# Step Coverage and Material Properties of CVD Titanium Nitride Films from TDMAT and TDEAT Organic Precursors

Anthony J. Toprac[1], Shi-Qing Wang[1,2], Joshua Musher[3] and Roy G. Gordon[3]
[1] SEMATECH, 2706 Montopolis, Austin, TX 78741-6499
[2] Also with Fairchild Research Center, National Semiconductor, Santa Clara, CA 95052
[3] Harvard University, Dept. of Chemistry, Cambridge MA 02138

Titanium nitride (TiN) films serve an important function as an adhesion layer and diffusion barrier in contact and via plug structures of ULSI devices. In this work, TiN films were deposited by chemical vapor deposition (CVD) at atmospheric pressure using the tetrakis (dimethylamido) titanium (TDMAT) and tetrakis (diethylamido) titanium (TDEAT) organic precursors over a range of temperatures and ammonia partial pressures. The step coverage and morphology of these films was evaluated at these various conditions by SEM of cross-sectioned contacts. In addition, material properties such as resistivity, surface roughness, and stoichiometry were assessed at some of the operating conditions.

## Introduction

Chemical Vapor Deposition (CVD) of titanium nitride (TiN) films produces more conformal films in contact and via structures than those deposited by the current technology of Physical Vapor Deposition (PVD). Chlorine-free titanium nitrides can be produced at relatively low temperatures (less than 400 °C) by CVD using metal-organic compounds. CVD TiN from two of these compounds, TDMAT and TDEAT, is currently being developed for commercial application. In this work, CVD films deposited from both these precursors were evaluated.

## Experimental

Films were deposited at atmospheric pressure in a prototype belt furnace from the Watkins-Johnson Company, model WJ-956. An inconel mesh belt, heated from below, delivered substrates to the deposition zone at 190-480 °C. Reactant gases were injected perpendicular to the substrates through three nozzles located approximately 3 mm above the substrate. Diluted $NH_3$ passed through the center nozzle, and diluted metal-organic precursor vapor passed through the adjacent outer nozzles. Laminar flow conditions were used (Reynolds number $< 30$), though some turbulent mixing occurred near the inlets when dilution flows were too high. The injector head was cooled to 110-130 °C, providing a cold wall reactor configuration. A series of high volume nitrogen curtains and exhausts prevented atmospheric air from reaching the deposition zone.



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TDMAT (99.999 % purity, Schumacher Corp.) was vaporized in a heated stainless steel bubbler. Precursor vapor pressures were calculated based on measurements by Schumacher Corp., with an estimated variability of $\pm$ 5 % from a value of 3.36 torr at 80 $\pm$ 1 °C bubbler temperature. Carrier gas ( $N_2$ ) flow rates were varied to change TDMAT flow rate. The bubbler effluent was further diluted with 4.4 to 14 standard liters/minute (slm) of $N_2$ .

For the TDEAT precursor, bubbler delivery was not possible due to the very low vapor pressure of TDEAT at temperatures low enough to avoid precursor decomposition over time. Instead, a prototype Direct Liquid Injection system developed by MKS Instruments was used to evaporate TDEAT. This system consisted of a precision metering pump delivering liquid precursor to a vaporizer designed to volatilize the precursor with minimal exposure to elevated temperature. With full volatilization, 1.06 $\times 10^{-3}$ slm of gas-phase TDEAT was delivered using a pumping rate of 20 microliters/min of liquid precursor.

Depositions were performed on sections of silicon wafers with blanket thermal oxide or patterned PETEOS oxide with contact holes etched in the oxide. Average contact aspect ratio was 2.1 with a standard deviation of 0.2 for the nominal 0.45 $\mu$ contacts used in this study. Bottom step coverage (deposition in contact bottom as a percent of deposition on field) was determined by SEM of cross-sectioned contact structures.

Stoichiometry of CVD TiN films was determined by Auger Electron Spectroscopy (AES) analysis calibrated against RBS analysis. AES analyses were performed in the PHI 670 FE-Auger system using a 10 keV 10 nA electron beam. The samples were sputtered with a 3 keV Ar ion beam rastered over a 2x2 mm area. These sputter conditions removed 77 Å of $SiO_2$ per minute. The Auger sputter depth profile data was treated with a data massage program to compensate for the spectral overlap of Ti and N. The quantification is still very rough (because of the difficulties in characterizing a standard), but we believe the trends indicated by this data are accurate.

### Experimental Results

The results of bottom step coverage measurements at three different deposition temperatures are indicated in Figure 1 as a function of the ratio of $NH_3$ and TDEAT inlet flow rate. At 370 °C, there was a steep fall from 80 % step coverage with no $NH_3$ to 45 % with the addition of 3.5:1 $NH_3$ /TDEAT. A similar fall in step coverage with the addition of 30:1 $NH_3$ /TDEAT was seen for deposition at 280 °C; subsequent decrease in step coverage with a large increase in $NH_3$ (113:1) was much smaller. The trend of decreasing step coverage with increasing $NH_3$ was not seen in the high temperature deposition using TDEAT at 420 °C. This trend was, however, exaggerated in the results using TDMAT (not shown), with a drop from 94 % step coverage with no ammonia to 15 % step coverage with the addition of 1.1 $NH_3$ /TDMAT at 370 °C. In all the films, conformality in terms of sidewall coverage was improved over PVD results [4], with approximately the same coverage on the sidewall as on the bottom itself.

Results for resistivity of the deposited TiN films versus $NH_3$ /TDEAT ratio are shown in Figure 2. The same trend exhibited in the step coverage results are observed for

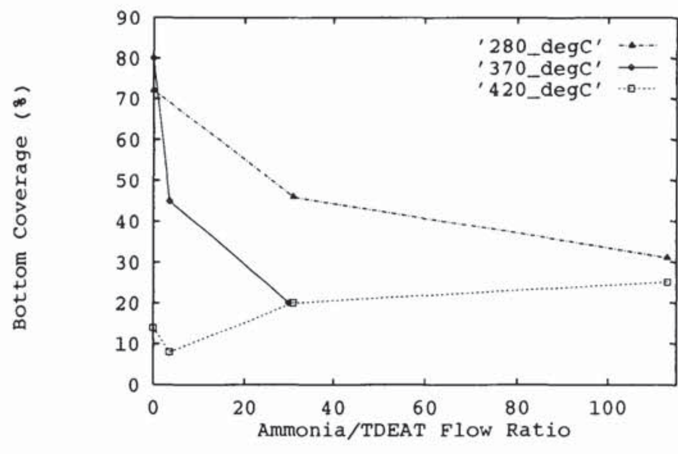


Figure 1: Bottom coverage of CVD TiN in contacts versus Ammonia:TDEAT flow ratio.

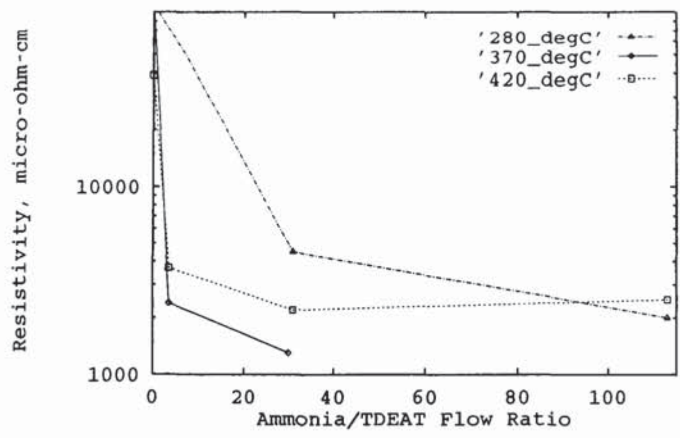


Figure 2: Resistivity of CVD TiN versus Ammonia:TDEAT flow ratio.

Table 1: Atmospheric deposition of titanium nitride from TDEAT and TDMAT precursors on $SiO_2$ surface, N, C, and O content relative to Ti from Auger analysis.

| precursor | temp. degC | $NH_3$ /precursor sccm/sccm | N:Ti | C:Ti | % O | %bottom coverage |
|---|---|---|---|---|---|---|
| tdeat | 280 | 0 | 0.91 | 0.20 | 42 | 72 |
| | 280 | 31 | 1.01 | 0.09 | 25 | 46 |
| | 280 | 113 | 1.06 | 0.08 | 17 | 31 |
| | 370 | 0 | 0.83 | 0.33 | 41 | 80 |
| | 370 | 3.5 | 1.05 | 0.14 | 19 | 45 |
| | 370 | 30 | 1.07 | 0.11 | 16 | 20 |
| | 420 | 0 | 0.89 | 0.39 | 39 | 14 |
| | 420 | 3.5 | 0.96 | 0.28 | 27 | 8 |
| | 420 | 31 | 1.07 | 0.12 | 14 | 20 |
| | 420 | 113 | 1.11 | 0.10 | 3 | 25 |
| tdmat | 190 | 27.7 | | | | $\leq$10 |
| | 280 | 0.9 | 1.06 | 0.14 | 28 | 20 |
| | 280 | 7.2 | 1.12 | 0.11 | 20 | $\leq$5 |
| | 370 | 0 | | | | 94 |
| | 370 | 1.1 | | | | 15 |

resistivity; resistivity falls sharply from off-scale (greater than $10^5\mu$ohm-cm) at the no ammonia condition to values in the thousands with the addition of 3.5:1 $NH_3$ : TDEAT. Further increases in $NH_3$ concentration lower resistivity further but with a less pronounced effect. Results with the TDMAT precursor followed similar trends to those of TDEAT.

Auger analysis results are summarized in Table 1. Again, the general trend shows a large step change from zero to 3.5:1 $NH_3$ /TDEAT ratio, with increasing amounts of $NH_3$ having a more limited effect. With the addition of ammonia, the N:Ti ratio increases; carbon and oxygen impurity levels decrease. In the case of TDMAT, addition of as little as 0.9:1 $NH_3$ /TDMAT produced nitrogen rich, low carbon TiN films at 280 °C. Oxygen levels, which result primarily from air exposure previous to analysis and are believed to reflect film porosity, were higher in the TDMAT plus ammonia films versus the films produced by TDEAT plus ammonia. Consistent trends in the compositional analysis with increasing temperature are also apparent in Table 1. Increasing temperature resulted in higher carbon levels and, in general, lower oxygen levels in the film analysis. No clear trend is exhibited in the temperature variation of the N:Ti ratio.

A more detailed analysis was performed on the TDEAT titanium nitride deposition at 370 °C and 3.5 $NH_3$ /TDEAT ratio, which was judged to have produced the best results in step coverage and resistivity among the operating conditions examined. TEM evaluation of step coverage in a 2.4 aspect ratio contact indicated sidewall and bottom coverage of 31 %, close to the value of 35 % to 45 % determined by SEM's of contact

cross-sections. Surface roughness was determined by AFM to be *circa* 10 angstroms, with an estimated average grain size of 700 angstroms. SEM micrographs of the surface indicated an apparent grain size of 800 angstroms on a fairly smooth surface. XRD scan showed weak and broad peaks, indicating poor crystalline or small grain structures in the deposited film. The d-spacings were estimated to be 2.496, 2.105, and 1.501 angstroms, which match the TiN (JCPDS # 6-0642) phase best.

## Discussion

Previous studies of the reaction of TDMAT and TDEAT with $NH_3$ furnish an interpretation of the data in this work. The reaction of TDMAT with $NH_3$ has been shown by Weiller and Partido [6] to be very fast even at 25 °C. The observed product was dimethylamine, consistent with the transamination mechanism proposed by several investigators [2], [3]. In the transamination reaction [1], the ammonia-bound nitrogen replaces the titanium-bound nitrogen, resulting in the elimination of organic carbon from the metal-organic compound. In addition to the dimethylamine product, the gas-phase reaction of TDMAT/TDEAT with $NH_3$ produces as yet unidentified intermediates which are highly surface reactive, depositing even on relatively cold teflon surfaces [5]. The high sticking coefficient of these gas-phase products results in preferential deposition at the top of a contact hole and poor coverage at the bottom. The extent of the gas-phase reaction of the TDMAT/TDEAT metal-organic precursors therefore correlates to the improvement in film properties (lower carbon content and resistivity) and the degradation of good conformality of the deposited film.

The surface reactivity of the gas-phase intermediate produced by the TDMAT and $NH_3$ reaction appears higher than that produced by TDEAT and $NH_3$ (Table 1). At 370 °C, a 1.1:1 $NH_3$:TDMAT ratio reduces step coverage to 15 %, whereas the same temperature and 3.5:1 $NH_3$:TDEAT ratio results in 45 % step coverage. While the deposited film step coverage from TDMAT declined precipitously with the addition of relatively little $NH_3$, the rate of decline in the C:Ti ratio with ammonia addition was not correspondingly as steep. The net result was lower carbon and better conformality in the deposited films using the TDEAT precursor with $NH_3$ relative to the TDMAT precursor with $NH_3$. The steric hindrance of the ethyl groups in the TDEAT precursor most likely result in lower gas phase reaction rates with $NH_3$ and lower surface reactivity of the resulting gas-phase intermediates relative to the TDMAT and $NH_3$ case.

## Conclusions

With the addition of $NH_3$, titanium nitride films using the TDEAT precursor had better step coverage conformality and improved material properties over the films produced using the TDMAT metal-organic precursor. While deposited TiN film quality was seen to improve with the addition of increasingly high levels of ammonia, the step coverage of this deposited film correspondingly worsened. There appears to be an intrinsic trade-off between the CVD TiN film quality in terms of resistivity, nitrogen, carbon and oxygen

content, and the step coverage of the film. The "best" process will represent a compromise between film quality and conformality, and will therefore vary according to the individual application requirements.

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