

CVD Reaction of Metal Nitride Precursors

Chemical vapor deposition (CVD) is an important technique that has found wide utilization in modern industry to produce a broad range of novel materials. A simplified scheme to describe the process is depicted in Fig. 1. Gaseous CVD precursor molecules are transferred by carrier gases to a heated substrate on which the decomposition of the molecules and ensuing growth of thin films are to take place. Whereas the precursors do not decompose to a significant degree in the gas phase, various bond breaking processes mediated by substrate surface can proceed via selective bond-activation channels. By means of a sequence of bond breakings that lead to ligand losses, the remaining surface adsorbed species then nucleate and thin film growth can proceed. However, an incomplete ligand removal can result in the contamination of the films. Therefore, an understanding of how the precursor undergoes thermolysis in terms of elementary processes is extremely useful in refining the molecular-design of the precursors and achieving a low impurity incorporation in the films.

Metal nitrides are of particular interest in microelectronic device fabrication because of the unusual properties associated with nitride materials such as high mechanical hardness, high

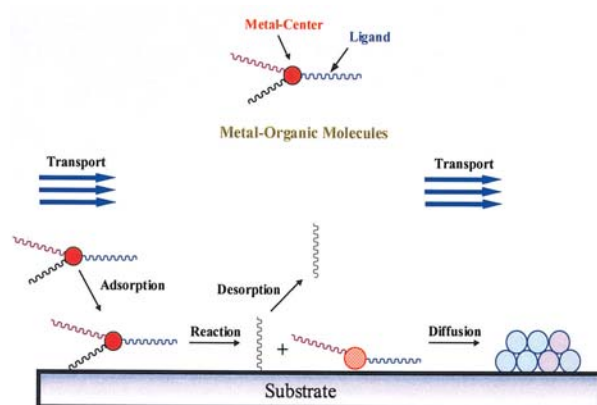


Fig. 1: A schematic illustrating the elementary processes involved in a chemical vapor deposition method.

thermal and chemical stability. Continuous shrinking of the feature dimension in ultra-large-scale-integrated (ULSI) circuits mandates a transition from aluminum to copper metallization scheme to keep pace with the device performance enhancement. However, copper is not only mobile in Si but also reactive with Si and SiO₂. A utilization of copper interconnect technology necessitates the deployment of barrier materials that effectively retard Cu diffusion into underneath structures. In this aspect, nitrides of heavier refractory metals like tantalum and tungsten have shown great promise as robust barrier materials. A recent employment of TaN via atomic layer epitaxy attests to the wide utilization of this class of the materials. For the past few years, we have studied surface reaction of metal nitride precursors on Si(100), SiO₂ and Cu(111) and the precursors investigated include both tantalum- and tungsten-based precursors. For brevity, only the surface chemistry of tungsten-based precursors is reported here.

We have been particularly interested in designing metal nitride precursors and achieving a CVD deposition of metal nitride films. The synthesis strategy consists of joining amido (-NR, R = alkyl group) and/or imido (=NR) ligands to the metal center. The double bond of the imido ligand is expected to survive the thermolysis better owing to its higher bond strength than the single bond of amido ligand. Most CVD precursors contain many hydrocarbon-based organic ligands to increase their volatility. As a result, it can be painfully difficult to delineate surface chemistry due to the coexistence of complex molecular species that contain C, N, and O elements. In the present report, we describe an in-situ surface science study aimed to illuminate the thermal decomposition of the precursors and resultant thin film growth in its early stage using XPS and temperature programmed reaction spectroscopy

(TPRS) to characterize both thin films and gaseous desorption products. The synchrotron based XPS is indispensable owing to its superior energy resolution and an order-of-magnitude increase in photoionization cross-section achieved through the energy tunability of photon source.

Standard procedures were adopted to clean Cu(111) and Si(100) samples. Photoemission measurements were carried out at wide range spherical grating monochromator beamline (WR-SGM) of NSRRC. All the reported XPS spectra were first normalized to photon flux by dividing recorded XPS signal by photocurrent derived from a gold mesh situated in the beamline. Binding energy scale was referenced to respective bulk core levels such as Si 2p_{3/2} or Cu 3p_{3/2}. The chemical structure of the synthesized precursor, ((CH₃)₃CN=)₂W(-NHC(CH₃)₃)₂, bis(tertbutylamido) bis (tertbutylimido) tungsten, or TATIT, is presented in Fig. 2. The work covering the other precursor ((CH₃)₃CN=)₂W(-N(C₂H₅)₂)₂, bis (diethylamido) bis (tertbutylimido)tungsten, or DATIT, is also mentioned in the text. DATIT and TATIT are structural isomers (compounds having the same molecular formula but different bonding sequence) and expected to exhibit similar surface chemistry. One difficult aspect in performing this type of the experiments is related to how to transfer thermally labile precursor molecules, instead of already decomposed molecular fragments, to the substrate. Gas manifold was constructed from glass as much as possible to minimize the potential precursor decomposition on metallic parts. Immediately prior to the dosing, the headspace in the precursor reservoir was

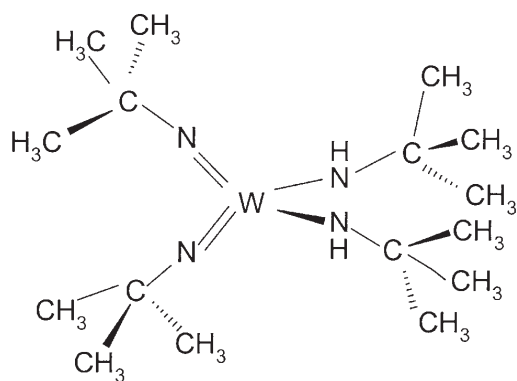


Fig. 2: Chemical structure of tungsten nitride precursor, ((CH₃)₃CN=)₂W(-NHC(CH₃)₃)₂, or TATIT for short.

evacuated again to remove any volatile ligand species that might have accumulated owing to the decomposition of the precursor. Even with all these precautions, a successful adsorption of the intact precursor, evidenced by the emergence of W-containing desorption peaks from physisorption layers, does not commence until a full passivation of the transfer line is reached.

Figure 3 shows the change of selective W 4f, N 1s, and C 1s XPS spectra with the annealing temperature for a submonolayer of TATIT on Cu(111). Also presented are the results obtained from nonlinear least squares fitting algorithm that employs a polynomial background in conjunction with line shape functions generated by a convolution of the Gaussian function with the Doniach-Sunjic function broadened by a finite lifetime. The spin-orbit-splitting is optimized at 2.18 eV and an intensity ratio for two components in the doublet is also fixed at its statistical value of 4:3. In a given spectrum, the Gaussian width (Γ_G), Lorentzian width (Γ_L) and Doniach-Sunjic asymmetric parameter (α) were allowed to vary in the fits but were constrained to be the same for all the peaks. For brevity, only the binding energy value of W 4f_{7/2} peak is reported here.

For 100 K data, W 4f spectrum shows a well defined spin-orbit doublet with its W 4f_{7/2} component occurring at 34.15 eV, characteristic of intact chemisorbed TATIT. In comparison, more components are found in both C 1s and N 1s spectra due to the coadsorption of amine ligands. Two N 1s components associated with W=N and

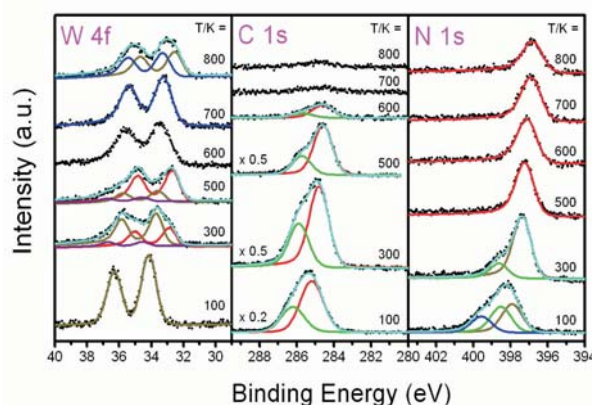


Fig. 3: Change of W 4f, C 1s and N 1s SR-XPS spectra with annealing temperature for a submonolayer of TATIT on Cu(111). Also plotted are the results from nonlinear least squares fitting.

W-N can be resolved at 398.5 and 399.5 eV, respectively. A warmup to 300 K sees a shifting of the peak centroid toward lower binding energy and a splitting of the W 4f peaks into several components, consistent with the labile nature of this type of CVD precursors. The W 4f spectra can be best described with three components, corresponding to the precursor losing one or two ligand(s) and/or a possible formation of oxygen-containing species produced from the reaction the precursor and the chamber moisture. After annealing to 700 K, W 4f peak appears at 33.2 eV and N 1s is at 396.8 eV, in agreement with the reported binding energy values for tungsten nitrides. After 800 K annealing, the W 4f spectrum broadens noticeably, suggesting the (inter) conversion among different tungsten nitride species like WN and WN₂, etc. The amount of residual carbon is small and it exists in graphitic form. The chemical composition departs from the ideal tungsten nitride formula owing to the ease of oxygen incorporation via moisture attack and the chemical formula for the final tungsten nitride can be represented as WN_{1.5}O.

As one major application of metal nitride in semiconductor industry is to serve as a barrier that prevents the diffusion of Cu interconnect into silicon substrate. Therefore it is of paramount importance to study the growth of the metal nitride films on silicon surface. Fig. 4 shows the adsorption and decomposition of the same TATIT at elevated temperatures. Due to the space limitation, only selective W 4f spectra acquired with photon energy of 200 eV are presented. Thanks to improved energy resolution at this photon energy, the W 4f spectra are better resolved, as compared with those taken using 600 eV photons. For 100 K spectrum, two W 4f_{7/2} components appear at 33.41 and 34.36 eV, respectively. The former is assigned to TATIT chemisorbed on Si(100), whereas the latter is to physisorbed TATIT. Higher annealing temperature shifts the W 4f peaks toward lower binding energy, consistent with the decrease of W oxidation state as the ligands are lost through metal-nitrogen bond breaking. Both amido and imido ligands are expected to exhibit electron-withdrawing character because the

nitrogen atom in the ligand has highest electronegativity.

Most amazing finding is the formation of metallic component that appears at a low binding energy of 31.1 eV at 500 K. The formation of metallic W requires the scission of four strong metal to nitrogen bonds at the same time, which should be energetically costly in view of stronger metal to nitrogen double bonds. This metallic W peak continuously gains intensity at higher annealing temperature, and after 800 K annealing, metallic W is formed exclusively. The temperature at which metallic W emerges seems to depend on the TATIT coverage as well as the type of precursor. For instance, metallic W can be observed for DATIT even at around room temperature. A complete stripping of all the ligands from the precursor at relatively low temperature underlines the reactive nature of Si(100), presumably due to the presence of dangling bonds on the dimerized silicon surface. It is noted that the binding energy for the metallic tungsten observed here, 31.1 eV, is lower than the binding energy value of 31.4 eV cited for bulk W metal. This unusually low binding energy is a manifestation of the predominance of surface over bulk W atoms for smaller W clusters in which a

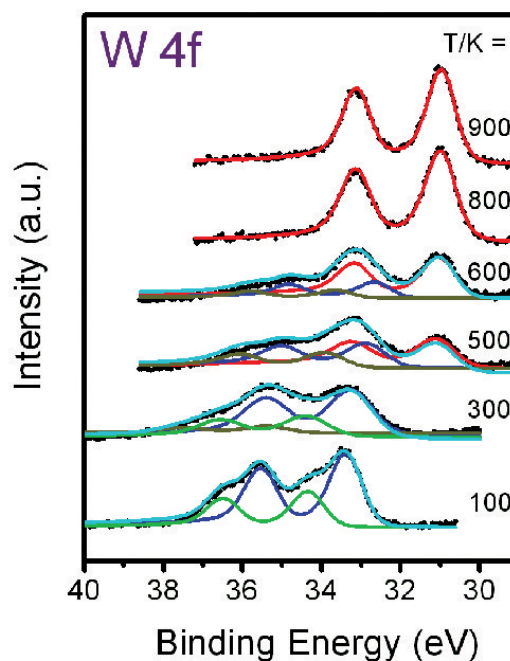


Fig. 4: Change of W 4f XPS spectra as TATIT precursor thermally decomposed on Si(100)-(2×1).

negative core level shift of -0.4 eV, relative to the bulk W, is found for surface W atoms.

The same phenomenon of a complete ligand transfer from the precursors to metal substrate has been reported in previous surface reaction studies of hexafluoroacetylacetonato complexes of transition metals like Rh, Pd, and Pt deposited on Cu(111) as well as metal complexes of Pd and Pt deposited on supports. We believe that the present results mark the first time that this type of so-called redox transmetalation reaction, metal atoms transferred from the precursor to the substrate while being reduced, can be observed on semiconductor surface as well.

As for the amido and imido ligands that are dissociated from the precursors and subsequently adsorbed onto Si(100), they seem to follow a decomposition pathway similar to that on clean Si(100). The story for their decomposition can be boiled down to the following. Amine ligands chemisorb strongly on Si(100) via nitrogen lone pair and a heating to higher temperature leads to characteristic bond breaking. Specifically, the most prevalent pathway is to form isobutylene via γ -H elimination, which is very effective in removing surface carbon species. The remaining surface adsorbed nitrogen and carbon species eventually form silicon nitrides with its N 1s at 397.5 eV and silicon carbides with its C 1s at 282.9 eV. However, the formation of small amount of carbonitride cannot be ruled out.

Thus far, completely different reaction pathways governing the end product formation are noted for different surfaces, viz., tungsten nitride formed on Cu(111) and metallic tungsten on Si(100). Why is there so much difference in reaction pathway? Will different products be formed on Si surface for a much higher TATIT dosage as the Si surface is gradually covered with silicon carbides and silicon nitrides that exhibit different electronic properties? We will answer the second question first and, based on this answer, the answer for the first question will be speculated on. A continuous dosing of Si(100) with a large quantity of TATIT is difficult in practice owing to the low volatility of the precursor and ease of the contamination for the silicon surface. As a result, we simulate the aftergrowth of TATIT by dosing

TATIT on a freshly prepared SiO₂ surface that is conveniently prepared by low-energy oxygen sputtering of Si(100). The justification comes from the fact that the inert nature of carbide- and nitride-covered silicon surface can be emulated with SiO₂.

Presented in Fig. 5 is the respective core levels as DATIT precursor undergoes thermal decomposition at elevated temperatures. Shown in the inset is the Si 2p spectrum for the SiO₂ surface, indicating the dominating dioxide species on the Si surface. All three core levels indicate pronounced change in spectrum feature like a considerable spectral broadening, as compared with the corresponding spectra for Cu(111) (Fig. 3) and Si(100) (Fig. 4). XPS peak fit reveals the presence of four major components: 32.2, 33.1, 34.3, and 35.8 eV. The former two peaks are assigned to WN_xC_y and WN_x, respectively and the latter two peaks are due to WO_x. C 1s spectrum shows the formation of WC_x and graphitic carbons; N 1s spectrum shows a broad peak centered at 397.5 eV, assigned to WN_x. Most importantly, during the course of annealing the sharp metallic W has never been observed, implying that a detachment of amido and imido ligands from W metal center never occurs to a completion on SiO₂ surface.

The switching from the formation of metallic tungsten to tungsten nitride upon a change of substrate from Si(100) to SiO₂ has several implications. The fact that sharper core levels are always observed for the reaction products formed

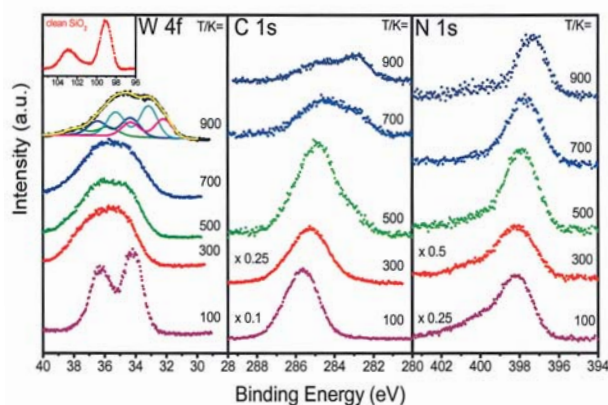


Fig. 5: Variation of W 4f, C 1s, and N 1s XPS spectra with the annealing temperature for DATIT adsorbed on SiO₂ surface.

on both Si(100) and Cu(111) surfaces indicate that the characteristic bond breaking must be operative on these surfaces, thereby producing selective few products. In contrast, the broad core level peaks observed for products on SiO₂ is a manifestation of the reduced selectivity in bond-breaking process inherent in the thermolysis, that is to assume a larger role on a non-reactive surface like SiO₂. With this understanding in mind, the earlier observation of WN_x, instead of metallic W, from a cold wall CVD reactor can be rationalized in terms of the precursor decomposition on a continuously generated, non-reactive SiN_x and SiC_x surfaces.

Beamline:

24A1 Wide Range beamline

Experimental Station:

Surface-interface end station

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