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

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Titanium nitride (TiN) thin films are utilized as the diffusion barriers for Co and W metal layers as well as the gate metal barrier in CMOS and memory devices due to their low resistivity and good electrical conductivity. TiN is also used as a 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, deposition by thermal ALD is needed because of the high conformality of the thermal ALD process and for back-end compatible deposition below 350 ^oC. Previously Wolf *et al.* demonstrated that at 400 ^oC, ALD of TiN with $TiCl_4$ and N_2H_4 resulted in a film with a resistivity of 500 μohm-cm[2]. In this work, it is shown that the resistivity can be decreased below 200 μohm-cm when deposited at 300 ^oC - 350 ^oC by reducing the oxygen in the films.

Titanium tetrachloride ($TiCl_4$) and anhydrous hydrazine (Rasirc, Brute Hydrazine®) were employed as the precursors with ultra-high purity nitrogen purge gas. To produce low resistivity films, a turbo molecular drag pump (Edwards EPX) was employed to maintain a high compression ratio during ALD pulsing. The TiN ALD chamber was connected to an *in-vacuo* Auger electron spectrometer (RBD Instruments), which was used to determine the atomic composition of ALD TiN after 50 cycles of deposition. Pulse lengths and purge times were optimized at sample temperatures of 300 ^oC and 350 ^oC on HF-cleaned Si (100) or 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.

The result of AES studies are shown in Figure 1 for varying pulse length of the precursors at 300^oC. 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. As shown in Fig 1, the film with the lowest oxygen concentration also produced the lowest sheet resistance. The effect of post deposition ambient atmosphere exposure time was quantified at the optimized pulse length (Fig 2). As the exposure time 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, element content measured by in-situ Auger Electron Spectroscopy is shown. At 300^oC, the surface oxygen content is ~8% and the corresponding N/O ratio is 5.5. For 350^oC 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. As shown Figure 4, the thickness as determined by XRR was 13.8 nm, which is consistent with the SEM-derived thickness of 13.5 nm and ellipsometry-derived growth rate of 3 Å per cycle. The optimal resistivity of the TiN deposited at 350 ^oC was 160 μohm-cm which is the lowest reported resistivity of any

TiN film deposited by thermal ALD. Note the reported oxygen concentration are for surface oxygen and the bulk oxygen is likely to be much lower consistent with the low resistivity. These experiments indicate that minimizing oxygen concentration using an ultra-clean ALD process with minimum backround oxidants is key in producing TiN thin films with desirable electrical properties.. This work was supported in part by the SRC.

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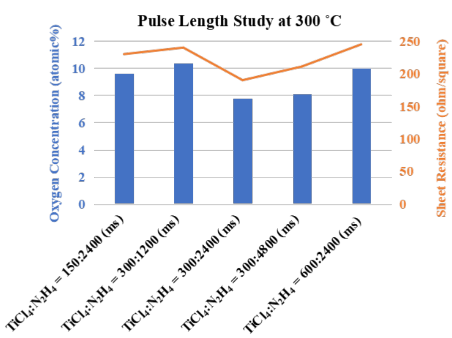

Fig. 1. Oxygen concentration and resistivity vs pulse length at 300 °C. N_2H_4 was saturated at 2400 ms. TiN had both the lowest oxygen concentration and resistivity for 300 ms of $TiCl_4$.

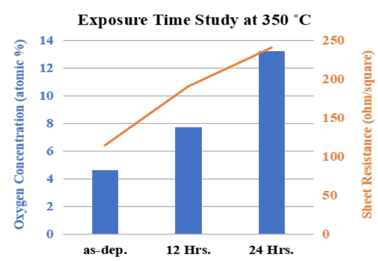

Fig. 2. Oxygen concentration and resistivity vs exposure time at 350°C. The exposure study was performed at 350 °C with optimized pulse lengths: 300 ms for $TiCl_4$ and 2400 ms for N_2H_4. As the exposure time increased, the oxygen concentration increased leading to an increase in sheet resistance.

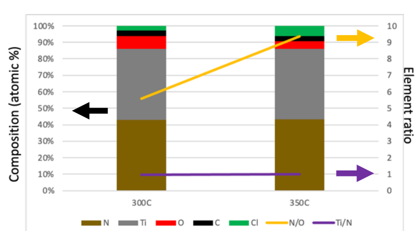

Fig. 3 Composition study of TiN film with optimal pulse lengths at different temperatures. AES shows that the N/O increase up to 9 as the temperature rise to 350°C. Also, oxygen content can be reduced to 4.6% at 350°C. Ti/N is close to 1, indicating that the film is stoichiometric.

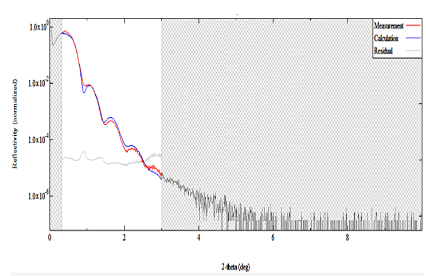

Fig. 4 XRR of the 350 °C TiN film with optimal pulse lengths. XRR shows that the thickness of the TiN thin film was 13.77 nm in agreement with SEM and ellipsometry (not shown). This was employed to calculate the reported 160 μohm-cm resistivity.

[1]C. H. Ahn. et al. *Metals and Materials International*, 7 (2001)

[2]Steven Wolf et al. *Applied Surface Science* 462 (2018)