Controlled Growth of TaN, Ta_3N_5, and TaO_xN_y Thin Films by Atomic Layer Deposition

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TaN, Ta_3N_5, and TaO_xN_y films were deposited by the atomic layer deposition technique. The alternate surface reactions between $TaCl_5$ and NH_3 resulted in Ta_3N_5 films, but when elemental zinc, serving as an additional reducing agent, was supplied on the substrates between the $TaCl_5$ and NH_3 pulses, TaN with a resistivity of 9×10^{-4} Ω cm was obtained. TaO_xN_y films were grown by depositing first thin Ta_3N_5 layers which were then partially oxidized by single water pulses. By varying the number of the Ta_3N_5 deposition cycles between the water pulses, the oxygen-to-nitrogen ratio of the films was controlled. The permittivity of the TaO_xN_y films was around 30 which is somewhat higher than that of Ta_2O_5.

Introduction

Metallic tantalum nitride is a potential material for many thin-film applications. In microelectronics, TaN has been used as a thin-film resistor and recently it has gained quite a lot of interest as a diffusion barrier between metals and silicon[1−6] and as passivation layer against copper oxidation.[7] In addition, TaN has been considered as an electrode material for those dynamic random access memory (DRAM) storage capacitors where Ta_2O_5 is used as a dielectric material.[8] TaN has also been investigated as a nonmagnetic interlayer in NiFeCo/TaN/NiFeCo nonvolatile magnetic random access memories.[9] In addition to microelectronics, TaN films have been also examined for high-temperature ceramic pressure sensors because of their good stability and piezoresistive properties.[10] Other potential uses of TaN comprise protective and hard coatings.

Reactive sputtering[1−4,7,9,10] and chemical vapor deposition (CVD)[5,11−16] are the main techniques used for depositing TaN films. The advantage of reactive sputtering is a good control of the N/Ta ratio over a broad range from metallic Ta through Ta_2N to TaN and further on toward the semiconducting Ta_3N_5,[1,3] and in addition, controlled addition of oxygen is possible.[2] However, sputtering has a poor step coverage which is a serious shortcoming especially for the use in microelectronics with continuously decreasing device dimensions. CVD, in turn, is known to give a good conformality when operated in the surface reaction limited regime[5] but the stoichiometry of the resulting films has often been Ta_3N_5 rather than the desired TaN. For example, $TaCl_5$−NH_3[14] and $Ta(NMe_2)_5$−NH_3[11,13] precursor combinations have resulted in Ta_3N_5. An imido−amido−amine single source precursor $[TaCl_2(=N^tBu)(NH^tBu)(NH_2tBu)]_2$ gave Ta_3N_5 at 500 and 600 °C, but at 1000 °C TaN was obtained.[12] By contrast, another rather similar single-source precursor $[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_n$ afforded TaN already at 400 °C because of the reducing action of the hydrazido ligands.[12] Other single source precursors resulting in TaN are the imido−amido complexes $Ta(=NEt)(NEt_2)_3$ above 500 °C[15] and $Ta(=N^tBu)(NEt_2)_3$ above 450 °C.[5] Also the $TaCl_5$−N_2−H_2 process resulted in TaN above 700 °C, although Ta_2N was obtained if the N_2 partial pressure was not high enough.[14,16]

In this work, we have examined controlled deposition of TaN, Ta_3N_5, and TaO_xN_y films by the atomic layer deposition (ALD) technique.[17−19] ALD was originally

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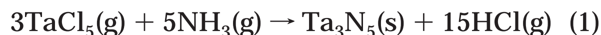
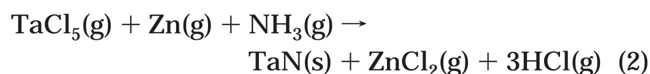
introduced with a name of atomic layer epitaxy (ALE)[20] but because of clarity reasons it has recently increasingly been called as ALD when dealing with nonepitaxial films. In ALD, the gaseous precursors are dosed alternately onto the substrate surface where they react with each other saturatively forming the desired film. Because the film growth proceeds via saturative surface reactions, it is self-limiting, ensuring excellent conformality, large area uniformity, and simple and accurate film thickness control. These features make ALD a promising technique for the future generation integrated circuit technology.

ALD deposition of the related transition metal nitrides TiN[21−24] and NbN[23−25] has been examined in detail previously but the deposition of TaN_x has only briefly been mentioned.[24] In the studies on ALD deposition of TiN and NbN from $TiCl_4$[21] and $NbCl_5$,[25] it was observed that the use of zinc as an additional reducing agent is crucial for achieving low resistivity films. However, the mechanism behind these improvements was found to be more complicated than the anticipated reducing and chlorine removing action of zinc; also structural effects were involved.[23] On the other hand, from TiI_4 low resistivity TiN films were obtained without using zinc.[22]

In the present study, it was observed that in ALD deposition of tantalum nitrides from $TaCl_5$ and NH_3, the importance of zinc is even more crucial than in the above-mentioned chloride based processes of TiN and NbN. The films obtained without zinc were Ta_3N_5, whereas with zinc TaN was deposited, the net reactions being:



$$3TaCl_5(g) + 5NH_3(g) \rightarrow Ta_3N_5(s) + 15HCl(g) \quad (1)$$



$$TaCl_5(g) + Zn(g) + NH_3(g) \rightarrow TaN(s) + ZnCl_2(g) + 3HCl(g) \quad (2)$$

Thus the reducing power of NH_3 is too weak to reduce tantalum(V) in $Ta^{V}Cl_5$ into tantalum(III) in $Ta^{III}N$ but zinc being a more powerful reducing agent is able to do that.

Deposition of TaO_xN_y films was also examined in an attempt to increase the permittivity of Ta_2O_5, which is a widely examined dielectric thin-film material.[8] The TaO_xN_y deposition was realized by depositing first a thin layer of Ta_3N_5 (eq 1) and then oxidizing that with water.

Experimental Section

Films were deposited in a commercial flow type F-120 ALE reactor (Microchemistry Ltd., Finland) operated under a pressure of 10 mbar using nitrogen (99.999%) as a carrier and purging gas. The precursors used were $TaCl_5$ (Merck), Zn (extra pure, Merck), NH_3 (99.999%, Messer Griesheim), and ion-exchanged H_2O. $TaCl_5$ and Zn were evaporated from open boats held at 90 and 380 °C, respectively, and pulsed onto the substrates by inert gas valving.[17] Ammonia and water were led into the reactor from their external reservoirs through needle and solenoid valves. The ammonia flow was adjusted to 8 std $cm^3\ min^{-1}$, during a continuous flow. Soda lime glass substrates measuring $5 \times 5\ cm^2$ were used as substrates. For dielectric measurements, the films were deposited onto indium−tin−oxide (ITO) electrodes sputtered on glass substrates, and were covered by evaporated aluminum electrodes.

Film thicknesses of the transparent films were determined by measuring transmittance spectra in a wavelength region of 370−1100 nm with a Hitachi U-2000 spectrophotometer. The spectra were fitted using a program developed and described by Ylilammi and Ranta-aho.[26] This procedure also gave the refractive indices and absorption coefficients in the region of weak absorption. To obtain the absorption coefficients in the strong absorption region, the procedure described by Swanepoel[27] was used. Film crystallinity was studied with a Philips MPD 1880 powder X-ray diffractometer with Cu Kα radiation. Morphology and cross sections of the films were examined using a Zeiss DSM 962 scanning electron microscope (SEM). A Link ISIS energy-dispersive X-ray spectrometer (EDX) installed to the SEM equipment was used for measuring film thicknesses and their impurity contents. The EDX results were analyzed with a GMR Electron Probe Thin-Film Microanalysis program.[28]

Elemental depth profiles of the films were measured by time-of-flight elastic recoil detection analysis (TOF-ERDA),[29−31] except for hydrogen which was analyzed by nuclear resonance broadening (NRB) technique.[30,31] A 5-MV tandem accelerator EGP-10-II of the Accelerator Laboratory was used for the both measurements. TOF-ERDA analysis were performed with 28 MeV $^{107}Ag^{5+}$ primary ions, whereas in NRB $^{15}N^{2+}$ ions were used for exciting the 6.39-MeV resonance of the reaction $^{1}H(^{15}N,\alpha\gamma)^{12}C$. Because of multiple scattering from heavy elements, their quantitative determination by TOF-ERDA is complicated and unreliable, thus making it impossible to determine accurate Ta concentrations. Rather, the Ta contents were evaluated from the measured nitrogen contents assuming a composition of Ta_3N_5 or TaN, against which the impurity contents were normalized. As an exception, the elemental contents in the most heavily contaminated Ta_3N_5 films deposited at 200 and 250 °C were calculated from a charge neutrality in a film consisting of the measured H^+, N^{3-}, O^{2-}, and Cl^- and the unmeasured Ta^{5+} ions. In the case of the TaO_xN_y films, the O/N ratio was determined.

Resistivities of the conducting films were measured by using the standard four-point probe technique. The dielectric properties of the insulating films were evaluated by sandwiching them between ITO and Al electrodes patterned in the form of stripes perpendicular to each other. The crossing points of the electrode stripes formed capacitors with an area of 29.4 mm^2. Capacitances were measured at 10 kHz frequency using a HP 4275A multifrequency LCR meter, and current−voltage characteristics with an HP 4140 pA meter/dc source.

Results and Discussion

1. Ta_3N_5 Films. Transparent and colored Ta_3N_5 films were deposited by an alternate supply of $TaCl_5$ and NH_3.

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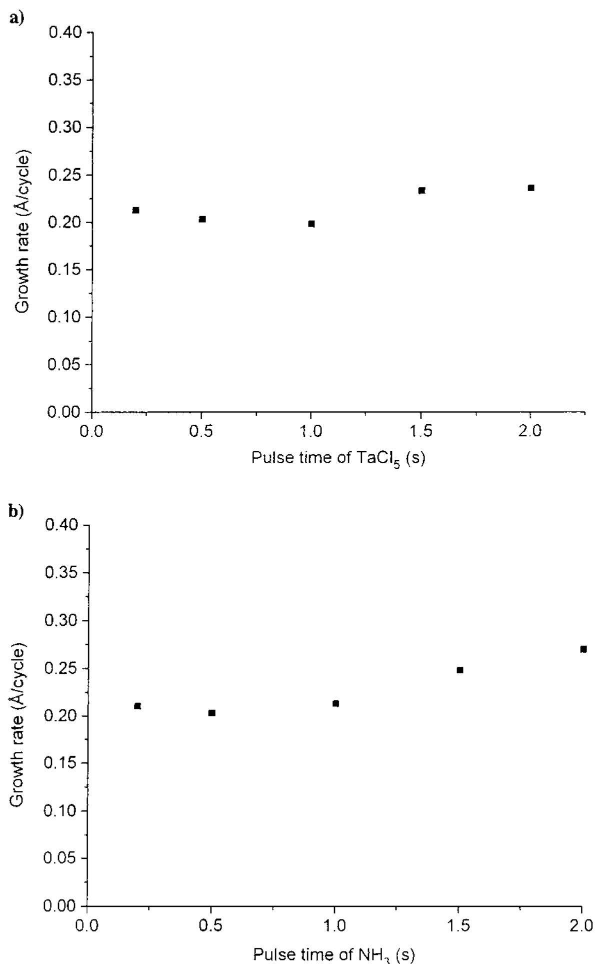

Figure 1. Growth rate of Ta_3N_5 films as a function of $TaCl_5$ (a) and NH_3 (b) pulse times at 400 °C.

To confirm that the film deposition occurs by a self-limiting mechanism as characteristic of ALD, the growth rate was examined as a function of pulse time of both precursors at 400 °C (Figure 1). Despite some scattering in the data, it is evident that in both cases the growth rate saturates to a level of 0.22−0.24 Å/cycle. The saturation is reached already with 0.2 s pulse times, thereby indicating fast surface reactions. On the other hand, the growth rate is low, far below one monolayer per cycle. Such a low growth rate is very typical for ALD growth of transition metal nitrides,[21−25] whereas for the main group nitrides much higher deposition rates above 1 Å/cycle have usually been measured.[32−38] Reasons for the low deposition rates of the transition metal nitrides are not known, however; but obviously they are related to unfavorable interactions between transition metal nitride surfaces and the corresponding halides used as precursors. Fundamental studies on the chemisorption and reaction mechanisms of the transition metal halides on the nitride surfaces will be needed for a thorough understanding of the film growth. In addition, desorption, readsorption and other possible reactions of hydrogen halides formed as byproducts should be examined.

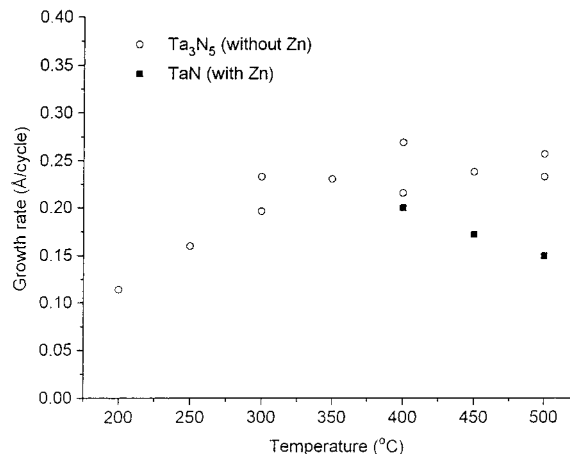

Figure 2. Growth rates of Ta_3N_5 and TaN as a function of growth temperature for processes using 0.2-s pulse times for all precursors. The double points given for Ta_3N_5 at three temperatures represent repeated experiments.

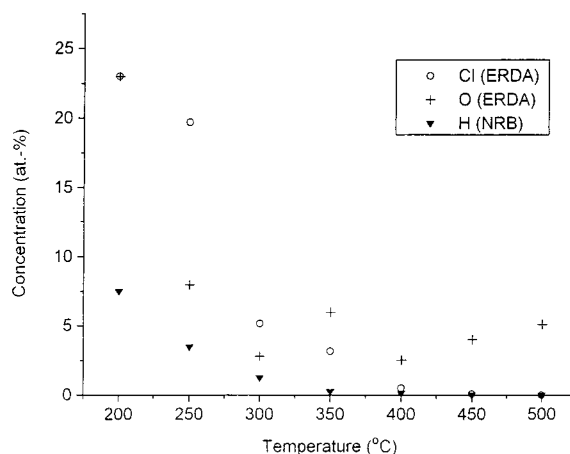

Figure 3. Growth temperature dependence of impurity contents in Ta_3N_5 films as analyzed by TOF-ERDA and NRB.

Figure 2 depicts the Ta_3N_5 deposition rate as a function of the growth temperature. Above 300 °C the deposition rate is constant but below that it decreases with decreasing temperature. This decrease is apparently caused by kinetic reasons, i.e., the surface reactions are too slow to reach the saturation within the given pulse times of 0.2 s.

Film composition was a strong function of deposition temperature (Figure 3). The films deposited at 200 and 250 °C were heavily contaminated with chlorine, oxygen, and hydrogen, whereas the films grown at 300 °C or above were rather pure, containing only a few atomic percentages of impurities. The purest films were obtained at 450 and 500 °C, where the chlorine and hydrogen contents were below 0.1 atom %. However, these films contained still 3−5 atom % of oxygen, the content of which showed no temperature dependence above 300 °C. The chlorine and hydrogen impurities apparently originate from the precursors due to incom-

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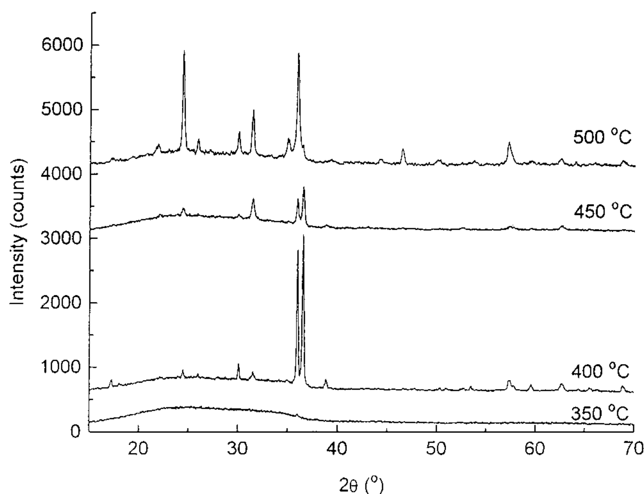


Figure 4. XRD diffractograms of Ta_3N_5 films deposited at different temperatures. All the reflections match with the orthorhombic Ta_3N_5 reference data[39] which is, however, incompletely indexed and, therefore, also these diffractograms are presented without indexing.

plete reactions at low temperatures. Oxygen, in turn, is most probably incorporated during air exposure after the film growth, even though impurities in the nitrogen carrier gas are also a possible source of oxygen. For comparison, the Ta_3N_5 films deposited by CVD from $Ta(NMe_2)_5$ and NH_3 at 200−400 °C contained somewhat less oxygen, 1−2 atom %, than the present films, but their hydrogen contents were much higher: 25 and 11 atom % at 200 and 400 °C, respectively.[11]

XRD measurements revealed that the films deposited at 400 °C and above were polycrystalline Ta_3N_5 while those deposited at lower temperatures were amorphous (Figure 4). The polycrystalline structure was verified by SEM which also showed that the grains formed a densely packed film structure.

The resistivities of the Ta_3N_5 films were highly dependent on the deposition temperature. For films deposited below 400 °C, resistivities higher than 200 Ω cm were measured while above that the resistivities decreased into a range of 0.5 Ω cm. This change in resistivity is obviously connected to the crystallization of the films (cf., Figure 4). The Ta_3N_5 films deposited by CVD were reported to have resistivities higher than 1 Ω cm.[11,14]

Optical properties of the films were evaluated from transmittance spectra. Both an indirect and direct band gap could be detected by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ vs $h\nu$, respectively, where α is the absorption coefficient and $h\nu$ the photon energy, i.e., the both plots showed a linear part which was extrapolated to obtain the band gap as an intercept with the abscissa. The indirect band gap varied in the range of 1.9−2.1 eV and the direct band gap within 2.7−2.9 eV (Figure 5a). Only the film deposited at 200 °C had higher band gaps of 2.7 eV (indirect) and 3.1 eV (direct) because of its high oxygen content (cf., Figure 3), i.e., the film was more like TaO_xN_y rather than Ta_3N_5. However, a similar band gap value was reported for Ta_3N_5 films deposited by CVD even though their oxygen content was below 1−2 atom %.[11] The reason for this difference is unclear. Refractive index and absorption coefficient, both given for a reference wavelength of 1 μm, increased with increasing

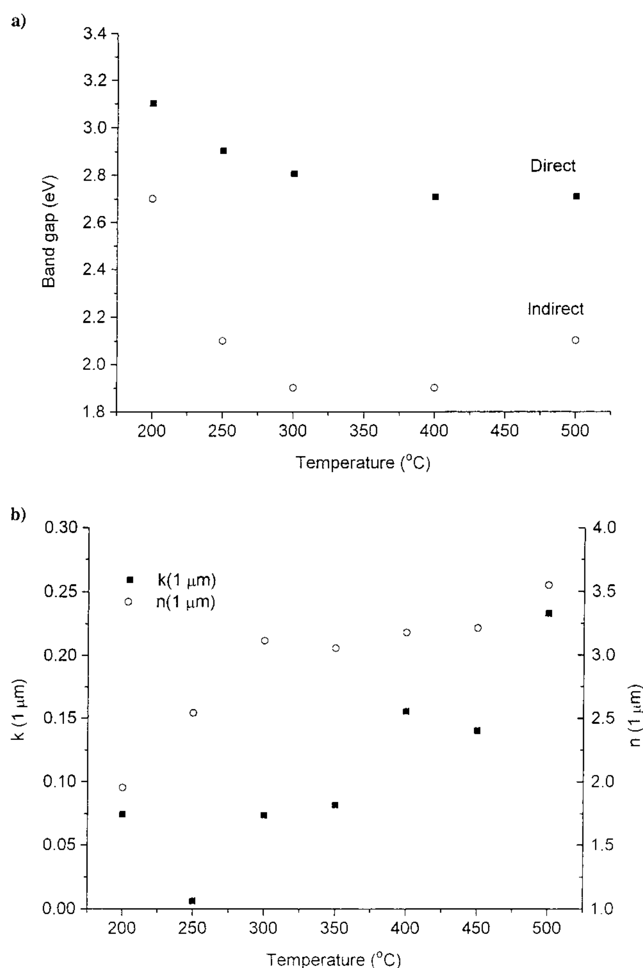


Figure 5. Optical properties of Ta_3N_5 films: (a) direct and indirect band gaps, and (b) refractive indices and absorption coefficients at a wavelength of 1 μm.

deposition temperature (Figure 5b). Improvements in both film density and purity are thought to be responsible for the increase of the refractive index. Because the absorption coefficient includes not only the true absorption but also scattering losses, its increase may arise from scattering caused by surface roughening accompanying the crystallization (cf. Figure 4). On the other hand, the observed 2 orders of magnitude decrease of the resistivity around 400 °C has no direct counterpart in the optical properties. This seems to confirm that the change in resistivity is due to the crystallization of the film.

2. TaN Films. TaN films with a metallic shine were obtained using an exposure sequence $TaCl_5$−Zn−NH_3. The difference in comparison with the $TaCl_5$−NH_3 process is clear; unlike NH_3, zinc is capable of reducing tantalum from its formal oxidation state of +V to +III. The temperature region for the TaN growth was in this study relatively narrow 400−500 °C, being limited by the low volatility of zinc and softening temperature of the glass substrates and the glassware in the reactor. It was observed that similar to $TaCl_5$ and NH_3 (Figure 1), also for Zn 0.2-s pulse time was long enough for reaching the growth rate saturation (Figure 6). At 400 °C, the growth rate was the same as the one obtained for Ta_3N_5, i.e., about 0.2 Å/cycle, but it decreased slightly with increasing temperature to 0.15 Å/cycle at 500 °C (Figure 2).

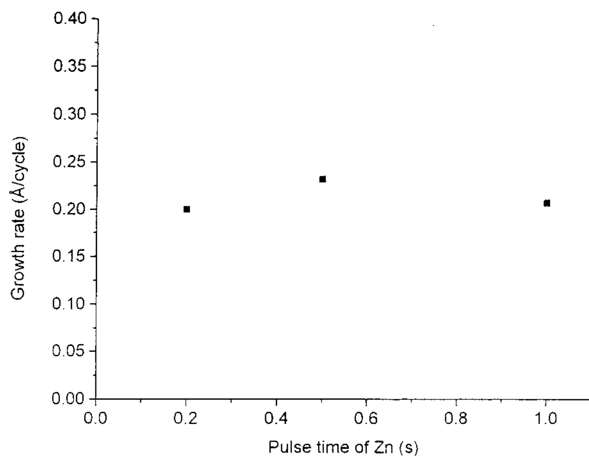


Figure 6. Growth rate of TaN versus the zinc pulse time at 400 °C.

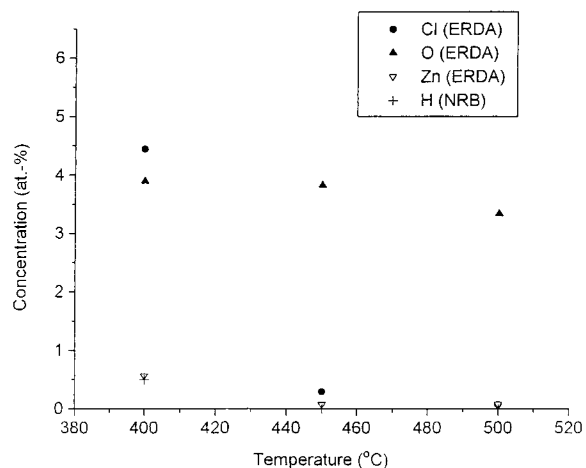


Figure 7. Impurity contents in TaN films as measured by TOF-ERDA and NRB.

TaN films contained 3−4 atom % oxygen independent of the deposition temperature (Figure 7). The film deposited at 400 °C contained about 4 atom % chlorine, but in the films deposited at 450 and 500 °C, the chlorine content decreased to 0.3 atom % and below 0.1 atom %, respectively. The film grown at 400 °C contained also about 0.5 atom % both hydrogen and zinc, whereas in the other films the contents of these impurities were below or at the level of the detection limits of NRB and TOF-ERDA, respectively, i.e., below 0.1 atom % (Figure 7). TaN films deposited by CVD from $Ta(=N^tBu)(NEt_2)_3$ were reported to contain 5−10 atom % oxygen and 10 atom % carbon[5] while those obtained from $[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_n$ contained about 3 atom % oxygen and undetectable (by XPS) amounts of carbon.[12] The carbon content of the films made from the single-source $Ta(=NEt)(NEt_2)_3$ precursor varied strongly as a function of reactor pressure and temperature, being at lowest around 5−10 atom %.[15]

TaN films were polycrystalline with the cubic structure (Figure 8). The peak intensities and widths imply that the film deposited at 400 °C was only weakly crystalline and had a small crystallite size, whereas those deposited at higher temperatures were more properly crystallized. SEM images again confirmed the polycrystalline and dense structure.

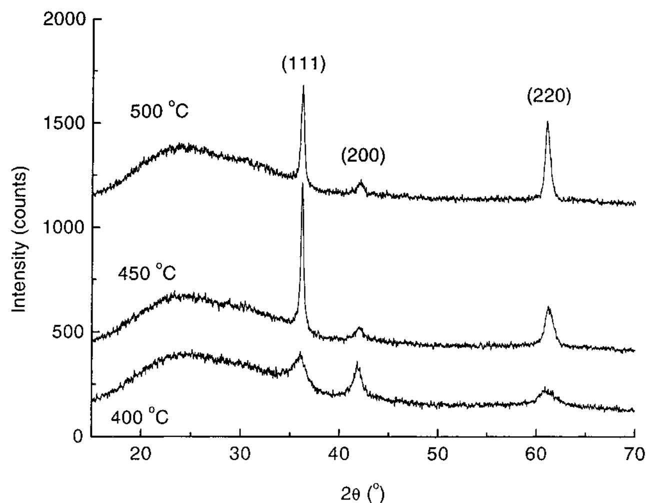


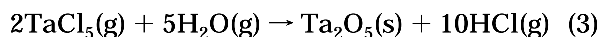
Figure 8. XRD diffractograms of TaN films deposited at different temperatures. The indexing refers to the cubic TaN (data from ref 40).

Table 1. Composition of TaO_xN_y as a Function of the $TaCl_5-NH_3$ to $TaCl_5-H_2O$ Cycle Ratio As Analyzed by TOF-ERDA

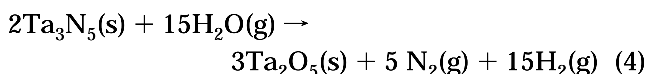
$TaCl_5-NH_3$ to $TaCl_5-H_2O$ cycle ratio	O/(O+N)	Cl (atom %)
10/1	0.999	0.6
100/1	0.82	1.3
500/1	0.63	4
1000/1	0.23	8

The resistivities of the TaN films were about 9×10^{-4} Ω cm with no significant temperature dependence. For comparison, the TaN films deposited by CVD at high temperatures around 1000 °C from $TaCl_5$, N_2, and H_2 had somewhat lower resistivities of $(2-3) \times 10^{-4}$ Ω cm.[14] The resistivities of the films made by CVD from $Ta(=N^tBu)(NEt_2)_3$ decreased with increasing deposition temperature from 1×10^{-2} Ω cm at 500 °C to 2×10^{-3} at 600 °C, and eventually to 9×10^{-4} Ω cm at 650 °C.[5] By contrast, a surprisingly high resistivity of 0.21 Ω cm was reported for the films grown from $[TaCl_2(NNMe_2)(NHNMe_2)(NH_2NMe_2)]_n$ by CVD at 600 °C.[12] For sputtered TaN films resistivities of 5.7×10^{-4} and 2.6×10^{-4} Ω cm have been measured.[1,3]

3. TaO_xN_y Films. TaO_xN_y films were deposited at 300 °C using varying amounts of $TaCl_5-NH_3$ and $TaCl_5-H_2O$ deposition cycles. The former cycles deposit Ta_3N_5 (eq 1) but the latter both deposit Ta_2O_5 (eq 3) and oxidize the underlying Ta_3N_5 (eq 4):



$$2TaCl_5(g) + 5H_2O(g) \rightarrow Ta_2O_5(s) + 10HCl(g) \quad (3)$$



$$2Ta_3N_5(s) + 15H_2O(g) \rightarrow 3Ta_2O_5(s) + 5\,N_2(g) + 15H_2(g) \quad (4)$$

The latter reaction was found to be favorable which may be understood by the high affinity of tantalum toward oxygen. For example, when the $TaCl_5-NH_3$ to $TaCl_5-H_2O$ cycle ratio was 10:1, the resulting film was completely oxidized, and even with a cycle ratio of 100:1, the O/(O+N) ratio in the film was as high as 0.82 (Table 1). In a separate experiment a 120-nm-thick Ta_3N_5 film was first deposited and then exposed to water vapor for 10 min. In this film the O/(O+N) ratio

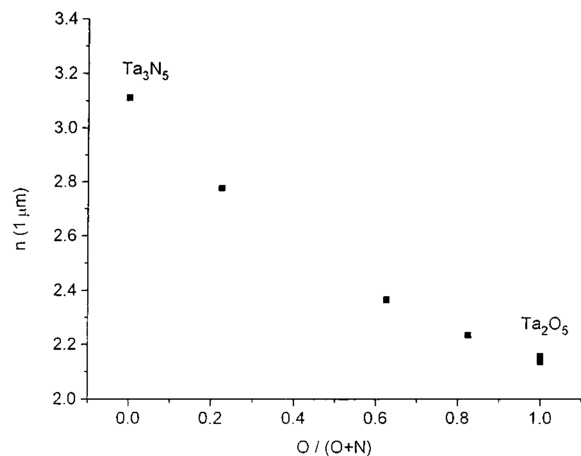


Figure 9. Refractive indices of TaO_xN_y films as a function of the O/(O+N) ratio.

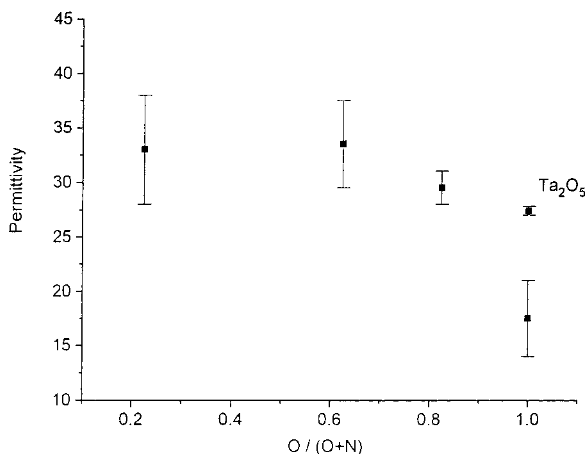


Figure 10. Dielectric permittivity of TaO_xN_y films as a function of the film composition.

remained rather low at 0.13 which implies that oxidation of Ta_3N_5 by water vapor is efficient only for thin Ta_3N_5 layers. On the other hand, despite the periodic oxidation by a single water pulse after as many as 1000 $TaCl_5-NH_3$ pulses which are supposed to result in a Ta_3N_5 thickness of about 20 nm, no periodic variation was observed in the oxygen depth profile by TOF-ERDA. The chlorine residue content in the TaO_xN_y films correlated with the nitrogen content increasing with it (Table 1). Although the deposition rate of Ta_2O_5 (about 0.6 Å/cycle) is much higher than the 0.2 Å/cycle of Ta_3N_5, the deposition rate of TaO_xN_y was only 0.10–0.15 Å/cycle.

The refractive index of the TaO_xN_y films varied nearly linearly as a function of the oxygen content from 3.1 for Ta_3N_5 to 2.1 for Ta_2O_5 (Figure 9). Dielectric permittivities of the TaO_xN_y films were somewhat higher (30–34) than the permittivity of Ta_2O_5 (26) but there existed quite a bit of scatter in their values (Figure 10). The difference between the Ta_2O_5 made directly from $TaCl_5$ and H_2O and that obtained with a $TaCl_5-NH_3$ to $TaCl_5-H_2O$ cycle ratio of 10:1 should be noted. The leakage currents of the Ta_2O_5 and TaO_xN_y were similar and rather high as it is common for high permittivity materials, like Ta_2O_5, especially in their as-deposited state.[8] Nonetheless, in all the TaO_xN_y films the leakage current density did not exceed 4 mA/cm^2 at an electric field of 1 MV/cm, the value of which we have measured for Ta_2O_5 deposited by ALD at 250 °C,[41] and the film made with a $TaCl_5-NH_3$ to $TaCl_5-H_2O$ cycle ratio of 100:1 (O/(O+N) = 0.82) exhibited even a slight improvement in comparison with Ta_2O_5. Together with the increased permittivity (Figure 10), these results imply that TaO_xN_y could be a potential dielectric material. However, the scatter in the permittivity needs to be eliminated and also the growth rate should be increased.

Conclusions

TaN, Ta_3N_5, and TaO_xN_y films were deposited by the atomic layer deposition technique. When only $TaCl_5$ and NH_3 were used as precursors, Ta_3N_5 films were obtained, but addition of elemental zinc as an additional reducing agent gave TaN films. TaO_xN_y films were obtained by depositing first thin Ta_3N_5 layers and then oxidizing them by single water pulses.

The Ta_3N_5 films deposited at the lowest temperatures were rather heavily contaminated with oxygen, chlorine, and hydrogen but the impurity contents decreased along with the deposition temperature. The films grown at 450 and 500 °C were the purest with less than 0.1 atom % hydrogen and chlorine and about 3 atom % oxygen. Ta_3N_5 films were amorphous when deposited below 400 °C above which they became polycrystalline. The film resistivity was obviously connected to the film crystallinity since the amorphous films deposited below 400 °C had a resistivity of 200 Ω cm while the polycrystalline ones grown above 400 °C had much lower resistivity of 0.5 Ω cm.

Since TaN films could be obtained only with zinc which has rather low vapor pressure, these films could be grown only at 400 °C and above. Again the highest purity was achieved at the highest growth temperature examined, 500 °C, where only about 0.1 atom % chlorine was left in the films and no zinc or hydrogen could be detected. However, also these films contained about 3 atom % oxygen, the origin of which is attributed to postdeposition oxidation. The TaN films were polycrystalline and their resistivity was in the order of 9×10^{-4} Ω cm.

The composition of the TaO_xN_y films could be controlled by the number of the Ta_3N_5 deposition cycles between the oxidizing water pulses. The permittivities of these films were somewhat higher (30–34) than the permittivity of Ta_2O_5 (26), and because the leakage current properties were equal or better, TaO_xN_y offers a potential alternative to Ta_2O_5 as a high permittivity insulator.

The low deposition rate below 0.25 Å/cycle is a major problem shared by all the above processes. In fact, the low deposition rate is common to all transition metal nitride ALD processes studied so far. Since by now only metal halides have been studied as precursors in these ALD processes, it is important to examine in the future whether the deposition rate may be increased by using other metal compounds, like alkyl amides.

(39) Joint Committee on Powder Diffraction Standards, card 19-1291.

(40) Joint Committee on Powder Diffraction Standards, card 32-1283.

(41) Kukli, K.; Ritala, M.; Leskelä, M. *J. Electrochem. Soc.* **1995**, *142*, 1670.

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