Deposition of molybdenum carbonitride thin films from $Mo(NBu^t)_2(NHBu^t)_2$

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$Mo(NBu^t)_2(NHBu^t)_2$ is used as a single-source precursor to deposit thin films of cubic phase molybdenum carbonitride, MoC_xN_y (x: 0.2–0.55, y: 0.1–0.47), by chemical vapor deposition on silicon substrates. In general, the C/Mo ratios increased from 0.2 to 0.55 and the N/Mo ratios decreased from 0.47 to 0.1 with increasing the temperature of deposition from 773 to 923 K. Based on the elemental composition and the composition of the gas phase products, it is proposed that the carbon atoms were incorporated through β-methyl activation of the ligands.

Transition metal carbides and nitrides are interesting materials with many useful physical and chemical properties.[1] Many research results of growing thin films of early transition metal carbides, nitrides, and carbonitrides from single-source precursors by chemical vapor deposition (CVD) have been published.[2–7] Recently, we have shown that tungsten nitride thin films can be prepared employing a bistertbutylimido complex of tungsten, $W(NBu^t)_2(NHBu^t)_2$.[8] In this communication, we wish to report our preliminary findings applying an analogous molybdenum complex, $Mo(NBu^t)_2(NHBu^t)_2$, **1**, as a single-source precursor of CVD.

1, synthesized according to a literature route with slight modification,[9] can be vaporized easily at 323 K in vacuum. Deposition of thin films on silicon and glass substrates was performed in a low-pressure cold-wall reactor at 723–923 K and 5–25 Pa depending on the carrier gas flow rate. Initial attempts to grow thin films on silicon substrates were difficult, possibly due to lack of suitable nucleation sites. Thus, we applied hydrogen plasma to etch the substrates before the depositions because our previous experience indicated that this procedure can assist thin film growth, probably by increasing nucleation sites on the surface.[10] After this process, grey metallic shining thin films with good adhesion to the substrates (Scotch tape test) were obtained. The surface morphology was smooth with very fine grains as shown by the scanning electron micrograph (SEM) in Fig. 1. Thin films with similar properties were grown on glass substrates without difficulty.

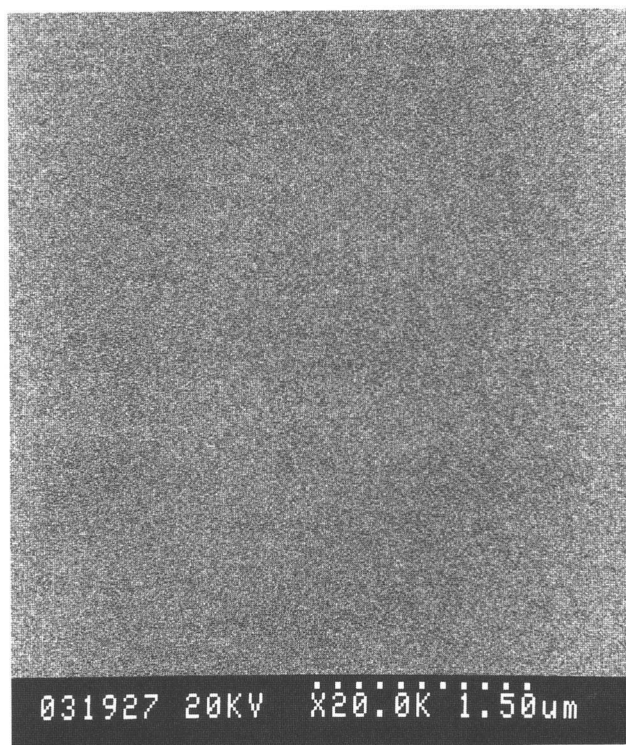

FIG. 1. SEM photograph of a thin film deposited at 773 K.

X-ray diffraction (XRD) studies, such as the one shown in Fig. 2, showed major Cu K_α diffraction peaks at angles 2θ equal to 36.99–37.35°, 43.19–43.52°, 62.38–63.07°, and 74.74–75.47° for the films. These peaks, characteristic of (111), (200), (220), and (311) reflections of cubic structures, are close to the values of γ–Mo_2C (37.77°, 43.69°, 63.39°, and 75.72°) and γ–Mo_2N (37.38°, 43.44°, 63.10°, and 75.72°).

High resolution x-ray photoelectron spectra (XPS) of a typical sample deposited at 773 K showed major signals assignable to the binding energies of the following electrons, $Mo_{3d5/2}$ and $Mo_{3d3/2}$ (228.4 and 231.6 eV), $Mo_{3p3/2}$ and $Mo_{3p1/2}$ (394.4 and 412.0 eV), C_{1s}(282.6 eV), N_{1s} (397.0 eV), and O_{1s} (530.2 eV), after some of the contaminated surface layers were removed by Ar^+ sputtering. Auger depth profiling of the films, such as the one shown in Fig. 3, showed uniform distributions of Mo, C, and N atoms within the films. O concentration was low except at the surface. The XPS and Auger data indicate that the films are molybdenum

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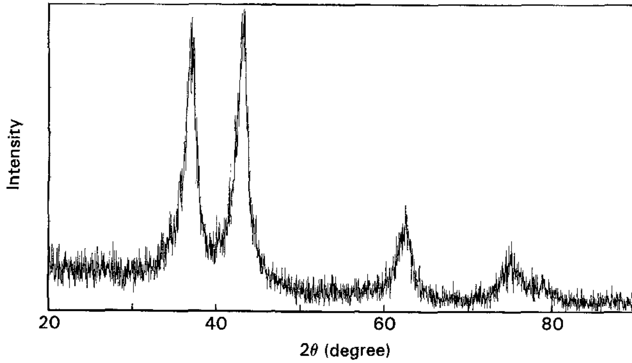


FIG. 2. XRD pattern of a thin film deposited at 823 K.

carbonitride of a formula MoC_xN_y. Bulk elemental composition of the films was determined by wavelength dispersive spectroscopy (WDS). C/Mo and N/Mo ratios of the films, derived from the WDS studies, are plotted against the temperature of deposition and shown in Figs. 4 and 5, respectively. Figure 4 shows that with increasing temperature of deposition from 773 to 923 K, the C/Mo ratios increased from 0.2 to 0.5 for the films grown without carrier gas. When either H_2 or Ar was employed as the carrier gas, which increased the pressure within the reactor, the C/Mo ratios increased from 0.45 at 773 K, a relatively high value, to 0.55 at 923 K. As shown in Fig. 5, the N/Mo ratios decreased from 0.47 to 0.1 with increasing temperature of deposition from 773 to 923 K for the films deposited without carrier gas. When H_2 or Ar was employed as the carrier gas, the N/Mo ratios lowered from 0.35 at 773 K to 0.1 at 923 K. These data suggest that both temperature and pressure of deposition influenced the C/Mo and the N/Mo ratios significantly while using either H_2 or Ar as the carrier gas affected the elemental compositions only slightly.

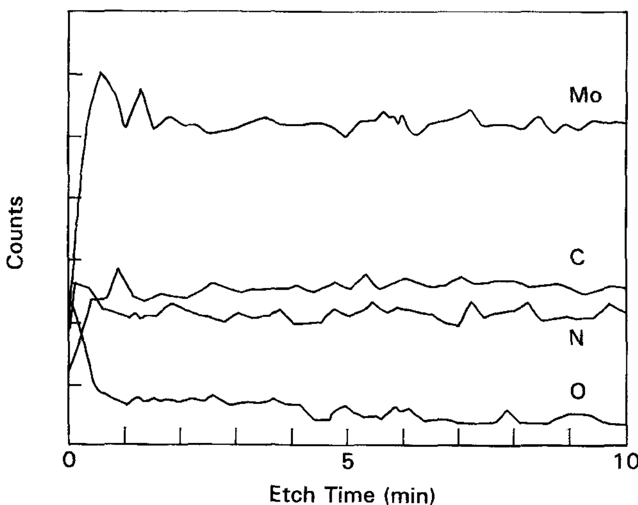


FIG. 3. Auger depth profile of a thin film deposited at 773 K.

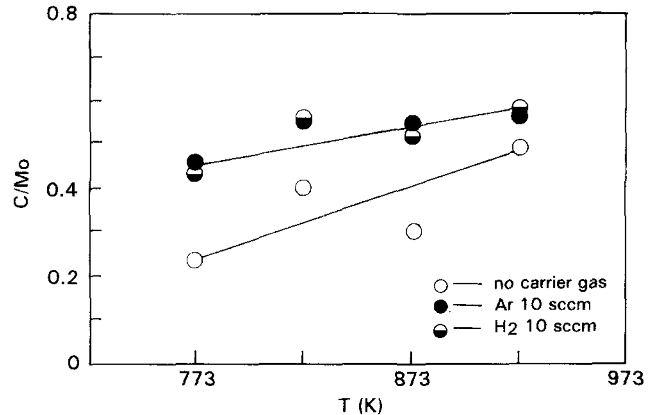
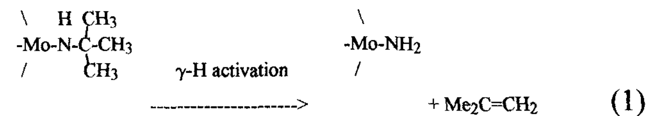
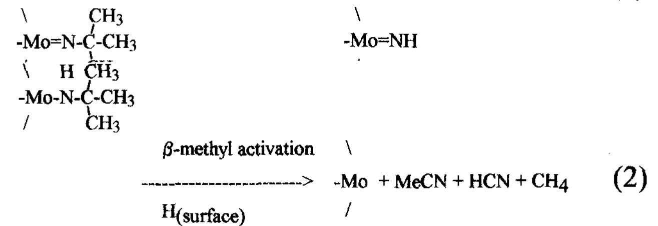
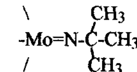


FIG. 4. Effect of temperature of deposition on C/Mo ratio of the films.

Volatile products, analyzed by a residual gas analyzer (RGA), were identified to be H_2, CH_4, HCN, N_2, CH_3CN, and $Me_2C{=}CH_2$. To account for the origins of these molecules, possible reaction pathways are proposed in Eqs. (1) and (2) below.







Analogous reaction pathways have been proposed previously.[8] In Eq. (1), γ-hydrogen activation of the

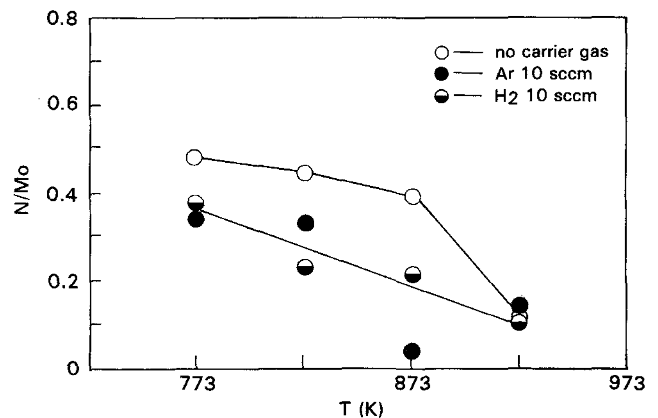


FIG. 5. Effect of temperature of deposition on N/Mo ratio of the films.

tertbutyl groups of both amido and imido ligands, followed by C—N bond dissociation, is suggested to be the origin of $Me_2C{=}CH_2$, and it appears to be unlikely to lead carbon atoms into the films through this pathway. On the other hand, as suggested in Eq. (2), MeCN and HCN are formed via β-methyl activation of the tertbutyl groups by successively removing two and three methyl groups, respectively, followed by Mo–N bond dissociation. These methyl groups may either combine hydrogen atoms on the surface to cause the evolution of CH_4 or undergo further C–H bond activation to form the carbidic atoms in the films. As shown in Fig. 6, $I_M{}^+/I_{Me_2C=CH_2}{}^+$, the ratios of the intensities of the ions formed in RGA from an evolved compound M and $Me_2C = CH_2$ are relatively constant for M = MeCN and HCN between 773 and 923 K, the temperature range employed for the deposition. This suggests that the amounts of the tertbutyl groups decomposed via Eq. (1) have an almost constant proportion to those decomposed via Eq. (2) between 773 and 923 K. Thus, it is reasonable to assume qualitatively that $I_{Me_2C=CH_2}{}^+$ is proportional to the amount of **1** decomposed at these temperatures. Consequently, the value of $I_M{}^+/I_{Me_2C=CH_2}{}^+$ in Fig. 6 can be correlated to the amount of M evolved versus the amount of **1** decomposed at a given temperature. As shown in Fig. 6, $I_{H_2}{}^+/I_{Me_2C=CH_2}{}^+$ increases with increasing temperature of deposition, suggesting that the films deposited below 773 K still contain some H atoms. When the temperature rose, these atoms combined to form hydrogen molecules. Thin films of metal nitrides containing H atoms have been grown by CVD from $M(NR_2)_4$ (M: Ti, Zr, Hf; R: Me, Et) and NH_3 at low temperatures.[11] On the other hand, with increasing temperature of deposition, $I_{CH_4}{}^+/I_{Me_2C=CH_2}{}^+$ decreases.

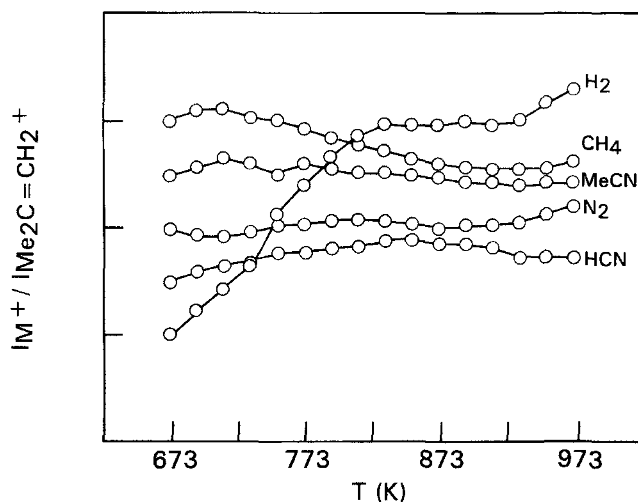


FIG. 6. Effect of temperature of decomposition on $I_M{}^+/I_{Me_2C=CH_2}{}^+$ ratios. For each M, the ratio at 673 K is normalized to 1. Each scale on the vertical axis is 0.5.

This trend correlates well with the variation of the C/Mo ratios with the temperature of deposition and supports the carbidic atom formation process proposed above. At a high pressure of deposition, removal of the methyl groups as methane molecules from the surface was hampered because diffusion of the gas was difficult. This rationalizes why the C/Mo ratios were high when either H_2 or Ar was employed as the carrier gas. It has been shown that molybdenum carbide can be prepared by reacting molybdenum nitride with methane at temperatures above 670 K, along with nitrogen evolution.[12] Compared to other early transition metal nitrides such as niobium nitride, molybdenum nitride is relatively unstable at high temperatures.[13] Complete decomposition of molybdenum nitride can be achieved below 1073 K. This explains why $I_{N_2}{}^+/I_{Me_2C=CH_2}{}^+$ increases (Fig. 6), although not significantly, and N/Mo decreases with increasing temperatures of deposition.

This study showed that **1** can be employed as a single-source precursor to molybdenum carbonitride thin films. CVD of thin films from other imido complexes of early transition metals is under investigation.

ACKNOWLEDGMENTS

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