

MOCVD of Titanium Nitride from a New Precursor, $\text{Ti}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$

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A new TiN precursor, tetrakis(ethylmethyamido)titanium (TEMAT), has been developed and characterized in terms of volatility and stability under CVD process conditions. In addition, titanium nitride thin films were prepared by means of metal organic chemical vapor deposition (MOCVD) technique, using TEMAT as a precursor. Depositions on SiO_2 patterned wafers were carried out at 250–350 °C and the pressure of 1 Torr, yielding growth rates from 50 to 1550 Å/min. Excellent bottom coverage of ~90% over 0.35 μm contacts with an aspect ratio of 2.9 was achieved at 300 °C. This excellent bottom coverage could be explained by the fact that the TiN deposition was surface reaction controlled with an activation energy of ~1.0 eV. AES analysis revealed the low carbon level (~18 at. %) in TEMAT-sourced TiN films, which was ~2 \times lower than that in TiN films prepared from tetrakis(diethylamido)titanium (TDEAT). We proposed the possible reaction mechanism responsible for the low carbon contents in the films, based on the byproduct gases detected by quadrupole mass spectrometer (QMS). TEMAT also produced better crystalline and less air-reactive films than tetrakis(dimethylamido)titanium (TDMAT). Consequently, the TEMAT compound can be a promising precursor for MOCVD TiN.

Introduction

TiN films have been employed for several technology applications because of its hardness, high temperature stability, chemical inertness, and electrical properties. A possible application of TiN films in microelectronics industry includes its use as an excellent barrier material^{1,2} for Al planarization gap filling of contacts and vias and as an adhesion and nucleation layer for chemical vapor deposition (CVD) of blanket tungsten.³ Physical vapor deposition (PVD) has been commonly used to deposit TiN films for these purposes. However, with decreasing feature size in ULSI, the further application of PVD TiN becomes increasingly difficult due to its poor conformality. The CVD of TiN has been proposed as an alternative to PVD TiN because CVD processes, unlike PVD processes, tend to be surface activated and provide conformal coatings over high aspect ratio structures.

Two types of titanium compounds such as titanium tetrachloride (TiCl_4) and metal–organic based chemis-

try have been widely used for CVD of TiN. TiCl_4 -based TiN has shown remarkable step coverage even in submicron contacts with an aspect ratio of 7.0, as well as excellent film properties including barrier properties and electrical resistivities.^{4–9} However, this inorganic chemistry for CVD TiN suffers from some severe drawbacks. Chlorine contamination in TiN films leads to serious corrosion in Al/Cu metallization. To reduce the chlorine content to a low level (<1 at. % Cl), high substrate temperatures of more than 600 °C are needed. The high-temperature process, however, cannot be applied in modern multilevel metallization schemes. An additional drawback of this chemistry is the formation of adducts and NH_4Cl salt particles, which brings severe particle generation in the production of microelectronic devices.¹⁰ Recently, high-quality TiN films from the reaction of metal–organic compounds and ammonia have been deposited at low temperatures (<400 °C) and

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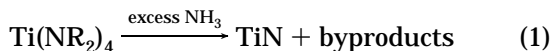
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high process pressures. This low-temperature process can be applied to vias as well as contacts, which makes this process very attractive in multilevel metallization. TDMAT^{11–17} and TDEAT^{18,19} are widely used as the Ti precursor in various MOCVD processes because of their commercial availability. It has been understood that TiN films are deposited between 200 and 400 °C via a transamination reaction of dialkylamido derivatives of titanium [Ti(NR₂)₄], where R = Me and Et complexes, and ammonia:



where R = methyl, ethyl, or butyl.

This process, however, reveals poor step coverage, probably due to the highly reactive intermediates produced in the gas phase. In addition, this binary chemistry process also suffers from particle contamination arising from high operating pressure (i.e., 50 Torr).

To address these problems encountered with these binary chemistries, recent work on CVD of TiN has been focused on a single-source-based process by using only a titanium–organic compound.^{11,12,20} MOCVD of TiN films from TDMAT has been well characterized. The process provides excellent step coverage. However, it produces unstable films, i.e., they are air-reactive and have high resistivity and a high level of oxygen contamination. In contrast, TiN films prepared from TDEAT have a lower resistivity and a negligible level of oxygen contamination and show excellent stability in resistivity upon air exposure. But the TDEAT process yields a relatively degraded conformality, compared with the TDMAT process. Therefore, a new process using a new Ti precursor needs to be developed to produce high-quality TiN films with improved conformality.

In this work, a new titanium compound (TEMAT) has been prepared and explored. This new chemistry, possessing chemical and physical properties between those of TDMAT and TDEAT, was expected to provide improved film quality without degraded conformality, compared with TDMAT, by using only their advantages in TDMAT and TDEAT. Therefore, the results of step coverage and TiN film quality will be described and compared with those obtained from TDMAT and TDEAT, respectively, to determine the advantages of TEMAT over TDEAT and TDMAT. In addition, we proposed the

Table 1. Deposition Variables for TiN Films from TEMAT

variables	range
substrate temp (°C)	250–350
source temp (°C)	65
chamber temp (°C)	85
carrier gas	He
He flow rate (sccm)	400
pressure (Torr)	1

reaction mechanism of precursor decomposition based on the byproduct gases detected by QMS.

Experimental Section

Synthesis. All manipulations were conducted under an atmosphere of dry nitrogen using Schlenk techniques. Solvents used in the preparation were dried and distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves. The compound LiN(CH₃)C₂H₅ was prepared by the published method.²² Microanalyses were performed at the Korea Advanced Institute of Science and Technology. NMR data were recorded on a Varian Gemini-200 NMR spectrometer by using the protio impurities of the deuterated benzene as the reference for the ¹H NMR spectroscopy.

The compound tetrakis(ethylmethyamido)titanium (TEMAT) was synthesized as follows. The compound LiN(CH₃)C₂H₅ (78.06 g, 1.20 mol) was placed in a 1000 mL Schlenk flask together with 500 mL of dry *n*-hexane. This suspension was cooled to ~78 °C by placing the Schlenk flask into a dry ice and acetone bath. Titanium tetrachloride (TiCl₄, 52.0 g, 0.27 mol) was added slowly to the cooled, rapidly stirred suspension. As the TiCl₄ was added, the mixture immediately turned amber. The mixture was allowed to warm to room temperature slowly and then stirred for 4 h to complete the reaction. The stirring was stopped and then the precipitant was settled down. After that, the solution was filtered through Celite and the solid washed with two 100 mL portions of *n*-hexane. The amber filtrates were combined, and then the volatile components were removed in vacuo leaving a dark amber oily liquid. The compound was purified by vacuum distillation under the condition of 75 °C and 10^{–2} Torr to give a yellow-orange liquid consisting of Ti[N(CH₃)C₂H₅] (bp 60 °C/10^{–2} Torr, yield 60%). ¹H NMR (200 MHz, 20 °C, C₆D₆) δ 1.10 (t, 7 Hz, –CH₂CH₃, 3H), 3.11 (s, –CH₃, 3H), 3.44 (q, 7Hz, CH₂CH₃, 2H). Anal. Calcd for C₁₂H₃₂N₄Ti: C, 51.40; H, 11.53; N, 19.99. Found: C, 51.31; H, 11.28; N, 20.65.

CVD. TiN films were deposited using only TEMAT in a load-locked single wafer type MOCVD reactor that has been previously described elsewhere.¹⁹ The base pressure of the reactor was maintained below 2 × 10^{–6} Torr. The gas delivery line, chamber, and showerhead were heated to prevent condensation of the precursor inside of them. A Baratron pressure gauge installed at the carrier gas line before the liquid bubbler system was used for calculating the flow rates of the precursor. Helium (<99.9999%) was used to deliver the metal–organic precursor to the chamber. In addition, a quadrupole mass spectrometer (MKS) connected to the exhaust line of the chamber was used for detecting byproduct gases as well as for monitoring the tightness of the system. CVD of titanium nitride from Ti[N(CH₃)C₂H₅]₄ was carried out under the conditions described in Table 1.

The sheet resistance and thickness were measured by the four-point probe and the surface profilometer, respectively. Cross-sectional scanning electron microscopy (SEM) was used to determine the step coverage over 0.35–5.0 μm contacts with 2.0–3.0 aspect ratios. Auger electron spectroscopy (AES) depth profiling of the samples revealed the contents of elements including titanium, nitrogen, carbon, and oxygen. X-ray photoelectron spectroscopy (XPS) and X-ray diffractometer

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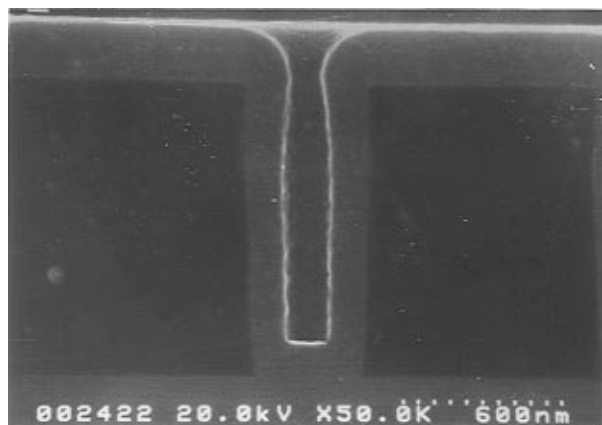
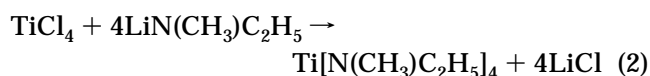


Figure 1. Step coverage of TiN film deposited using TEMAT at 300 °C.

(XRD) were employed to identify chemical bonding configuration of elements and the phases in TiN films, respectively.

Results and Discussion

Synthesis and Characterization. The compound $\text{Ti}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$ was prepared in high yield according to eq 2 and characterized by spectroscopic and analytical techniques:



The relevant physical and chemical properties are summarized briefly here. The compound $\text{Ti}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$ is a yellow-orange liquid at room temperature and changes into white solid immediately after exposure to air. Direct measurement of the vapor pressure of the compound as a function of temperature showed a vapor pressure of 1 Torr at 78 °C.

This vapor pressure is between that of TDMAT (2 Torr at 80 °C) and TDEAT (0.07 Torr at 80 °C). This new chemistry is expected to possess chemical and physical properties between that of TDMAT and TDEAT since the properties of amino group ligated to titanium in TEMAT possess the properties between that in TDMAT and TDEAT. In addition, the compound $\text{Ti}[\text{N}(\text{CH}_3)\text{C}_2\text{H}_5]_4$ has been heated to 90 °C in vacuo for 7 days to investigate the stability of the compound at 90 °C. No decomposition was observed with ^1H NMR spectroscopy, implying that the compound is very stable under these conditions.

Deposition Characteristics. CVD of TiN from TEMAT was carried out at 250–350 °C with He carrier gas. TiN films deposited in these experiments showed an excellent adhesion to silicon substrates as well as SiO_2 coated wafers. The step-coverage in 0.35 μm contacts with 2.9 aspect ratio ranged from 90% to 50%, depending on substrate temperature as well as TiN film thickness. Figure 1 shows the step coverage of ~90% in 0.35 μm contacts for a 1300 Å thick film deposited from TEMAT at 300 °C. It is noteworthy that Sinha et al. and Lee et al.¹⁹ reported the step coverage of 75% in 0.4 μm contact for a 1500 Å TiN film by the thermolysis of TDMAT and that of 50% in 0.5 μm contact for a 950 Å thick film from TDEAT, respectively. Comparison of those results of conformality indicates that the use of TEMAT as a precursor provided improved step coverage.

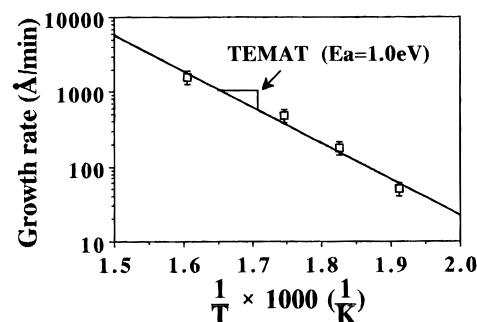


Figure 2. TiN growth rate as a function of reciprocal temperature.

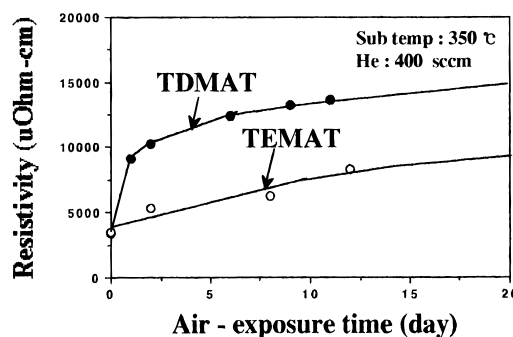


Figure 3. TiN resistivity variations as a function of air-exposure time.

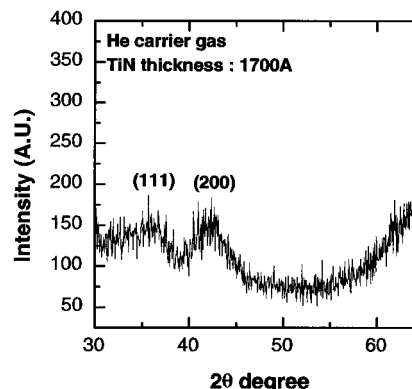


Figure 4. X-ray diffraction patterns of 1700 Å thick TiN film deposited at 250 °C.

The results of the deposition rate experiments at 250–350 °C can be seen in the Arrhenius plot of Figure 2. The curve shows the growth rate in the range 70–1050 Å/min as well as the high positive temperature activation energy of 1.0 eV. This high activation energy indicates that all the reactions at 250–350 °C are surface reaction limited, which can explain the excellent step coverage obtained using TEMAT.

The resistivity of as-deposited TiN films from TEMAT was in the range 2500–15 000 $\mu\Omega$ cm, depending on the substrate temperature. Increasing the temperature from 250 to 350 °C continued to decrease the resistivity to 2500 $\mu\Omega$ cm and further increase in temperature caused a slight increase of the resistivity by 50–100 $\mu\Omega$ cm. The resistivity of as-deposited MOCVD TiN films generally increases with air-exposure time, probably due to porous microstructures and impurities of the films. The experiments have been conducted at the substrate temperature of 350 °C to investigate the effect of the precursor type on the stability of TiN films in resistivity. Figure 3 reveals the variation of the resistivities of TiN

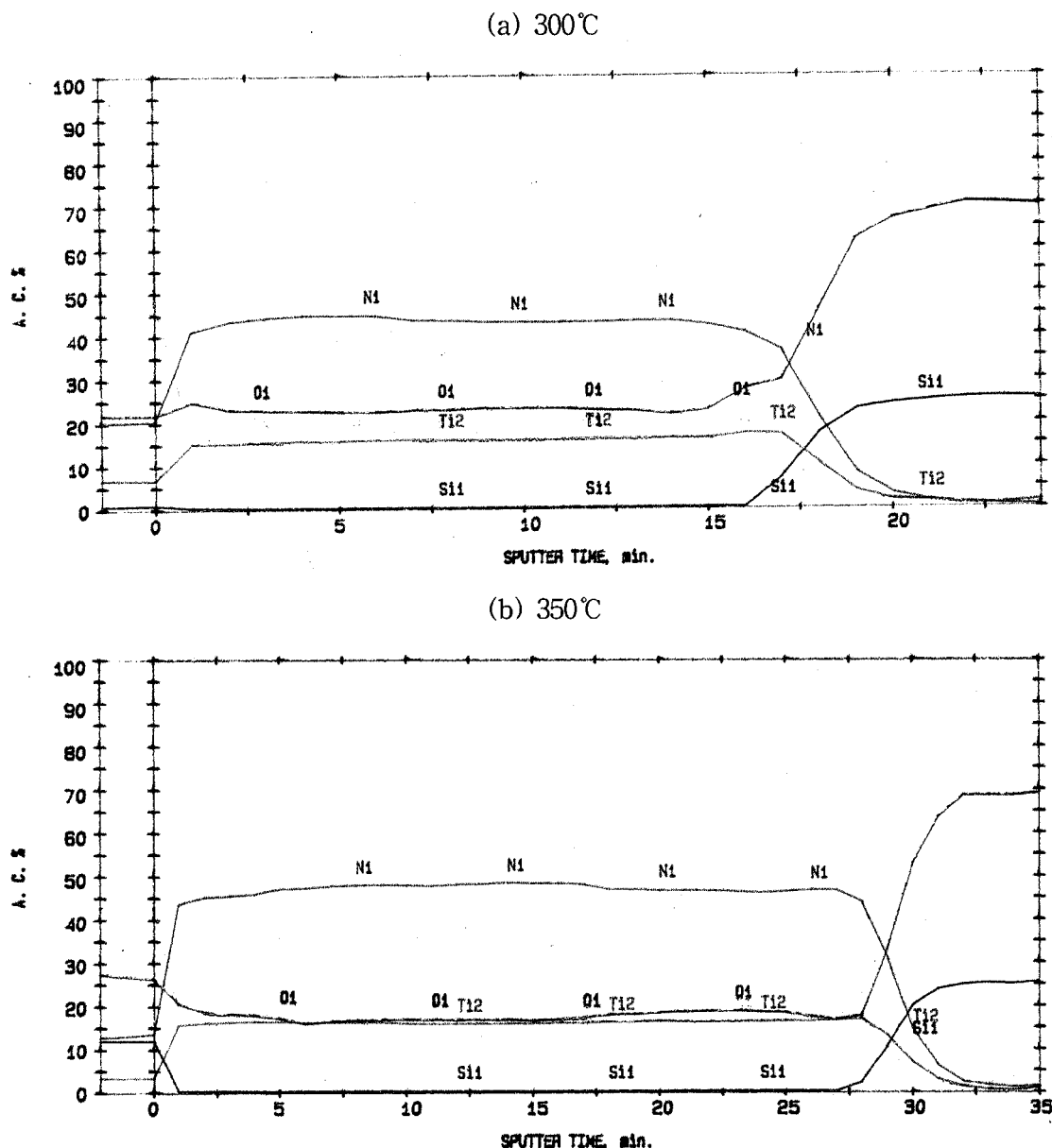


Figure 5. AES depth profiles of TiN films deposited using TEMAT at (a) 300 and (b) 350 °C.

films deposited from TEMAT and TDMAT, respectively, with air-exposure time. The resistivity of TDMAT-sourced TiN film was on the order of $3500 \mu\Omega \text{ cm}$ as-deposited and increased rapidly through $14\,000 \mu\Omega \text{ cm}$ further upon air exposure. In the case of a TEMAT-sourced TiN film, similar but less increase in resistivity during air-exposure was observed, probably indicating that TEMAT produced more dense TiN films than TDMAT.

Thin-film XRD patterns of 1700 \AA thick TiN film deposited at 350°C , as shown in Figure 4, reveal the microcrystalline TiN film whose grain size was estimated to be about 20 \AA by using a Scherrer formula.²⁴ The XRD peaks around 18° and 21° correspond to the TiN(111) peak and the TiN(200) peak, respectively.

The Auger depth profile of the TiN film from TEMAT in Figure 5, shows about 18 at. % carbon and 10 at. % oxygen in the film. Since the impurities distributions appear to be fairly uniform, it is obvious that carbon

came from the Ti precursor. However, oxygen incorporation into the film was not expected to result from the precursor; instead it came from the oxygen in air. Because of the use of tight-vacuum MOCVD system, high-purity precursor and carrier gas would not allow any oxygen incorporation into the films during the TiN deposition. TDMAT-sourced TiN²⁵ was also reported to undergo similar but more serious oxygen stuffing when exposed to air; the oxygen content of as-deposited films was ~ 2 at. % oxygen and increased up to the level of ~ 20 at. % or more during air exposure. Oxygen stuffing occurring in MOCVD TiN, especially at room temperature, may be attributed to the presence of titanium loosely connected with carbon (or nitrogen) in porous TiN films. The porous microstructure facilitates the diffusion of oxygen into the films and loosely bound titanium can capture the oxygen through easy breaking of the bonds to carbon (or nitrogen).

It is also noted that the use of the TEMAT precursor lowered the carbon content significantly to 18 at. % C,

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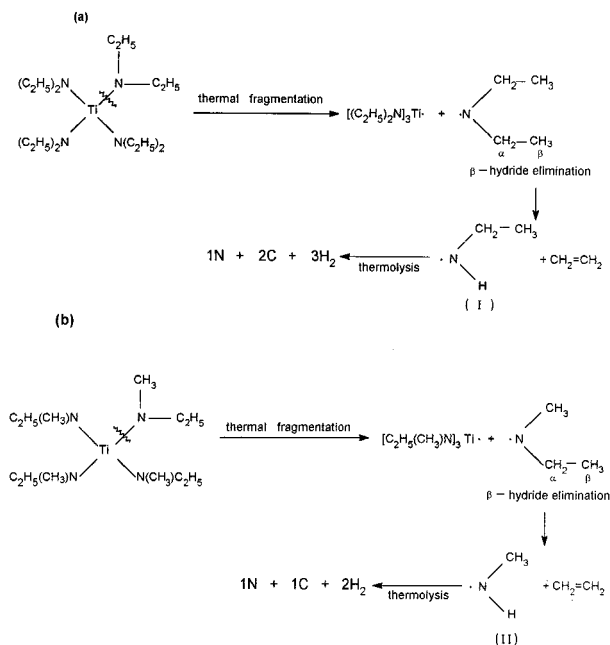


Figure 6. Hypothetical reaction schemes for single-source process CVD using the titanium alkylamino precursors: (a) TDEAT and (b) TEMAT.

compared with about 30 at. % C in TiN films prepared from TDEAT¹⁹ at 250–350 °C. We speculated that the β -hydride elimination reaction of the ethylmethyamido fragment occurring in the thermolysis of TEMAT accounted for the lower carbon contents in TEMAT-sourced TiN films. We proposed here the possible reaction mechanisms for the titanium alkylamido precursors as shown in Figure 6. TDEAT produces the alkylamido fragments (I) containing two moles of carbon while one mole of carbon is in the fragment (II) of TEMAT. These fragments might be the origin of the carbon in the films. These proposed reactions were supported by the QMS detection of the byproduct gas such as C_2H_4 in our experiments.

XPS data for the film show the element chemical bonding. In Figure 7, XPS carbon 1s region for the film deposited from TEMAT consists of two peaks at binding energies of 282 and 284.6 eV that are characteristic of carbon attached to titanium and organic carbon, respectively. It is observed that the amounts of organic and titanium-bound carbon are similar for the film deposited from TEMAT and the similar ratio of organic to titanium-bond carbon in amount was also reported for TiN film

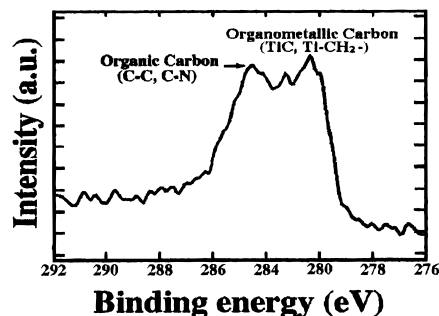


Figure 7. XPS C_{1s} spectra obtained for TiN film prepared from TEMAT at 350 °C.

from TDMAT, possibly indicating that the same reaction mechanism would be responsible for the deposition of TiN.

Conclusions

Thermal MOCVD of titanium nitride from tetrakis(ethylmethyamido)titanium was carried out at 250–350 °C and the pressure of 1 Torr. It is seen that the deposition occurs in a surface reaction controlled over the temperature range studied. As a result, an excellent step coverage of $\sim 90\%$ in $0.35\ \mu\text{m}$ contacts with 2.9 aspect ratios was obtained at the 300 °C deposition. In addition, TiN growth rate was in the range 50–1550 Å/min, depending on the substrate temperature. The resistivity of TiN films prepared at 350 °C was $\sim 2500\ \mu\Omega\ \text{cm}$ as-deposited and increased to $\sim 8000\ \mu\Omega\ \text{cm}$ 12 days after air exposure. XRD analysis indicated that TiN films consisted of microcrystalline structure with grain size of approximately 20 Å. It is also noted that TEMAT gave TiN films with very low carbon content (~ 18 at. %), compared ~ 30 at. % carbon in TDEAT-sourced TiN. We speculated that β -hydride elimination reaction might take place during the ethylmethyamido fragmentation in the thermolysis of TEMAT and allow deposition of titanium nitride films with lower carbon impurities.

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