embrittlement of the contact layer, and destruction of electrical connections to the chip. Furthermore, the diffusion of Cu in Si is extremely rapid at processing temperatures (e.g., $D_{Cu}$ at 1000°C in Si is $4 \times 10^{-6}$ cm$^2$/s). Thus, a local Cu source can impact a large area, destroying shallow junctions and contacts during subsequent thermal annealing. Long-term reliability of a multi-layer metallization device requires that there be little or no migration of copper through adjacent layers.

As a result, a diffusion barrier is required to separate Cu from the active areas on a device. This barrier must have minimal impact on the line and via resistance of each interconnect layer. Additionally, a suitable barrier should meet the demands of shrinking device sizes, such as minimum layer thickness, good conformality, low resistivity, low temperature deposition, and amorphous film structure.

Among the deposition techniques for barrier materials, metalorganic chemical vapor deposition (MOCVD) has shown promise due to low deposition temperatures, minimal halide incorporation into the barrier film, good conformality and negligible pitting of the underlying Cu line. The major challenge for MOCVD is minimizing contamination by carbon and oxygen from the precursor ligands (and solvent, when applicable). Carbon and oxygen, however, incorporation may not be fatal to barrier performance. Moderate levels of impurities such as carbon and oxygen in the grain boundaries may actually improve barrier integrity and are reported to improve thermal properties of transition metal diffusion barriers. Heavy impurity incorporation, however, can increase the resistivity of the barrier films, negating the benefits gained by switching from Al to Cu metallization.

Refractory metals have been tested as diffusion barriers, but failed because the film microstructure contained grain boundaries, which are easy diffusion paths for migration of Cu to the underlying Si substrate. In contrast, metal nitrides of Ta, Ti, and W are good candidates for reliable diffusion barriers that provide lower electrical resistivities than their pure metal counterparts. Excess nitrogen in these films migrates from the bulk polycrystals to the grain boundaries, where repulsive interactions between Cu and nitrogen “stuff” the boundary and halt Cu diffusion. Stuffed barrier quality may be further enhanced by low temperature film deposition. The structural advantages provided by low temperature deposition of metal nitrides are two-fold. First, low temperature deposition can eliminate grain boundaries by depositing amorphous films. Second, any grain boundaries that may form during subsequent processing are stuffed with excess nitrogen, which is more likely to be retained by films deposited at lower temperatures. Low temperature deposition ($\leq 500^\circ C$) also prevents damage to temperature sensitive components on the device.

Although TiN is commonly used as a barrier material in Al metallization schemes, both WN$_x$ and TaN appear to promise better copper interdiffusion barrier integrity at elevated temperatures. Deposition by physical vapor deposition (PVD) techniques has dominated TiN barrier growth, despite the resulting problems with non-uniform coverage of high aspect ratio structures due to step shadowing. Attempts to deposit TiN by MOCVD produced films with high impurity levels that required an additional plasma processing step to stabilize the films in a low resistivity form. As a result, TaN has generally been discussed as the barrier material of choice for copper metallization. Nevertheless, TaN presents challenges as well. While Ta/TaN dual layer barriers produced by PVD are currently utilized with intermediate level wiring on IC devices, the use of this technique will ultimately be limited due to the aforementioned problematic aspects of PVD. Moreover, TaN films deposited by MOCVD exhibit uniform coverage but high resistivity.

Tungsten nitride appears to have technological advantages over TaN as a Cu diffusion barrier. WN$_x$ is known to be an effective diffusion barrier against copper penetration at temperatures of up to 750°C and copper deposited by CVD exhibits superior adhesion to WN$_x$ as compared to TaN. In addition, WN$_x$ outperforms TaN as a liner material for seedless electrochemical...
deposition (ECD), as ECD Cu shows a higher nucleation density on and stronger adhesion to WNx film layers [18,22,23]. A suitable liner material would enable seedless ECD of Cu, eliminating the need for a Cu seed layer.

There are also processing advantages for WNx. During chemical mechanical polishing (CMP), TaN is removed at a rate 18 times slower than copper while WNx is removed 1.5 times faster [15]. The slower TaN removal rate necessitates a time consuming two-step CMP process, which includes a slurry and pad changeout. Tungsten nitride (by virtue of a faster removal rate than copper) requires only a single CMP processing step, which provides a higher wafer per hour throughput. One report gives WNx removal rates of ~100 Å/min for a CMP pressure below 0.5 psi, while similar removal rates for TaN required a polishing pressure close to 2 psi [24]. Thus, WNx can be planarized with minimum dishing of the neighboring copper. The combination of these steps would result in cost savings per wafer, a higher wafer throughput, and a higher quality device for a WNx based system as compared to its TaN counterpart [15].

Tungsten nitride from CVD is therefore regarded as a promising diffusion barrier for Cu metallization. Prior CVD investigations have typically relied on the reduction of WF6, WCl6, or WO3 by ammonia (NH3) [16,25–31]. Several problems with these methods have been reported. The hydrogen halides (HX) produced upon reaction of WX6 with H2 are corrosive byproducts, which can rapidly etch the substrate or growing WNx film [32,33]. In addition, the move toward ultra-low k dielectric materials limits the barrier deposition temperature to 500–600°C (and in some contact schemes even lower) to avoid damaging the temperature sensitive low k materials. Thus, the minimum 800°C deposition temperature necessary for reaction of the halide precursors with ammonia is unacceptable. In an attempt to avoid these problems, tungsten nitride has recently been deposited by MOCVD using \((t\text{-BuN})_2\text{W(NH}t\text{-Bu})_2\) as a single-source precursor [34,35]. Two other MOCVD precursors for use with coreactants have been reported. Kelsey et al. reacted tungsten(0) hexacarbonyl \([W(CO)]_6\) with NH3, while Gordon et al. reacted tungsten(0) pentacarbonyl 1-methylbutylisonitrile \([W(CO)_5(C_5H_{11}NC)]\) with NH3 [36,37].

We now report the growth of WNx thin films from the single source tungsten imido precursor \(\text{Cl}_4(\text{CH}_3\text{CN})\text{W}(\text{N}^t\text{Pr})\) (1). The precursor structure was chosen so that the W–N multiple bond of 1 would survive while the ancillary ligands and the isopropyl imido substituent dissociated during deposition. Mass spectral data on the dissociation of gas phase ions of 1 and film growth studies provide support for this strategy.

![Diagram of WNx molecules](image)

2. Experimental procedure

2.1. General (precursor synthesis)

Standard inert atmosphere Schlenk, cannula, and glove box techniques were used in the preparation of 1 and 2. Tungsten oxychloride was purchased from Aldrich Chemical Co. Acetonitrile, benzonitrile and heptane were purchased as anhydrous reagents and stored over 4 Å molecular sieves under a N2 atmosphere. NMR solvents were degassed by three freeze–pump–thaw cycles and stored over 3 Å molecular sieves in an inert-atmosphere glove box. 1H and 13C NMR spectra were recorded on Gemini 300 or VXR 300 spectrometers. \(\text{Cl}_4(\text{CH}_3\text{CN})\text{W}(\text{N}^t\text{Pr})\) (1) was prepared as previously described [38]. All other chemicals were purchased in reagent grade and used with no further purification unless stated otherwise.
2.2. Synthesis of Cl₄(PhCN)W(N'iPr) (2)

Tungsten oxychloride (1.03 g, 3.00 mmol) was slurried in a solution of isopropyl isocyanate (0.435 g, 5.11 mmol) in heptane (35 ml) in a sealed pressure vessel. The mixture was heated for 2 days at 110°C. The solvent was removed from the resulting dark orange-red solution in vacuo. The orange residue was dissolved in a minimal amount of benzonitrile (approximately 5 ml). The resulting solution was stirred for 2 h and then added to stirring pentane in the glove box to precipitate the dark orange product. The solid was filtered and washed with 25 ml of additional pentane to afford 0.829 g (58.4% yield) of 2. ¹H NMR (CDCl₃) δ 7.92 (d, J = 8 Hz, 2H, Ho), 7.81 (t, J = 8 Hz, 1H, Hp), 7.63 (t, J = 8 Hz, 2H, Hₚ); 7.13 (heptet, J = 6 Hz, 1H, NCH(CH₃)₂); 1.76 (d, J = 6 Hz, 6H, NCH(CH₃)₂). ¹³C NMR (CDCl₃) δ 135.5, 133.6, 129.8, 119.6, 109.2, 68.8 (NCH(CH₃)₂), 23.4 (NCH(CH₃)₂).

2.3. Mass spectrometry

All mass spectral analyses were performed using a Finnigan MAT95Q hybrid sector mass spectrometer (Thermo Finnigan, San Jose, CA). Electron ionization (EI) was carried out in positive ion mode using electrons of 70 eV potential and a source temperature of 200°C. Negative ion electron capture chemical ionization (NCI) used methane as the bath gas at an indicate pressure of 2 × 10⁻⁵ Torr, an electron energy of 100 V and a source temperature of 120°C. All samples were introduced via a controlled temperature probe with cooling capability to maintain the sample temperature as low as 35°C. The mass resolving power (m/Δm) was 5000 full-width half-maximum (FWHM).

2.4. Film growth studies

The solid precursor (1) was dissolved in benzonitrile solvent at a concentration of 7.5 mg/ml, loaded into a syringe and pumped into a nebulizer. The nebulizer contained a quartz plate vibrating at a frequency of 1.44 MHz, which created a mist of precursor-containing solvent droplets. Carrier gas flowed through the nebulizer, conveying the droplets into a heated impinging jet. This mixture then traveled through the jet and out of a showerhead to the substrates, which rested on a heated graphite susceptor inside the reactor. Deposition time was varied from 30 to 150 min.

Experiments were conducted in a custom-built vertical quartz cold wall CVD reactor system. A graphite susceptor, heated by RF induction coils, maintained the substrates at the desired reaction temperature. Wacker Chemitronic p-type boron doped Si (100) substrates with resistivity of 1–2 Ω cm were used for the film growths. Growths were conducted at temperatures ranging from 400 to 750°C. The system was pumped by a mechanical roughing pump, with operating pressure ranging from 200 to 350 Torr. Hydrogen (H₂) carrier gas was used for the depositions.

After growth, film structure was examined by X-ray diffraction (XRD) on a Philips APD 3720, operating from 5 to 85 2θ degrees with Cu Kα radiation. Film composition was checked by Auger electron spectroscopy (AES) using a Perkin-Elmer PHI 660 Scanning Auger Multiprobe, while film resistivity was measured with an Alessi Industries four-point probe. Film thickness was estimated by cross-sectional scanning electron microscopy (X-SEM) on a JEOL JSM-6400, with growth rate calculated by dividing film thickness by deposition time.

3. Results and discussion

3.1. Mass spectrometry

Although the precursor solutions were prepared from Cl₄(CH₃CN)W(N'iPr) (1), the CVD process utilizes benzonitrile as the solvent. We have demonstrated by ¹H NMR experiments that exchange of the acetonitrile ligand of 1 with benzonitrile to yield Cl₄(PhCN)W(N'iPr) (2) occurs to some extent in the solutions used for MOCVD. Therefore, mass spectrometry experiments were carried out with both 1 and 2. These experiments yielded information about the fragmentation characteristics of the complexes under gas phase ionization conditions. The utilization of mass
spectral data to predict possible mechanisms for CVD processes has been previously established [39]. As has been discussed in the literature, care must be taken in extrapolating any fragmentation information from mass spectral data to the CVD process since the latter is thermal in nature [40]. Nevertheless, MS data have provided insights into probable fragmentation patterns of the tungsten imido precursors.

Fig. 1a shows the positive ion electron-impact ionization (EI) and negative ion electron capture chemical ionization (NCI) mass spectra of 1. The molecular ion could not be observed in either case. As expected, the EI spectrum displays more fragmentation than the NCI spectrum. The base peak in the EI spectrum occurs at $m/z$ 348 and is assigned to the [Cl$_3$W(N$i$Pr)]$^+$ fragment. The isotopic pattern is consistent with a moiety

![Fig. 1. Positive ion electron-impact ionization (EI) and negative ion electron capture chemical ionization (NCI) mass spectra of Cl$_4$(CH$_3$CN)W(N'i'Pr). (a) EI, (b) NCI.](image-url)
containing three chlorines. The only organic ion observed in the EI spectrum occurs at \( m/z = 41 \), corresponding to the fragment \([\text{CH}_3\text{CN}]^+\). Another tungsten fragment at \( m/z = 306 \) demonstrates a high relative abundance (\( \sim 80\% \)). This ion corresponds to the \([\text{Cl}_3\text{W(NH)}]^+\) fragment. The only other significant peaks occur at \( m/z = 291 \) and 326. These represent the loss of both the nitrile and imido ligands to form \([\text{Cl}_3\text{W}]^+\) and \([\text{Cl}_4\text{W}]^+\), respectively (abundances for both \(< 30\% \)).

Only two peaks of consequence are observed in the NCI experiment (Fig. 1b). The first occurs at \( m/z = 383 \) (\( \sim 42\% \) abundance), and involves the loss of the acetonitrile ligand to form \([\text{Cl}_4\text{W(NPr)}]^+\). The base peak of the NCI spectrum appears at \( m/z = 340 \), corresponding to the formation of \([\text{Cl}_4\text{WNN}]^-\). Thus, the NCI spectrum indicates cleavage of both the nitrile ligand and the isopropyl moiety to afford a tungsten nitrido fragment.

The benzonitrile complex 2 was subjected to similar mass spectral analysis. Again, the positive ion EI spectrum contains a base peak at \( m/z = 348 \), corresponding to the \([\text{Cl}_3\text{W(NPr)}]^+\) fragment. All of the other tungsten-containing fragments observed for the acetonitrile complex were also found in the spectrum of 1. Interestingly, the NCI experiment again exhibited the base peak at \( m/z = 340 \) (\([\text{Cl}_4\text{WNN}]^-\)); however, only a small amount (~1% relative abundance) of the \([\text{Cl}_4\text{W(NPr)}]^-\) fragment was observed. Table 1 summarizes the fragments and the relative abundances observed for 1 and 2.

The mass spectral data collected for the tungsten imido complexes offer some perspectives about these systems as CVD precursors. Most importantly, the cleavage of the isopropyl moiety from the imido group is relevant due to the necessity of this process in forming tungsten nitride films. Furthermore, the absence of a molecular ion in either the EI or NCI mass spectra suggests facile loss of the nitrile ligand. The observation of the \([\text{WC}_3\text{W}]^+\) and \([\text{WC}_4]\) fragments may be problematic since this indicates cleavage of the W–N bond; however, similar fragments were not present in the NCI spectrum. Thus, these fragments may be a result of the more energetic electron-impact process. Based on these results and the deposition of tungsten nitride from the imido complexes, there appears to be a correlation between the mass spectral data and behavior under CVD conditions.

### 3.2. Volatilization of the precursor

Once structure and fragmentation analyses were complete, the precursor was used for preparation of thin films by MOCVD. Deposition requires transport of the solid isopropylimido precursor 1 to the reactor in the vapor phase. Tests with a solid source delivery system resulted in minimal precursor transport, due to the low vapor pressure of the precursor compound. Transport difficulties were overcome by using a nebulizer to deliver a benzonitrile solution of the precursor to the reactor.

### 3.3. Film structure

The films typically had a smooth, shiny metallic appearance with color varying from a gold to black tint, depending on deposition conditions. The X-ray diffraction (XRD) spectrum in Fig. 2a indicates amorphous film deposition at 450°C, evidenced by a flat profile without any characteristic \( \beta\)-\( \text{W}_2\text{N} \) peaks. The spectrum shown in Fig. 2b reveals polycrystalline \( \beta\)-\( \text{W}_2\text{N} \) film deposition at 700°C. Four characteristic peaks are evident, with

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Table 1

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<th>( m/e )</th>
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<td>348</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>([\text{Cl}_4\text{W}]^+)</td>
<td>326</td>
<td>26</td>
<td>41</td>
</tr>
<tr>
<td>([\text{Cl}_3\text{W(NH)}]^+)</td>
<td>306</td>
<td>78</td>
<td>90</td>
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<tr>
<td>([\text{Cl}_3\text{W}]^+)</td>
<td>291</td>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td>([\text{C}_6\text{H}_5\text{CN}]^+)</td>
<td>103</td>
<td>n/a</td>
<td>97</td>
</tr>
<tr>
<td>([\text{CH}_3\text{CN}]^+)</td>
<td>41</td>
<td>24</td>
<td>n/a</td>
</tr>
<tr>
<td>([\text{Cl}_4\text{WNN}]^-)</td>
<td>383</td>
<td>42</td>
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</tr>
<tr>
<td>([\text{Cl}_4\text{WNN}]^-)</td>
<td>340</td>
<td>100</td>
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*Relative abundances were adjusted by summing the observed intensities for the predicted peaks of each mass envelope and normalizing the largest sum to 100%.
relative peak intensities indicating that no preferred crystal orientation exists. Primary reflections at 37.42 and 43.12 2θ degrees are consistent with (1 1 1) and (2 0 0) β-W2N growth planes, while additional reflections at 62.52 and 75.22 2θ degrees indicate (2 2 0) and (3 1 1) planes, respectively. No peaks consistent with the hexagonal WN phase or the α-W phase were evident for any of the films.

Fig. 2. XRD plots of WN_x grown on Si (100) in a H_2 atmosphere at (a) 450°C and (b) 700°C; (c) shows a standard powder diffraction plot for β-W2N.

growth. This is consistent with a previous report that amorphous WN_x films transform into polycrystalline W_2N between 450°C and 500°C [41]. As the deposition temperature increases to 550°C, this peak sharpens and a broad peak at 44.42 2θ degrees appears, indicating β-W_2N (2 0 0) growth. Films deposited between 475°C and 600°C displayed two additional peaks at 33.03 and 61.67 2θ degrees, representing Si (2 0 0) Kα and Si (4 0 0) Kβ radiation, respectively. Broad peaks emerge at 63.00 and 75.82 2θ degrees for deposition at 650°C, indicating β-W_2N (2 2 0) and (3 1 1) growth. The peaks sharpen further as the temperature approaches 700°C, indicating increasing polycrystalline grain growth. The formation of polycrystalline films is highly undesirable, since grain boundaries are facile paths for Cu transport to the underlying Si. Hence, deposition below 500°C is preferable for deposition of an amorphous film.

3.4. Film composition

AES results in Fig. 4 indicate that W, N, C and O were present in the deposited films. No chlorine was detected in the films by AES. Between 450°C and 500°C, the carbon level is constant at approximately 12 at%. Between 500°C and 600°C, carbon content increases steadily from 12 to 27 at%. Between 600°C and 650°C, the carbon level jumps from 27 to 43 at%, and then increases slowly to 49 at% at 700°C. The overall trend
reflects the increasing tendency of the hydrocarbon groups present in the precursor ligands and the solvent to decompose as the deposition temperature rises. Fragmentation of ligands and solvent would leave carbon-containing moieties at the film surface, resulting in carbon incorporation into the growing WN_x film.

The initial nitrogen content in films grown at 450°C was 8 at%. The nitrogen content increased to a maximum value of 11 at% at 500°C, as a consequence of decreased oxygen concentration through this range. The slight increase in nitrogen between 450°C and 500°C may reflect the stability of the W–N multiple bond in the precursor molecule. This bond likely endures at deposition temperatures up to 500°C, inhibiting release of nitrogen into the gas phase during deposition. Above 500°C, the nitrogen levels decrease, dipping to ~3 at% at 700°C. Metal nitride barriers typically show a decrease in nitrogen content with increasing deposition temperature, because higher temperatures impart more energy to the film lattice, inducing nitrogen atoms in the film to desorb as N_2 gas. Nitrogen release from WN_x films has been reported at temperatures above 700°C [42], consistent with AES results in this range.

Oxygen contamination resulted from post-growth exposure of the film samples to air. Incremental AES sputtering showed a steady decrease in oxygen levels with increasing depth into the WN_x films. The oxygen concentration was highest at 450°C, reaching 22 at%, and decreased slightly to 18 at% at 475°C. The amorphous films deposited below 500°C may have low density and high porosity, allowing substantial amounts of oxygen to penetrate into the film lattice. High oxygen concentrations (~20%) attributed to air exposure have been reported for porous TiN, TiC and TiCN barriers [43–45]. As the deposition temperature rises from 475 to 500°C, the oxygen content drops sharply down to 7 at%, while the carbon and nitrogen levels are fairly steady. This indicates crystallization of the film in this temperature range. As the film crystallizes, its microstructure becomes denser [20], thereby inhibiting post-growth oxygen diffusion into the lattice. As deposition temperature increases above 500°C, the oxygen concentration drops further. This results from film densification (by polycrystal grain growth) and increased carbon levels at higher deposition temperatures stuffing the grain boundaries. Porosity of amorphous films grown below 500°C may be problematic, as defects in the film may degrade the barrier’s resistance to Cu diffusion. A previous report, however, indicates that diffusion barrier performance depends more strongly on film microstructure than film density [46].

Fig. 5 depicts the ratios of W to C, N and O in the deposited films. The W/N ratio was quite high, ranging from 6 to 18. This is much higher than the ratio of 2 for β-W_2N, and contrasts sharply with XRD results indicating β-W_2N growth. The trend followed by the W/N ratio is expected, since higher deposition temperatures liberate nitrogen from the films to form N_2 gas, causing W/N to increase. Although the general trend of nitrogen content with deposition temperature is discernible from the AES data, exact measurement of the nitrogen level is difficult. Preferential incorporation of carbon and removal of nitrogen by Ar⁺ sputtering during AES analysis has been reported to cause artificially high carbon and low nitrogen concentration readings [47]. The AES data were collected after 2.0 min of sputter time, so it is likely that nitrogen atoms were sputtered and replaced by carbon atoms, causing the W/N and W/C ratios to be artificially high and low, respectively. The W/C

![Fig. 4. Variation of nitrogen, carbon and oxygen content in the WN_x films with deposition temperature. Data are from AES after 2.0 min sputter time.](image-url)
ratio increases slightly between 450°C and 500°C, and then decreases. This reflects the enhanced decomposition of hydrocarbon moieties in the precursor and in the solvent with increased deposition temperature. The W/C ratio drops to 1 at 700°C due to significant decomposition of the ligand alkyl moieties or of the solvent. The W/O ratio increases from 3 to 10 between 450°C and 500°C, due to the aforementioned film crystallization, and then rises from 10 to 27 between 500°C and 650°C. This increase is directly related to the jump in carbon content in this temperature range (Fig. 4), which leads to further stuffing of the grain boundaries, preventing oxygen diffusion into the films. The W/N and W/O ratios reached their maximum values at 650°C, and decreased above this temperature.

3.5. Lattice parameter

The dependence of lattice parameter on deposition temperature was determined by XRD using the 20 position of the β-W₂N (111) diffraction peak, with peak position calibrated to the Si (100) diffraction peak. Fig. 6 shows the lattice parameter increasing from 4.11 to 4.17 Å as deposition temperature increases from 500 to 650°C, and then decreasing to 4.16 Å at 700°C. Shifts in the lattice parameter reflect either a composition change in the polycrystals or a variance in the residual film stress. Since AES yields area averaged film concentrations, compositions in the polycrystals and at the grain boundaries cannot be resolved. Shifts in the lattice parameter cannot therefore be attributed solely to film composition without considering the possible influence of residual film stress. If we assume, however compositional variation dominates the shift in lattice parameter, the likely cause for lattice expansion between 500°C and 650°C would be incorporation of additional carbon into the polycrystals. As shown in Fig. 4, only the carbon content increases continuously with temperature in this range. The existence of a continuous β-Wₙ₋ₓNₓCₙ solid solution, where x + y ≈ 0.5, has been predicted [48]. As x decreases, the lattice parameter of β-Wₙ₋ₓNₓCₙ polycrystals would increase from a = 4.126 Å at x = 0.5 (β-W₂N) to a = 4.236 Å at x = 0 (β-W₂C). Above 650°C, the lattice parameter decreases. Again, this may indicate a change in film stress or in film composition. If we again assume that compositional variation dominates, we note that nitrogen and oxygen levels are essentially unchanged in this temperature range, while carbon levels continue to increase with temperature. Lattice parameter decrease may indicate a solubility limit for carbon in the β-Wₙ₋ₓNₓCₙ polycrystals at 650°C, with additional
carbon incorporated above 650°C preferring to reside at grain boundaries rather than bulk polycrystals.

3.6. Film growth rate

Growth rates were estimated by dividing the total film thickness (from X-SEM) by deposition time. Fig. 7 depicts two sample X-SEM photographs. The surface of the deposited films appeared to be fairly smooth, and film thickness varied from 1500 Å for the deposition at 450°C up to 4000 Å for deposition at 700°C. These film thicknesses correspond to deposition rates ranging from 10 to 27 Å/min. The growth rate of the WNₓ films (as determined by X-SEM) varied with temperature, as shown in Fig. 8. From this figure, two growth regimes are apparent. The plot depicts a region with a shallow slope and another region with a steep slope. The region with the shallow slope exhibits a weak dependence on temperature consistent with a mass-transfer controlled regime. The region with a steep slope suggests that growth rate increases exponentially with temperature, which is indicative of a kinetically controlled regime. In this regime, the rate-determining step for film growth is reaction on the substrate surface.

Growth rate in the kinetically controlled regime can be modelled by the Arrhenius expression for growth rate:

\[ G = A e^{-E_a/RT} \]  

(1)

where \( G \) is growth rate (Å/min) and \( E_a \) is the apparent activation energy (eV). From this expression, we can calculate \( E_a \) for the precursor molecule by plotting \( \ln G \) vs. \( 1/T \) according to

\[ \ln G = -\left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) + \ln A \]  

(2)

where \( A \) is a constant, \( -E_a/R \) is the slope of the line in the kinetically controlled regime, and \( E_a \) is the apparent activation energy for film growth. The calculated \( E_a \) for film growth from the isopropyl precursor was 0.84 eV in the kinetically controlled regime, compared to 0.9 eV reported for the bis(tertbutylimido)bis(tertbutylamido) tungsten complex [35]. This value falls within the typical activation energy range for CVD growth in the kinetic regime, which is 0.5–1 eV [49]. The growth rate variation with temperature in the

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Fig. 7. Cross-section SEM photo depicting thickness of WNₓ film on a Si(1 0 0) substrate grown at (a) 450°C and (b) 700°C.

Fig. 8. Plot of WNₓ film growth rate on Si(100) vs. inverse temperature. Error bars indicate uncertainty due to deposition temperature variation (±10°C) and thickness measurement from X-SEM photos.
kinetic regime was roughly 1% $\Delta T$ yielding a 10% $\Delta G$. The kinetically controlled regime appears to have an upper temperature limit near 600°C. Above 600°C, the region’s shallower slope indicates diffusion controlled growth. Depositions at 400°C and 750°C were done to establish the temperature boundaries for film growth with the precursor. Although the results of these growths were not included in Fig. 8, they do provide some useful information. Films deposited at 400°C were not visible by X-SEM, but AES depth profiling indicated a nominal film thickness of $\sim 100$ Å. This thickness value was used to estimate $E_a$ for the kinetic regime. The growth rate at 750°C dropped to 10 Å/min, with black particulates visible on the substrates after deposition. Particulate formation and reduced growth rate are characteristic of gas phase decomposition of the precursor, due to upstream heating at the higher temperatures.

3.7. Film resistivity

Film resistivity was calculated from the following relation:

$$\rho = R_s t$$  \hspace{1cm} (3)

where $\rho$ is resistivity (Ω·cm), $R_s$ is sheet resistance from 4-point probe (Ω/□), and $t$ is film thickness from X-SEM (cm). The variation of film resistivity with deposition temperature is shown in Fig. 9. Deposition at 450°C produced films with the lowest resistivity value (750 µΩ·cm) despite carbon and oxygen contamination levels of 13 and 22 at%, respectively. This is slightly higher than 620 µΩ·cm reported for film growth from the single-source bis(tertbutylimido)bis(tertbutylamido) tungsten precursor at 650°C [35]. Resistivity climbs steadily from 750 to 4800 µΩ·cm as the deposition temperature increases from 450°C to 550°C. The rise in resistivity is most likely due to the combined effects of increasing carbon levels and polycrystal formation. Carbon contamination increases film resistivity by scattering electrons as they travel through the WN$_x$ lattice, and carbon levels increased from 13% to 20% over this temperature range. In addition, transitioning from an amorphous to polycrystalline film structure causes formation of grain boundaries, which scatter electrons and increase film resistivity. Once polycrystal grains have formed, the film resistivity is typically lowered by grain growth, which decreases the number of grain boundaries. Between 550 and 675°C, the resistivity increases gradually from 4800 to 5500 µΩ·cm, despite grain growth in this temperature range (evident in Fig. 3). This can be attributed to increasing carbon contamination through this temperature range (evident in Fig. 4) and increasing film thickness (evident from Fig. 8). In this range, interplay between grain growth (which decreases resistivity), increasing carbon content and film thickness (which both increase resistivity), leads to the gradual rise in film resistivity. Between 675°C and 700°C, film resistivity jumps to 15 000 µΩ·cm, due to massive carbon contamination, which overtakes the tungsten concentration near 700°C. Decreasing the deposition temperature decreases the amount of carbon present in the film and therefore should decrease the WN$_x$ film resistivity. This trend provides an additional incentive to move to lower deposition temperature.

3.8. Film sheet resistance

Film resistivities calculated with Eq. (3) depend on both the sheet resistance and thickness of the analyzed films. As deposition temperature increases, both the film resistivity and the film
thickness increase. To decouple the impact of film thickness from carbon contamination on the film’s electrical properties, the sheet resistance was plotted as a function of deposition temperature in Fig. 10. The sheet resistance increases with deposition temperature from 47 Ω/square at 450 °C to 184 Ω/square at 500 °C, decreases to 145 Ω/square at 675 °C, and increases sharply to 371 Ω/square at 700 °C. The increase in sheet resistance up to 550 °C is attributed to polycrystal formation and increased carbon contamination. Between 550 °C and 675 °C, the decrease in sheet resistance is due to grain growth, which overcomes any increase caused by additional carbon contamination. At 700 °C, overwhelming carbon contamination dominates the sheet resistance, driving it up sharply. Given these sheet resistances, a 100 Å thick film grown at 450 °C would have a resistivity of ~47 μΩ cm.

4. Conclusions

Use of the tungsten imido complex Cl₄(CH₃CN)W(N₃Pr) (1) as a single-source precursor for low temperature growth of WNₓ thin films was demonstrated. Mass spectral analysis indicates that the precursor may cleave in a manner consistent with retaining a tungsten nitrido (WN) fragment, thus ensuring a steady nitrogen supply to the film at lower temperatures. The optimal structural and electrical film properties were achieved at the lowest deposition temperature. Carbon and oxygen contamination of the films did occur with carbon contamination increasing with deposition temperature and oxygen contamination occurring during post-growth exposure of the films to air. Appreciable deposition was possible down to 450 °C, with the resulting film being X-ray amorphous. The amorphous films did appear to be porous, allowing significant levels of oxygen to diffuse into them after exposure to air. Activation energy for film growth in the kinetically controlled regime was 0.84 eV, with the transition temperature between kinetic and diffusion control was near 600 °C. The amorphous film had resistivity and sheet resistance values of 750 μΩ cm and 47 Ω/square, respectively. This resistivity was achieved by growth at a deposition temperature of 450 °C, which produced material that incorporated some carbon and oxygen. Further testing of the films for Cu barrier integrity and conformality in small features is underway.

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