2012 NNIN ALD Symposium
Harvard University
November 29-30

Vince Genova

Research Staff

Cornell NanoScale Facility

Cornell University

ALD at Cornell NanoScale Facility

- Current capabilities:
  - system sources and gases
  - established processes
- Electrical characterization of dielectric films
- Conformal coating of high aspect ratio (HAR) features
- Silicon nitride PEALD development
- ALD of novel gate dielectrics
- Ongoing and planned research

Oxford FlexAL ALD system

- Remote plasma (RPEALD) and thermal ALD
- Automated loadlock for samples up to 200mm
- 4 organic based precursors: procured from SAFC specialty gases
  - Al: TMA
  - Hf: TEMAH
  - Ta: PDMAT
  - Si: 3DMAS
- H2O thermal source
- Process gases: O2, N2, H2, NH3, Ar, SF6 (MFC controlled)
- Dimethylamine (DMA) for selective area ALD
- Electrode temperatures up to 400C
- Precursor source temps up to 200C (oven and jacket)

ALD film	status	tool	precursor 1	precursor 2	deposition temp. C	refractive index(630nm)	deposition rate A/loop	XPS data
Plasma Al2O3	established	Oxford FlexAl	trimethylaluminum TMA	O2 plasma	110	1.625	1.369	Yes
					200	1.65	1.173	Yes
					300	1.655	0.998	Yes
Thermal Al2O3	established	Oxford FlexAl	trimethylaluminum TMA	H2O	110	1.6	0.848	Yes
					200	1.66	0.94	Yes
					300	1.66	1.04	Yes
Plasma AlN	established	Oxford FlexAl	trimethylaluminum TMA	N2 + H2 plasma	300	1.86	0.585	Yes
					400	1.94	0.6	Yes
Plasma HfO2	established	Oxford FlexAl	tetrakisethylmethylamide hafnium TEMAH	O2 plasma	110	1.85	1.16	Yes
					200	1.97	1.04	Yes
					300	2.075	0.854	Yes
Thermal HfO2	established	Oxford FlexAl	tetrakisethylmethylamide hafnium TEMAH	H2O	110	1.9	1.2	Yes
					200	2.08	1.03	Yes
					300	2.1	0.83	Yes
Plasma HfN	established	Oxford FlexAl	tetrakisethylmethylamide hafnium TEMAH	N2 + H2 plasma	275	2.4	0.82	Yes
Plasma SiO2	established	Oxford FlexAl	trisdimethlyaminosilane 3DMAS	Ar + O2 plasma	110	1.505	0.92	Yes
					200	1.52	0.9	Yes
					300	1.48	0.8	Yes
					350	1.53	0.75	Yes
Plasma Si3N4	established	Oxford FlexAl	trisdimethylaminosilane 3DMAS	Ar + N2 plasma	350	2.1	0.2	Yes
Thermal TaN	established	Oxford FlexAl	pentakiskimethlyamino-Ta PDMAT	NH3	225	2	0.413	Yes
					255	2	0.482	Yes
					300	2.1	0.462	Yes
Plasma TaN	established	Oxford FlexAl	pentakiskimethlyamino-Ta PDMAT	H2 plasma	110	2.4	0.23	Yes
					225	2.7	0.28	Yes
					300	2.7	0.32	Yes
Thermal Ta2O5	established	Oxford FlexAl	pentakiskimethlyamino-Ta PDMAT	H2O	110	2.057	2.52	Yes
					200	2.142	1.97	Yes
					300	2.201	1.29	Yes
Plasma Ta2O5	established	Oxford FlexAl	pentakiskimethlyamino-Ta PDMAT	O2 plasma	110	2.04	1.53	Yes
					200	2.185	1.1	Yes
					300	2.2016	1.04	Yes
Plasma HfSiO2	established	Oxford FlexAl	TEMAH + 3DMAS 2:1	O2 plasma	200	1.925	0.91	Yes
			TEMAH + 3DMAS 1:1	O2 plasma	200	1.7164	0.94	Yes
Plasma HfSiON	established	Oxford FlexAl	TEMAH + 3DMAS 2:1	O2 +N2 plasma	200	1.84	0.85	Yes
			TEMAH + 3DMAS 1:1	O2 +N2 plasma	200	1.7288	0.86	Yes
Plasma HfAlOx	established	Oxford FlexAl	TEMAH + TMA 2:1	O2 plasma	200	1.86	1.01	Yes

MIMCAP Fabrication Process

- Grow 500nm thermal SiO2 for isolation
- 1st metal contact process
  - spin LOR (liftoff resist) 10A
  - dice/cleave into quarters
  - contact lithography exposure/develop
  - ebeam evaporation Cr(5nm)/Pt(100nm)
  - liftoff
- ALD film deposition
- Anneal at 500C/30min in Argon if needed

MIMCAP Fabrication Process

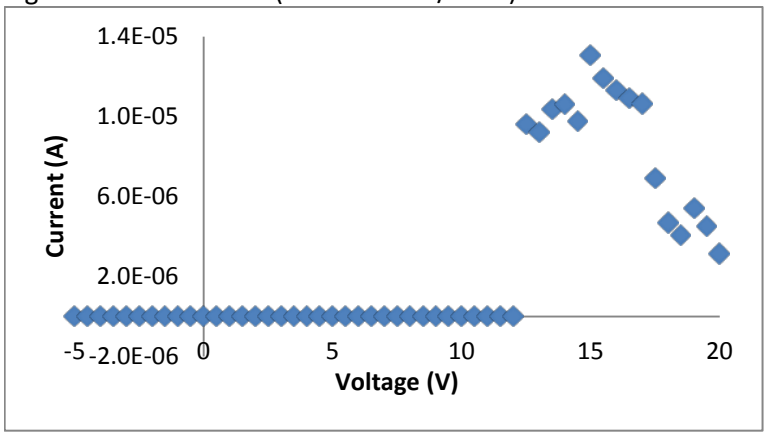
- 2nd metal contact process
  - repeat the lithography steps above
  - ebeam evaporation Cr(5nm)/Pt(100nm)
  - liftoff
- Wet etch ALD film
  - 30:1 BOE: Al2O3, HfO2, SiO2
  - 6:1 BOE: HfAlOx, HfSiOx, HfSiOxNy
  - 49% HF: TaOx

MIMCAP Device IV Curve: HfO_2 plasma ALD thin film (std. recipe) at 300°C

Fig: 1: No anneal, 240 loops (25.08 nm thick)

Fig. 2: Annealed at 500°C in Ar atmosphere for 30 min, 240 loops (25.08 nm thick)

Fig. 1: Without anneal (data from 03/2011)



Breakdown voltages:

1. Without anneal (n=6):

7.0 V	4.5 V	7.0 V	12.5 V	4.5 V
8.5 V				

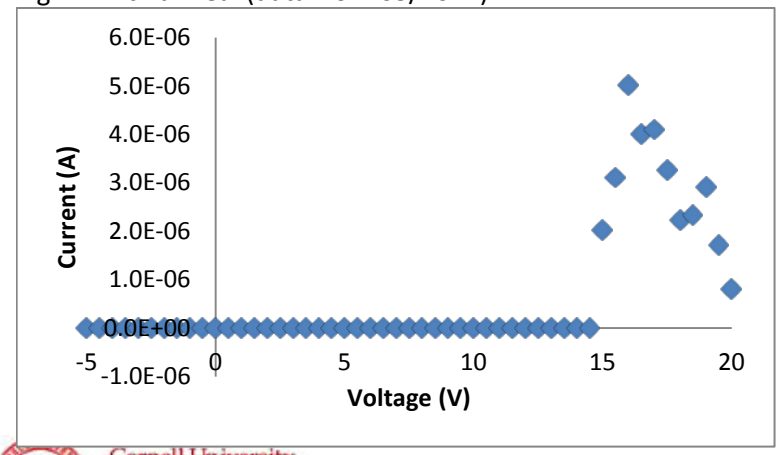
Average breakdown voltage:
7.33 ± 2.98 V

2. With anneal (n=7):

17.0 V	4.5 V	14.0 V	13.5 V	9.0 V
15.0 V	16.5 V			

Average breakdown voltage:
12.79 ± 4.59 V

Fig. 2: With anneal (data from 03/2011)



MIMCAP Device IV Curve: HfO_2 thermal ALD thin film (std. recipe) at 300°C

Fig: 1: No anneal, 270 loops (24.07 nm thick)

Fig. 2: Annealed at 500°C in Ar atmosphere for 30 min, 270 loops (24.07 nm thick)

Fig. 1: Without anneal (data from 03/2011)

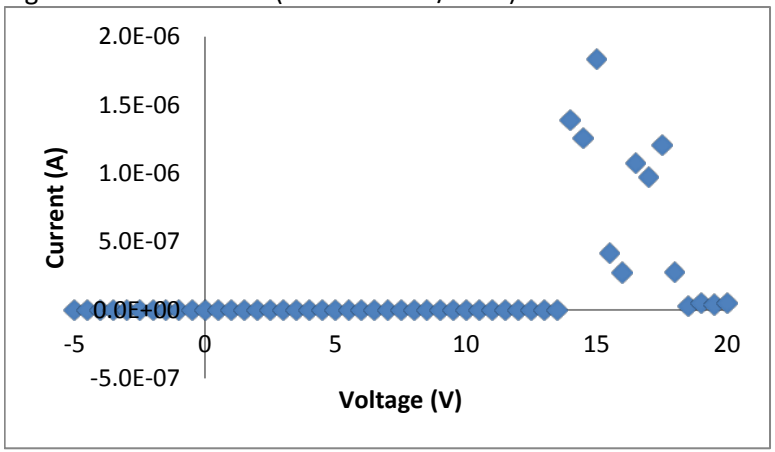
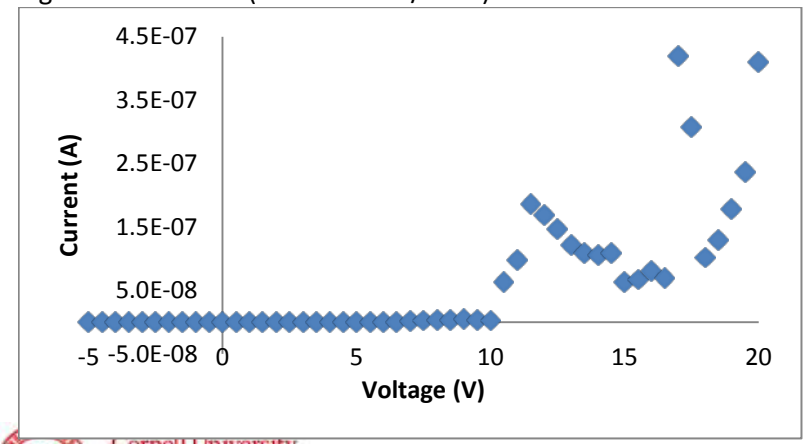


Fig. 2: With anneal (data from 03/2011)



Breakdown voltages:

1. Without anneal (n=6):

7.0 V	14.0 V	7.0 V	5.5 V	12.0 V
12.0 V				

Average breakdown voltage:
7.25 ± 7.71 V

2. With anneal (n=4):

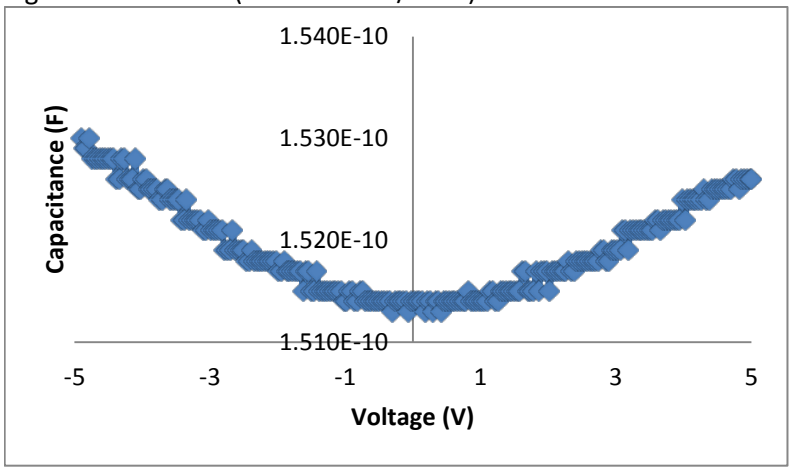
10.5 V	5.5 V	10.5 V	10.5 V	

Average breakdown voltage:
9.25 ± 2.50 V

MIMCAP Device CV Curve: HfO_2 plasma ALD thin film (std. recipe) at 300°C

Fig: 1: Annealed at 500°C in Ar atmosphere for 30 min, 240 loops (25.08 nm thick)

Fig. 1: With anneal (data from 03/2011)



Dielectric constants:

1. With anneal (n=1):

19.1				

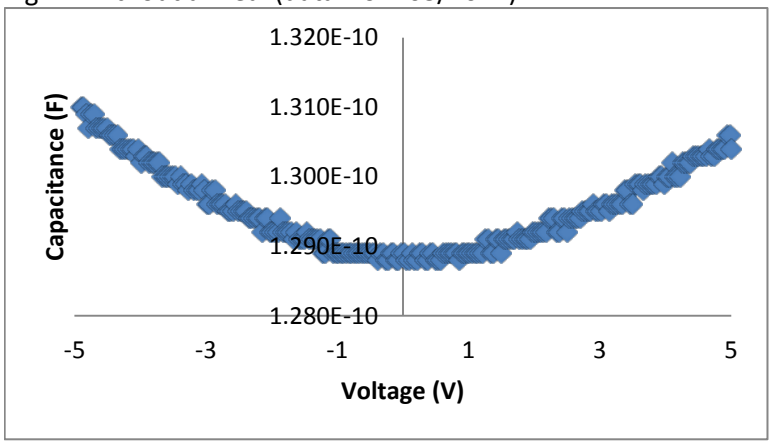
Dielectric constant:
19.1

MIMCAP Device CV Curve: HfO_2 thermal ALD thin film (std. recipe) at 300°C

Fig: 1: No anneal, 270 loops (24.07 nm thick)

Fig. 2: Annealed at 500°C in Ar atmosphere for 30 min, 270 loops (24.07 nm thick)

Fig. 1: Without anneal (data from 03/2011)



Dielectric constants:

1. Without anneal (n=6):

17.0	15.9	15.7	15.3	10.9
15.3				

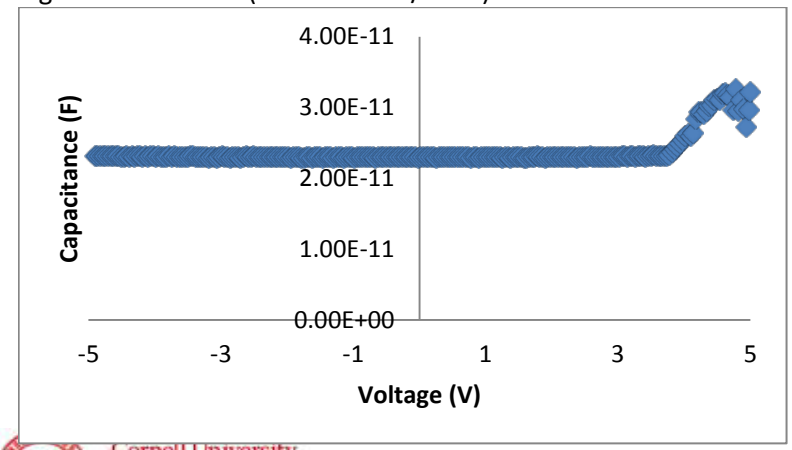
Average dielectric constant:
15.0 ± 2.1

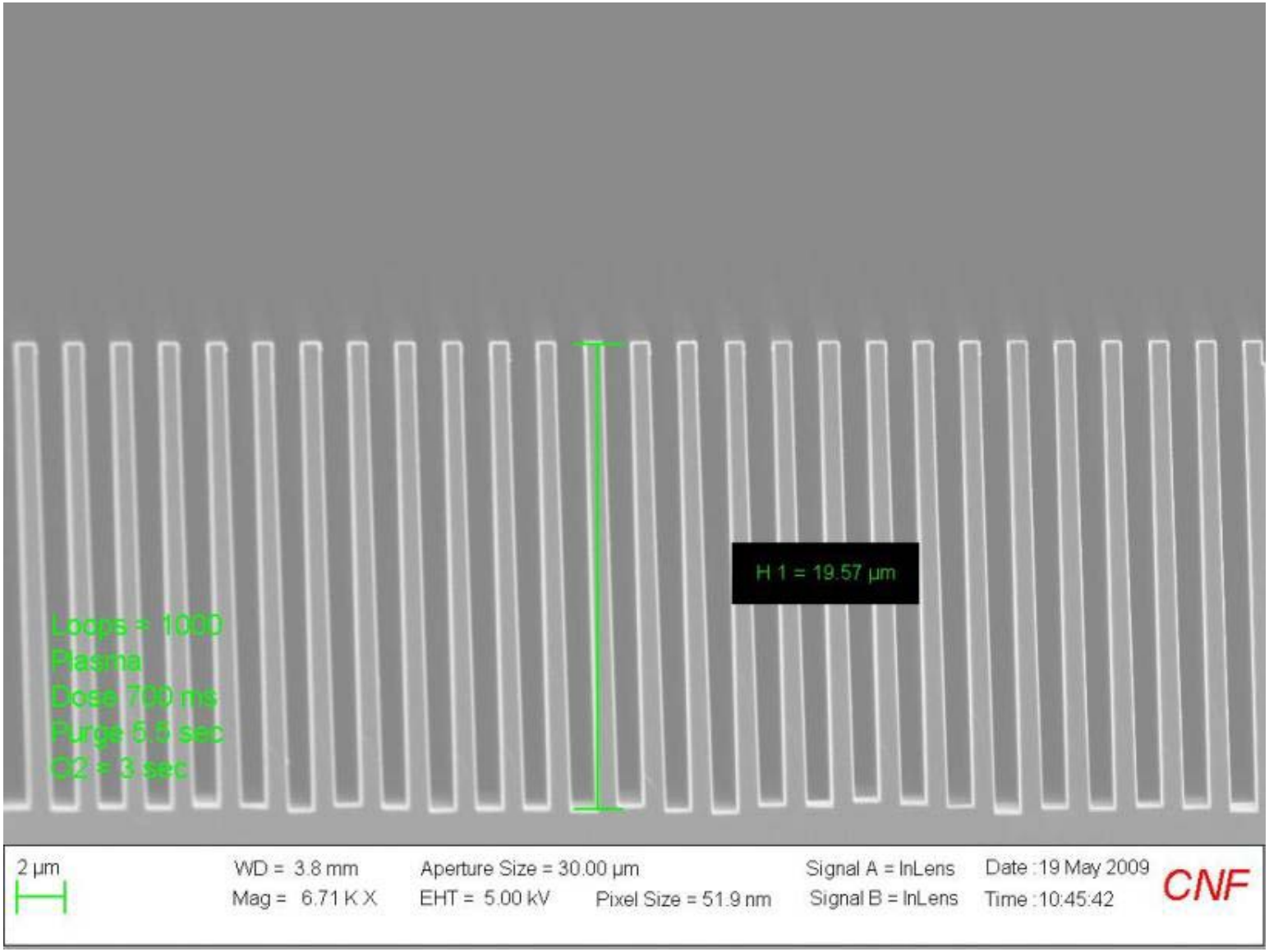
2. With anneal (n=2):

25.0				

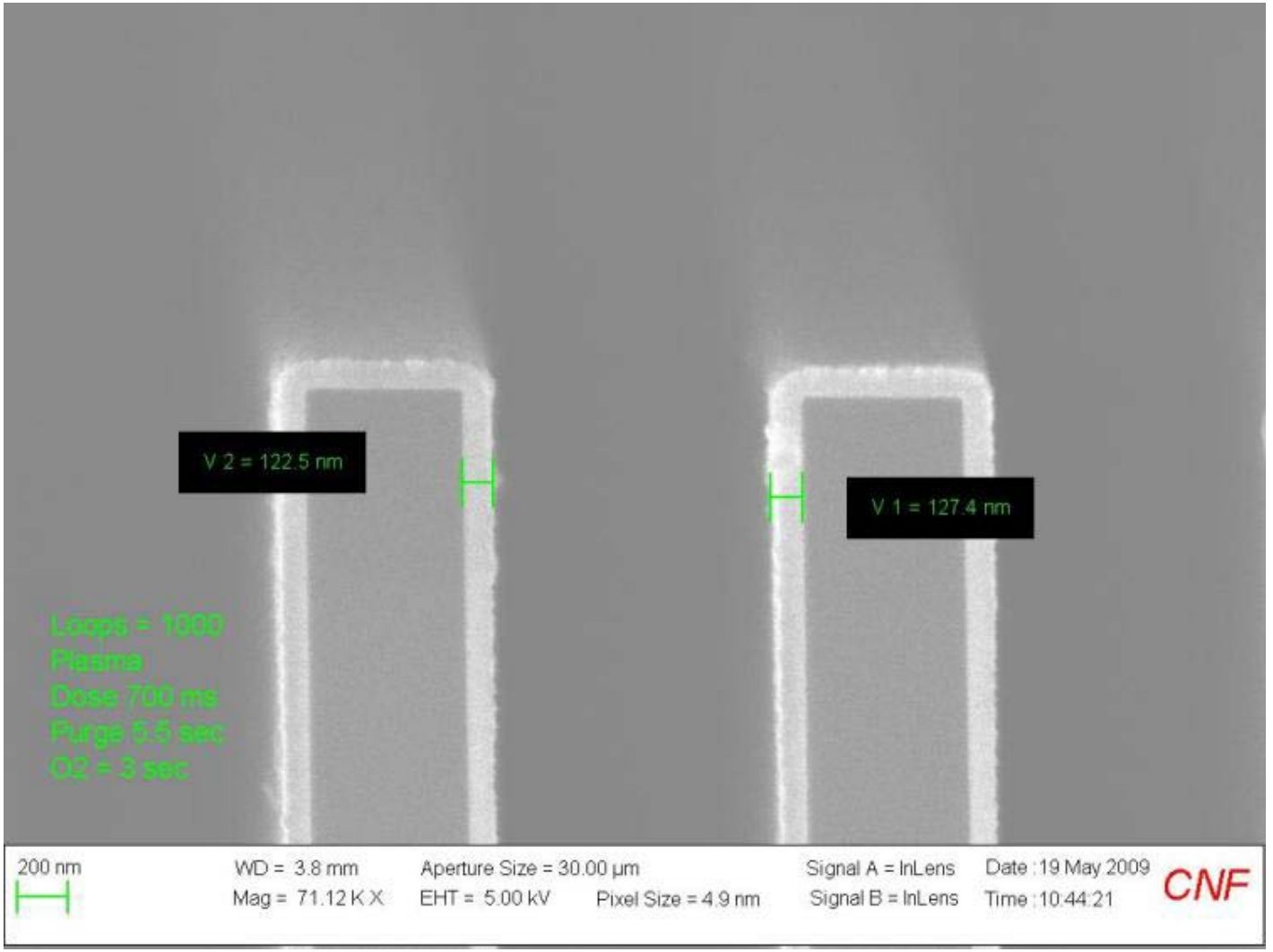
Average dielectric constant:
25.0

Fig. 2: With anneal (data from 03/2011)

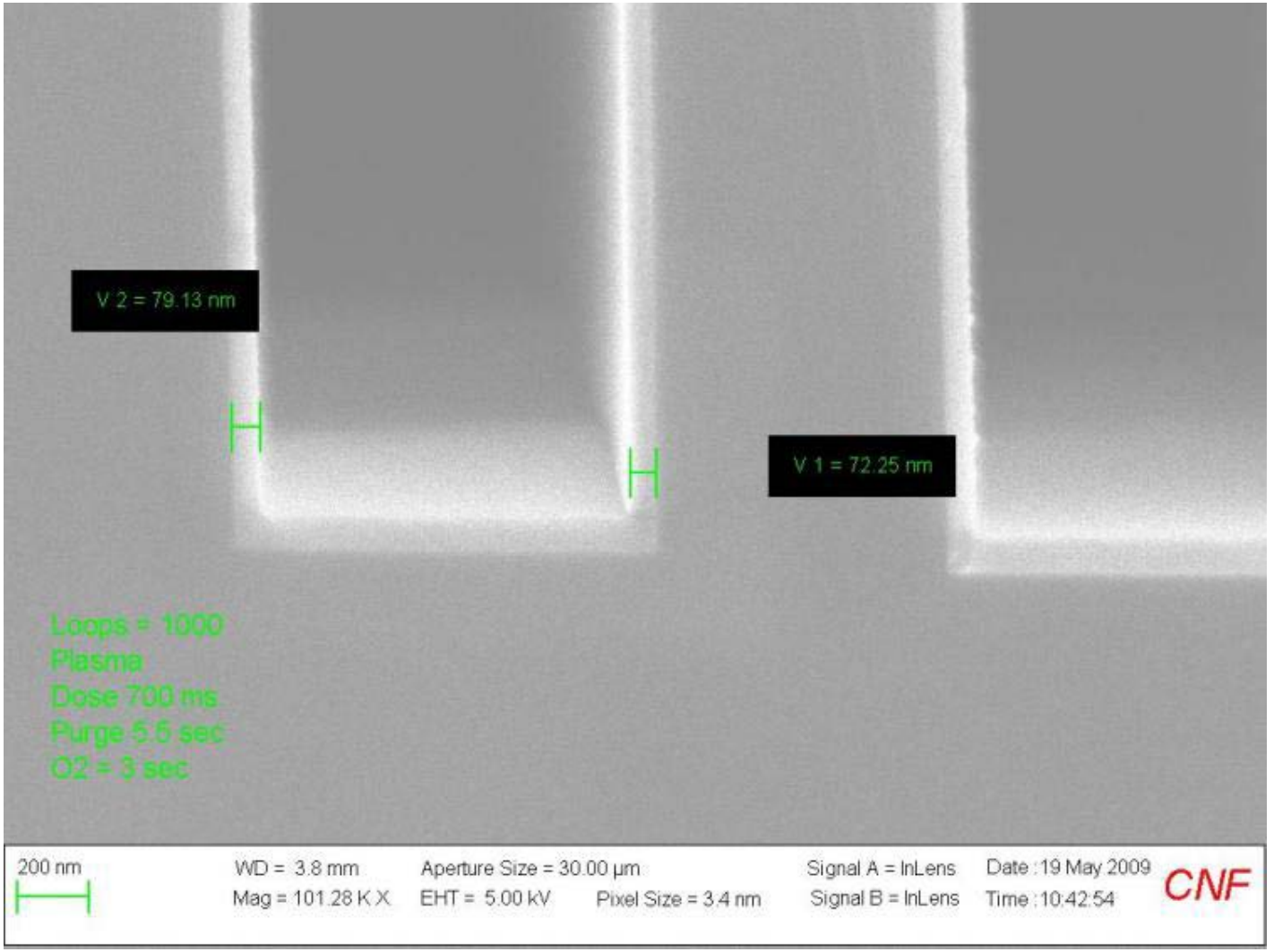




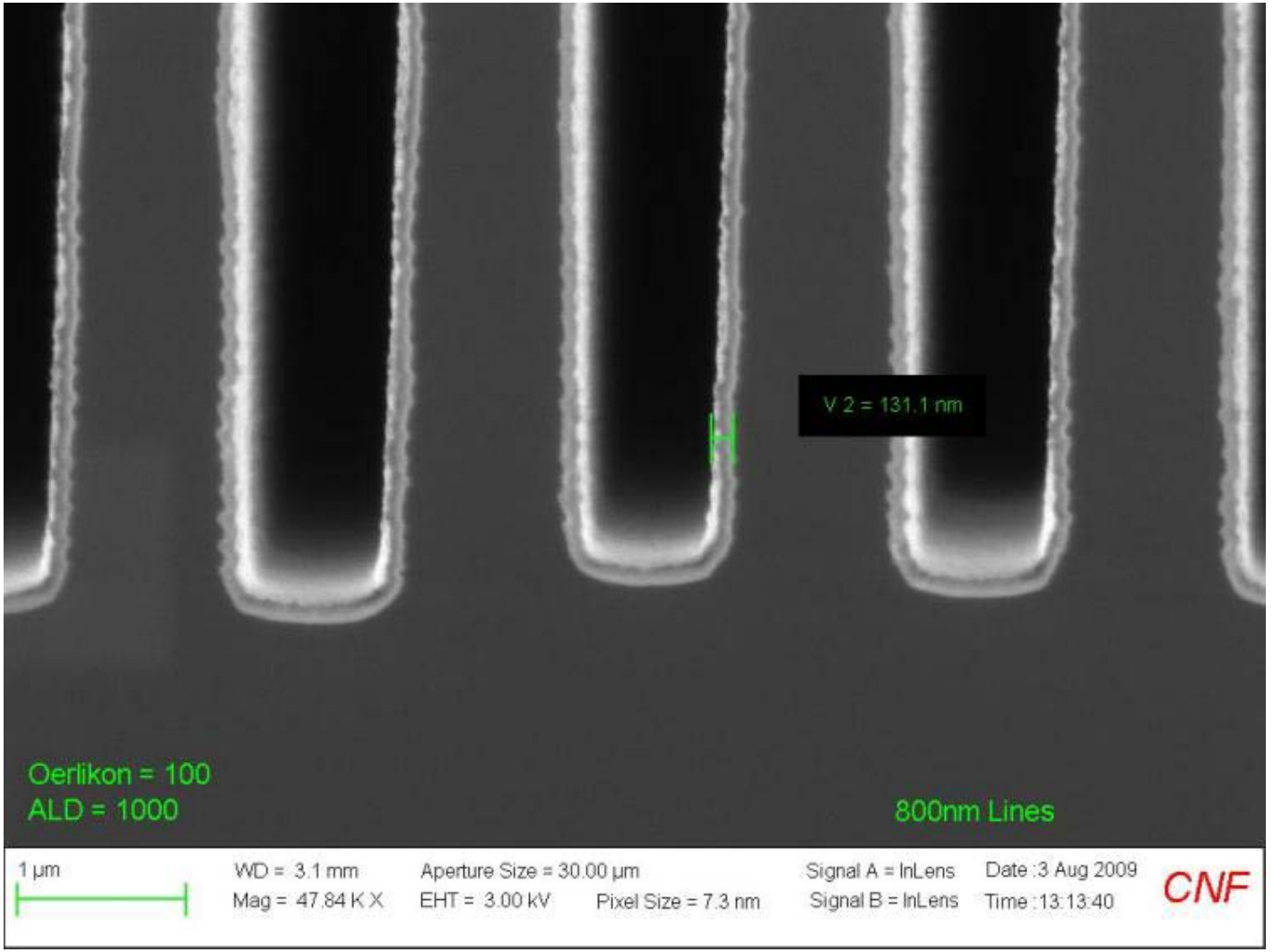
20 micron deep KOH etch. 1 micron line/space
300C HfO2 plasma, 5 sec. hold time



300C HfO2 plasma, 5 sec. hold time, 125nm at the top edge.



Approximately 75nm at the bottom edge,
HfO2 plasma 300C, 5 sec. hold time



Modified ALD recipe:

Approximately 130nm at the bottom 50um DRIE trench.

ALD alumina and Plasmatherm Versaline DRIE etching

ALD alumina has shown to be a good etch mask for the new Versaline DRIE silicon etcher. The selectivity to silicon has been shown to be 2000:1. In the image above 15nm of ALD alumina was used to etch 25 microns into silicon. The alumina can be etched in a chlorine plasma or wet etched in basic developer.

Silicon nitride PEALD

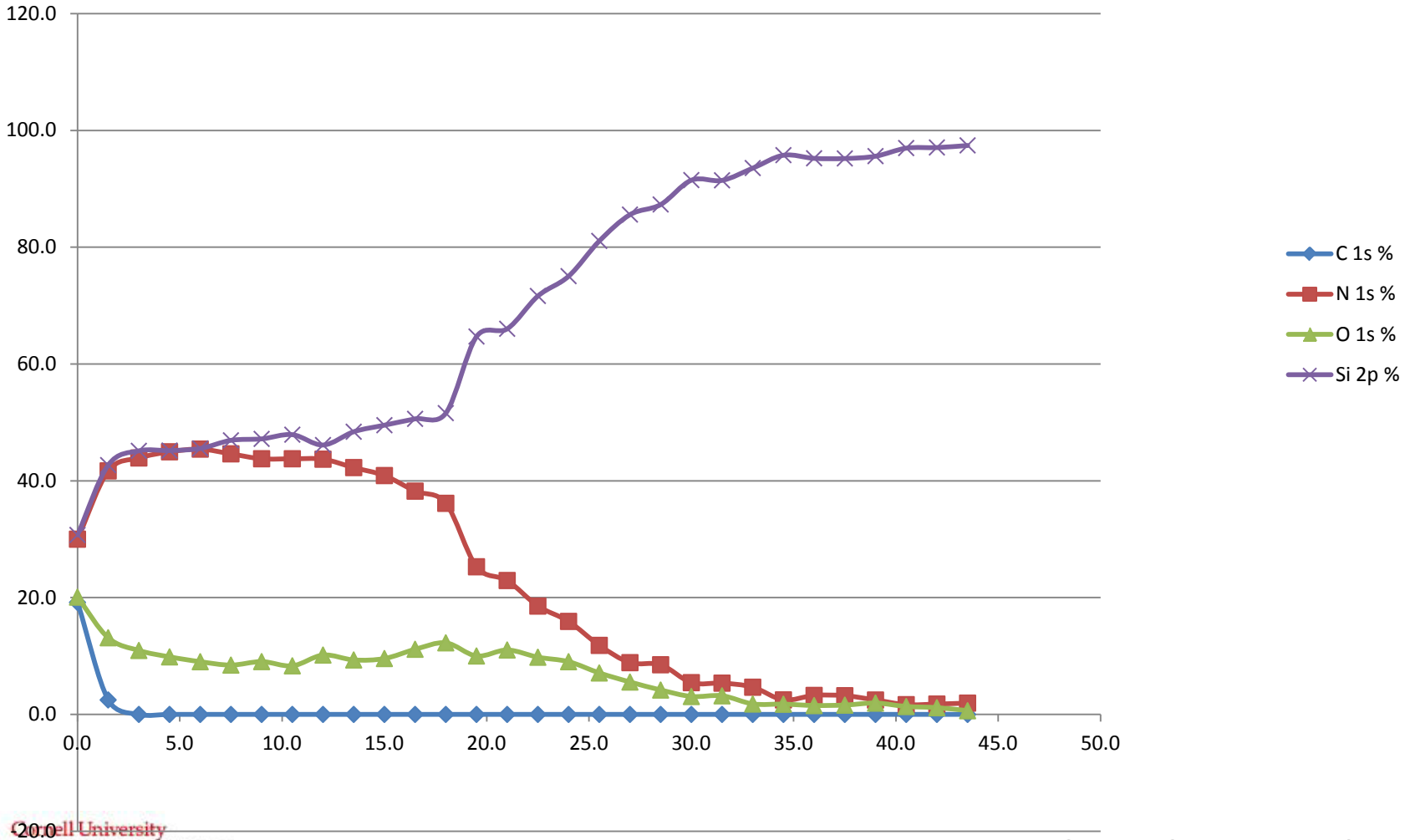
Pre-processing steps:

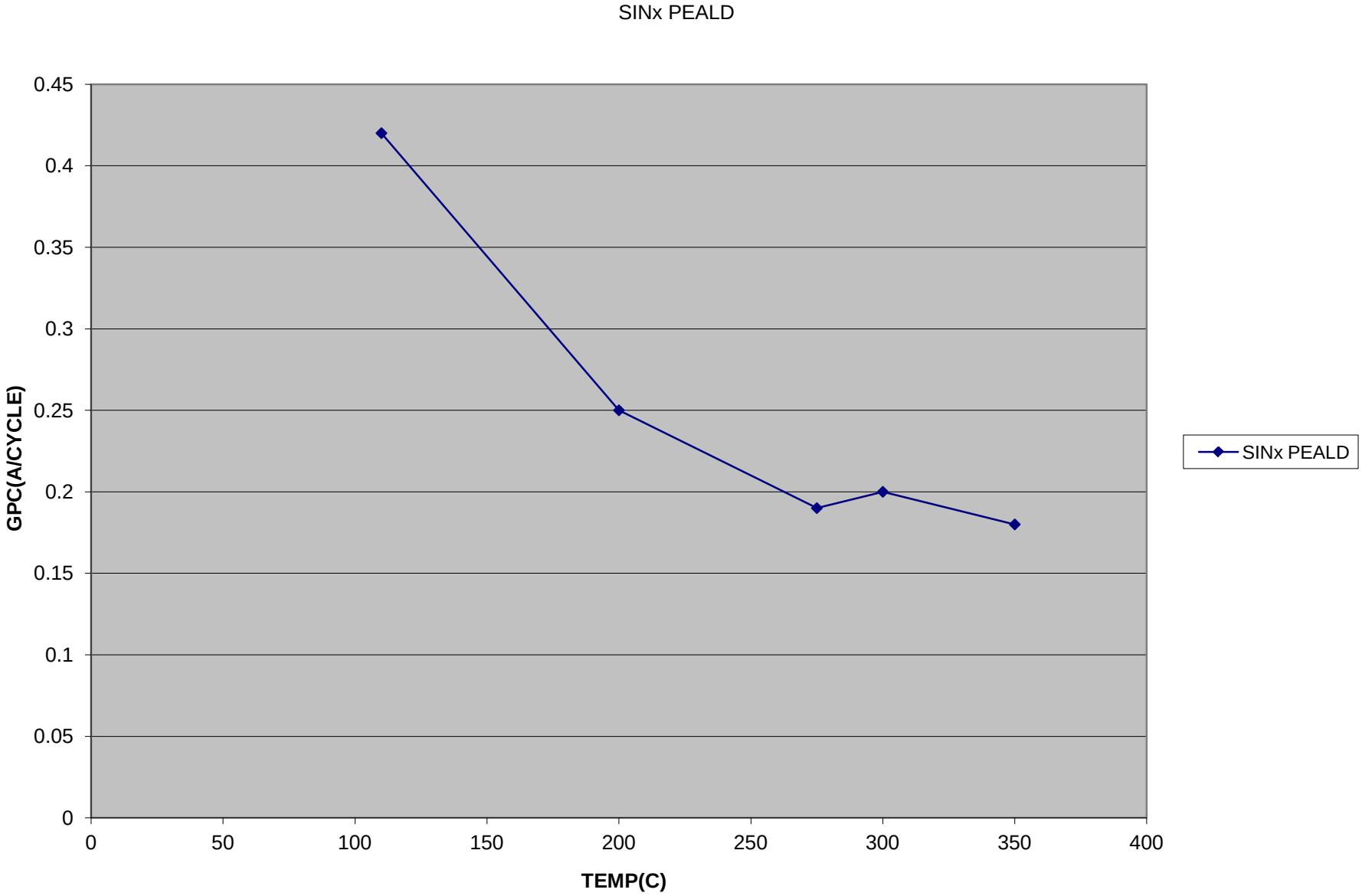
- FlexAl chamber conditioning: 30 loops of aluminum oxide plasma deposition (TMA/O2) to reduce the oxygen level in the main chamber followed by a series of pump/purge cycles.
- In-situ NH3 plasma surface pre-treatment at 110C for 5 min to induce nitridation of the silicon surface.

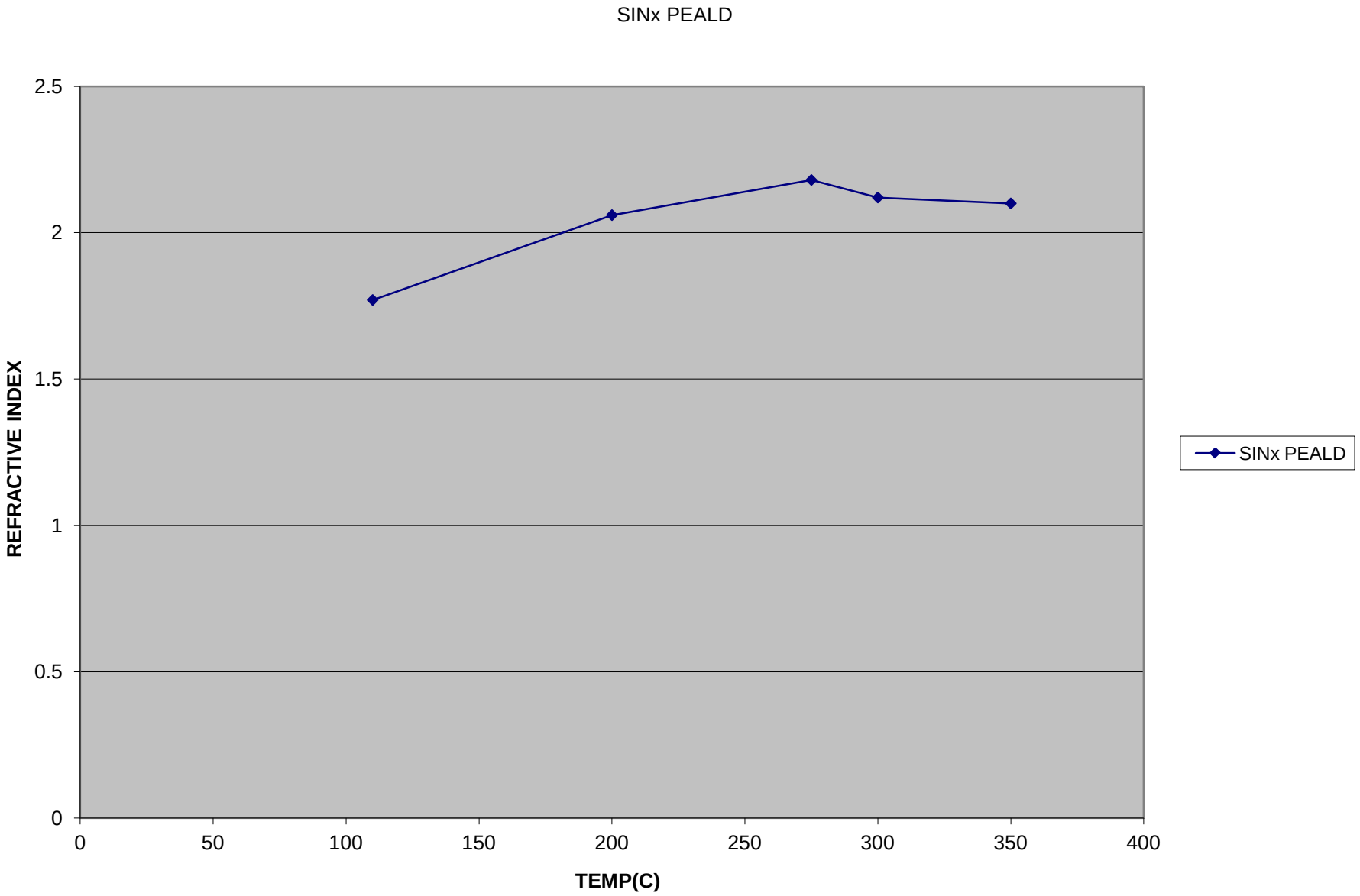
Silicon nitride PEALD process

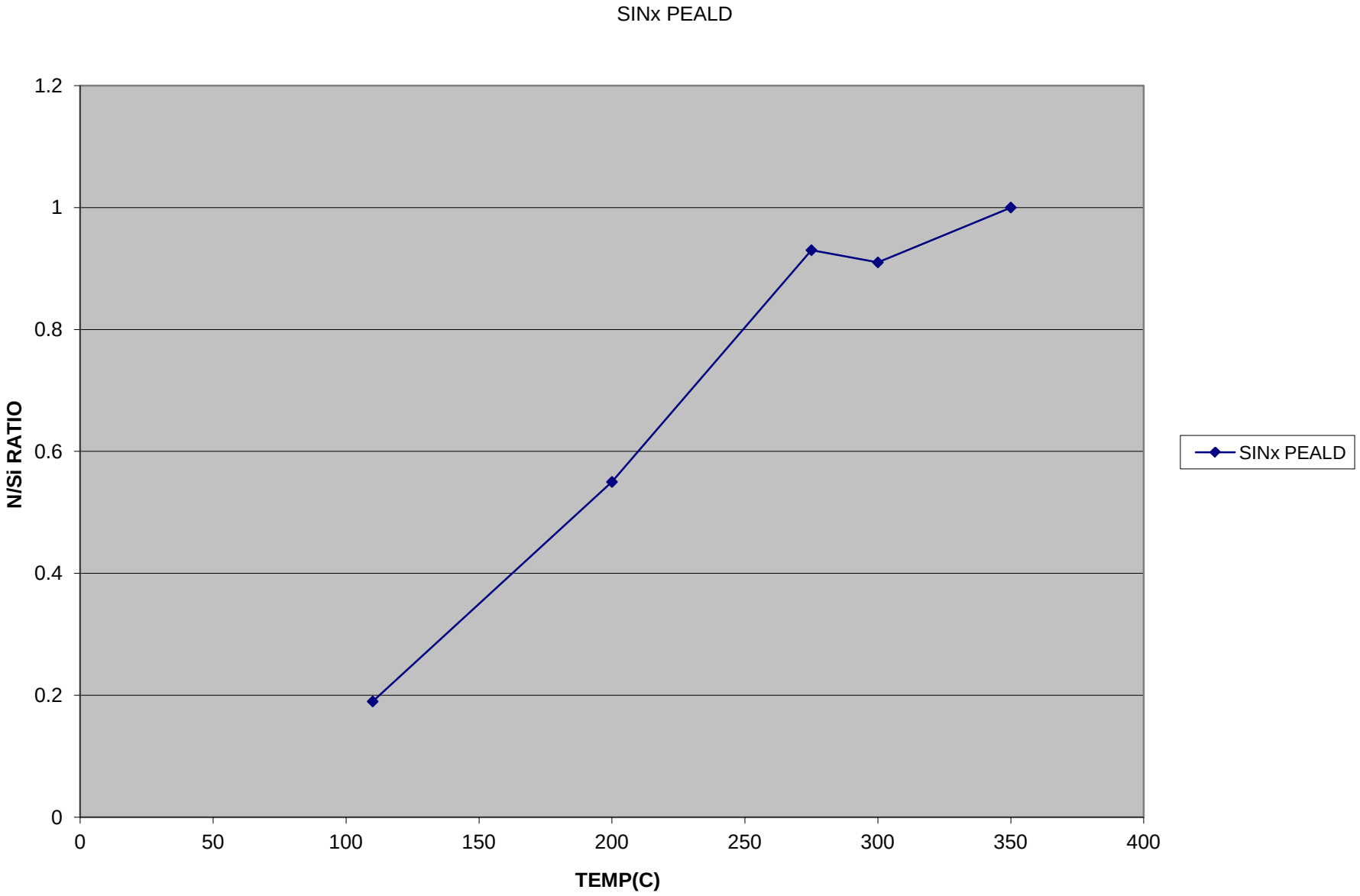
- 3DMAS dosage: 1.6 sec
- Hold 3DMAS (APC valve closed): 10 sec.
- 3DMAS purge: 2 sec.
- Ar/N2 (20/40) plasma: 300W, 10mT, 15 sec.

XPS Silicon Nitride PEALD, 350C, 64A, 10/19/2010




SINx PEALD
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
GPC(A/CYCLE)
0
50
100
150
200
250
300
350
400
TEMP(C)
SINx PEALD


SINx PEALD
REFRACTIVE INDEX
2.5
2
1.5
1
0.5
0
0
50
100
150
200
250
300
350
400
TEMP(C)
SINx PEALD


SINx PEALD
1.2
1
0.8
0.6
0.4
0.2
0
N/Si RATIO
0
50
100
150
200
250
300
350
400
TEMP(C)
SINx PEALD

Silicon nitride experimental observations

- 200C deposition temperature threshold for minimal oxygen incorporation.
- No residual carbon detected in the film, suggesting complete ligand exchange.
- Argon presence in the plasma half reaction (Ar/N2) has importance.
- NH3 plasma wafer pre-treatment important for growth initiation.

Silicon nitride experimental observations

- Nitrogen content shows dependence on higher temperatures.
- Further experimentation needed to obtain a stoichiometric nitride Si3N4.
- Higher temps > 350C and/or adjustment of plasma composition (note: plasma power limited to 300W generator)

Novel Gate Dielectrics

- Hf aluminates (HfAlOx)
- Hf silicates (HfSiOx)
- Hf silicon oxynitrides (HfSiOxNy)

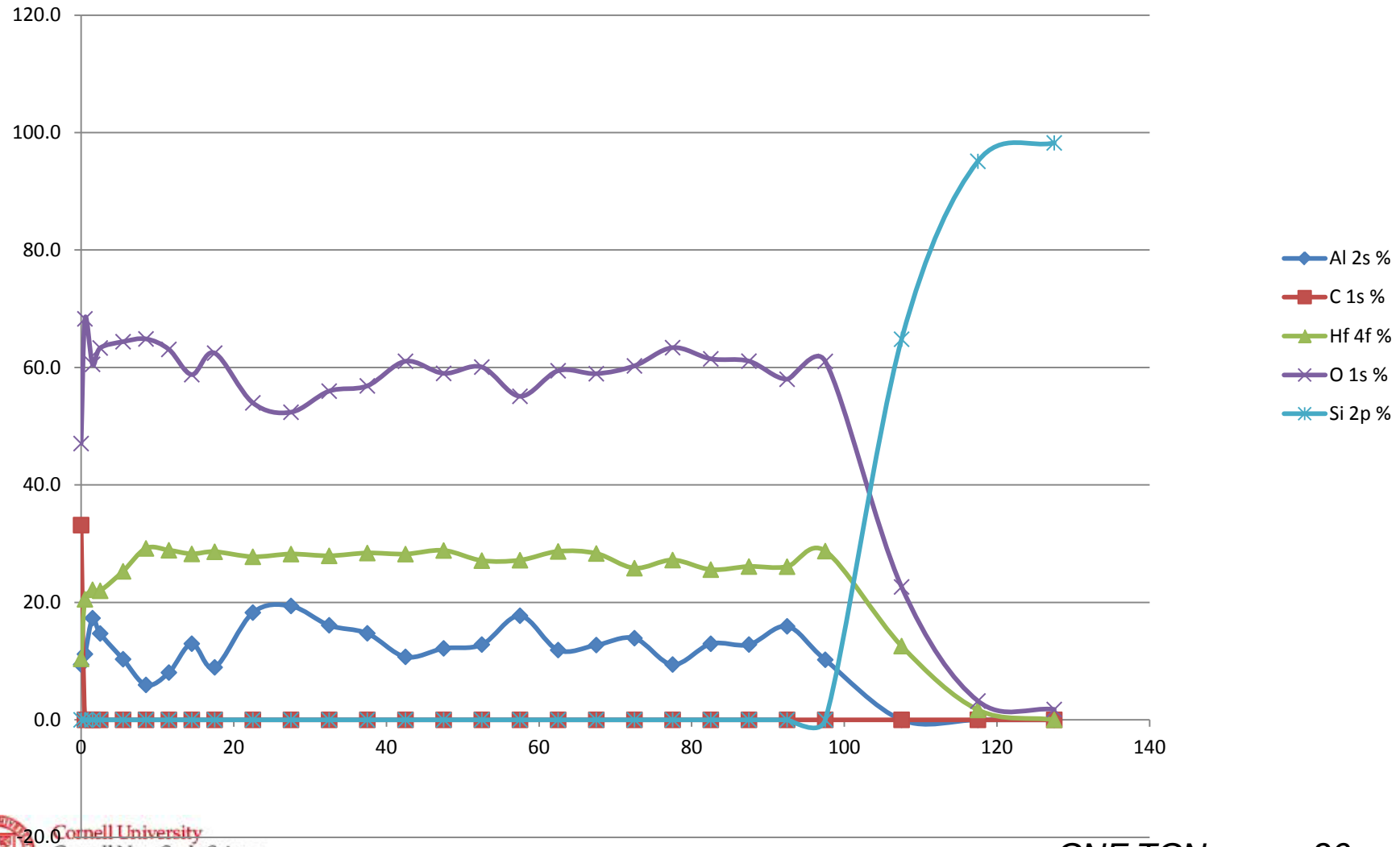
Motivation:

- Adjustable dielectric constant k
- Higher thermal stability
- Higher electron mobilities

HfAlOx PEALD

- 200C
- TEMAH:TMA = 2:1
- 600/300 cycles
- GPC = 1.01A/cycle
- Index = 1.86
- XPS at.%: Hf(28%), Al(18%), O2(54%)

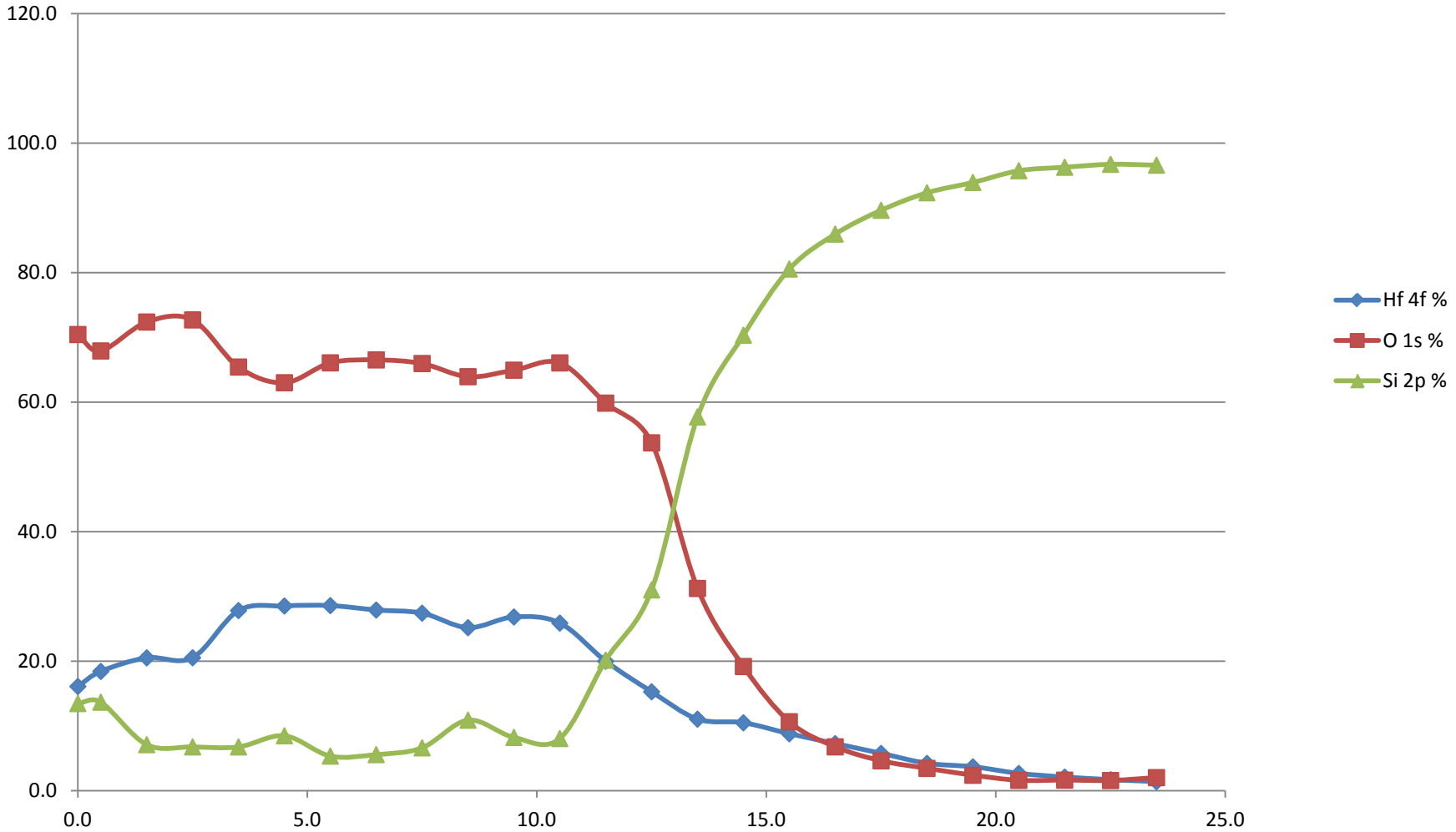
HfAlOx 200C , TEMAH/TMA (2:1)



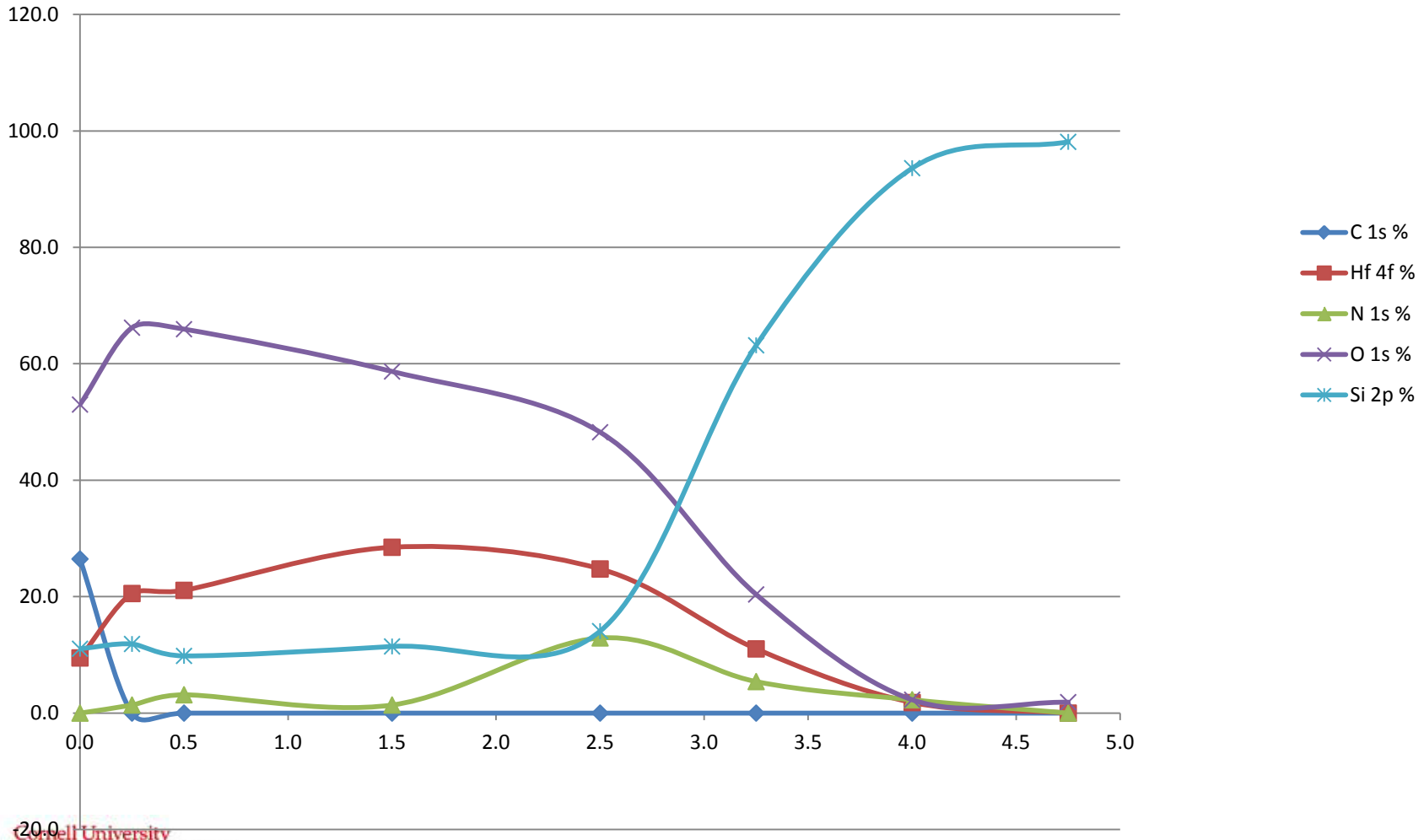
HfSiOx PEALD

- 200C
- TEMAH:3DMAS = 2:1, 100/50 cycles
- XPS at.%: Hf(28%), Si(10%), O2(62%)
- GPC = 0.91A/cycle, index = 1.925
- TEMAH:3DMAS = 1:1, 200/200 cycles
- XPS at.%: Hf(25), Si(14), O(48), N(13) at interface
- GPC = 0.94A/cycle, index = 1.7164

HfSiOx-200C
TEMAH:3DMAS (2:1)



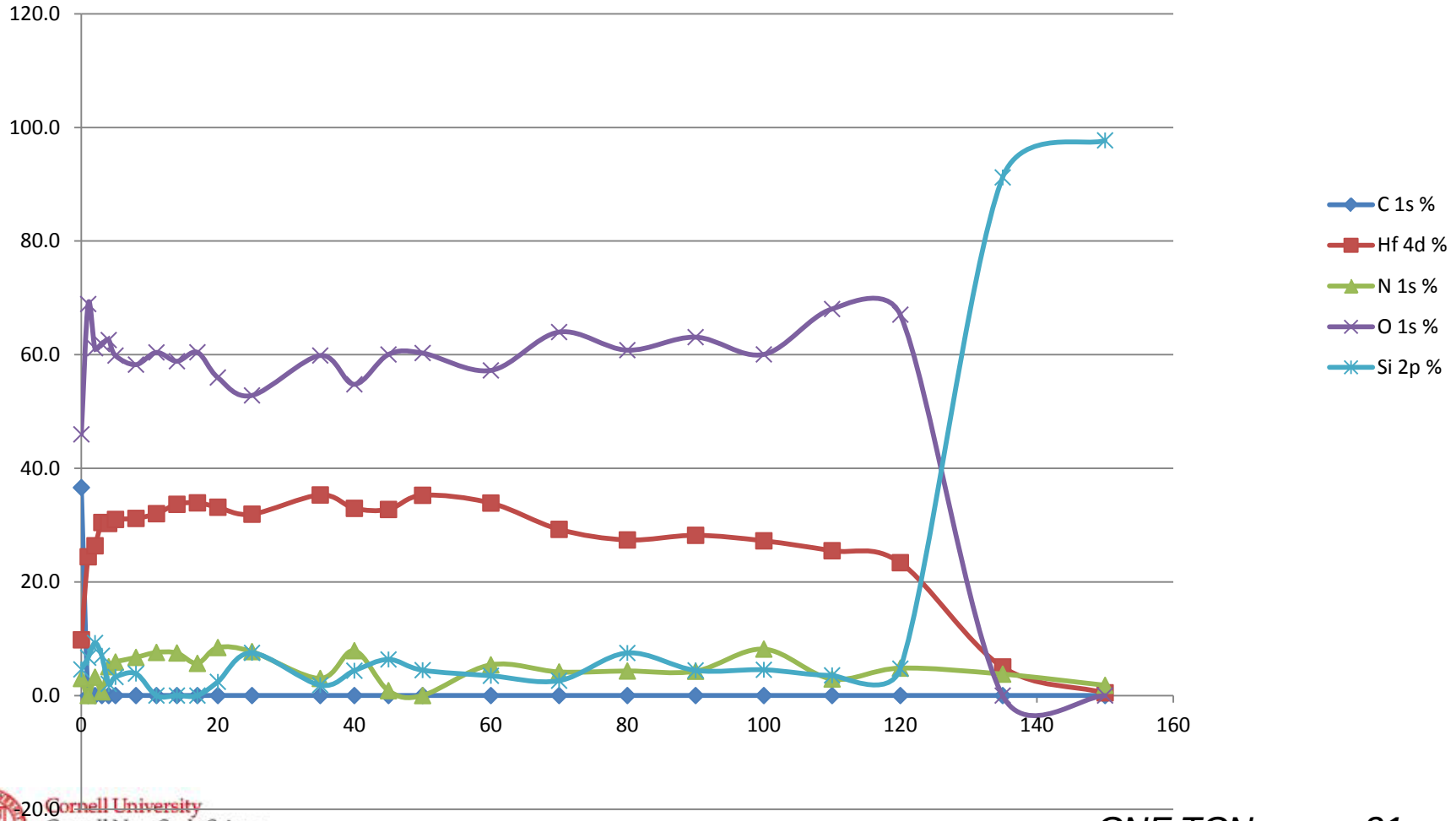
HfSiOx, 200C, TEMAH/3DMAS (2:2)
4keV N 1s peak used



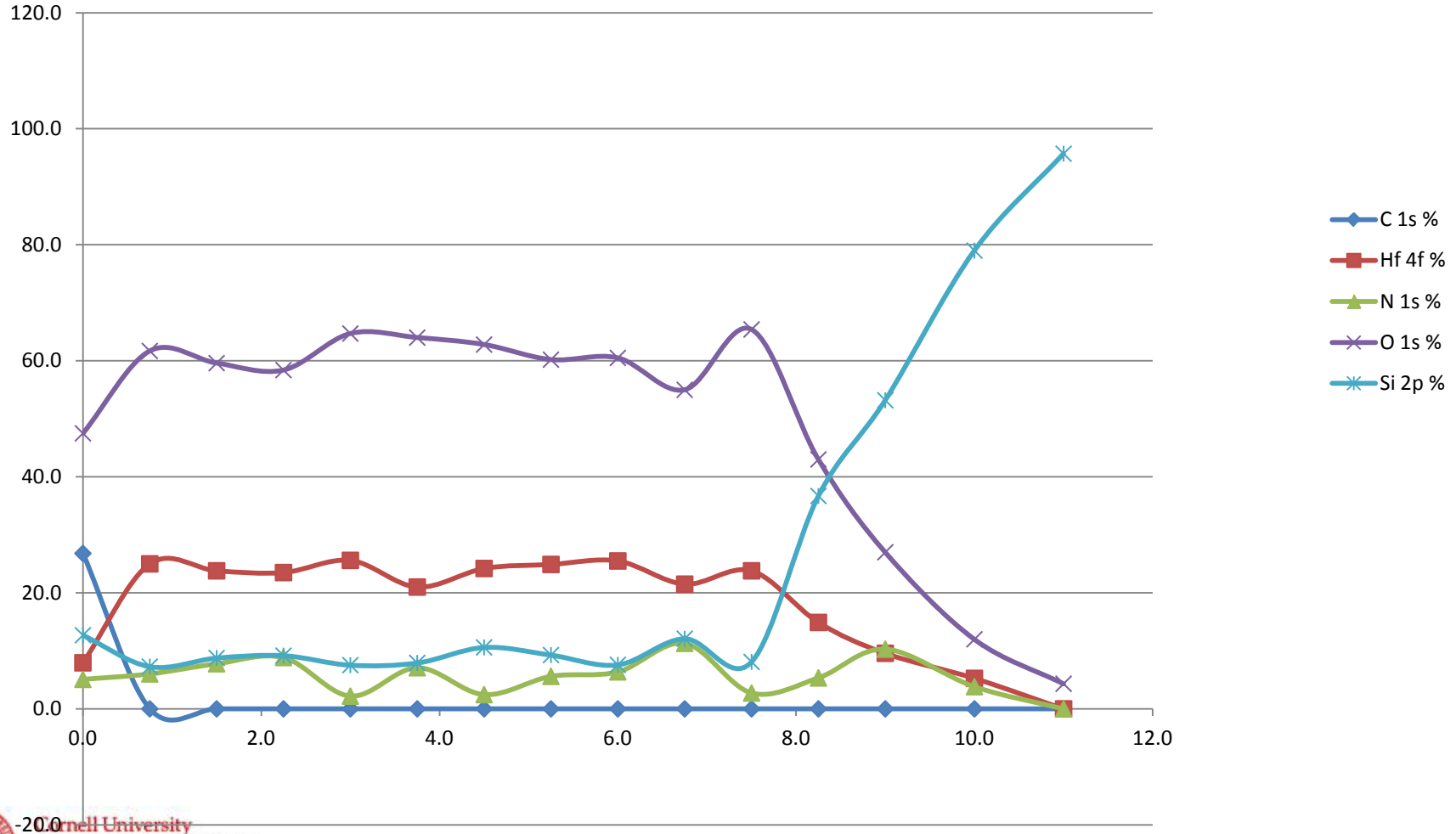
HfSiON PEALD

- TEMAH:3DMAS = 2:1, 800/400 cycles
- 200C
- XPS at.% = Hf(32), Si(6), O(54), N(8)
- GPC = 0.85A/cycle
- TEMAH:3DMAS = 1:1, 500/500 cycles
- 200C
- XPS at.% = Hf(22), Si(12), O(55), N(11)
- GPC = 0.86A/cycle, index = 1.7288

HfSiON-200C
TEMAH:3DMAS (2:1)



HfSiOxNy, 200C, TEMAH/3DMAS (2:2)



Future research and activities

- Selective area ALD using dimethylamine (DMA)
- Graphene functionalization and seeding for dielectric ALD
- Continued work on high aspect ratio coatings of DRIE structures
- Purchase of additional system for metals and other user desired materials