

EE412 Report: Team ALD Nitride

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Initial goal

The initial goals of this project are to develop the recipe for four nitride films, TiN, Hf₃N₄, WN, and AlN in the Savannah system, and characterize their deposition rate, compositions, and sheet resistances. Table 1 shows the precursors for each target material.

Target material	Precursor 1	Precursor 2
TiN	Tetrakis(dimethylamido)titanium(IV)	NH ₃
Hf ₃ N ₄	tetrakis(dimethylamido)hafnium(IV)	NH ₃
WN	Bis(tert-butylimino)bis(dimethylamino)tungsten(VI)	NH ₃
AlN	Trimethylaluminum	NH ₃

Table 1. Precursors for each target material

Initial deposition results

Standard nitride recipes for Savannah were tried first. Woollam M2000 spectroscopic ellipsometer (Woollam) and SSI S-Probe X-Ray Photoemission Spectrometer (XPS) were used for thickness and composition measurements. However, the results were undesirable. For example, the results of Woollam showed that Hf₃N₄ films with 500, 375, and 250 cycles well matched to the corresponding HfO₂ models. Furthermore, the resultant growth rate was similar to that of HfO₂ film from the ALD oxide group. XPS results of the Hf₃N₄ films deposited with standard recipes showed no nitrogen signature but a huge amount of oxygen even after 12 seconds of Ar sputtering, which was calibrated to sputter 10 nm/min of SiO₂. TiN deposited with standard recipes showed similar results. The results of Woollam showed that TiN films with 500, 375, and 125 cycles fitted well to the corresponding TiO₂ models. The XPS measurements showed that the ratio of oxygen over titanium is approximately two, confirming stoichiometric TiO₂. Also, no nitrogen signature exhibited.

Table 2 shows the summary of the initial depositions. Most films were hydrophilic and contained no nitrogen but a great amount of oxygen. Thus, we concluded that our initial depositions only yielded oxides potentially due to serious oxygen leakage. Therefore, the focus of the project switched to reducing oxygen contamination. With the help of SNF staff members, O₂ filters were set up on different gas lines, one by one, for us to investigate the O₂ leakage.

Recipe	TiN	Hf ₃ N ₄	WN	AlN
Deposition rate	0.44 Å/cyc	0.92 Å/cyc	No film observed	0.8 Å/cyc
Contact angle	~2°	~3.5°	35-46°	~1.5°
Woollam	Fit with TiO ₂	Fit with HfO ₂	Fit with Si	Fit with Al ₂ O ₃
XPS	O ₂ /Ti = 2.5 ± 0.3	O ₂ /Hf = 5.1 ± 0.5	Trace amount of W	-
Film most likely deposited	TiO ₂	HfO ₂	Nothing	Al ₂ O ₃

Table 2. Summary of initial deposition results

Oxygen leak in Savannah

Figure 1 shows the schematic of the Savannah system. O₂ contaminations observed in our initial depositions might be caused by the air leak from the O-ring, N₂ line, NH₃ line, or metal precursor line. To identify the sources of oxygen leak, the deposition rates of HfO₂ in different system configurations are compared (Table 3). The experimental results show the deposition rate of HfO₂ reduced >93% when only N₂ and metal precursors lines are opened, which demonstrates that the majority of O₂ leak is from the NH₃ line. After removing the NH₃ line, an O₂ filter was installed on the N₂ line to further reduce the amount of O₂ leakage. The 0.02-Å/cyc reduction of the HfO₂ deposition rate is confirmed (Table 3). Based on these comparisons, the minimum air leak rates in different leak sources are estimated as shown in Table 4. The calculation

result shows the minimum air leak rate in the Savannah system is 3.35×10^{-3} sccm. The result can be improved by installing an O₂ filter on the NH₃ line (the filter was on order and not installed before the end of the quarter). Further improvements would require reducing the O-ring leak rate by improving the seal or creating a reduced oxygen environment around the chamber. Filters do not exist for the metal precursors.

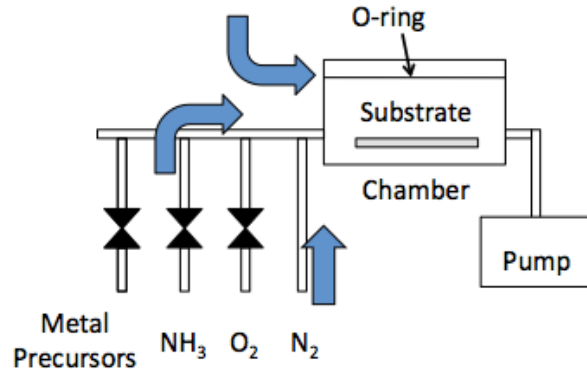


Figure 1. Schematic of the Savannah system

Recipe	Condition	Open valves	Results
HfO ₂	Normal	N ₂ , metal precursor, O ₂	HfO ₂ , 1.0 Å/cyc
Hf ₃ N ₄	Normal	N ₂ , metal precursor, NH ₃	HfO ₂ , 0.97 Å/cyc
HfO ₂	H ₂ O source off	N ₂ , metal precursor	HfO ₂ , 0.07 Å/cyc
Hf ₃ N ₄	NH ₃ line removed, O ₂ filter is installed in N ₂ line	N ₂ , metal precursor	HfO ₂ , 0.05 Å/cyc

Table 3. Comparison of HfO₂ deposition rates in different system configurations

Location of air leak	Estimated minimum air leak	Current condition
Old NH ₃ line	6.43×10^{-2} sccm	New NH ₃ line is installed
N ₂ line w/o O ₂ filter	1.64×10^{-3} sccm	O ₂ filter is installed
O-ring, metal precursor	3.35×10^{-3} sccm	-

Table 4. Estimated minimum air leak rate in the Savannah system

Deposition results with the new ammonia line

Five TiN films were deposited after the installation of the new NH₃ line. The TiN standard recipe was used as a baseline while the number of cycles and the temperatures were changed as shown in Table 5. Note these films were still subject to oxygen contamination because the NH₃ line was not filtered and O-ring leakage.

T(°C) \ Cyc	100	200	300
150	#1		
180 (standard)	#3	#4	#5
250	#2		

Table 5. TiN films deposited with the new NH₃ line

Sample #	T (°C)	Cyc	Ti%	O%	N%
1	150	100	18	76	6.4
2	250	100	20	77	2.9
3	180	100	22	70	8.4
4	180	200	23	68	8.4
5	180	300	21	71	8.3

Table 6. XPS results of samples deposited with the new ammonia line

Table 6 shows the results of XPS of these samples. Ti%, O%, and N% are the atomic concentrations of titanium, oxygen, and nitrogen, respectively. Note these were only surface concentrations because the authors were unable to access the in-situ ion sputter gun of XPS by the time of writing. Also note the concentration of carbon was ignored because all previous tests showed carbon only existed within 2 nm from the surface. The high oxygen concentration was also believed to be only on the surface but further investigation is necessary. Lastly, except for sample #2, the ratio Ti/N was consistent among all other samples. Figure 2 shows the actual XPS spectra.

Table 7 shows the results from Woollam on the last five films. Here we improved the fitting by employing a linear model $x \text{TiN} + (1-x) \text{TiO}_2$, the reason being our observations that the TiO_2 model fits better the long-wavelength tails of polarization curves, and that the TiN model better fits the short-wavelength parts. Interestingly, the fitting results from Woollam confirmed that sample #2 was low in nitrogen content. Figure 3 shows the actual fitted and measured polarization curves. Figure 4 shows the growth curve of sample #3, #4, and #5. Figure 5 shows the growth rate per cycle.

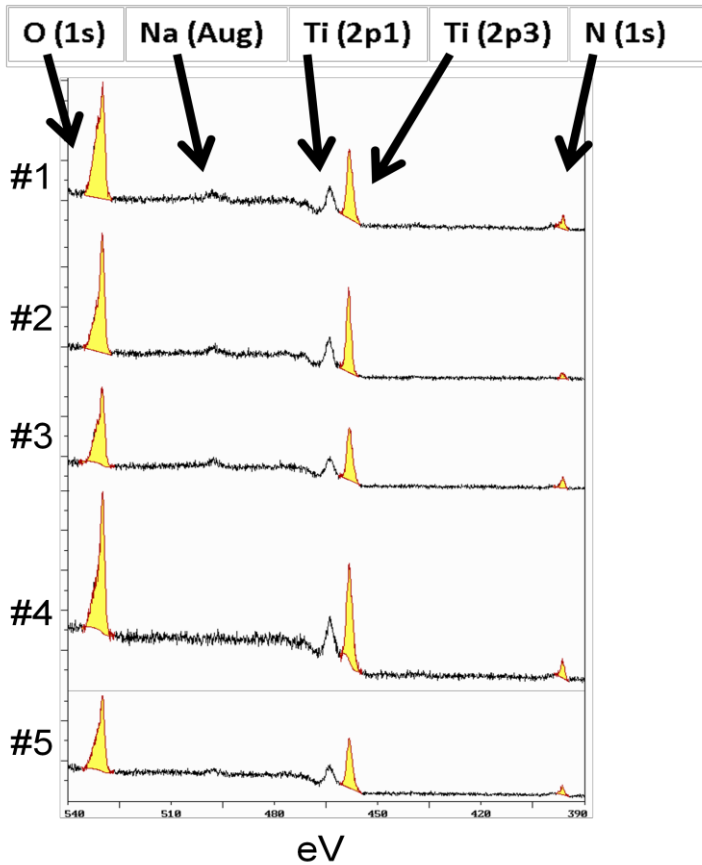


Figure 2. XPS spectra of the last five samples

#	T (°C)	Cyc	Thickness (Å)	x
1	150	100	55	0.15
2	250	100	50	0.02
3	180	100	45	0.13
4	180	200	87	0.17
5	180	300	119	0.19

Table 7. Woollam results of the last five samples. A linear model $x \text{TiN} + (1-x) \text{TiO}_2$ was used.

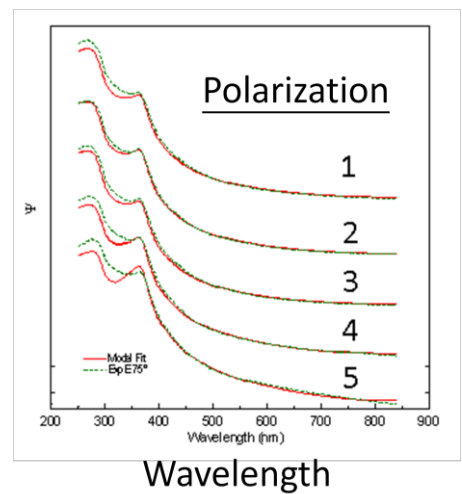


Figure 3. Woollam fitting of the last five samples

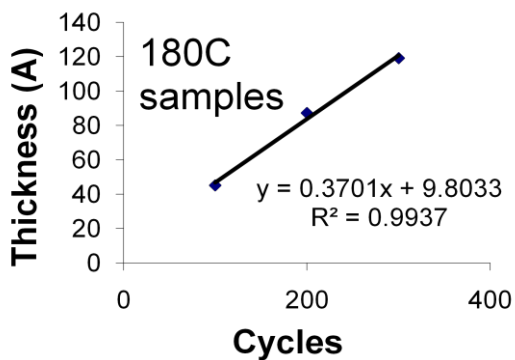


Figure 4. Growth curve of sample #3, #4, and #5

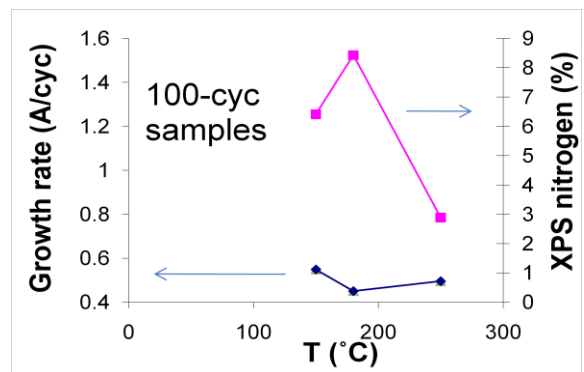


Figure 5. Growth rates and nitrogen contents of sample #1, #2, and #3

Comparison with literature

The final TiN depositions showed a growth rate of $\sim 0.5 \text{Å}/\text{cycle}$ (Fig. 5) comparable to the growth rate of thermal ALD TiN found in literature of about $\sim 0.55 \text{Å}/\text{cycle}$ (Fig. 6) [2]. Furthermore, according to the literature, a higher growth rate would

have been obtained for TiO₂ [1]. The thermal ALD TiN films in other works showed 35% oxygen concentration (Fig. 7) [2]. It is difficult to compare these exactly to the TiN films obtained from the Savannah since XPS was performed only on the surface since the sputter gun was unavailable.

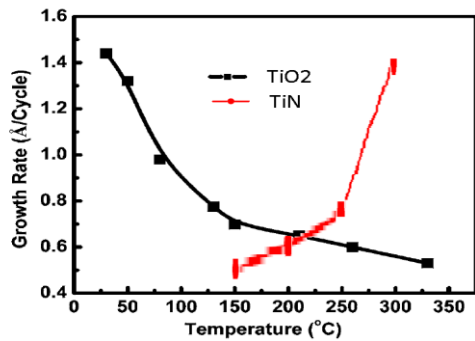


Figure 6. (From literature) Growth rates vs. T for TiO₂[1] and TiN[2]

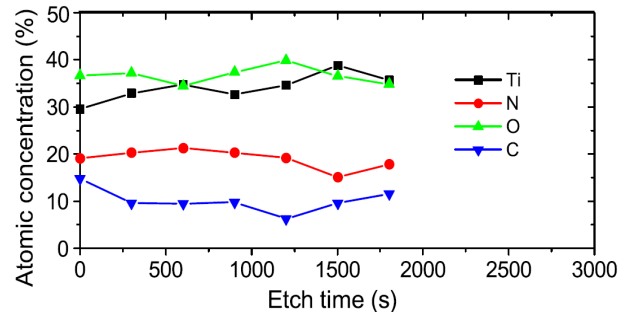


Figure 7. (From literature) Atomic concentrations of a thermal-ALD TiN film[2]

Conclusions and Recommendations

The initial goal of the project was to characterize four nitride films: TiN, Hf₃N₄, WN, and AlN. The films contained a negligible amount of nitrogen and severe oxygen contamination. The focus of the project transitioned to finding and reducing the source of the oxygen contamination and increasing the nitrogen concentration in the films. After a series of experiments, we determined that the major oxygen source was from the NH₃ line. After repairing the NH₃ line and adding an O₂ filter to the N₂ carrier gas line, the nitrogen concentration increased to ~8% with an O₂ concentration of ~70% on the surface of the TiN films. Further characterization is necessary to determine the stoichiometry below the surface. Further experiments should be done with the O₂ filter on the NH₃ line. Other methods to reduce the oxygen contamination would require reducing the oxygen leakage through the O-ring. Once the Fiji is operational, an interesting experiment would be to run the same thermal TiN recipe and observe the oxygen contamination. The Fiji uses a load lock so the oxygen contamination should decrease significantly. In its current state, the oxygen contamination limits the usefulness of the Savannah for depositing TiN films. Other films will most likely suffer from oxygen contamination as well.

References

- [1] Q. Xie, et al., *Journal of Applied Physics*, **102**, 085321, (2007).
- [2] J. Musschoot, et al., *Microelectronic Engineering*, **86**, 72-77, (2009).