Use of 1,1-Dimethylhydrazine in the Atomic Layer Deposition of Transition Metal Nitride Thin Films

Marika Juppo,[z] Mikko Ritala,* and Markku Leskelä

The Laboratory of Inorganic Chemistry, University of Helsinki, 00014 Helsinki, Finland

Atomic layer deposition (ALD) of TiN, TaN_x, NbN, and MoN_x thin films from the corresponding metal chlorides and 1,1-dimethyl-hydrazine (DMHy) was studied. Generally, the films deposited at 400°C exhibited better characteristics compared to the films deposited at the same temperature using NH_3 as the nitrogen source. In addition, films could be deposited at lower temperatures down to 200°C. Even though the carbon content in the films was quite high, in the range of 10 atom %, the results encourage further studies. Especially the effect of carbon on the barrier properties and the use of other possibly less carbon-contaminating hydrazine derivatives should be studied.

© 2000 The Electrochemical Society. S0013-4651(00)03-044-5. All rights reserved.

Transition metal nitride thin films are important in many areas of microelectronics. The most important challenge today is the adoption of copper interconnects in the integrated circuits, which requires the use of a diffusion barrier because copper is known to diffuse through silicon dioxide-based dielectrics. The most promising diffusion barrier materials are transition metals, metal nitrides, metal silicides, and metal-silicon-nitrides. Because for a long time the semiconductor industry has used Ta-, Ti-, and W-based materials, these transition metals and their compounds are also the most studied materials for barrier applications.[1]

In addition to the important barrier film properties, like low resistivity and dense microstructure, there are several other requirements for barrier deposition techniques to be used in future microelectronic circuits manufacturing. The thickness of the films must be well controlled because the films need to be very thin, preferably below 100 Å. The films should be conformal and exhibit good uniformity over large wafers. Also the future requirements for the deposition temperature are quite demanding. The films should preferably be deposited below 400°C, considering the tolerance of the other, polymer-based low-*k* materials used in the circuits.
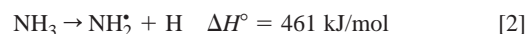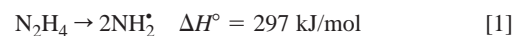
The deposition of nitride thin films has mainly been performed with various physical vapor deposition (PVD) and chemical vapor deposition (CVD) techniques. These, however, suffer from various difficulties. Films can be grown at quite low temperatures using the PVD techniques, but their step coverage is poor and therefore their use in manufacturing the future generation integrated circuits is limited. More conformal films are achieved by using the CVD techniques, but unfortunately the needed growth temperatures are often too high. In addition good conformality and good electric properties are often difficult to achieve at the same time. In the traditional CVD deposition processes, titanium nitride (TiN) films are deposited from $TiCl_4$, H_2, and N_2 at temperatures above 750°C.[2] If NH_3 is used instead of H_2 and N_2, high conductivity films with low chlorine contamination levels can usually be deposited at temperatures exceeding 550°C.[3-9] Nowadays alternative precursors, particularly alkyl amines,[10-15] additional energy sources,[16] and post- or intermediate deposition plasma treatments[17,18] have been widely examined in order to reduce the CVD growth temperature.

Atomic layer deposition (ALD), also known as atomic layer epitaxy (ALE),[19-21] is one of the most promising techniques to fulfill the above mentioned requirements. It is a CVD-related technique and therefore the name atomic layer chemical vapor deposition (ALCVD) is also sometimes used. The most important difference between CVD and ALD is that in ALD the precursors are introduced onto the substrates alternately. Between the reactant pulses the reactor is purged with an inert carrier gas. Under properly adjusted experimental conditions the surface reactions are self-controlled, and the film grows in a self-limiting manner with no detrimental gas phase reactions. As a result, the film thickness can be accurately controlled by the number of deposition cycles and conformality is excellent.[22] In addition, practise has also proven that usually the temperatures needed for depositing high quality thin films are lower than in the alternative methods.[23,24] Perhaps the most severe disadvantage of ALD is that it is rather slow. On the other hand, the uniformity of the deposited films over large batches is a clear advantage. In the future, the device dimensions will continue to shrink and very thin films are needed. So, the slowness of the method will no longer be a big problem.

TiN,[25-28] TaN,[27,29] NbN,[27,30] MoN,[27] WN,[31] and Ti-Si-N[32] films have already been deposited by the ALD method. Except for Ti-Si-N and one TiN process, where alkyl amines were used,[28] halides have been used as the metal source and ammonia as the nitrogen source. An intermediate zinc pulse between the chloride and ammonia pulses has been proven to be effective in improving the electrical properties of the TiN,[25,33] TaN,[29] and NbN[30,33] films. However, the use of zinc in electronic applications is undesirable, because it has a tendency to dissolve into silicon producing electronically active defect sites which weaken the properties of the electric circuit. On the other hand, without the intermediate zinc pulse the resistivity of the films is higher and the deposition temperatures that have to be used to achieve comparable film qualities are higher, though still quite comparable to CVD.

The oxidation number of the metal in the conventional precursors is higher than in the desired nitride and therefore reduction is required. At the present time ammonia has been the most often used and studied nitrogen source in ALD. However, NH_3 is quite stable and not a very effective reducing agent and therefore, alternative more reactive nitrogen sources should be sought. One of the possible choices is hydrazine, N_2H_4, which is more reactive than NH_3. The radical formation enthalpies[34] are

$$N_2H_4 \rightarrow 2NH_2^\bullet \quad \Delta H° = 297 \text{ kJ/mol} \tag{1}$$

$$NH_3 \rightarrow NH_2^\bullet + H \quad \Delta H° = 461 \text{ kJ/mol} \tag{2}$$

which are favorable for using N_2H_4, especially at lower temperatures. The advantages of N_2H_4 have been successfully demonstrated especially in the CVD growth of GaN.[34-36] Also in the ALD growth of Si_3N_4, N_2H_4 has proven to be effective.[37] The problem with using N_2H_4 is that it is a carcinogen, highly flammable, and even explosive under certain conditions.[38] Therefore methylized derivatives, for example, $(CH_3)(H)NNH_2$,[39,40] $(CH_3)_2NNH_2$,[41-44] and $(CH_3)_3C(H)NNH_2$,[45] are somewhat safer to use and have been examined in the growth of nitrides.

In this paper studies on the use of unsymmetrical dimethylhydrazine, $(CH_3)_2NNH_2$ (DMHy), in the ALD growth of some nitrides,

* Electrochemical Society Active Member.
z E-mail: marika.juppo@helsinki.fi

namely, TiN, TaN, NbN, and MoN are presented. The goal of these studies is to evaluate the potential of DMHy as a nitrogen precursor to replace NH_3 for the low temperature growth of these nitrides.

Experimental

The films were grown on 5 × 5 cm soda-lime glass substrates using a commercial flow-type F120 ALD reactor (ASM-Microchemistry Ltd., Espoo, Finland)[23] operated under a pressure of 10 mbar. Nitrogen (99.9995%), generated by Nitrox UHPN 3000, was used both as a carrier and a purging gas. The metal precursors were chlorides $TiCl_4$ (99.9%, Aldrich), $MoCl_5$ (Cerac, 99.5%), $TaCl_5$ (Merck), and $NbCl_5$ (99.9%, Aldrich). All the other chlorides except $TiCl_4$ are solid at room temperature and therefore seldom utilized in CVD. $TiCl_4$ vapor was generated in an external reservoir held at 19°C and pulsed into the reactor with the aid of a solenoid valve. All the other metal precursors were evaporated from an open boat held at 90°C inside the reactor, and their pulsing was realized by means of inert gas valving.[23] Unsymmetrical dimethylhydrazine (DMHy) (98%, Aldrich), $(CH_3)_2NNH_2$, is a liquid with a vapor pressure of >80 Torr at room temperature. In these experiments DMHy vapor was generated in an external reservoir held at −20°C (vapor pressure about 8 Torr) and its pulsing was accomplished in the similar manner as that of the $TiCl_4$ vapor. The effects of the pulse and purge lengths were not examined in detail in this study. For titanium, niobium, and molybdenum chlorides 0.2 s, and for tantalum chloride 0.5 s pulse lengths were used because they were known to be appropriate from the previous studies with NH_3-based processes. For DMHy a pulse length of 0.3 s was chosen. The purge length after each reactant pulse was 0.5 s, and all the films were grown using 5000 deposition cycles. The films were deposited at different temperatures, TiN between 200-500°C, TaN between 300 and 400°C, and both NbN and MoN at 400°C.

Impurities and film thicknesses were determined at approximately 3 cm from the leading edge of the substrate with energy dispersive X-ray spectroscopy (EDX) using a Link ISIS EDX spectrometer installed in a Zeiss DSM 962 scanning electron microscope (SEM) and a GMRFILM program.[46] In the EDX analysis only the chlorine and titanium could be measured and nitrogen was calculated from the stoichiometry. In other words in these routine analyses it was supposed that those were the only constituents in the films. Because the films also contain carbon, hydrogen, and oxygen residues, a more detailed impurity analysis was performed on selected samples with time-of-flight elastic recoil detection analysis (TOF-ERDA).[47,48] In the TOF-ERDA analysis, the samples were bombarded with 53 MeV I^{10+} ions.

Film crystallinity was examined with a Bruker AXS D8 advance powder X-ray diffractometer (XRD) using Cu Kα radiation. Film resistivity was measured with the standard four-point probe method.

Results and Discussion

In this paper the main focus is on the properties of the metal nitride films deposited from the corresponding metal chlorides and DMHy. The possible reaction mechanisms are not discussed or speculated any further, but on the basis of the recent study on the WF_6-NH_3 process,[31] the film growth may be suggested to take place as follows. When the metal chloride (MCl_a) is pulsed to the reactor, it reacts with surface $-NH_y^*$ groups (* denotes all the possible surface species after adsorption step) forming adsorbed $-NMCl_x^*$ and gaseous reaction product HCl, which is pumped away. During the DMHy pulsing sequence gaseous DMHy reacts with surface $-NMCl_x^*$ groups forming adsorbed $-NMNH_y^*$ species and again HCl.

TiN films were studied in the most detail, not only because it may be the most promising diffusion barrier material, but also because its ALD deposition has earlier been studied most thoroughly.[25-27] The summary of the present and previous results is given in Table I.

TiN.—The deposition rate, the chlorine contents, and the resistivity of the films were strongly dependent on the deposition temperature (Fig. 1 and 2). The chlorine content, determined by EDX,

decreases strongly with increasing temperature so that at 200°C it is as much as 23 atom % but at and above 400°C only about 2 atom %. The chlorine content at 400°C is three times lower than in the films deposited at the same temperature by the $TiCl_4$-Zn-NH_3 ALD process.[25] Also the growth rates are somewhat higher than those achieved by the ammonia-based processes. At 250°C the growth rate already exceeds 0.02 nm/cycle, which is slightly higher than the growth rate achieved with the $TiCl_4$-Zn-NH_3 process at 500°C.[25] Between 350 and 450°C the growth rate is the highest, 0.026-0.028 nm/cycle.

Figure 2 shows the resistivity of the films as a function of the deposition temperature. Conducting films are deposited already at 250°C, and the resistivity decreases with increasing temperature until 350°C where it is the lowest, about 500 μΩ cm. This is, however, about two times higher than the resistivity of the films grown at 400°C by the $TiCl_4$-Zn-NH_3 ALD process.[25] The rather high resistivity is most likely caused by high carbon and oxygen content of the films. TOF-ERDA analysis shows that the film deposited at 400°C contains 13 atom % carbon, 14 atom % oxygen, and 2 atom % chlorine, which are quite uniformly distributed through the whole film (Fig. 3). The carbon content is evidently caused by the decomposition of DMHy at 400°C because at 300°C the carbon content is much lower (6 atom %). The onset of DMHy decomposition is reported to occur at 370°C producing $(CH_3)_2N$ and NH_2 that decompose further to H_2CN and CH which are the most likely the reason for the high carbon contents.[49] Oxygen incorporation into the film can occur during and/or after the deposition and cooling steps, since nitride materials are known to be very sensitive to oxygen and the reaction of titanium nitride with oxygen-forming TiO_2 is thermodynamically favorable ($\Delta G° = −582$ kJ/mol).[50] The most potential oxygen sources during the deposition sequence are impurities in DMHy and in the N_2 carrier gas. On the other hand, it is more likely that most of the oxygen incorporation takes place after the deposition sequence when the film is exposed to air. The oxygen content of the previous ALD-grown TiN films was also quite high and this was thought to be caused by preferential oxidation through grain boundaries. This kind of oxygen incorporation mechanism is also supported by other groups[51,52] and most likely also takes place with the films deposited in this study. Hydrogen content, on the other hand, is quite low, only 2 atom % at both 300 and 400°C as analyzed by TOF-ERDA. The much lower hydrogen content compared to the carbon content (6-13 atom %) suggests that carbon is present in the films as carbide rather than CH_x species. However, the high carbon content could possibly be considered only as a minor drawback, because carbides are known to be quite conducting and strongly bonded compounds, and therefore could be used as diffusion barriers.[53]

According to the XRD measurements the films grown at 250, 300, and 400°C are only weakly crystalline cubic TiN (Fig. 4). As a distinction to the other ALD TiN processes,[25,26] the only reflection is [200], which is quite weak. This is a rather promising result since amorphous films work better as diffusion barriers as they contain no grain boundaries through which copper and silicon could migrate. Thinner films might very well be amorphous because the films grown in this study were quite thick (>100 nm).

TaN_x—Earlier it was shown that the reducing power of NH_3 is too weak to reduce Ta(V) in $TaCl_5$ into Ta(III) in TaN and only semiconducting (ρ = 0.5 Ω cm at 400°C) Ta_3N_5 film was deposited. However, the contamination levels of the films deposited at higher temperatures were quite low, for example, at 400°C, Cl, H, O <3 atom %. On the other hand, the films obtained at 400 and 500°C by using an intermediate zinc pulse between $TaCl_5$ and NH_3 pulses were conducting TaN with a resistivity of $9 × 10^{−4}$ Ω cm. So, unlike NH_3, Zn is capable of reducing Ta(V) to the oxidation state +III. Also with Zn the contamination levels were quite low, for example, at 400°C, Cl, O < 5 atom % and Zn, H < 1 atom %.[29] Because zinc was previously found to be crucial in obtaining conductive TaN films, the idea of replacing NH_3 by a more reactive and reducing nitrogen source that could reduce Ta(V) into Ta(III) is especially important.

Table I. Summary of the present and previous results. The chlorine content is determined by TOF-ERDA, if not otherwise indicated.

Material/Precursors	Deposition temperature (°C)	Growth rate (nm/cycle)	Resistivity (μΩ cm)	Cl content (atom %)	Ref.
TiN					
$TiCl_4$, NH_3	500	0.017	250	<0.5	25
$TiCl_4$, Zn, NH_3	400	0.013	200	6	25
	500	0.019	50	<0.5	25
$TiCl_4$, DMHy	200	0.011	—	23 (EDX)	This study
	250	0.022	3,200	18 (EDX)	This study
	300	0.022	990	7	This study
				9 (EDX)	
	350	0.026	530	6 (EDX)	This study
	400	0.026	650	2	This study
				2 (EDX)	
	450	0.028	670	3 (EDX)	This study
	500	0.021	1,500	2 (EDX)	This study
TaN$_x$					
$TaCl_5$, NH_3	400	0.024	500,000	<1	29
	500	0.024	500,000	<0.1	29
$TaCl_5$, Zn, NH_3	400	0.020	900	4	29
	500	0.015	900	<0.1	29
$TaCl_5$, DMHy	300	0.031	—	14 (EDX)	This study
	400	0.013	—	<0.5(EDX)	This study
NbN					
$NbCl_5$, NH_3	300	0.011	—	24 (EDX)	This study
	400	0.010	>10,000	15 (EDX)	This study
	500	0.025	550	<0.3	30
$NbCl_5$, Zn, NH_3	500	0.018	200	<0.3	30
$NbCl_5$, DMHy	400	0.023	2900	5 (EDX)	This study
MoN$_x$					
$MoCl_5$, NH_3	400	0.0020	—	10 (EDX)	This study
	500	0.031	100	1 (EDX)	This study
$MoCl_5$, Zn, NH_3	400	0.078	3,600	7 (EDX)	This study
	500	0.040	490	<1 (EDX)	This study
$MoCl_5$, DMHy	400	0.057	930	3	This study
				5 (EDX)	

Unfortunately, DMHy did not bring any improvement to the conductivity as compared with the NH_3-based ALD process, but rather the resistivity was so high that it could not be measured with the standard four-point probe method. In addition, the films were partly transparent, which indicates that they were Ta_3N_5 rather than TaN. According to the XRD analysis the films deposited at both temperatures were amorphous. Clearly, DMHy is not efficient enough for reducing tantalum. The growth rate, however, was rather good (0.03 nm/cycle) at 300°C but the chlorine content was also high (14 atom

%, determined by EDX). At 400°C the situation was inverse as the growth rate was lower (0.01 nm/cycle) but only below 0.5 atom % chlorine was detected by EDX.

NbN.—In the previously reported studies on the ALD growth of NbN, the films were deposited from $NbCl_5$ and NH_3 with and without the intermediate Zn pulses only at 500°C.[30] Without the intermediate Zn pulses the resistivity was higher, 550 μΩ cm, than with the Zn pulse, 200 μΩ cm. On the other hand, the use of zinc caused
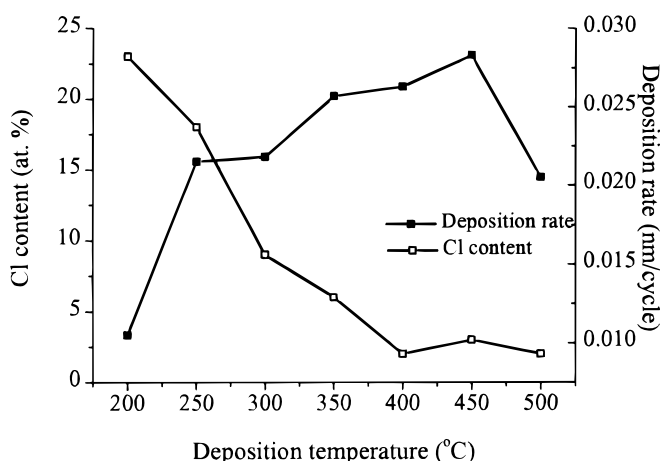

Figure 1. Chlorine content and deposition rate of the TiN films as a function of deposition temperature. The chlorine content and the film thickness are determined by EDX.
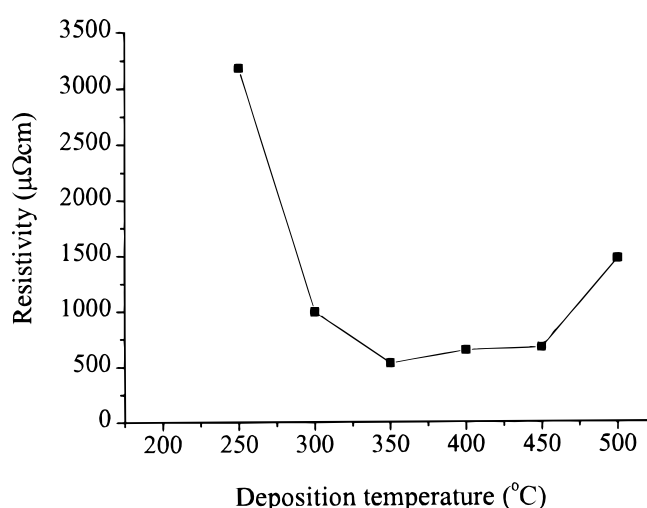

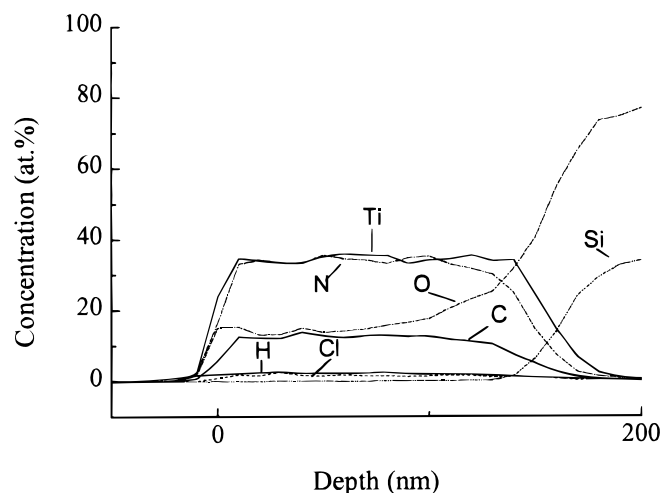**Figure 2.** Resistivity of the TiN films as a function of deposition temperature.

Figure 3. TOF-ERDA analysis of the elemental depth profiles of the TiN film deposited at 400°C.

Figure 4. XRD patterns of the TiN films.

the growth rate to decrease (0.025 nm/cycle *vs.* 0.018 nm/cycle). Because the future demands for the growth temperature are below 500°C, for comparison some NbN films were grown also from NbCl$_5$ and NH$_3$ at 300 and 400°C. The growth rate of those films was rather low, only 0.010 nm/cycle at both temperatures. According to the EDX analysis, the films contained quite a lot of chlorine, 24 atom % at 300°C and 15 atom % at 400°C, and the conductivity of the films was very poor (resistivity over 10,000 μΩ cm).

The resistivity of the film deposited from NbCl$_5$ and DMHy was approximately 2,900 μΩ cm, which is much higher than the resistivity achieved in the previous study at 500°C[30] but considerably lower than was obtained with the NbCl$_5$-NH$_3$ process at 400°C. However, the deposition rate is comparable (0.023 nm/cycle) to the 500°C processes and according to the EDX analysis the film contained 5 atom % of chlorine. In the XRD analysis only one peak was detected. Because this peak was broad, it could not be distinguished as to whether it corresponded to either the [200] or [002] or even both reflections of the tetragonal Nb$_4$N$_3$ or the [200] reflection of the cubic δ-NbN.

MoN$_x$—The growth of MoN$_x$ by ALD has earlier been reported only briefly.[27] Both cubic Mo$_2$N and hexagonal MoN films could be grown from MoCl$_5$ and NH$_3$ at 500°C. As no further details had been reported, we also studied the MoCl$_5$-NH$_3$ process for comparison. MoN films were grown from MoCl$_5$ and NH$_3$ with and without the intermediate Zn pulses at 400 and 500°C. The film grown at 500°C without the intermediate Zn pulses with a rate of 0.03 nm/cycle had a resistivity of only about 100 μΩ cm. With a Zn pulse the resistivity increased to about 500 μΩ cm, most likely because of Zn residues (2 atom % as determined by EDX). The films deposited at 400°C were of quite poor quality. Only very thin (9 nm with 5,000 deposition cycles) could be grown without Zn. The films grown with the intermediate zinc pulses had a high resistivity (about 3600 μΩ cm) and also rather high chlorine (7 atom %) and zinc (2 atom %) content. On the other hand, the growth rate of the MoCl$_5$-Zn-NH$_3$ process was quite high (0.08 nm/cycle) at 400°C and only half of that at 500°C. The decrease in the growth rate may result from an increased etching of MoN$_x$ by MoCl$_5$ at higher temperatures.[54]

The resistivity of the film deposited from MoCl$_5$ and DMHy was about 930 μΩ cm which is much lower than those achieved with the previous processes at 400°C. Also the deposition rate (0.06 nm/cycle) was higher than those of the films deposited by the previous processes at both 400 and 500°C, if the higher resistivity film deposited with zinc at 400°C is excluded. According to the TOF-ERDA analysis, a quite large amount of carbon (10 atom %) is incorporated into the film. However, the amounts of the other impurities are quite low (oxygen 2 atom %, hydrogen 2 atom %, and chlorine 3 atom %).
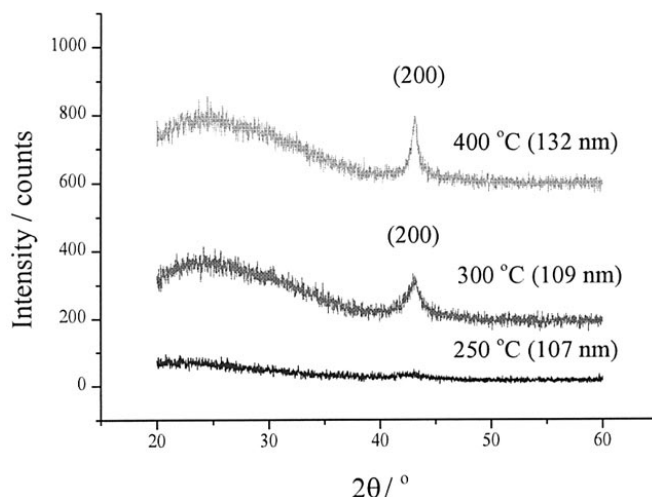
According to the XRD analysis the film exhibited quite weak (111) and (200) reflections typical for the cubic Mo$_2$N, although the XRD peaks were slightly shifted and quite broad. The difference between the d values of the obtained peaks (d_{111} = 2.44 Å, d_{200} = 2.10 Å) and the reference values (d_{111} = 2.404 Å, d_{200} = 2.081 Å) is 0.04 Å for (111) and 0.02 Å for (200) orientation. In addition, the (111) reflection of the cubic Mo$_2$N is quite close to the (200) reflection of the hexagonal MoN (d_{200} = 2.479 Å). The TOF-ERDA analysis showed that the Mo:N ratio was close to 1:1. It could be possible that the extra nitrogen is present in the Mo$_2$N matrix or the matrix is in fact amorphous MoN with nanocrystallites of Mo$_2$N. Extensive conclusions, however, cannot be drawn since the XRD peaks are only weak and shifted.

Conclusions

TiN, TaN$_x$, NbN, and MoN$_x$ films were deposited by ALD from the corresponding metal chlorides and 1,1-dimethylhydrazine (DMHy). The aim of this study was to find out if by using a more reactive nitrogen source instead of the normally used NH$_3$, better quality films could be prepared at 400°C.

In the case of TiN and MoN$_x$, reasonably good quality films were indeed deposited, although the resistivities measured were quite high (about 500 μΩ cm for TiN and about 900 μΩ cm for MoN$_x$). This is due to the rather high impurity contents of the films. In addition to chlorine (in both films about 2-3 atom % at 400°C) and oxygen (about 14 atom % in TiN and about 2 atom % in MoN$_x$ at 400°C) which are known to have a negative effect on the electrical properties, the decomposition of DMHy also results in carbon incorporation (about 10 atom % in both films at 400°C). On the other hand, the hydrogen content of the films is quite low (2 atom % in all cases), which is an indication of the carbidic nature of the incorporated carbon.

The deposited TaN$_x$ and NbN films were not as good as the TiN and MoN$_x$ films. The TaN$_x$ films prepared were not even conducting, and the resistivity of the NbN film was nearly 3000 μΩ cm.

Although the use of DMHy in the growth of nitrides by ALD did not bring any major improvement as compared to the films deposited with NH$_3$ at 500°C, one very important issue is the low growth temperature. The films deposited at 400°C with DMHy were almost without exception better than the films deposited with NH$_3$ at the same temperature, although the films contained rather large amounts of carbon. The carbon impurities could probably be decreased by using other hydrazine derivatives.

References

1. S-O. Wang, *MRS Bull.,* 30 (Aug 1994).
2. S. Chatterjee, S. Chandrashekhar, and T. Sudarshan, *J. Mater. Sci.,* **27,** 3409 (1992).
3. A. S. Herman, *Jpn. J. Appl. Phys.,* **30,** 3553 (1991).
4. N. Yokoyama, K. Hinode, and Y. Homma, *J. Electrochem. Soc.,* **136,** 882 (1989).
5. R. I. Hegde, R. W. Fiordalice, E. O. Travis, and P. J. Tobin, *J. Vac. Sci. Technol. B,* **11,** 1287 (1993).
6. R. I. Hegde, P. J. Tobin, R. W. Fiordalice, and E. O. Travis, *J. Vac. Sci. Technol. A,* **11,** 1692 (1993).
7. R. I. Hegde, R. W. Fiordalice, and P. J. Tobin, *Appl. Phys. Lett.,* **62,** 2326 (1993).
8. T. Kaizuka, H. Shinriki, N. Takeyasu, and T. Ohta, *Jpn. J. Appl. Phys.,* **33,** 470 (1994).
9. J. T. Hillman, D. W. Studiner, M. J. Rice, Jr., and C. Arena, *Microelectronic Eng.,* **19,** 375 (1992).
10. J. P. Endle, Y.-M. Sun, J. M. White, and J. G. Ekerdt, *J. Vac. Sci. Technol. A,* **16,** 1262 (1998).
11. G. S. Sandhu, S. G. Meikle, and T. T. Doan, *Appl. Phys. Lett.,* **62,** 240 (1993).
12. A. Weber, R. Nikulski, C.-P. Klages, M. E. Gross, W. L. Brown, E. Dons, and R. M. Charatan, *J. Electrochem. Soc.,* **141,** 849 (1994).
13. J. A. Prybyla, C.-M. Chiang, and L. H. Dubois, *J. Electrochem. Soc.,* **140,** 2695 (1993).
14. A. Intemann, H. Koerner, and F. Koch, *J. Electrochem. Soc.,* **140,** 3215 (1993).
15. I. J. Raaijmakers, *Thin Solid Films,* **247,** 85 (1994).
16. S. V. Deshpande, J. L. Dupuie, and E. Gulari, *Adv. Mater. Opt. Electron.,* **6,** 135 (1996).
17. M. Eizenberg, *Mater. Res. Soc. Symp. Proc.,* **427,** 325 (1996).
18. S.-H. Kim, D.-S. Chung, K.-C. Park, K.-B. Kim, and S.-H. Min, *J. Electrochem. Soc.,* **146,** 1455 (1999).
19. M. Ritala and M. Leskelä, *Nanotechnology,* **10,** 19 (1999).
20. M. Ritala, *Appl. Surf. Sci.,* **112,** 223 (1997).
21. M. Leskelä and M. Ritala, *J. Phys. IV,* C5-937 (1995).
22. M. Ritala, M. Leskelä, J.-P. Dekker, C. Mutsaers, P. J. Soininen, and J. Skarp, *Chem. Vap. Dep.,* **5,** 7 (1999).
23. T. Suntola, *Thin Solid Films,* **216,** 84 (1992).
24. T. Suntola, J. Antson, A. Pakkala, and S. Lindfors, in *SID 80 Dig.,* **11,** 109 (1980).
25. M. Ritala, M. Leskelä, E. Rauhala, and P. Haussalo, *J. Electrochem. Soc.,* **142,** 2731 (1995).
26. M. Ritala, M. Leskelä, E. Rauhala, and J. Jokinen, *J. Electrochem. Soc.,* **145,** 2914 (1998).
27. L. Hiltunen, M. Leskelä, M. Mäkelä, L. Niinistö, E. Nykänen, and P. Soininen, *Thin Solid Films,* **166,** 149 (1988).
28. J-S. Min, Y-W. Son, W-G. Kang, S-S. Chun, and S-W. Kang, *Jpn. J. Appl. Phys.,* **37,** 4999 (1998).
29. M. Ritala, P. Kalsi, D. Riihelä, K. Kukli, M. Leskelä, and J. Jokinen, *Chem. Mater.,* **11,** 1712 (1999).
30. K-E. Elers, M. Ritala, M. Leskelä, and E. Rauhala, *Appl. Surf. Sci.,* **82/83,** 468 (1994).
31. J. W. Klaus, S. J. Ferro, and S. M. George, *J. Electrochem. Soc.,* **147,** 2658 (2000).
32. J-S. Min, H-S. Park, W. Koh, and S-W. Kang, *Mater. Res. Soc. Symp. Proc.,* **564,** 207 (1999).
33. M. Ritala, T. Asikainen, M. Leskelä, J. Jokinen, R. Lappalainen, M. Utriainen, L. Niinistö, and E. Ristolainen, *Appl. Surf. Sci.,* **120,** 199 (1997).
34. D. Gaskill, N. Botka, and M. Lin, *J. Cryst. Growth,* **77,** 418 (1986).
35. S. Fujieda, M. Mizuta, and Y. Matsumoto, *Jpn J. Appl. Phys.,* **26,** 2067 (1987).
36. D. K. Gaskill, N. Bottka, and M. C. Lin, *Appl. Phys. Lett.,* **48,** 1449 (1986).
37. S. Morishita, S. Sugahara, and M. Matsumura, *Appl. Surf. Sci.,* **112,** 198 (1997).
38. *Kirk-Othmer Encyclopedia of Chemical Technology,* Vol. 10, 4th ed., J. I. Kroschwitz, Executive Editor, John Wiley & Sons, Inc., New York (1993).
39. H. Tsuchiya, A. Takeuchi, M. Kurihara, and F. Hasegawa, *J. Cryst. Growth,* **152,** 21 (1995).
40. S. Yonemura, T. Yaguchi, H. Tsuchiya, N. Shimoyama, T. Sucmasu, and F. Hasegawa, *J. Cryst. Growth,* **188,** 81 (1998).
41. Y. Kobayashi, F. Scholz, and N. Kobayashi, *Jpn J. Appl. Phys.,* **36,** 2592 (1997).
42. H. Sato, H. Takahashi, A. Watanabe, and H. Ota, *Appl. Phys. Lett.,* **68,** 3617 (1996).
43. S. Miyoshi, K. Onabe, N. Ohkovehi, H. Yoguchi, R. Ho, S. Fukatsu, and Y. Shiraki, *J. Cryst. Growth,* **124,** 439 (1992).
44. J. Luv, H. Yaguchi, H. Nagasawa, Y. Yamaguchi, K. Onabe, Y. Shiraki, and R. Ho, *Jpn J. Appl. Phys.,* **36,** 4241 (1997).
45. U. W. Pohl, C. Möller, K. Knorr, W. Richter, J. Gottfriedsen, H. Schumann, K. Rademann, and A. Fielicke, *Mater. Sci. Eng.,* **B59,** 20 (1999).
46. R. A.Waldo, *Microbeam Anal.,* 310 (1988).
47. J. Jokinen, J. Keinonen, P. Tikkanen, A. Kuronen, T. Ahlgren, and K. Nordlund, *Nucl. Instrum. Methods Phys. Res., Sect. B,* **119,** 533 (1996).
48. J. Jokinen, P. Haussalo, J. Keinonen, M. Ritala, D. Riihelä, and M. Leskelä, *Thin Solids Films,* **289,** 159 (1996).
49. U. W. Pohl, C. Möller, K. Knorr, W. Richter, J. Gottfriedsen, H. Schumann, K. Rademann, and A. Fielicke, *Mater. Sci. Eng.,* **B59,** 20 (1999).
50. J. Demaison, P. Lefort, and M. Billy, *Oxid. Met.,* **13,** 203 (1979).
51. C. Ernsberger, J. Nickerson, T. Smith, A. E. Miller, and D. Banks, *J. Vac. Sci. Technol., A,* **4,** 2784 (1986).
52. S. Logothetides, E. I. Meletis, G. Stergioudis, and A. A. Adjaottor, *Thin Solid Films,* **338,** 304 (1999).
53. H. O. Pierson, *Handbook of Chemical Vapor Deposition,* Noyes Publications, Park Ridge, NJ (1992).
54. M. Juppo, M. Vehkamäki, M. Ritala, and M. Leskelä, *J. Vac. Sci. Technol., A,* **16,** 2845 (1998).