Process Report

This report is a summary of the Process Visit carried out at

California Institute of Technology

Films: Al_2O_3 (plasma and thermal), TiO_2 (plasma), HfO_2 (plasma)

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System number	220302

1.0 ABSTRACT

Plasma and thermal Al_2O_3 films and plasma TiO_2 and HfO_2 films were deposited on bare Si wafers. The plasma Al_2O_3 process was demonstrated at 200ºC using the standard recipe with the following changes: TMA dose was reduced to 15ms, TMA was increased to 2s. The thermal Al_2O_3 process was demonstrated at 200ºC using the standard recipe with the following changes: TMA dose was reduced to 15ms, TMA purge was increased to 2s, the water purge was increased to 6s. The plasma TiO_2 process was demonstrated at 250ºC using the standard recipe with the following changes: O_2 plasma dose was increased to 6s, O_2 plasma purge was increased to 4s. The HfO_2 process has not been fully demonstrated.

All results are described in Section 4.

2.0 System Configuration

The work was carried out on the FlexAL system in at California Institute of Technology.
System number 220302.

3.0 Samples

3.1 ALD Process Description

No. Wafers:	>30	No. samples / batch: (if not single)	NA
Wafer size (size / shape if not wafers):	150 mm	Flat / notch specification:	Semi standard
Substrate material [1]:	Si	Substrate orientation:	<100>
Was substrates broken for extra samples / analysis?	No		
Film type details: (e.g. NH_3-free):	Uniform film deposition to meet Oxford process specifications.		

3.2 Plasma Al_2O_3 Process Specifications

Parameter	Target Value	Result
Process	Plasma Al_2O_3	
Number of Cycles	300	300
Target Thickness	360 A	366.4 A
Dep. Rate	~1.2 A/cycle	~1.2 A
Non-Uniformity	1.5%	0.17%
Expected RI	1.64	1.638

3.3 Thermal Al_2O_3 Process Specifications

Parameter	Target Value	Result
Process	Thermal Al_2O_3	
Number of Cycles	300	300
Target Thickness	300 A	294.3 A
Dep. Rate	~1.0 A/cycle	~0.98 A
Non-Uniformity	1.5%	0.56%
Expected RI	1.64	1.638

3.4 Plasma TiO_2 Process Specifications

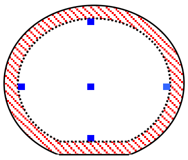
Parameter	Target Value	Result
Process	Plasma TiO_2	
Number of Cycles	400	400
Target Thickness	200 A	216.7 A
Dep. Rate	~0.5 A/cycle	~0.51 A
Non-Uniformity	2.0%	0.44%
Expected RI	2.4	2.378

3.5 Plasma HfO_2 Process Specifications

Parameter	Target Value	Result
Process	Plasma HfO_2	
Number of Cycles	300	200-300
Target Thickness	330	
Dep. Rate	~1.1 A/cycle	
Non-Uniformity	2.0%	>11%
Expected RI	>1.8	>1.8

4.0 Process Results

Film thickness and refractive index was measured using a Woollam ellipsometer. Film thickness uniformity was based on the inner 100mm of a 150mm wafer using the following equation:



$$\text{\% Within Wafer Uniformity} = \pm \frac{\text{max} - \text{min}}{2 \times \text{average}} \times 100\%$$

4.1 Plasma Al_2O_3 Process Results

Run Number	5	6	7	8	11	12	13	14	14x
Date/time		Selected run for repete							
# cycles	300	300	300	300	300	300	300	900	900
TMA DOSE Time (sec)	0.02	0.03	0.015	0.015	0.015	0.03	0.03	0.03	0.03
Purging time TMA	2	2	2	2	2.5	2	2	2	2
Plasma stab time	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Plasma Time (sec)	2	2	2	2	2	2	2	2	2
Post plasma purge time	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Growth Cycle (Å/cycle)	1.36	1.27	1.33	1.28	1.27	1.28	1.28	1.24	1.25
Average Thickness (A)	40.9	38.2	39.9	38.5	38.2	38.5	38.5	111.6	112.5
100mm Thx Uniformity +/-%	1.32	0.15	0.46	0.19	0.24	0.22	0.22	0.42	0.18
Repeatability (+/-%)							0.32		

Plasma Al_2O_3 thin films were run by Chris Georgiou under the guidance of Craig Ward and Felicia McGuire. Multiple wafers were used to determine in-wafer uniformity and to find the correct ellipsometry model to determine wafer thickness. After some iterations, the process that gave the best uniformity had a TMA dose increased from 20ms to 30ms and a TMA purge increased from 1s to 2s. Increasing the dose allowed for a more uniform coating of the wafer surface, and increasing the purge time minimized the excess TMA in the lines helping to improve in-wafer uniformity. The final process had a pressure of 30mT, The GPC of the improved wafers was ~1.3 Angstroms/cycle with variations in the thickness across a four inch wafer of less than 0.25%. The refractive indices for the 3 wafers in in the run-to-run were 1.635, 1.639, 1.639 for an average RI of ~1.638. The process from wafer 6 was selected to demonstrate the process repeatability, with the variations in the thickness across 3 wafers of 0.32%, below the repeatability specification of 2.0%.

2019.04.30 Addition:

Cycles	Thickness	Max	Min	RI	Non-Uniformity %	GPC (Ang/cycle)
300	36.64	36.75	36.63	1.638	0.1637555	1.22133333

One plasma Al_2O_3 thin film was grown on a blank Si wafer using the same process as before. The results were as follows: the in-wafer non-uniformity was <0.17%, the growth per cycle (GPC) was 1.22 A/cycle, and the refractive index was 1.638. These are all within the process specifications outlined in the PA.

4.2 Thermal Al_2O_3 Process Results

Process	TMA - Thermal	TMA - Thermal	TMA - Thermal	TMA - Thermal	TMA - Thermal	TMA - Thermal	TMA - Thermal
Wafer #	1	2	3	4	RTR	RTR	RTR
Cycles	300	300	300	300	300	300	300
TMA Dose (ms)	15	15	20	20	15	15	15
TMA Purge (s)	2	2	1.5	2.5	2	2	2
H2O Dose (ms)	100	100	100	100	100	100	100
H2O Purge (s)	4	6	4	4	6	6	6
Total Time	35m 39s	45m 39s	33m 11s	38m 11s	45m 39s	45m 39s	45m 39s
Thickness	30.86	30.36	31.88	32.40	31.51	31.44	31.89
Max-Min	0.912	0.439	0.605	0.536	0.456	0.396	0.359
RI	1.633	1.635	1.633	1.632	1.635	1.635	1.635
Average Non-Uniformity %	1.477641	0.722991	0.948871	0.82716	0.72358	0.62977099	0.56287237
Average GPC (Angstom/cycle)	1.0286667	1.012	1.062667	1.08	1.050333	1.048	1.063
Run-to-Run %							0.71172501
Average RI							
Comments							

Thermal Al_2O_3 thin films were run initially using the standard Oxford Instruments Plasma Technology process and the TMA dose with purge obtained from the plasma Al_2O_3 process. The in-wafer uniformity was in spec, but on the high side. Additional wafers were run with an increased plasma purge (wafer 2) to remove any excess reactive oxygen species that was could not be removed in the initial 4s. This improved the in-wafer non-uniformity to 0.72%. Two additional wafers were demonstrated with the standard Oxford Instruments Plasma Technology process (wafer 3) and the starting process with a longer TMA purge (wafer 4).

After reviewing the results, it was determined that Process 2 would be used to demonstrate the three wafer repeatability test as it provided the best uniformity and a refractive index closest to that expected. The three wafers in the repeatability process had thicknesses of 31.51nm, 31.44nm, and 31.89nm, giving a variation in the thickness of 0.7%, below the repeatability standard of 2%.

The final process loaded onto the FlexAL is the same as for wafer 2 and wafers 5-7.

2019.04.30 Addition:

Process	Wafer #	Cycles	TMA Dose (ms)	TMA Purge (s)	H2O Dose (ms)	H2O Purge (s)	Total Time	Thickness	Max	Min	RI	Average Non-Uniformity %	Average GPC (Angstom /cycle)
TMA - Thermal	9	300	15	2	100	6	45m 39s	29.43	29.47	29.14	1.638	0.5606524	0.981

One thermal Al_2O_3 thin film was grown on a blank Si wafer using the same process as before. The results were as follows: the in-wafer non-uniformity was <0.57%, the growth per cycle (GPC) was 0.98 A/cycle, and the refractive index was 1.638. These are all within the process specifications outlined in the PA.

4.3 Plasma TiO_2 Process Results

Process	TDMAT - Plasma	TDMAT - Plasma	TDMAT - Plasma	TDMAT - Plasma	TDMAT - Plasma	TDMAT - Plasma	TDMAT - Plasma
Wafer #	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Cycles	400	400	400	400	400	400	400
TDMAT Dose (ms)	500	750	500	500	500	500	750
TDMAT Purge (s)	3	4.5	3	3	3	3	4.5
Plasma Gas Stab (s)	1.5	1.5	1.5	1.5	1.5	1.5	1.5
O2 Plasma Dose (s)	4	4	6	6	6	6	6
Plasma Purge (s)	2	2	4	4	4	4	4
Total Time	1h 17m 55s	1h 29 35s	1h 44 35s	1h 44 35s	1h 44 35s	1h 44 35s	1h 44 35s
Thickness	21.94	23.18	21.17	20.61	20.7	20.28	21.81
Max	22.286	23.28	21.573	20.647	20.707	20.554	21.838
Min	21.674	23.034	21.14	20.18	20.276	20.115	21.585
RI	2.37	2.38	2.34	2.36	2.36	2.37	2.35
Average Non-Uniformity	1.39471285	0.53062985	1.0226736	1.1329452	1.0410628	1.0823471	0.580009
Average GPC (Angstom/cycle)	0.5485	0.5795	0.52925	0.51525	0.5175	0.507	0.54525
Run-to-Run						1.0228933	

Plasma TiO_2 thin films were run initially using the standard Oxford Instruments Plasma Technology process. The in-wafer uniformity was in spec, but it was requested that a few process parameters be adjusted to determine the best process prior to moving on to the repeatability test. Additional wafers were run with 50% increased TDMAT dose and purge times (wafer 2) and 50% increased O2 dose and purge times (wafer 3). The increased dose times were to ensure there was sufficient precursor deposition on the wafer, while the longer purge times were used to remove the excess precursor before the next dose. Lengthening the TDMAT dose and purge times improved the in-wafer non-uniformity to 0.53%, while elongating the O_2 plasma dose and purge times improved the in-wafer non-uniformity to 1.1%.

Ultimately, Process 3 was chosen to demonstrate repeatability due to the more standard refractive index of 2.34. The test demonstrated a process repeatability of 1% and an average RI of 2.353.

A final wafer was demonstrated by combining the two tests, increasing all dose and purge times by 50% (wafer 7). This wafer gave a non-uniformity measure of <0.6%, a refractive index of 2.35, and a GPC of 0.545 Angstroms/cycle. It was decided that this would process would be the one uploaded onto the FlexAL.

2019.04.30 Addition:

Process	Wafer #	Cycles	TDMAT Dose (ms)	TDMAT Purge (s)	Plasma Gas Stab (s)	O2 Plasma Dose (s)	Plasma Purge (s)	Total Time	Thickness	Max	Min	RI	Average Non-Uniformity	Average GPC (Angstom /cycle)
TDMAT - Plasma	**8**	400	750	4.5	1.5	6	4	1h 44 35s	21.67	21.74	21.55	2.39	0.4383941	0.54175

One plasma TiO_2 thin film was grown on a blank Si wafer using the same process as outlined above. The results were as follows: the in-wafer non-uniformity was <0.44%, the growth per cycle (GPC) was 0.54 A/cycle, and the refractive index was 2.39. These are all within the process specifications outlined in the PA.

4.4 Plasma HfO_2 Process Results

Process	TDMAH - Plasma	TDMAH - Plasma	TDMAH - Plasma	TDMAH - Plasma	TDMAH - Plasma	TDMAH - Plasma	TDMAH - Plasma
Wafer #	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Cycles	300	300	200	200	300	200	300
TDMAH Dose (ms)	400	1000	1000	1000	1000	1000	1500
TDMAH Purge (s)	1	4	4	6	4	3	6
Plasma Gas Stab (s)	3	3	3	3	3	3	3
O2 Plasma Dose (s)	5	5	5	5	7	7	7
Plasma Purge (s)	8	8	12	8	10	10	10
Total Time	1h 31m 35s	1h 43m 35s	1h 31m 15s	1h 21m 15s	2h 9m 35s	1h 24m 35s	2h 34m 35s
Thickness	12.44	32.93	16.58	20.55	31.82	17.37	14.41
Max	22.35	39.03	21.9	23.75	35.99	21.56	17.62
Min	11.27	31.52	15.72	18.24	28.96	16.59	10.27
RI	1.86	2.01	1.99	1.99	2	1.99	
Average Non-Uniformity	44.53376	11.40298	18.6369119	13.40633	11.04651	14.30628	25.50312
Average GPC (Angstom/cycle)	0.414667	1.097667	0.829	1.0275	1.060667	0.8685	0.480333

Plasma HfO_2 thin films were run initially using the standard Oxford Instruments Plasma Technology process. With this process, the in-wafer non-uniformity was >44%, and the GPC was 2.5x lower than the anticipated growth rate. The TDMAH dose was increased by 2.5x and the purge by 4x in Process 2 to allow a more complete layer of TDMAH to deposit each dose. This improved the process results to an average GPC of ~1.1 Angstroms/cycle, but the variations in thickness across the wafer showed clear CVD growth marked by a non-uniformity measurement of 11.4% and a film thickness reading of 39.03nm (GPC of ~1.3 Angstroms/cycle) on the side of the wafer closes to the TDMAH dose.

In Process 3, the TDMAH dose and purge were kept at the increased values, and the post plasma purge was increased from 8s to 12s to ensure all reactive O_2 was removed from the chamber prior to TDMAH dosing. 200 cycles of this process were run to allow for more process to be run each day. The increase in the post plasma purge resulted in the in-wafer thickness non-uniformity increasing from 11.4% to 18.6%, and the film growth changed from slightly parasitic CVD (closest to the TDMAH dose) to A GPC of 0.83 Angstroms per cycle (furthest from the TDMAH), signalling there was not enough precursor in the chamber.

The post plasma purge was returned to 8s in Process 4, and the TDMAH purge was increased from 4s to 6s under the assumption that the TDMAH was not being removed from the chamber during the purge time and that an increased purge would help improve the non-uniformity of the film. After 200 cycles, the process was shown to have a more reasonable GPC, but the non-uniformity measure was now at 13.4%. Additionally, on this wafer, the side of the wafer closest to the TDMAH dose had a thickness slightly higher than expected, while the opposite side of the wafer demonstrated a lower than expected growth.

A fifth process was run for 300 cycles overnight with the TDMAH dose and purge returned to 1s and 4s, and the O2 dose and purge were increased by 2s each to 7s and 10s, respectively. The thought here was that the film was oxygen deficient, resulting in the high non-uniformities. While this process demonstrated the lowest non-uniformity, it was only at 11%. Additionally, the GPC of HfO_2 ranged from ~1.2

on the nearest the TDMAH dose to ~0.96 Angstroms/cycle, again signalling a lack of precursor in the chamber.
A seventh process maintained the same parameters as #6, with only a reduction in the TDMAH purge to try to leave more of the TDMAH present in the chamber. This process had a non-uniformity of 14.3%, and still demonstrated lower than expected growth.

The shift in these results from being slightly parasitic to a lower than expected GPC even with the same or more precursor/plasma and less purge is opposite what is expected. For example, comparing Process 2 to Process 4, Process 4 should have had an improved non-uniformity due to the longer purge for the TDMAH, however, the non-uniformity across wafer 4 was calculated to be less uniform. A similar statement can be made for the Processes 2 and 3, where in elongated post plasma purge in process 3 should have improved the in-wafer uniformity, yet the results show the non-uniformity degraded from 11% to >18%.

From Processes 5 to 6, a reduced TDMAH purge time should have increased the GPC, as more TDMAH would be present in the chamber. The results are opposite what was expected, as the reduced purge time led to a large decrease in the GPC from 1.06 Angstroms/cycle to 0.868 Angstroms/cycle.

The inability for the process to produce a reasonable result using conventional ALD methods is concerning. Despite this, the previous results were demonstrated on the same chamber, indicating a probable breakdown/degradation on the TDMAH precursor prior to use in the ALD tool. Replacing the TDMAH should provide more anticipated results with shorter deposition times.

These results were also sent to the OPT ALD team in Europe for examination.

5.0 Summary

- Plasma and thermal Al_2O_3 thin films and plasma TiO_2 thin films were demonstrated within OPT process specifications.
- HfO_2 films were not able to meet OPT specifications.

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