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Low temperature chemical vapor deposition of titanium nitride films from tetrakis(ethylmethyamido)titanium and ammonia

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Abstract

Titanium nitride films were deposited from tetrakis(ethylmethyamido)titanium and ammonia at 250–350°C and 0.7–2 Torr by thermal chemical vapor deposition. The effect of process parameters such as deposition temperature, precursor temperature, carrier gas flow, and ammonia flow on the film properties was studied, the apparent activation energy of film growth was calculated and the film composition was determined. The film step coverage was better than for films grown from tetrakis(dimethylamido)titanium and ammonia. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chemical vapor deposition; Diffusion barrier; Nitrides; Titanium nitride

1. Introduction

Titanium nitride (TiN) is thermally stable and has low contact resistance, low electrical resistivity, etch-stop capability and resistance to corrosion [1]. It is recognized as an excellent barrier material in microelectronics applications where it serves to prevent damage to Si during plug filling by tungsten. It also acts as an adhesion layer for tungsten, which is needed because tungsten adheres poorly to silicon dioxide due to formation of tungsten oxide. TiN also serves as a barrier against diffusion of aluminum in plugs and interconnects, and as an anti-reflection coating in the interconnect stack. Finally, TiN, along with other early transition metal nitrides, is under consideration as a diffusion barrier material for copper metallization.

Good conformality is essential for optimizing TiN barrier properties [2,3]. Until recently, TiN films have been deposited for microelectronics applications by physical vapor deposition (PVD) processes such as reactive sputtering [4,5] and reactive evaporation [6]. The directional nature of these processes can result in non-conformal deposition and discontinuities in severe cases. Thin non-uniform film

deposition on the bottom and sidewalls of vias causes degradation of the barrier properties. These types of problems are more severe in sub-0.5 μm contacts and vias.

In contrast to the PVD processes, chemical vapor deposition (CVD) offers the possibility of both low temperature deposition with the use of suitable precursors and excellent conformality because the reactants and intermediates have the ability to diffuse over and on the surface. The chemical vapor deposition of TiN from metal halides and metal-organic precursors has been reported.

A precursor combination of TiCl₄ and NH₃ is commonly used to grow TiN by CVD [7–11]. There are several factors, however, that limit the application of this chemistry. Films grown below 550°C, for example, contain more than 5 at.% chlorine [10] and incorporation of chlorine impurity is deleterious to the reliability of devices. Higher deposition temperatures lower the chlorine concentration [10] but the temperatures are too high for metallization and step coverage deteriorates as well. Another drawback of the TiCl₄–NH₃ system is the formation of ammonium salts in the cold zones of the reactor, which causes particle formation.

The limitations of the TiCl₄-based route led to a study of TiI₄ as an alternative inorganic precursor. Highly conformal (90% conformality) films were grown by using a TiI₄–NH₃ system at low temperatures (< 450°C) [12,13]. The iodine concentration in the films was less than 2 at.%. The iodine

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contamination did not affect the performance of TiN as a diffusion barrier because the activation energy for iodine diffusion is high due to its size. TiI_4 is a solid at room temperature, however, and has to be sublimed into the CVD reactor. This provides less control over precursor delivery compared to liquid precursors [14].

Interest in the use of metal-organic precursors to TiN has grown because of the problems associated with the use of titanium halide precursors and the realization that metal-organic precursors offer the possibility of lower deposition temperatures compatible with multi-level metallization schemes. The titanium amide compounds tetrakis(dimethylamido)titanium (TDMAT; $Ti[N(CH_3)_2]_4$) [15–28] and tetrakis(diethylamido)titanium (TDEAT, $Ti[N(CH_2CH_3)_2]_4$) [16,18,28–30] are the most studied metal-organic precursors to TiN but other related precursors [31,32] have been examined as well. The first use of a metal amide compound and ammonia as precursors to nitride films was in 1990 by Fix et al. [15,16], who deposited TiN from TDMAT- NH_3 in an atmospheric-pressure CVD process. Later, Raaijmakers [18] found that films grown by low pressure CVD using TDMAT- NH_3 were inferior to those obtained from TDEAT- NH_3 under similar growth conditions. Films from TDMAT- NH_3 had higher resistivity, lower film density, higher oxygen and carbon content and lower conformality compared to those grown using TDEAT- NH_3 . The TDMAT- NH_3 films could be grown with higher growth rates, however, due to the higher volatility of TDMAT compared to TDEAT. Sun and Tsai [19] have recently studied the effect of deposition parameters in the TDMAT- NH_3 and TDEAT- NH_3 systems on film properties. Metal-organic CVD (MOCVD) processes appear to overcome most of the problems of the $TiCl_4$ - NH_3 based process, but carbon contamination and step coverage are still issues. In addition, films grown by MOCVD may be porous, which causes film properties to vary on exposure to air.

Another approach is plasma-assisted CVD using either metal-organic [33–35] or halide [36,37] precursors. Intemann et al. [33] attributed the poor step coverage of films grown from metal-organic precursors in thermal processes to the high reactivity of the precursors with ammonia. Apparently rapid consumption of the precursor at the surface results in the process not being in the surface-reaction-controlled regime, which is necessary for conformal deposition. In place of ammonia, Intemann et al. [33] used reactive but long lived radicals that were created by activating mixtures of N_2/H_2 in a downstream microwave plasma. Highly conformal depositions were obtained when only hydrogen was used but film resistivity was high. Weber et al. [34,35] used an ECR plasma to obtain low resistivity films but the conformality was low. Similarly, Akahori et al. [36] used the $TiCl_4$ - NH_3 system in an ECR plasma process to deposit low resistivity films ($<200 \mu\Omega \text{ cm}$) at temperatures $>450^\circ\text{C}$, but the sidewall coverage was low. Increasing the plasma power decreased the film resistivity, but the deposition rate decreased.

In this paper we describe the preparation of titanium nitride in a thermal low-pressure CVD reactor by using tetrakis(ethylmethylamido)titanium (TEMAT, $Ti[N(CH_3)(CH_2CH_3)]_4$), a hybrid of TDMAT and TDEAT, and ammonia as precursors. The effects of deposition temperature, precursor temperature, carrier gas flow, and ammonia flow on film properties are reported. In previous work involving TEMAT, Shin et al. [38] thermally decomposed TEMAT in the absence of ammonia to prepare highly conformal films that had high resistivities (2500–15000 $\mu\Omega \text{ cm}$). In addition, Min et al. [39] have deposited TiN films by using an atomic layer deposition technique that alternately supplied TEMAT, argon and ammonia at 0.5 Torr and substrate temperatures of 150–400°C. The highly conformal films contained about 4 at.% carbon but film resistivities were not reported.

2. Experimental

Experiments were carried out in a cold-wall vertical quartz reactor, which is shown schematically in Fig. 1. Ammonia (Matheson ULSI grade) and argon (UHP grade) were introduced through a 0.5 cm diameter inlet at the top of the reactor. The gas flow rates were regulated by mass flow controllers (MFC). The 20-cm long top portion of the reactor has a diameter of 4 cm and the 27-cm bottom portion has a diameter of 7.5 cm, with the transition region being 3.5 cm. The flask containing the precursor was placed in a heated silicone oil bath. The bath temperature was controlled by a thermostat and the oil was stirred by using a magnetic stirrer. Argon carrier gas was bubbled through the liquid TEMAT precursor and was delivered into the chamber through a quartz annular ring, which was positioned over the wafer. This ring design was used to provide a uniform distribution of the precursor over the wafer. The annular ring had an outer diameter of 3.5 cm, inner diameter of 2 cm, and six 1 mm holes along the inner diameter, facing the ring center. The delivery line between the precursor flask and the ring was wrapped with heating tape and kept at a temperature of about 80°C to prevent condensation of the precursor vapor.

The substrate was held in place by two spring-loaded clamps on a 4 cm diameter stainless steel susceptor that was heated to the desired temperature using a cartridge heater (Omega, 120 W). The temperature of the susceptor was measured by using a K-type thermocouple and was controlled with a thermostat. The susceptor was positioned 5 cm below the ring. The chamber was evacuated through a side arm near the bottom of the reactor using an Edwards E2M40 pump. A throttle valve was used to control the pressure, which was measured by a pressure transducer (MKS, Baratron) gauge. The reactor leak rate was 1.66×10^{-4} Torr/min. A liquid nitrogen trap was placed between the reactor outlet and the pump to condense unreacted precursor, reaction by-products, and ammonia.

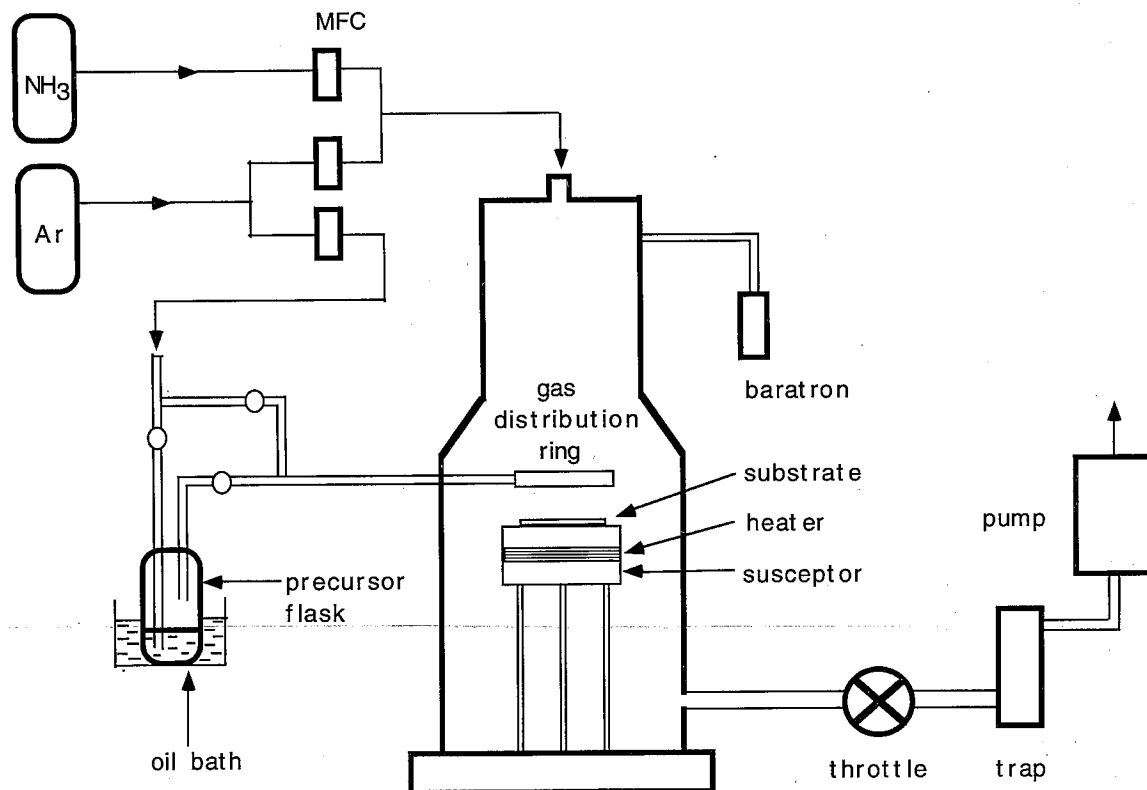


Fig. 1. Schematic of the experimental apparatus.

Before the start of each film deposition, argon gas was introduced into the reactor for about 2 h, and then ammonia for about 10 min. At the end of each experiment, the ammonia flow was continued for 10–15 min after the precursor flow was stopped to ensure complete reaction of precursor trapped in the delivery line. The wafer was removed from the reactor after it had cooled to room temperature, which took about 2 h. Ar gas flow was maintained during the cool down period. Depositions were carried out in the temperature range 250–350°C at pressures of 0.7–2 Torr. The carrier gas flow was varied between 5 and 20 sccm. The Ar diluent gas flow was maintained at 600 sccm while ammonia flows of 600 sccm and 800 sccm were used.

Unpatterned boron-doped (100) silicon wafers were used as substrates (2 × 2 cm). The wafers were prepared by soaking them in a 4:1 solution of H₂SO₄/H₂O₂ for 10 min, rinsing with de-ionized water and then drying with nitrogen gas. The wafers were then soaked in a 10% HF/90% deionized water solution for 2 min followed by a rinse of deionized water to remove the native oxide. The wafers were dried again before being placed immediately in the reactor. Wafers with a SiO₂ pattern from Texas Instruments (Dallas, TX) were used for step coverage studies.

TEMAT was synthesized in the following way [38]. A solution of TiCl₄ (7.59 g, 0.04 mol) in benzene (10 ml) was added dropwise to a cold (0°C) slurry of LiNMeEt (10.9 g, 0.168 mol) in ether (200 ml). The mixture was allowed to warm slowly to room temperature after the addition of TiCl₄

was completed. The mixture was then refluxed for 3 h, which resulted in a white solid precipitating from the solution. The volatile components were removed under vacuum, the residue was extracted with benzene (10 × 10 ml), and the extracts were combined and filtered through dry Celite. Benzene was removed from the filtrate by vacuum distillation, and the residue, a dark green-orange viscous liquid, was held under vacuum for 6 h. Vacuum distillation (85°C, 0.05 mm Hg) afforded the product as a light-orange viscous liquid (yield 7.16 g, 70%). The purity was checked by ¹H NMR (>98%). All manipulations were carried out under inert atmosphere and dry oxygen-free solvents were used.

Sheet resistances were measured by the four-point probe method immediately after removing the substrate from the reactor to minimize the effect of film exposure to air. Scanning electron microscopy (SEM) was used to evaluate step coverage. Film composition was determined using X-ray photoelectron spectroscopy (XPS). The XPS system was equipped with a 5-keV Ar⁺ sputter gun. An aluminum X-ray source at 3 kV and 400 W was used. The electron energy analyzer was calibrated to the Ag 3d_{5/2} line at 368.3 eV.

The estimated error in the activation energy was ±0.4 kJ/mol. The error is mostly due to the uncertainty in the growth rates (±5 Å/min), which in turn is the result of the variation observed in the film thicknesses. Film thicknesses were measured by using scanning electron microscopy and step profilometry. Thicknesses used in the calculation of growth

rates varied from 800–1800 Å depending on the growth conditions and the time the film was grown. Thickness measurements were taken at several points on the individual samples and for different samples deposited under the same experimental conditions. The SEM data indicated the surface roughness was small compared to the film thickness; hence, errors in film thickness measurement due to film roughness were negligibly small. The susceptor temperature varied $\pm 1^\circ\text{C}$, which also had little effect on the calculation of the activation energy.

3. Results and discussion

Fig. 2 shows the film growth rate plotted against the susceptor temperature. The growth rate decreased from 66 Å/min at 350°C to 42 Å/min at 250°C. The oil bath temperature was 40°C and base case values (shown in Table 1) were used for other parameters. The apparent activation energy was calculated from an Arrhenius plot to be about 12.3 (± 0.4) kJ/mol. This value is between the activation energies calculated from growth rates in the literature for films grown from TDEAT-NH₃ and TDMAT-NH₃. Films grown, for example, by Raaijmakers [18] at 10 Torr from TDMAT-NH₃ at 200–400°C and TDEAT-NH₃ at 60–450°C had activation energies of 14.4 and 5.8 kJ/mol, respectively. Katz et al. [23] obtained an activation energy of 14.4 kJ/mol for films grown from TDMAT-NH₃ at 300–350°C. Activation energies for surface reaction controlled CVD processes are on the order of 50–100 kJ/mol, while those for transport controlled processes are on the order of 10 kJ/mol [18]. Thus, the process reported here appears to be transport limited. Sun and Tsai [19] obtained a value of 6.75 kJ/mol for the TDEAT-NH₃ system, which is in the transport-controlled regime. They used a pressure of 0.8 Torr, which is close to the pressure (1 Torr) used in this work.

Fig. 3 shows a plot of film resistivity as a function of the susceptor temperature. The oil bath temperature was 40°C and Table 1 values were used for the other deposition parameters. The resistivity increased with decreasing tempera-

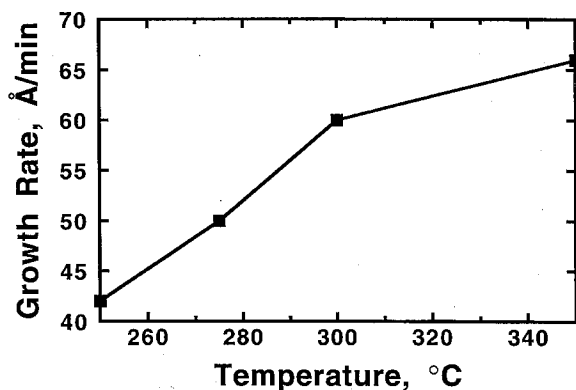


Fig. 2. Plot of film growth rate as a function of susceptor temperature. The precursor temperature was 40°C and the other parameters are those listed in Table 1.

Table 1
Base case deposition parameters

| | |
|----------------------------|-----|
| Ammonia flow (sccm) | 600 |
| Argon, diluent (sccm) | 600 |
| Argon, carrier (sccm) | 10 |
| Pressure (Torr) | 1 |
| Precursor temperature (°C) | 30 |
| Susceptor temperature (°C) | 350 |

ture; for example, the resistivity increased from 1450 $\mu\Omega$ cm at 350°C to 2500 $\mu\Omega$ cm at 250°C. Also plotted in Fig. 3 are the resistivities obtained by Raaijmakers for TDEAT-NH₃ and TDMAT-NH₃ depositions at 10 Torr [18]. Compared to our films, the sensitivity of the resistivity to the deposition temperature is less than for films grown by Raaijmakers from TDEAT-NH₃ and comparable to those grown from TDMAT-NH₃. Films grown from TDEAT-NH₃ by Sun and Tsai [19] and from TDMAT-NH₃ by Ishihara et al. [22], Katz et al. [23], and Sandhu et al. [26] showed similar behavior. For MOCVD TiN films, a higher susceptor temperature decreases the hydrogen content [16] and carbon content, and makes the film more crystalline [22]. All these factors contribute to decreased resistivities at higher deposition temperatures.

The oil bath (precursor) temperature and the carrier gas flow rate regulate the amount of precursor delivered to the system. Fig. 4 shows the growth rates and resistivities obtained at different oil bath temperatures under otherwise identical conditions. The resistivity increased from 1000 to 1450 $\mu\Omega$ cm and the growth rate increased from 37.5 to 66 Å/min as the oil bath temperature was raised from 30 to 40°C. The increased growth rate can be attributed to higher precursor flow at the higher oil bath temperatures. For a constant ammonia flow rate, however, increasing the precursor flow also decreases the ammonia-to-precursor ratio, which results in films with higher resistivity. Precursor delivery is also regulated by the carrier gas flow rate.

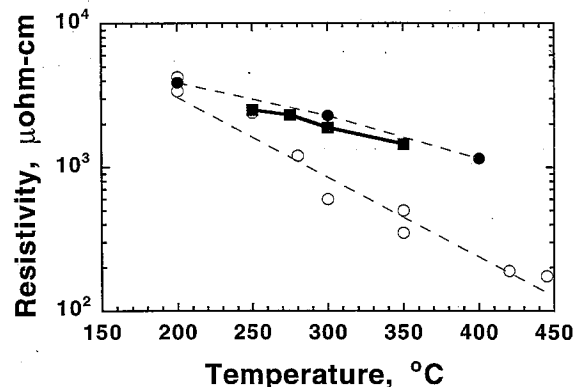


Fig. 3. A plot of film resistivity as a function of the susceptor temperature is shown by the filled squares. The precursor temperature was 40°C and other parameters were those in Table 1. Also plotted are the resistivities of films deposited from TDMAT-NH₃ (●) and TDEAT-NH₃ (○), as reported by Raaijmakers [18].

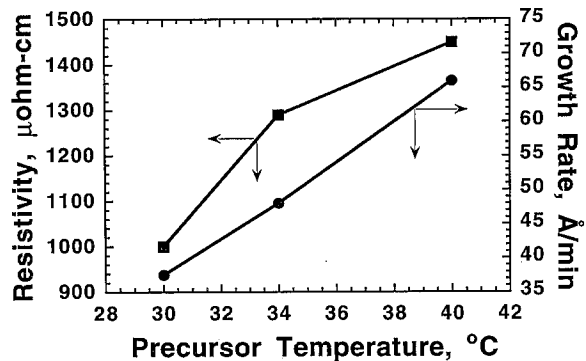


Fig. 4. Plots of growth rate and resistivities at different precursor temperatures. The other parameters were those listed in Table 1.

Increasing the carrier gas flow increased the amount of precursor delivered and resulted in higher growth rates, but the resistivity increased from $700 \mu\Omega \text{ cm}$ at 5 sccm Ar to $1150 \mu\Omega \text{ cm}$ at 20 sccm Ar carrier gas flow under otherwise identical conditions. The increased resistivity with increasing bubbler temperature and carrier gas flow is probably due to an increase in carbon content of the films, which increases because the ammonia-to-precursor ratio is lowered. The effect of lowering the ammonia-to-precursor ratio is to allow precursor intramolecular decomposition (via β -hydrogen activation) to become competitive with the intermolecular transamination chemistry and intramolecular α -hydrogen activation that serves to rid the titanium amide compound of the carbon containing ethyl methyl amide ligands [15,16,28].

Experiments were conducted at different NH_3 /precursor flow ratios to study the effect of ammonia concentration. NH_3 flow rates of 600 and 800 sccm were used. The total pressure (1 Torr) was unaffected by the difference in NH_3 flow rate. The results are shown in Fig. 5. The higher NH_3 flow rate resulted in films with lower resistivity ($700 \mu\Omega \text{ cm}$) and a lower growth rate ($28 \text{ \AA}/\text{min}$). The decreased resistivity is probably due to a lower carbon content in the films [15,16]. Katz et al., found that increasing NH_3 flow resulted in lower carbon content and resistivity for films prepared from TDMAT- NH_3 [23], and Raaijmakers and

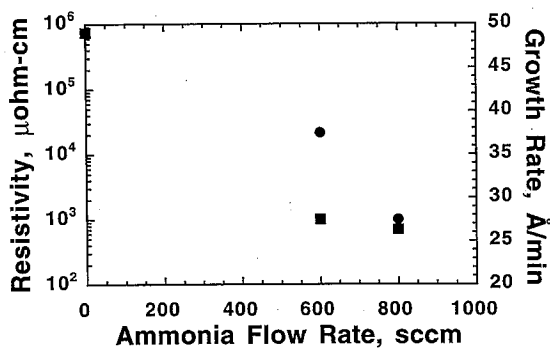


Fig. 5. Plots of growth rate (circles) and resistivities (squares) at different ammonia flow rates. The other parameters were those listed in Table 1.

Yang [29] and Sun and Tsai [19] reported decreasing film resistivity with increasing ammonia flow. The resistivity of a film prepared by thermally decomposing TEMAT in the absence of ammonia was $\approx 10^6 \mu\Omega \text{ cm}$. The high resistivity is undoubtedly due to a high carbon content in the film. High resistivities in films grown from $\text{Ti}(\text{NR}_2)_4$ ($R = \text{CH}_3, \text{CH}_2\text{CH}_3$) without ammonia have previously been observed [19,23,40]; for example, Fix et al., showed that thermal decomposition of TDMAT in the absence of ammonia results in films with carbon contents of 30–35 at.% [40].

Fig. 6 shows film resistivity plotted as a function of growth rate for films grown at 350°C under different conditions of pressure (0.7–2 Torr) and precursor temperature (30– 40°C). Data points from Fig. 5 are included. Although there is an appreciable scatter in the data, there is a trend of obtaining a lower resistivity with a lower growth rate. Presumably, this is a result of decreasing carbon and/or hydrogen content.

Fig. 7 shows the change in resistivity with time on exposure to air of a film grown by using the base case conditions in Table 1. The resistivity increased rapidly initially, reaching a value about 40% higher than the initial value after 8 h. Beyond this time, the rate of increase in resistivity was not as rapid. The resistivity was about 56% higher than the initial value after 72 h.

An XPS depth profile of a film grown under base conditions is shown in Fig. 8. To avoid possible degradation of the film by exposure to air, prior to the analysis the film was stored under argon and the transfer to the XPS vacuum chamber was carried out quickly. After sputtering into the bulk, the film contained about 47 at.% titanium, 40 at.% nitrogen ($\text{Ti}/\text{N} = 1.2$), 9 at.% oxygen and 2 at.% carbon. The source of oxygen in the film is presumably air that leaked into the CVD system during deposition and the carbon is a result of intramolecular decomposition of TEMAT via β -hydrogen activation [15,40]. The hydrogen content was not determined but it is expected to be high based on work by Fix et al. [16] who measured about 9–33 at.% hydrogen in TiN films grown by atmospheric pressure CVD from TDMAT- NH_3 . Titanium nitride films grown

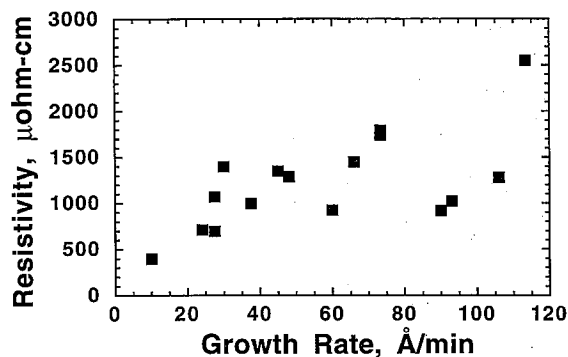


Fig. 6. Plot of film resistivity as a function of the growth rate at various pressures (0.7–2 Torr), precursor bath temperatures (30– 40°C) and ammonia flow rates (600–800 sccm). The susceptor temperature was 350°C .

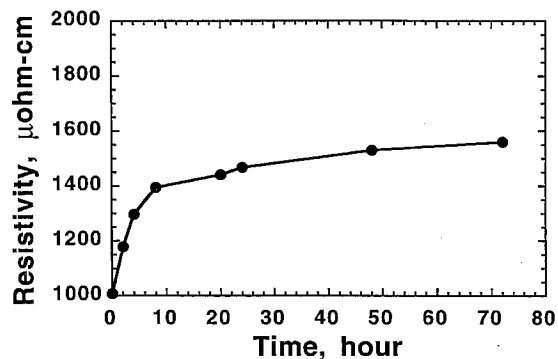


Fig. 7. Plot showing the variation of film resistivity as a function of time upon exposure to air. The film was grown under the conditions listed in Table 1.

by Prybyla et al. [27] from TDMAT-NH₃ at 10⁻⁴ Torr and 300°C had a Ti/N ratio of about 1.15, and those grown by Fix et al. [15,16] from TDMAT-NH₃ at 300°C and atmospheric pressure had a Ti/N ratio of around 0.9:

Fig. 9a shows an SEM of a film deposited on a 1:1 trench. The deposition temperature was 300°C with the other conditions being those in Table 1. A step coverage (defined as the ratio of the film thickness at the center of the trench bottom to that on the top surface) of 33% was obtained. Raaijmakers [18] deposited TiN films from TDMAT-NH₃ and TDEAT-NH₃ at 300°C on a trench with a similar aspect ratio but at a higher pressure of 10 Torr. He found that films deposited from TDMAT-NH₃ had a step coverage of 20% while those deposited from TDEAT-NH₃ had a step coverage of 85%. We would expect the step coverage of our films to be greater than 33% at higher deposition pressures since it has been reported that better step coverage is obtained at higher pressures [18], but due to limitations in our reactor design we could not test this hypothesis. Fig. 9b shows the SEM of a film deposited from TEMAT without

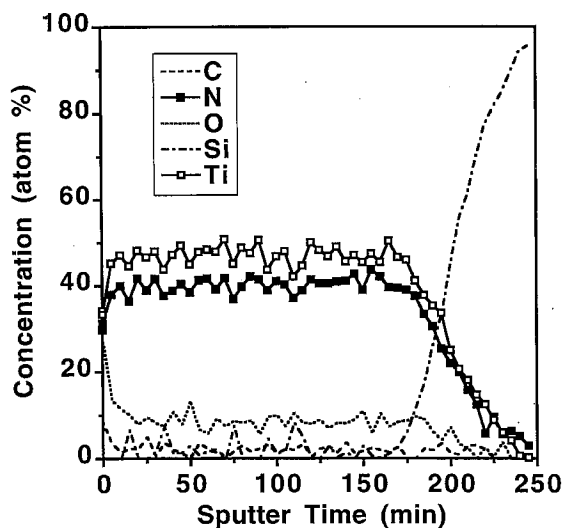


Fig. 8. Depth profile from XPS data for a film grown under the conditions listed in Table 1.

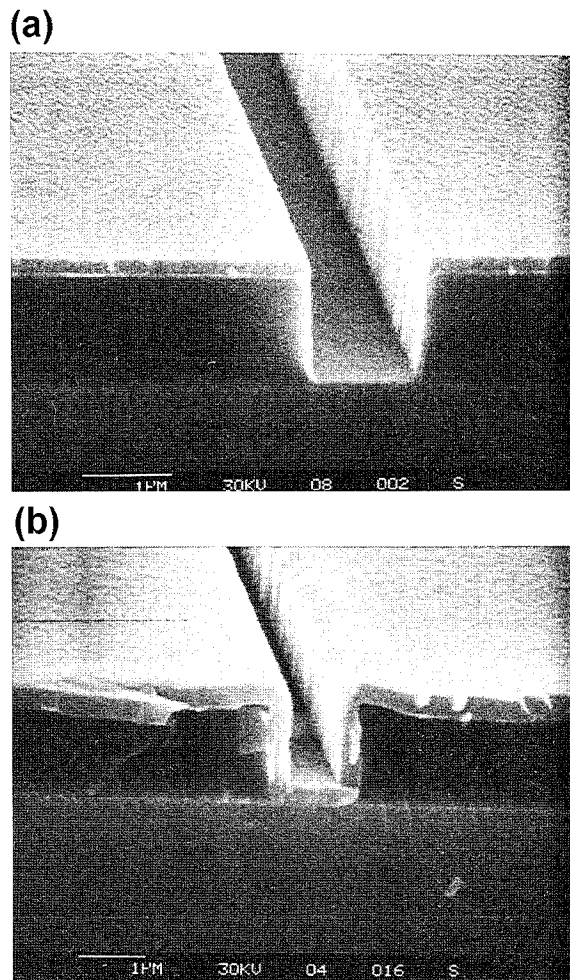


Fig. 9. Scanning electron micrographs of films grown (a) with and (b) without ammonia on a 1:1 trench. The susceptor temperature was 300°C and the other parameter values were those in Table 1.

ammonia. Nearly 100% step coverage was obtained. This is consistent with the work of Raaijmakers and Yang [29] who obtained highly conformal films by thermally decomposing TDEAT without ammonia. They attributed the high conformality to the decomposition being in the surface controlled regime.

4. Conclusion

Titanium nitride films were grown by thermal CVD from tetrakis(ethylmethylamido)titanium (TEMAT) and ammonia at 250–350°C in a cold wall reactor at pressures of 0.7–2 Torr. The apparent activation energy was found to be about 12.3 kJ/mol, a value that is between those reported for films grown from TDMAT-NH₃ and TDEAT-NH₃. The effect of deposition temperature, precursor temperature, carrier gas flow, and ammonia flow on the film properties was studied. Film resistivity decreased with increasing deposition temperature, decreasing precursor temperature,

decreasing carrier gas flow and increasing ammonia flow. At a constant deposition temperature and system pressure, the film growth rate can be regulated by the precursor temperature and the carrier gas flow. The growth rate appears to be a factor governing film resistivity. The film resistivity increased with time upon exposure to air. A film grown at 350°C and 1 Torr was nearly stoichiometric ($Ti/N = 1.2$) and contained 9 at.% oxygen and 2 at.% carbon. The step coverage of the films grown from TEMAT-NH₃ was better than that of films grown from TDMAT-NH₃.

Acknowledgements

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