2022 IEEE International Interconnect Technology Conference (IITC)
San Jose, California, June 27-30, 2022

Low Resistivity Titanium Nitride Thin Film Fabricated by Atomic Layer Deposition with $TiCl_4$ and Metal-Organic Precursors in Horizontal Vias

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Titanium nitride (TiN) thin films are utilized as diffusion barriers for Co and W metal layers as well as the gate metal barrier in CMOS and memory devices due to the material's low resistivity; TiN is also used as a coating for hard disk drives[1]. Low resistivity TiN in commercial devices has been deposited by plasma-enhanced ALD (PE-ALD) and by physical vapor deposition. However, for high aspect ratio features and horizontal vias, deposition by thermal ALD is needed to enhance the conformality of the deposition process. In the present work, it is shown that the resistivity can be decreased below 220 uΩ-cm with a non-halogenated precursor at 425 ^{o}C by using a Ti precursor with high thermal stability and by reducing the oxygen and carbon contents in the films using a highly reactive co-reactant, anhydrous hydrazine (N_2H_4).

Titanium tetrachloride ($TiCl_4$), as well as three metal-organic precursors and anhydrous hydrazine (N_2H_4, Rasirc, Brute Hydrazine), were employed with ultra-high purity nitrogen purge gas. Films formed with the three halogen-free precursors, TDMAT (tetrakis(dimethylamino)titanium), TDEAT (tetrakis(diethylamino)titanium), and TEMATi (tetrakis(ethylmethylamido)titanium) were compared to $TiCl_4$ for resistivity and conformality. The TiN ALD chamber was connected to an *in-situ* Auger electron spectrometer (RBD Instruments), which determined the atomic composition of ALD TiN. Pulse lengths and purge times were optimized on HF-cleaned Si (100) or degreased SiO_2. For $TiCl_4$, the optimized deposition temperature was 425 ^{o}C and the optimal pulse times were 300 ms for $TiCl_4$ and 3600 ms for N_2H_4, but for the metal-organic precursors, different optimized pulsed lengths and deposition temperatures were needed. Four-point probe (Ossila) measurements were performed to determine the resistivity of TiN thin films on degreased SiO_2 substrates. Nanoscale patterned samples with horizontal vias (aspect ratio: 1:5) were used to verify the conformality of the low resistivity TiN thin films. TEM was employed to analyze the conformality of TiN thin films. Fig. 1 illustrates the structure of horizontal vias in the patterned samples. As shown by the blue lines, the goal of the process was to conformally deposit 4 nm TiN thin films on all the walls.

Comparisons of TiN using N_2H_4 with $TiCl_4$, TDMAT, TDEAT, and TEMATi using in-situ Auger and ex-situ resistivity are shown in Fig 2, 3, 4, and 5. The data in Fig 2 for $TiCl_4$ was employed as a benchmark; the low resistivity was ascribed to the high deposition temperature (425 ^{o}C) and low O and C contaminant content allowing for good crystalline structures. Note, the resistivity was only constant for N_2H_4 pulse lengths greater than 3.6s consistent with the need for excess N_2H_4 to reduce O and Cl contaminants.

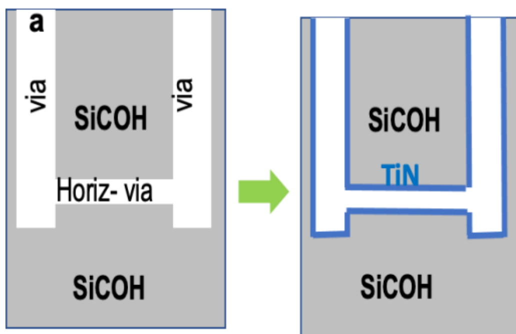
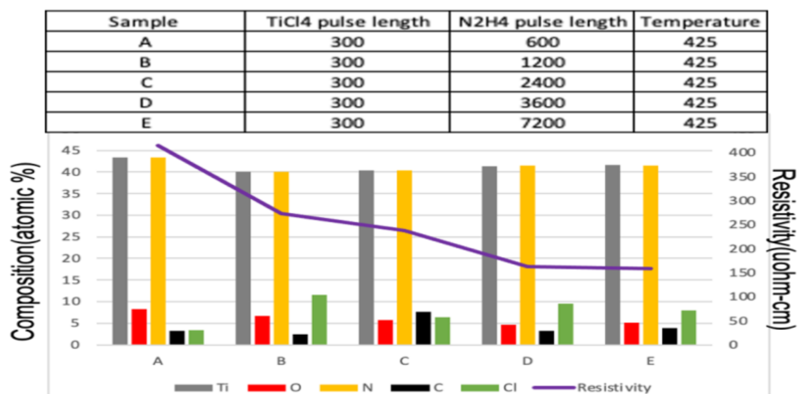


Fig. 1. Illustration of vertical vias and horizontal vias in patterned sample. A TiN thin film which is shown in blue region requires high nucleation density and high conformality on SiCOH or SiO_2 depending on the sample.



Sample	TiCl4 pulse length	N2H4 pulse length	Temperature
A	300	600	425
B	300	1200	425
C	300	2400	425
D	300	3600	425
E	300	7200	425

Fig. 2 Pulse length study of TiN using $TiCl_4$ and N_2H_4. By increasing the pulse length of N_2H_4, oxygen was suppressed resulting in low resistivity.

Sample	TDMAT	N2H4	Temp
A	500	6000	350
B	250	6000	350
C	125	6000	350
D(300cyc)	60	6000	350
E(750cyc)	30	6000	350

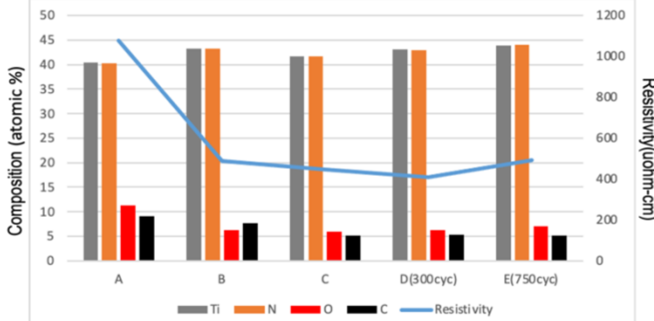


Fig. 3. Pulse length study of TiN using TDMAT and N_2H_4. Surface carbon was reduced for a shorter pulse length of TDMAT. However, to reach a similar thickness, extra cycles were needed.

Sample	TDEAT	N2H4	Temp
A	600	6000	300
B	300	6000	300
C	150	6000	300
D	150	6000	350
E	150	6000	400

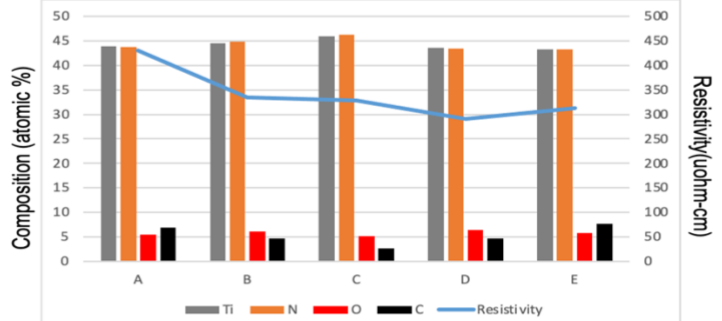


Fig. 4. Pulse length and deposition temperature study of TiN using TDEAT and N_2H_4. At 350ºC and 150ms pulse length of TDEAT, the lowest resistivity of TiN was observed.

Sample	Pulse length TEMATi	Pulse length N2H4	Temp
A	300	1200	300
B	300	1200	350
C	300	3600	350
D	300	3600	400
E	300	6000	400
F	300	6000	425

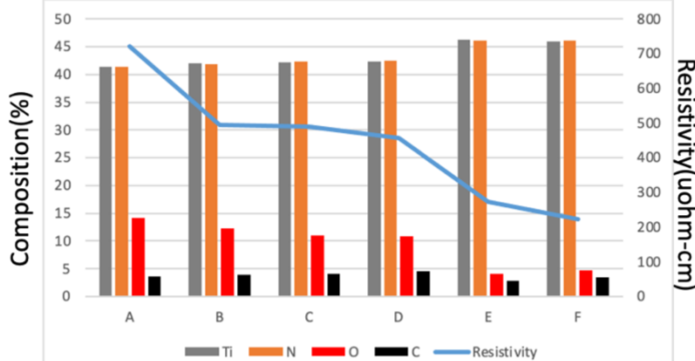


Fig. 5. Pulse length study of TiN using TEMATi and N_2H_4. Surface oxygen was reduced at higher temperatures and with a longer pulse length of N_2H_4. Lowest resistivity was for 425ºC ALD.

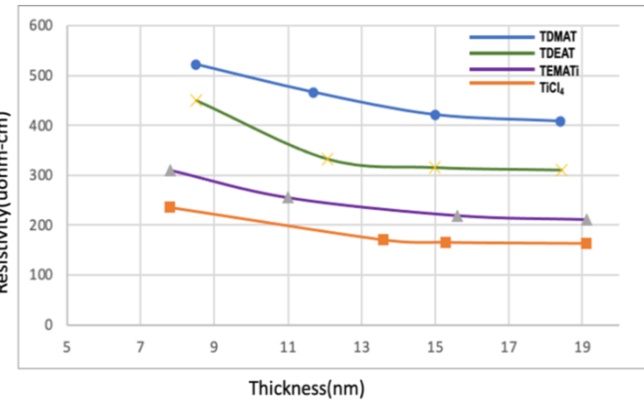


Fig. 6. Resistivity vs. Thickness of ALD TiN using different Ti precursors. All precursors had the same trend: as the thickness increased, the resistivity decreased and became stable above 15nm. $TiCl_4$ had the lowest resistivity ~160 uΩ-cm. For metal-organic precursors, TEMATi had the lowest resistivity ~220 uΩ-cm

The deposition of TiN using TDMAT at 350 ºC is shown in Fig. 3; this low temperature was needed to prevent decomposition and carbon contamination. At shorter TDMAT pulse lengths, the TiN resistivity was reduced due to the decrease in carbon content. Even for optimized pulse lengths, the surface oxygen and carbon for TDMAT based films are greater than for $TiCl_4$ based films. The data shows that TDMAT is a poor precursor for thermal TiN ALD because it cannot be employed at a sufficiently high temperature which are hypothesized to be required for a good crystalline structure.

TDEAT has higher temperature stability (350 ºC) than TDMAT so it was tested at 350 ºC and 400 ºC as shown in Fig 4. While the TDEAT films had lower resistivity than TDMAT films at 350ºC, the TDEAT film resistivity increased for 400ºC deposition temperature due to the high carbon content resulting from the decomposition of the TDEAT precursor at 400ºC (note higher C content in experiment E).

The optimal metal-organic precursor was found to be TEMATi as shown in Fig 5. TEMATi is still thermally stable at 425 °C; therefore, it is hypothesized that the crystallinity can be improved relative to TDEAT or TDMAT by higher temperature processing without carbon incorporation. It is noted that the residual C and O in the optimized TEMATi + N_2H_4 films are comparable to that in the optimized $TiCl_4$ + N_2H_4 films. A comparison of resistivity for TiN using $TiCl_4$ as well as metal-organic precursors is shown in Fig. 6. As the thickness decreased, resistivity increased, consistent with surface oxidation and surface scatting in the thin films. Among all metal-organic precursors, TEMATi had the lowest resistivity, ~220 uΩ-cm at 425 °C.

As shown in Fig 7, a conformal TiN thin film (~3.8nm) was deposited in horizontal vias using $TiCl_4$ + N_2H_4 at 425 °C. EDX results support that a TiN thin film was grown on the walls in the horizontal vias. Bright-field TEM (BF-TEM) is shown in Figs 7 a-c. EDX mapping showed that the fin was SiO_2/SiCOH and the thin film conformally grown in the horizontal via was TiO_xN_y (Fig.7 d-g). BF-TEM images of TiN using TDMAT + N_2H_4 at 350 °C are shown in Fig.8. Conformal TiN was again deposited on the fins with thickness around 6 nm. The TEM images of other metal-organic precursors will be presented.

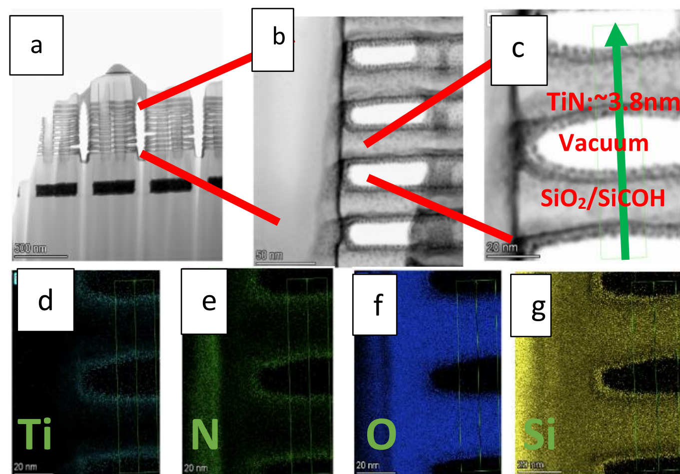


Fig. 7. a-c, bright-field TEM and d-g, EDX mapping analysis of TiN thin film in horizontal vias using $TiCl_4$ + N_2H_4 at 425 °C.

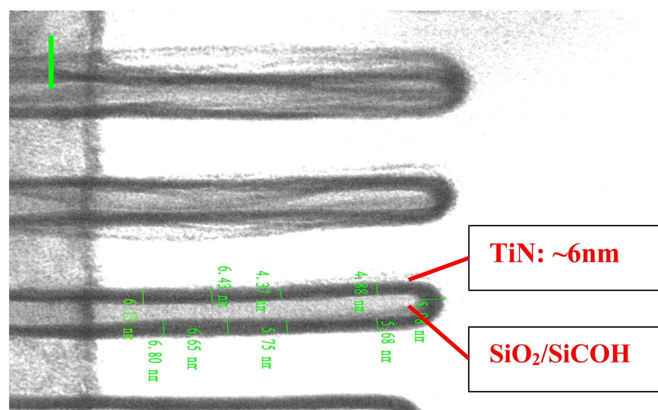


Fig. 8. Bright-field TEM images of TiN using TDMAT + N_2H_4 at 350 °C in the horizontal vias. It shows that conformal TiN thin film with ~6nm thickness is deposited in the vias.

Previously Wolf *et al.* demonstrated 400 °C, ALD of TiN with $TiCl_4$ and N_2H_4 with a resistivity of 500 uΩ-cm[2]. The lowest resistivity thermal ALD TiN films reported using a metal-organic precursor employed TDEAT and NH_3 and had 450 uΩ-cm resistivity[3]. Elam et. al. synthesized TiN using TDMAT and NH_3 had 10000 uΩ-cm[4]. The lowest resistivity PEALD TiN films reported using a metal-organic precursor employed TDMAT and NH_3 had 180 uΩ-cm resistivity[5]. The lowest resistivity thermal ALD TiN films reported using $TiCl_4$ and NH_3 and had 120 uΩ-cm resistivity but employed a toxic chemical, H_2S, to minimize the residual Cl[6]. Therefore, the present work with TEMATi + N_2H_4 at 425 °C showing resistivity below 220 uΩ-cm represents the lowest reported TiN resistivity for thermal ALD with a non-halogenated precursor. The reported ALD films using $TiCl_4$ and N_2H_4 represent the lowest reported TiN resistivity for thermal ALD with a halogenated precursor while avoiding the use of H_2S.

Acknowledgment: Special thanks to Micron for the patterned samples.

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