Low Resistivity Titanium Nitride Thin Film Fabricated by Atomic Layer Deposition on Silicon

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***Abstract*—A low temperature (300°C-350°C) TiN thermal ALD process using titanium tetrachloride ($TiCl_4$) and anhydrous hydrazine was developed to yield films with resistivities below 200 μohm-cm. Surface treatments such as Ar plasma and atomic hydrogen were applied to further reduce the surface impurities including all halogens. These experiments indicate that minimizing oxygen concentration using an ultra-clean ALD process with minimum background oxidants and high purity precursors are keys in producing TiN thin films with low resistivity.**

***Keywords*—thermal ALD, thin film, atomic hydrogen, Ar plasma, low resistivity, TiN**

I. Introduction

Titanium nitride (TiN) thin films are utilized as diffusion barriers for Co and W metal layers as well as gate metal in CMOS devices due to their high electrical conductivity. TiN is also used as coating for hard disk drives[1]. Low resistivity TiN has been deposited in commercial devices by plasma enhanced ALD (PEALD) and by physical vapor deposition. However, for high aspect ratio features and back-end applications, high conformality requirements and a low thermal budget below 350°C necessitate low temperature thermal ALD. Previously Wolf *et al.* demonstrated that at 400 °C, ALD of TiN with $TiCl_4$ and N_2H_4 resulted in a film with a resistivity of 500 μohm-cm[2].

II. Experimental Section

In this work, titanium tetrachloride ($TiCl_4$) and anhydrous hydrazine (Rasirc, Brute Hydrazine®) were employed as the precursors with ultra-high purity nitrogen purge gas. Hydrazine was employed since previous work had shown it produces lower resistivity films than NH_3[2] To produce the lowest resistivity films, a turbo molecular drag pump (Edwards EPX) was employed to maintain a high compression ratio during ALD pulsing. The ALD chamber was connected to an *in-vacuo* Auger electron spectrometer (RBD Instruments) which was used to determine the chemical composition of ALD TiN after 50 cycles of deposition. Pulse lengths and purge times were optimized at sample temperatures of 300 °C and 350 °C on HF-cleaned Si(100) and degreased SiO_2; the optimized pulse times were 300 ms for $TiCl_4$ and 2400 ms for N_2H_4. Surface morphology was measured by *ex-situ* atomic force microscopy (AFM). To determine resistivity, four-point probe (Ossila) measurements were performed on TiN thin films on degreased SiO_2 substrates. Scanning electron microscopy (SEM), ellipsometry, and X-ray reflectivity (XRR) were used to measure TiN film thicknesses.

III. Results and Discussions.

To study the properties of TiN films, several characterization tools were applied. The AES results are shown in Figure 1 for varying pulse length of the precursors at 300°C. The films showed nitrogen saturation with 2400 ms N_2H_4 pulse length. The TiN thin films had the lowest oxygen concentration with a $TiCl_4$ pulse length of 300 ms.

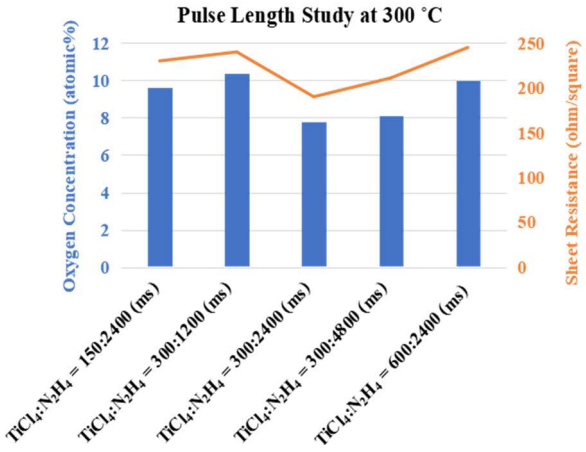

Fig. 1. Oxygen concentration and resistivity vs pulse length at 300 °C. N_2H_4 was saturated at 2400 ms. TiN had both the lowest oxygen concentration and resistivity for 300 ms of $TiCl_4$.

As shown in Figure 1, the film with the lowest oxygen concentration also produced the lowest sheet resistance.

The effect of exposure time was quantified at the optimized pulse length (Fig 2). As the exposure time to ambient atmosphere increased, (as-dep, 12 hrs, 24 hrs), the oxygen concentration increased from 4.6% to 13.2 %, and the increased oxygen content resulted in higher sheet resistance.

In Figure 3, elemental content measured by in situ Auger Electron Spectroscopy is shown. At 300°C, the surface oxygen content is ~8% and the corresponding N/O ratio is 5.5. For 350°C deposition temperature, the surface oxygen content can be reduced, and N/O ratio can be further increase to over 9. The thickness of the TiN thin film was measured by SEM, XRR, and ellipsometry.

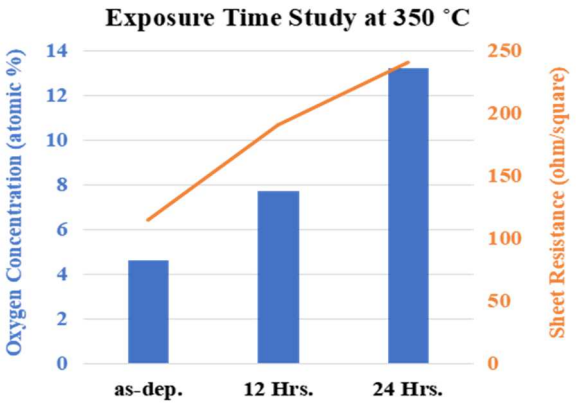

Fig. 2. Oxygen concentration and resistivity vs exposure time at 350°C. The exposure study was performed at 350 °C with optimized pulse lengths: 300 ms for $TiCl_4$ and 2400 ms for N_2H_4. As the exposure time increased, the oxygen concentration increased leading to an increase in sheet resistance.

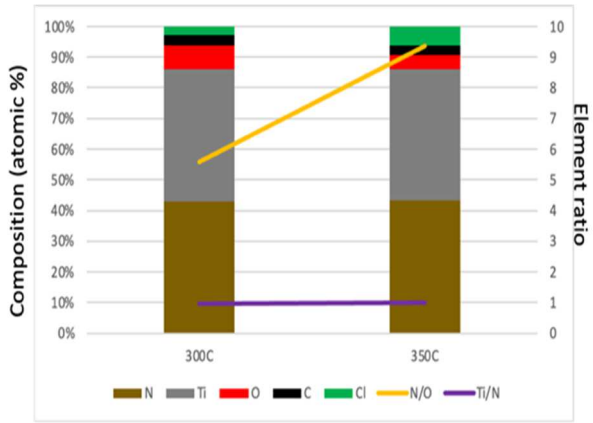

Fig. 3. Composition study of TiN film with optimal pulse lengths at different temperatures. AES shows that the surface N/O increases up to 9 as the temperature rises to 350°C. The oxygen content can be reduced to 4.6% at 350°C. The Ti/N ratio is close to1, indicating that the film is stoichiometric.

In Figure 4, the thickness as determined by XRR was 13.8 nm, which is consistent with the SEM measured thickness of 13.5 nm and ellipsometry measured growth rate of 3 Å per cycle.

In Figure 5, Ar plasma treatment was applied to clean the surface impurities. One of the major challenges with the use of $TiCl_4$ as a TiN precursor is the presence of residual chlorine which can induce corrosion especially in Cu and Co vias and interconnects. Simple Ar sputter was first tested. The sample was at -100V DC bias, and sample stage was maintained at 300 °C. Ar plasma (50W) removed all surface chlorine and lowered the surface oxygen content.

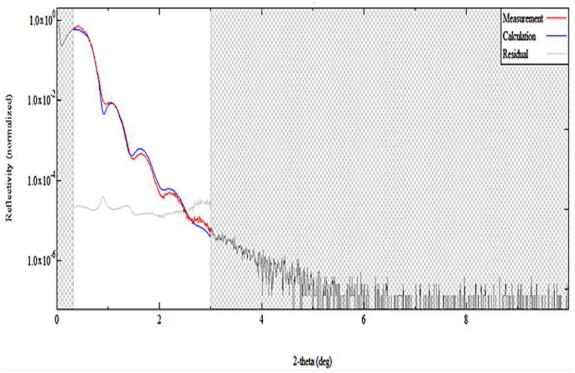

Fig. 4. XRR of the 350 °C TiN film with optimal pulse lengths. XRR shows that the thickness of the TiN thin film was 13.77 nm which agreed with SEM and ellipsometry (not shown). This was employed to calculate the reported 160 µohm-cm resistivity.

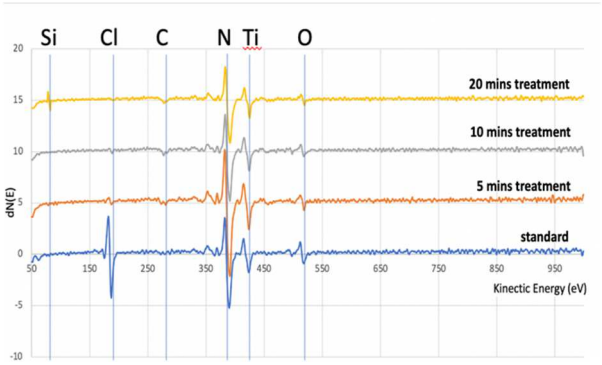

Fig. 5. Ar plasma treatment for surface impurities cleaning at different treatment time. AES shows that surface Cl can be removed after the sputtering treatment for 5 mins.

Table 1. Chemical composition of standard, 5 min, 10 min and 20 min Ar plasma treatment samples.

	Ti	N	O	C	Si	Cl
std	39.9%	40.0%	6.1%	3.4%	0.0%	10.5%
5mins	43.9%	44.0%	3.8%	7.6%	0.0%	0.7%
10mins	45.6%	45.7%	3.3%	4.8%	0.0%	0.6%
20mins	40.5%	40.6%	3.6%	6.0%	9.0%	0.3%

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The chemical composition of standard and different Ar plasma treatment time samples were listed in Table 1. We concluded that as the treatment time increased, the surface chlorine can be reduced from 10.5% to less than 1%.

Atomic H treatment was also tested since atomic H should combine with Cl to remove surface chloride and atomic H can be isotropically directed at substrates which can be useful on 3D features. The effect of atomic hydrogen treatment is illustrated in Figure 6. The sample was at 300 ºC with no applied bias and pure atomic hydrogen (140 mtorr, 50W) was employed. After 10 mins of treatment, the Cl was reduced from 10% to less than 2%. The optimal resistivity of the TiN deposited at 350ºC even without post deposition clean was 160 µohm-cm which is the lowest reported resistivity of any TiN film deposited by thermal ALD.

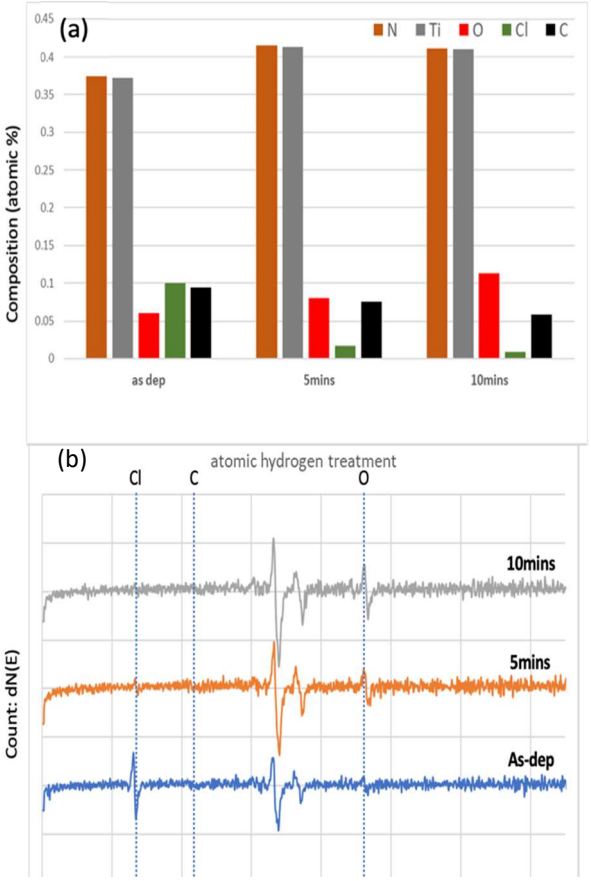

Fig. 6. (a) Atomic Hydrogen treatment for surface Cl purification. (b) Auger Spectrum data of as-dep, 5mins treatment and 10 mins treatment samples. AES shows that after 10 mins of atomic hydrogen treatment, the Cl on the surface was be reduced from 10% to less than 2%. The C content was also slightly reduced due to the reaction with atomic hydrogen.

CONCLUSIONS

These experiments indicate that minimizing oxygen concentration using an ultra-clean ALD process with minimum background oxidants is key in producing TiN thin films with low resistivity. Surface treatments such as the atomic hydrogen and Ar can further reduce the surface impurities such as chlorine, carbon and oxygen. The atomic H treatment maybe favorable for high aspect ratio features since the flux on the sidewalls will be greater than for an ion based cleaning method. The key to low oxygen content was careful control of background water by optimizing the pumping with a drag pump, careful control of wall temperatures, use of high purity precursors, and careful optimization of precursor pulse time for oxygen content instead of growth rate. The low surface Cl and O are consistent with the high purity N_2H_4 being able to efficiently remove surface Cl and for stable _NHx termination which prevents background H_2O from reacting with the surface during the ALD process. The resistivities of the films are the lowest reported for a thermal ALD of TiN at 350C.

ACKNOWLEDGMENT

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