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Low-temperature atmospheric-pressure metal–organic chemical vapor deposition of molybdenum nitride thin films

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Abstract

Amorphous molybdenum nitride thin films were deposited from tetrakis(dimethylamido)molybdenum(IV), $Mo(N(CH_3)_2)_4$, and ammonia at low substrate temperatures (200–400 °C). The films were characterized by Rutherford backscattering spectroscopy, elastic recoil detection and X-ray photoelectron spectroscopy. Rutherford backscattering gave a N/Mo = 1.4–1.5 stoichiometry that did not vary significantly with deposition temperature. The hydrogen content, determined by elastic recoil detection, varied from H/Mo = 1.0 to 0.45 with the content decreasing as the deposition temperature was increased. Carbon contamination was not observed in the film bulk. The films had high resistivities ($\approx 10^4$ μΩ cm).

Keywords: Chemical vapour deposition; Molybdenum; Nitrides; Organometallic vapour deposition

1. Introduction

Molybdenum forms a variety of nitrogen-containing compounds MoN_x with x ranging from 0 to at least 1. Molybdenum nitrides are candidates for use as a diffusion barrier film in microelectronic devices [1,2]. In this application, the barrier film must be deposited at low temperature (< 450 °C) and with high conformality. Chemical vapor deposition (CVD) is the preferred method for obtaining conformal coatings, and the use of metal–organic precursors offers the possibility of low-temperature depositions. A recent example of this approach is the metal–organic chemical vapor deposition of titanium nitride as a diffusion barrier material in very large-scale and ultra-large-scale integrated devices [3,4]. Hard, wear-resistant coatings, potentially useful on machine tools, have also been formed from molybdenum nitrides [5–7].

There appears to be only one report in the literature on the preparation of CVD molybdenum nitride. It involves a high-temperature (500–900 °C) plasma-assisted chemical vapor deposition process using $MoCl_5$ and NH_3 [8]. Other molybdenum nitride film preparation methods include the direct nitridation of molybdenum layers with NH_3 [9,10] and physical techniques such atomic layer epitaxy [11], reactive sputtering [2,5,7,12,13], ion-assisted deposition [14,15] and electron-beam evaporation [16].

Group IV and V transition-metal homoleptic dialkylamido complexes ($M(NR_2)_n$, M = Ti, Zr, Hf, V, Nb, Ta; R = CH_3 or CH_2CH_3) and ammonia have been successfully used as precursors for the low-temperature (< 450 °C) CVD of high-quality metal nitride thin films [2,3,17–19]. Given this precedent, the known Group VI metal–organic compound tetrakis(dimethylamido)molybdenum(IV), $Mo(N(CH_3)_2)_4$, appeared to be a promising precursor for the low-temperature CVD of molybdenum nitride thin films. We report here on the successful low-temperature atmospheric-pressure CVD of molybdenum nitride films from $Mo(N(CH_3)_2)_4$ and ammonia precursors [20].

2. Experimental

$Mo(N(CH_3)_2)_4$ was prepared by the reaction of $MoCl_5$ with $LiN(CH_3)_2$ as described in the literature [21]. The compound is an oxygen- and moisture-sensitive volatile solid. It was purified by vacuum sublimation (40–70 °C at 0.1 mm Hg). The purity was checked by ^1H NMR (> 98%).

Depositions were carried out in an atmospheric-pressure laminar-flow rectangular glass reactor heated from below, which was described previously in detail [18]. Deposition temperatures were in the range 200 to 450 °C. Ultra high purity helium, passed through a gettering furnace (Matheson Hydrox model 8301) and a Nanochem purifier (Model L-50 t, resin type IV), was used as carrier gas for the metal–organic compound and as diluent for the ammonia. The ammonia

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(Matheson USLI grade, 99.9995% min) was purified using a Nanochem purifier (Model L-50 t, resin type 1400). The CVD system, loaded with the substrates, was purged with helium for at least 2 h before each deposition. After purging in this manner, the helium outflow contained less than 0.1 ppm O_2 and H_2O as measured separately with oxygen and moisture analyzers. During the deposition process, helium was passed through a heated stainless steel sublimator vessel containing the metal–organic compound, and the metal–organic vapor/He mixture then flowed through a 2 mm i.d. delivery line to the reaction chamber. Approximately 2 cm before the delivery line entered the reaction chamber, the metal–organic vapor/He mixture was combined with ammonia gas diluted in helium (≈ 10% NH_3 in He). The combined mixtures then flowed over the hot substrate. Outflow from the reaction chamber exited to an oil bubbler, which prevented air from flowing back into the reactor. After depositions the films were allowed to cool slowly in the reactor under a flow of helium.

Silicon and glass substrates were cleaned by immersion in H_2O_2:H_2SO_4 (1:4) for 10 min and then rinsed with de-ionized water. The glass substrates were either Corning 7059 low sodium glass or normal soda lime glass. The silicon substrates were <100> test-grade p- or n-doped wafers.

Rutherford backscattering spectroscopy (RBS) analysis (General Ionics Model 4117) was used to measure film composition (Mo, N, C and O). RBS spectra were obtained by using a 2.0 MeV He^+ beam. Elastic recoil spectrometry (ERS) was used to measure the hydrogen content of the films. A 2 MeV He^+ beam was used for the ERS experiments. For the ERS experiments, the sample was tilted so that the incident beam arrived at a 15° angle. In this configuration the detector and incident beam were at an angle of 150°. A previously calibrated TiN film with a hydrogen content of 33 at.% was used as the standard. An identical hydrogen scattering cross-section was assumed for all samples. RBS and ERS spectra were analyzed using the programs SPECTRUM ANALYSIS and RUMP, respectively [22,23].

X-ray photoelectron spectroscopy (XPS) was carried out by using a Surface Science Lab SSX-100 system equipped with a 3 keV Ar^+ sputter gun. The electron-energy analyzer was referenced to the Au $4f_{7/2}$ line at 84 eV. XPS spectra depth profiles were collected in the unscanned mode by using the monochromatized Al Kα excitation with a spot size 600 μm and the electron-energy analyzer set for a pass energy of 150 eV. The experimental detector width was 18.6 eV in this configuration. The base pressure was 10^{-7} Torr with the sputter gun on. After sputtering into the bulk, high-resolution spectra were collected in the scanned mode (20 eV window) with a spot size of 300 μm and a pass energy of 50 eV. In this configuration the Ar^+ gun was off during the data acquisition and the base pressure was below 10^{-8} Torr.

Transmission electron micrographs and electron diffraction patterns were obtained on a Philips EM420T scanning transmission electron microscope at 120 kV.

3. Results

3.1. General results

Films were deposited by atmospheric pressure CVD from $Mo(N(CH_3)_2)_4$ and ammonia (≈ 10% NH_3 in helium) at substrate temperatures ranging from 200 to 400 °C. The films showed good adhesion to low sodium (Corning 7059) and soda lime glass and silicon substrates. When the ammonia was omitted in control experiments, no deposition was observed in the temperature range 200–400 °C. Film growth rates were about 100–150 Å min^{-1} (film thicknesses from RBS spectra) when the sublimator vessel containing the metal–organic compound was heated to 50 °C to give a vapor partial pressure of about 0.1 mm Hg.

The coatings were gold-colored with a smooth mirror-like appearance. They were resistant to HCl but they dissolved readily in HF.

The films were not uniformly thick across the substrates. Also, as the deposition temperature was increased, the films grew thicker closer to the reactor inlet and covered a smaller area. Higher flow rates could be used to counteract the temperature effect to some extent.

3.2. Film characterization

Film stoichiometries (Mo, N, C, and O) were determined by using RBS. X-ray photoelectron spectroscopy depth profile data was used to evaluate the level of impurities that were not detected by the less-sensitive RBS technique.

The RBS data showed that the films deposited at 200–400 °C had N/Mo ratios of 1.4–1.5. Carbon and oxygen contamination levels were below the detection limit of RBS (<5–10 at.%). The film stoichiometries did not vary significantly with deposition temperature.

XPS analyses revealed the films had a superficial oxide layer, undoubtedly resulting from their routine handling in air. The oxide was removed by sputtering (3 keV Ar^+ gun) for 1–3 min. The XPS depth profile data indicated that the levels of C and O contamination in the bulk were each below 1 at.%. The amount of contamination did not depend on the deposition temperature. In the bulk of the films, the Mo $3d_{5/2}$ and N 1s electron binding energies were 228.4 and 397.3 eV, respectively (Fig. 1). These values were reproducible to ±0.2 eV throughout the bulk of the film. The observed N 1s binding energy is close to the values reported for TiN (396.9 eV), Zr_3N_4 (397.2 eV), Ta_3N_5 (396.9 eV) and other early transition metal nitrides [18,19]. Also, Fujimoto et al. reported a N 1s peak at 398 eV for a film with N/Mo = 1.3 [14]. They also observed a peak at 394.2 eV that they attributed to N 1s, but the peak probably was due to Mo $3p_{3/2}$ electrons.

The hydrogen content in the films as a function of deposition temperature was determined by hydrogen ERS. The ERS spectra indicated that the molybdenum nitride films con-

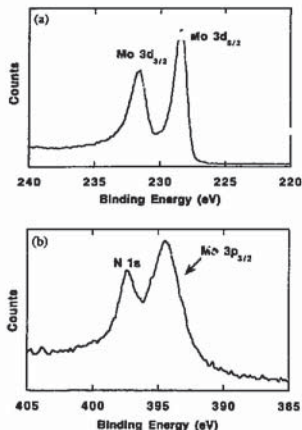

Fig. 1. X-ray photoelectron spectra for a film deposited at 200 °C on silicon from $Mo(N(CH_3)_2)_4$ and NH_3 in the Mo 3d (a) and N 1s (b) regions.

Table 1
Hydrogen-to-molybdenum ratios for films deposited on silicon

Deposition temperature (°C)	H/Mo atom ratios
200	1.0
300	0.8
400	0.45

tained hydrogen and that the hydrogen content decreased as the deposition temperature increased (Table 1).

The films were featureless by scanning electron microscopy. A transmission electron micrograph of a film deposited at 300 °C on mica has a granular structure with poorly defined grain boundaries. The grain size was <2 nm. An electron diffraction pattern for the same film showed broad rings indicative of an amorphous material. A film deposited at 400 °C has better defined grains, but the diffraction pattern was not any sharper.

The films had resistivities of around 10^4 $\mu\Omega$ cm (four-point probe method; film thicknesses from RBS measurements). The resistivities did not vary significantly with deposition temperature.

4. Discussion

Amorphous molybdenum nitride thin films were deposited from $Mo(N(CH_3)_2)_4$ and ammonia at 200–400 °C. The films had N/Mo ratios of 1.4–1.5 and H/Mo ratios of 0.45–1.0. The hydrogen content decreased as the deposition temperature increased. The decrease in hydrogen content with deposition temperature is consistent with earlier work on group IV and V nitrides prepared from $M(NR_2)_n$ compounds and ammonia [18,19].

The resistivities we observe ($\approx 10^4$ $\mu\Omega$ cm) are higher than those reported for crystalline hexagonal and cubic molybdenum nitride films made by atomic layer epitaxy (≈ 250 $\mu\Omega$ cm) [11], and as-deposited cubic molybdenum nitride prepared by reactive sputtering (500–850 $\mu\Omega$ cm) [5]. One or more factors may account for the high resistivities of our films, including their excess nitrogen content, small grain size, amorphous nature, and/or large hydrogen content.

Our results with molybdenum nitride parallel in many ways our previous studies on the use of homoleptic early transition metal amido complexes and ammonia to deposit Ti, Zr, Hf, V, Nb and Ta nitride films at low temperature (<450 °C) [18,19]. For example, as in the present study, the N/M ratios for the group IV and V nitride films did not vary significantly with deposition temperature. Also, significant amounts of hydrogen were observed in the group IV and V nitride films, and the hydrogen contents decreased markedly as the temperature of deposition was increased (e.g. the H/Ti ratio for TiN was 1.1 and 0.2 at deposition temperatures of 150 and 400 °C, respectively). In the previous studies, little or no carbon contamination was found in the films, and in two cases, niobium and tantalum nitride, the as-deposited films were amorphous.

The low-temperature deposition of molybdenum nitride from $Mo(N(CH_3)_2)_4$ and ammonia probably proceeds via a mechanism similar to the one proposed for TiN deposition from $Ti(NR_2)_4$ ($R=CH_3$ or CH_2CH_3) and ammonia [18–20,24–28]. Thus, the deposition process most likely involves substitution of one or more dimethylamido ligands with NH_2 groups by transamination reactions ($M–N(CH_3)_2+NH_3 \rightarrow M–NH_2+HN(CH_3)_2$). The NH_2-substituted species can eliminate an amine group intramolecularly by α-hydrogen activation involving a NH_2 ligand, leaving an imido (M=NH) linkage. Further reactions would lead to a nitrido (M≡N) species. The absence of carbon contamination in the films suggests that the transamination and α-hydrogen activation reactions occur rapidly and cleanly. The presence of hydrogen in the films, however, suggests incomplete reaction of the putative $Mo–NH_2$ and/or Mo=NH groups.

5. Conclusion

Amorphous molybdenum nitride thin films were deposited from tetrakis(dimethylamido)molybdenum(IV), $Mo(N(CH_3)_2)_4$, and ammonia at 200–400 °C. The N/Mo ratios were 1.4–1.5, and the ratios did not vary significantly with deposition temperature. The H/Mo ratios ranged from 0.45 to 1.0, and they decreased as the deposition temperature was increased. The films had high resistivities ($\approx 10^4$ $\mu\Omega$ cm).

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References

[1] M.-A. Nicolet, *Thin Solid Films, 52* (1978) 415.
[2] V.P. Anitha, A. Bhattacharya, N.G. Patil and S. Major, *Thin Solid Films, 236* (1993) 306.
[3] I.J. Raaijmakers and J. Young, *Appl. Surf. Sci., 73* (1993) 31.
[4] I.J. Raaijmakers, *Thin Solid Films, 247* (1994) 85.
[5] K.K. Shih and D.B. Dove, *J Vac. Sci. Technol. A, 8* (1990) 1359.
[6] J. Dandroc, A. Aubert and R. Gillet, *Thin Solid Films, 153* (1987) 281.
[7] J. Valli, U. Mäkelä and H.T.G. Hentzell, *J. Vac. Sci. Technol. A, 4* (1986) 2850.
[8] M. Tetsuro and N. Renpei, *Jpn. Patent 63072881 A2*, 1988; *Chem. Abstr., 109* (1988) 161128g.
[9] M. Maoujoud, M. Jardinier-Offergeld and F. Bouillon, *Appl. Surf. Sci., 64* (1993) 81.
[10] B.P. Kryzhanovskii, *Sov. J. Opt. Technol. (Engl. Transl.), 45* (1978) 96; *Opt.-Mekh. Prom., 45* (1978) 33.
[11] L. Hiltunen, M. Leskelä, M. Mäkelä, E. Niinistö, E. Nykänen and P. Soininen, *Thin Solid Films, 166* (1988) 149.
[12] G. Linker, R. Smithey and O. Meyer, *J. Phys. F: Met. Phys., 14* (1984) L115.
[13] H. Ihara, Y. Kimura, K. Senzaki, H. Kezuka and M. Hirabayashi, *Phys. Rev. B: Condens. Matter, 31* (1985) 3177.
[14] F. Fujimoto, Y. Nakane, M. Satou, F. Komori, K. Ogata and Y. Andoh, *Nucl. Instrum. Meth. Phys. Res. Sect. B, B19/20* (1987) 791.
[15] N. Savvides, *J. Appl. Phys., 62* (1987) 600.
[16] D.S. Easton, E.H. Henninger, O.B. Cavin and C.C. Koch, *J. Mater. Sci., 18* (1983) 2126.
[17] D.M. Hoffman, *Polyhedron, 13* (1994) 1169.
[18] R. Fix, R.G. Gordon and D.M. Hoffman, *Chem. Mater., 3* (1991) 1138.
[19] R. Fix, R.G. Gordon and D.M. Hoffman, *Chem. Mater., 5* (1993) 614.
[20] R. Fix, R.G. Gordon and D.M. Hoffman, *J. Am. Chem. Soc., 112* (1990) 7833.
[21] D.C. Bradley and M.H. Chisholm, *J. Chem. Soc. (A)*, (1971) 2741.
[22] SPECTRUM ANALYSIS, local program, P.M. Smith, Division of Applied Sciences, Harvard University, MA.
[23] RUMP, based on, L.R. Doolittle, *Nucl. Instrum. Meth., B9* (1985) 344.
[24] R. Fix, R.G. Gordon and D.M. Hoffman, *Mater. Res. Soc. Symp. Proc. Chemical Vapor Deposition of Refractory Metals and Ceramics, 168* (1990) 357.
[25] B.H. Weiller and B.V. Partido, *Chem. Mater., 6* (1994) 260.
[26] L.H. Dubois, B.R. Zegarski and G.S. Girolami, *J. Electrochem. Soc., 139* (1992) 3603.
[27] L.H. Dubois, *Polyhedron, 13* (1994) 1329.
[28] J.A. Prybyla, C.-M. Chiang and L.H. Dubois, *J. Electrochem. Soc., 140* (1993) 2695.