

## Expo Mode Al<sub>2</sub>O<sub>3</sub> on Fiji using trimethylaluminium (TMA) and H<sub>2</sub>O

Temperature (TMA) = unheated precursor line #2; unheated H<sub>2</sub>O on precursor line #0

Purge flows = 140 (plasma) + 40 (carrier) sccm

Expo flows = 60 (plasma) + 20 (carrier) sccm

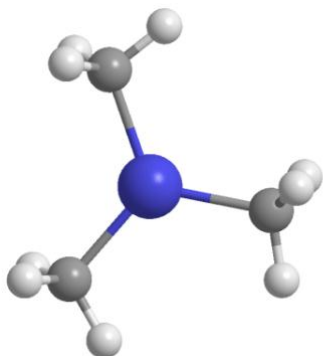
Reactor, chuck and trap temperature = 175°C

Expo time = 60 sec (line 9, 19)

Purge = 90 sec (line 13, 23)

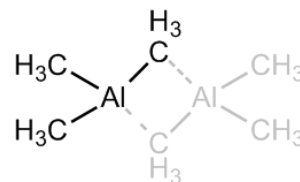
|    |           |   |      |
|----|-----------|---|------|
| 0  | wait      |   | 1800 |
| 1  | flow      | 0 | 40   |
| 2  | flow      | 1 | 140  |
| 3  | wait      |   | 30   |
| 4  | stopvalve |   | 0    |
| 5  | pulse     | 2 | 0.4  |
| 6  | wait      |   | 1    |
| 7  | flow      | 0 | 20   |
| 8  | flow      | 1 | 60   |
| 9  | wait      |   | 60   |
| 10 | flow      | 0 | 40   |
| 11 | flow      | 1 | 140  |
| 12 | stopvalve |   | 1    |
| 13 | wait      |   | 90   |
| 14 | stopvalve |   | 0    |
| 15 | pulse     | 0 | 0.12 |
| 16 | wait      |   | 1    |
| 17 | flow      | 0 | 20   |
| 18 | flow      | 1 | 60   |
| 19 | wait      |   | 60   |
| 20 | flow      | 0 | 40   |
| 21 | flow      | 1 | 140  |
| 22 | stopvalve |   | 1    |
| 23 | wait      |   | 90   |
| 24 | goto      | 4 | x    |
| 25 | flow      | 0 | 10   |
| 26 | flow      | 1 | 20   |

**Precursors:**



Trimethylaluminum, TMA, Al(CH<sub>3</sub>)<sub>3</sub>  
CAS #: 75-24-1

Water, H<sub>2</sub>O or O<sub>2</sub> plasma



**Note: Both Trimethylaluminum (TMA) and H<sub>2</sub>O are unheated**

**Door purge = 50sccm**

**0.06s room temperature TMA pulse ≈ 1.2mg**

**Fiji Thermal Al<sub>2</sub>O<sub>3</sub> Recipe**

A generic thermal Al<sub>2</sub>O<sub>3</sub> recipe is shown to the right. Depending on the desired process temperature, use values from the table below to create a recipe appropriate for your application.

| Temperature (C) | TMA Purge (s) | H <sub>2</sub> O Purge (s) |
|-----------------|---------------|----------------------------|
| 300             | 5             | 5                          |
| 250             | 8             | 8                          |
| 200             | 10            | 10                         |
| 150             | 20            | 20                         |
| 100             | 30            | 30                         |
| 75              | 60            | 60                         |
| 50              | 120           | 120                        |
| 25              | 180           | 180                        |

**APC Command Note:**

If Fiji system is equipped with a turbo pump and APC valve, set the APC valve so the system pressure is 200mTorr when the door purge is 50sccm, the carrier Ar is 60sccm, and the plasma Ar is 200sccm.

|    | Instruction | #   | Value     |                                                             |
|----|-------------|-----|-----------|-------------------------------------------------------------|
| 0  | flow        | 0   | 20        | Set precursor manifold stand-by Ar flow rate                |
| 1  | flow        | 1   | 40        | Set plasma source stand-by Ar flow rate                     |
| 2  | heater      | 12  | See table | Set trap/cone temperature                                   |
| 3  | heater      | 13  | See table | Set reactor zone 1 temperature                              |
| 4  | heater      | 14  | See table | Set reactor zone 2 temperature                              |
| 5  | heater      | 15  | See table | Set chuck temperature                                       |
| 6  | heater      | 16  | 150       | Set precursor delivery line to 150C                         |
| 7  | heater      | 17  | 150       | Set precursor manifold to 150C                              |
| 8  | stabilize   | 12  |           | Wait for trap/cone temperature to stabilize                 |
| 9  | stabilize   | 13  |           | Wait for reactor zone 1 temperature to stabilize            |
| 10 | stabilize   | 14  |           | Wait for reactor zone 2 temperature to stabilize            |
| 11 | stabilize   | 15  |           | Wait for chuck temperature to stabilize                     |
| 12 | wait        |     | 600       | Wait for substrate temperature to stabilize                 |
| 13 | flow        | 0   | 30        | Set precursor manifold Ar for expo step                     |
| 14 | flow        | 1   | 100       | Set plasma source Ar for expo step                          |
| 15 | APC         |     | See note  | Set throttle valve. If no throttle valve, remove this line  |
| 16 | wait        |     | 10        | Wait for Ar MFCs to stabilize                               |
| 17 | pulse       | TMA | 0.06      | Begin loop. Pulse TMA. TMA = TMA ALD valve number           |
| 18 | wait        |     | See table | Purge TMA and reaction by-products                          |
| 19 | pulse       | H2O | 0.06      | Pulse H2O. H2O = H2O ALD valve number                       |
| 20 | wait        |     | See table | Purge H2O and reaction by-products                          |
| 21 | goto        | a   | x         | a = TMA pulse line number, x = cycles, GPC ~ 1A/cycle       |
| 22 | flow        | 0   | 20        | Set precursor manifold stand-by Ar flow rate                |
| 23 | flow        | 1   | 40        | Set plasma source stand-by Ar flow rate                     |
| 24 | APC         |     | 100       | Open throttle valve. If no throttle valve, remove this line |

### Fiji Plasma Al<sub>2</sub>O<sub>3</sub> Recipe

A generic plasma Al<sub>2</sub>O<sub>3</sub> recipe is shown to the right. Depending on the desired process temperature, use values from the table below to create a recipe appropriate for your application.

| Temperature (C) | TMA Purge (s) | O <sub>2</sub> Purge (s) |
|-----------------|---------------|--------------------------|
| 300             | 5             | 5                        |
| 250             | 8             | 5                        |
| 200             | 10            | 5                        |
| 150             | 20            | 5                        |
| 100             | 30            | 5                        |
| 75              | 60            | 5                        |
| 50              | 120           | 5                        |
| 25              | 180           | 5                        |

#### APC Command Note:

If Fiji system is equipped with a turbo pump and APC valve, set the APC valve so the system pressure is 200mTorr when the door purge is 50sccm, the carrier Ar is 60sccm, and the plasma Ar is 200sccm.

|    | Instruction | #   | Value     |                                                                              |
|----|-------------|-----|-----------|------------------------------------------------------------------------------|
| 0  | flow        | 0   | 20        | Set precursor manifold stand-by Ar flow rate                                 |
| 1  | flow        | 1   | 40        | Set plasma source stand-by Ar flow rate                                      |
| 2  | heater      | 12  | See table | Set trap/cone temperature                                                    |
| 3  | heater      | 13  | See table | Set reactor zone 1 temperature                                               |
| 4  | heater      | 14  | See table | Set reactor zone 2 temperature                                               |
| 5  | heater      | 15  | See table | Set chuck temperature                                                        |
| 6  | heater      | 16  | 150       | Set precursor delivery line to 150C                                          |
| 7  | heater      | 17  | 150       | Set precursor manifold to 150C                                               |
| 8  | stabilize   | 12  |           | Wait for trap/cone temperature to stabilize                                  |
| 9  | stabilize   | 13  |           | Wait for reactor zone 1 temperature to stabilize                             |
| 10 | stabilize   | 14  |           | Wait for reactor zone 2 temperature to stabilize                             |
| 11 | stabilize   | 15  |           | Wait for chuck temperature to stabilize                                      |
| 12 | wait        |     | 600       | Wait for substrate temperature to stabilize                                  |
| 13 | flow        | 0   | 30        | Set precursor manifold Ar for expo step                                      |
| 14 | flow        | 1   | 100       | Set plasma source Ar for expo step                                           |
| 15 | APC         |     | See note  | Set throttle valve. If no throttle valve, remove this line                   |
| 16 | wait        |     | 10        | Wait for Ar MFCs to stabilize                                                |
| 17 | pulse       | TMA | 0.06      | Begin loop. Pulse TMA. TMA = TMA ALD valve number                            |
| 18 | wait        |     | See table | Purge TMA and reaction by-products                                           |
| 19 | flow        | 3   | 50        | Start O <sub>2</sub> flow.                                                   |
| 20 | plasma      |     | 300       | Turn on plasma.                                                              |
| 21 | wait        |     | 20        | Pulse H <sub>2</sub> O. H <sub>2</sub> O = H <sub>2</sub> O ALD valve number |
| 22 | plasma      |     | 0         | Turn off plasma.                                                             |
| 23 | flow        | 3   | 0         | Turn off O <sub>2</sub> .                                                    |
| 24 | wait        |     | See table | Purge O <sub>2</sub> and reaction by-products                                |
| 25 | goto        | a   | x         | a = TMA pulse line number, x = cycles, GPC ~ 1A/cycle                        |
| 26 | flow        | 0   | 20        | Set precursor manifold stand-by Ar flow rate                                 |
| 27 | flow        | 1   | 40        | Set plasma source stand-by Ar flow rate                                      |
| 28 | APC         |     | 100       | Open throttle valve. If no throttle valve, remove this line                  |

Prefilled cylinders compatible with Savannah™ ALD reactors available from:

#### Strem Chemicals

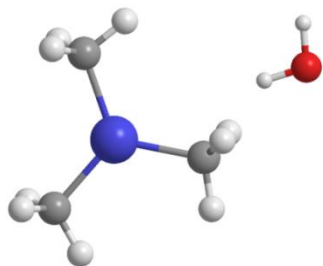
<http://www.strem.com/catalog/v/98-4003/1/>

#### Sigma-Aldrich

[http://www.sigmaaldrich.com/catalog/ProductDetail.do?N4=663301|ALDRICH&N5=SEARCH\\_CONCAT\\_PNO|BRAND\\_KEY&F=SPEC](http://www.sigmaaldrich.com/catalog/ProductDetail.do?N4=663301|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC)

## Fiji Film Recipe

### Precursors:



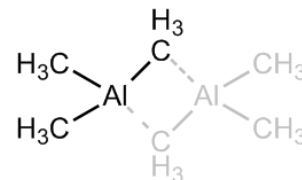
Trimethylaluminum, TMA,  $\text{Al}(\text{CH}_3)_3$

CAS #: 75-24-1, unheated

$\text{N}_2$  gas, Electronic grade 99.999+%

$\text{H}_2$  gas, Electronic grade 99.999+%

$\text{NH}_3$  gas, Electronic grade 99.999+%



Door purge = 50 sccm

Recommended idle flow rates: flow 0 = 15 sccm, flow 1 = 30 sccm

### Fiji Plasma AlN Recipe with $\text{NH}_3$

|    | Instruction | #     | Value     |                                                                        |
|----|-------------|-------|-----------|------------------------------------------------------------------------|
| 0  | heater      | 12    | T1        | Set temperatures for various heaters                                   |
| 1  | heater      | 13    | T2        | Refer to Table 1 for details                                           |
| 2  | heater      | 14    | T2        |                                                                        |
| 3  | heater      | 15    | T3        |                                                                        |
| 4  | stabilize   |       | 12        | Wait for temperatures to stabilize                                     |
| 5  | stabilize   |       | 13        |                                                                        |
| 6  | stabilize   |       | 14        |                                                                        |
| 7  | stabilize   |       | 15        |                                                                        |
| 8  | wait        |       | 3600/7200 | Prebake time (seconds) with/without loadlock                           |
| 9  | MFC valve   | NH3 # | 1         | Open $\text{NH}_3$ pneumatic valve                                     |
| 10 | APC         |       | 23        | Set throttle valve. Delete this line if no throttle valve <sup>1</sup> |
| 11 | flow        | 0     | 30        | Set precursor carrier Ar flow rate                                     |
| 12 | flow        | 1     | 100       | Set plasma source Ar flow rate                                         |
| 13 | wait        |       | 30        |                                                                        |
| 14 | pulse       | TMA # | 0.06      | Pulse TMA for 0.06 s, consumption rate $\approx 1.25\text{mg/pulse}$   |
| 15 | wait        |       | 10        | Purge 10 seconds                                                       |
| 16 | flow        | NH3 # | 20        | Set $\text{NH}_3$ plasma gas flow rate                                 |
| 17 | wait        |       | 1         | Wait for $\text{NH}_3$ flow to start                                   |
| 18 | plasma      |       | 300       | Light plasma, 300 W power                                              |
| 19 | wait        |       | 40        | 40 seconds plasma exposure time                                        |
| 20 | plasma      |       | 0         | Turn off plasma, 0 W power                                             |
| 21 | flow        | NH3 # | 0         | Turn off $\text{NH}_3$ plasma gas                                      |
| 22 | wait        |       | 10        | Purge 10 seconds                                                       |
| 23 | goto        | 14    | n         | Set # of cycles                                                        |
| 24 | MFC valve   | NH3 # | 0         | Close $\text{NH}_3$ pneumatic valve                                    |
| 25 | Flow        | 0     | 15        | Set precursor purge gas to idle flow rate                              |
| 26 | Flow        | 1     | 30        | Set plasma purge gas to idle flow rate                                 |

Table 1 Temperature settings, growth rate and refractive index of AlN from NH<sub>3</sub> plasma

| Deposition temp. (°C) | Trap heater (T1, °C) | Reactor zone heater(s) (T2, °C) | Chuck heater (T3, °C) | GPC (Å/cycle) | n(633nm) (300Å film) |
|-----------------------|----------------------|---------------------------------|-----------------------|---------------|----------------------|
| 200                   | 200                  | 200                             | 200                   | 0.54          | 1.90                 |
| 250                   | 250                  | 250                             | 250                   | 0.63          | 1.94                 |
| 300                   | 300                  | 250                             | 300                   | 0.73          | 1.95                 |
| 350                   | 300                  | 250                             | 350                   | 0.82          | 1.96                 |

Fiji Plasma AlN Recipe with N<sub>2</sub> + H<sub>2</sub>

|    | Instruction | #     | Value     |                                                                        |
|----|-------------|-------|-----------|------------------------------------------------------------------------|
| 0  | heater      | 12    | T1        | Set temperatures for various heaters                                   |
| 1  | heater      | 13    | T2        | Refer to Table 2 for details                                           |
| 2  | heater      | 14    | T2        |                                                                        |
| 3  | heater      | 15    | T3        |                                                                        |
| 4  | stabilize   |       | 12        | Wait for temperatures to stabilize                                     |
| 5  | stabilize   |       | 13        |                                                                        |
| 6  | stabilize   |       | 14        |                                                                        |
| 7  | stabilize   |       | 15        |                                                                        |
| 8  | wait        |       | 3600/7200 | Prebake time (seconds) with/without loadlock                           |
| 9  | MFC valve   | 2     | 1         | Open N <sub>2</sub> pneumatic valve                                    |
| 10 | MFC valve   | 4     | 1         | Open H <sub>2</sub> pneumatic valve                                    |
| 11 | APC         |       | 22.5      | Set throttle valve. Delete this line if no throttle valve <sup>1</sup> |
| 12 | flow        | 0     | 30        | Set precursor carrier Ar flow rate                                     |
| 13 | flow        | 1     | 100       | Set plasma source Ar flow rate                                         |
| 14 | wait        |       | 30        |                                                                        |
| 15 | pulse       | TMA # | 0.06      | Pulse TMA for 0.06 s, consumption rate ≈ 1.25mg/pulse                  |
| 16 | wait        |       | 10        | Purge 10 seconds                                                       |
| 17 | flow        | 2     | 20        | Set N <sub>2</sub> plasma gas flow rate                                |
| 18 | flow        | 4     | 20        | Set H <sub>2</sub> plasma gas flow rate                                |
| 19 | wait        |       | 1         | Wait for N <sub>2</sub> and H <sub>2</sub> flows to start              |
| 20 | plasma      |       | 300       | Light plasma, 300 W power                                              |
| 21 | wait        |       | 40        | 40 seconds plasma exposure time                                        |
| 22 | plasma      |       | 0         | Turn off plasma, 0 W power                                             |
| 23 | flow        | 2     | 0         | Turn off N <sub>2</sub> plasma gas                                     |
| 24 | flow        | 4     | 0         | Turn off H <sub>2</sub> plasma gas                                     |
| 25 | wait        |       | 5         | Purge 5 seconds                                                        |
| 26 | goto        | 15    | n         | Set # of cycles                                                        |
| 27 | MFC valve   | 2     | 0         | Close N <sub>2</sub> pneumatic valve                                   |
| 28 | MFC valve   | 4     | 0         | Close H <sub>2</sub> pneumatic valve                                   |
| 29 | Flow        | 0     | 15        | Set precursor purge gas to idle flow rate                              |
| 30 | Flow        | 1     | 30        | Set plasma purge gas to idle flow rate                                 |

Table 2 Temperature settings, growth rate and refractive index of AlN from N<sub>2</sub> and H<sub>2</sub> plasma

| Deposition temp. (°C) | Trap heater (T1, °C) | Reactor zone heater(s) (T2, °C) | Chuck heater (T3, °C) | GPC (Å/cycle) | n(633nm) (300Å film) |
|-----------------------|----------------------|---------------------------------|-----------------------|---------------|----------------------|
| 220                   | 220                  | 220                             | 220                   | 0.57          | 1.90                 |
| 250                   | 250                  | 250                             | 250                   | 0.70          | 1.93                 |
| 300                   | 300                  | 250                             | 300                   | 0.74          | 1.94                 |
| 350                   | 300                  | 250                             | 350                   | 0.80          | 1.95                 |

**Process Notes:**

1. The APC throttle valve is set to give approximately 200 mTorr of pressure with the carrier and plasma argon flowing, the door purge and N<sub>2</sub>/H<sub>2</sub> or NH<sub>3</sub> process gases on and plasma power off. Adjust the APC setting if necessary.
2. To minimize film impurities, the use of a hydride gas purifier for the NH<sub>3</sub> gas line to remove any trace quantities of O<sub>2</sub> and H<sub>2</sub>O is recommended. Cambridge NanoTech has successfully utilized the Entegris Gatekeeper hydride gas purifier 35KF1 ¼ FS, Part # CE35KFSK4R.  
<http://www.entegris.com/Resources/Images/15183.pdf>
3. Prefilled cylinders compatible with Fiji™ ALD reactors are available from:  
**Strem Chemicals**  
<http://www.strem.com/catalog/v/98-4003/1/>  
**Sigma-Aldrich**  
[http://www.sigmaaldrich.com/catalog/ProductDetail.do?N4=663301|ALDRICH&N5=SEARCH\\_CONCAT\\_PNO|BRAND\\_KEY&F=SPEC](http://www.sigmaaldrich.com/catalog/ProductDetail.do?N4=663301|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC)

**Application Notes:**

1. Thermal and plasma-enhanced ALD processes for AlN using TMA have been widely reported for the lack of an ALD temperature window within which film growth should be self-limiting,<sup>i</sup> and the growth rate per cycle (GPC) of AlN can be equipment and/or process-dependent even for a given temperature. Conflicting high-rate saturated-like growth of AlN in a wide temperature range of 100-400°C has been reported for the NH<sub>3</sub> plasma process, where a long pulse time of 2 seconds for TMA was applied,<sup>ii</sup> or a low-temperature ALD window below 200°C may exist for both NH<sub>3</sub> and N<sub>2</sub>+H<sub>2</sub> plasma processes.<sup>iii</sup> Whether or not a true ALD window exists has yet to be confirmed, and the quality of low-temperature AlN films is questionable. Hydrogen impurity concentration is known to increase with decreasing deposition temperature for the NH<sub>3</sub> plasma process.<sup>iv</sup> AlN deposited at 185°C with N<sub>2</sub>+H<sub>2</sub> plasma in Fiji was found to decompose gradually in atmosphere with a drastic increase in film thickness (doubled) and a drop in refractive index that eventually became even lower (1.55 at 633nm) than that of Al<sub>2</sub>O<sub>3</sub> (1.65).

**References:**

- i. Xinye Liu et. al., *Mat. Res. Soc. Symp. Proc.* **811**, 227(2004).
- ii. Kwang-Ho Kim et. al., *Electronic Mater. Let.* **5**(2), 83-86(2009). doi: 10.3365/eml.2009.06.083
- iii. Mustafa Alevli et. al., *J. Cryst. Growth* **335**(1), 51(2011). doi:10.1016/j.jcrysgro.2011.09.003
- iv. Markus Bosund et. al., *Appl. Surf. Sci.* **257**(17), 7827(2011). doi:10.1016/j.apsusc.2011.04.037

## Fiji System

### HfN<sub>x</sub> grown with Tetrakis(Dimethylamido)Hafnium (Hf(NMe<sub>2</sub>)<sub>4</sub>) and Plasma N<sub>2</sub>

Precursors: Hf(NMe<sub>2</sub>)<sub>4</sub> (TDMAHf)  
CAS# =19962-11-9, heated to 75°C  
Plasma N<sub>2</sub>

**Common Heaters:** ALD Valves=150°C  
Precursor Delivery=150°C  
Ti(NMe<sub>2</sub>)<sub>4</sub> Precursor=75°C

**Flows:** Argon Carrier (Flow 0) = 60sccm  
Argon Plasma (Flow 1) = 200sccm

**250°C Plasma Recipe:**  
Growth rate 0.2 Å/cycle

**Heaters:** Reactor 1&2=250°C  
Chuck=250°C  
Trap=250°C

**ALD Pulse:**  
Hf(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.25s

**Plasma:**  
Power 300Watts  
Nitrogen (Flow 2) 50sccm, flow 20s, wait 5s

HfN<sub>x</sub> film properties are strongly dependent upon the Hf:N ratio. HfN is conductive and Hf<sub>3</sub>N<sub>4</sub> is insulating. Longer N<sub>2</sub> plasma exposures increase the N incorporation into the film resulting in more insulating films.

|    | Instruction | #          | Value      |
|----|-------------|------------|------------|
| 0  | APC         |            | 100        |
| 1  | flow        | 0          | 20         |
| 2  | flow        | 1          | 40         |
| 3  | heater      | 12         | 250        |
| 4  | heater      | 13         | 250        |
| 5  | heater      | 14         | 250        |
| 6  | heater      | 15         | 250        |
| 7  | wait        |            | 3600       |
| 8  | stabilize   | 12         |            |
| 9  | stabilize   | 13         |            |
| 10 | stabilize   | 14         |            |
| 11 | stabilize   | 15         |            |
| 12 | MFCvalve    | 2          | 1          |
| 13 | flow        | 0          | 60         |
| 14 | flow        | 1          | 200        |
| 15 | flow        | 2          | 0          |
| 16 | APC         |            | 15         |
| 17 | wait        | 10         |            |
| 18 | pulse       | 75C TDMAHf | 0.25       |
| 19 | wait        |            | 2          |
| 20 | flow        | 1          | 400        |
| 21 | flow        | 2          | 50         |
| 22 | APC         |            | 100        |
| 23 | wait        |            | 3          |
| 24 | plasma      |            | 300        |
| 25 | wait        |            | 20         |
| 26 | plasma      |            | 0          |
| 27 | flow        | 1          | 200        |
| 28 | flow        | 2          | 0          |
| 29 | APC         |            | 15         |
| 30 | wait        |            | 5          |
| 31 | goto        | 18         | 0.2A/cycle |
| 32 | APC         |            | 100        |
| 33 | flow        | 0          | 20         |
| 34 | flow        | 1          | 40         |
| 30 | flow        | 2          | 0          |
| 31 | MFCvalve    | 2          | 0          |

## Fiji System

### HfO<sub>2</sub> grown with Tetrakis(Dimethylamido)Hafnium(Hf(NMe<sub>2</sub>)<sub>4</sub>) and plasma O<sub>2</sub>

**Precursors:** (Hf(NMe<sub>2</sub>)<sub>4</sub>) heated to 75°C  
CAS# =19962-11-9  
plasma O<sub>2</sub>

**Heaters:** ALD Valves: 16=17=150°C  
(Hf(NMe<sub>2</sub>)<sub>4</sub>) = 75°C

**Gas Flows:** Argon Carrier (Flow 0) = 60sccm  
Argon Plasma(Flow 1) = 200sccm

Pick a temperature and use these values in the recipe shown on the right.

| Temperature | A   | B   | C   | D   | E   | F   | G           |
|-------------|-----|-----|-----|-----|-----|-----|-------------|
| 90          | 90  | 90  | 90  | 90  | 120 | 120 | ~1.2A/cycle |
| 150         | 150 | 150 | 150 | 150 | 30  | 20  | ~1A/cycle   |
| 200         | 200 | 200 | 200 | 200 | 5   | 20  | ~0.9A/cycle |
| 250         | 250 | 250 | 250 | 250 | 5   | 20  | ~0.9A/cycle |

|    | Instruction | #  | Value |
|----|-------------|----|-------|
| 0  | flow        | 0  | 20    |
| 1  | flow        | 1  | 40    |
| 2  | heater      | 12 | A     |
| 3  | heater      | 13 | B     |
| 4  | heater      | 14 | C     |
| 5  | heater      | 15 | D     |
| 6  | stabilize   | 12 |       |
| 7  | stabilize   | 13 |       |
| 8  | stabilize   | 14 |       |
| 9  | stabilize   | 15 |       |
| 10 | wait        |    | 600   |
| 11 | MFCvalve    | 3  | 1     |
| 12 | flow        | 0  | 60    |
| 13 | flow        | 1  | 200   |
| 14 | wait        |    | 20    |
| 15 | pulse       | Hf | 0.25  |
| 16 | wait        |    | E     |
| 17 | flow        | 3  | 20    |
| 18 | plasma      |    | 300   |
| 19 | wait        |    | F     |
| 20 | plasma      |    | 0     |
| 21 | flow        | 3  | 0     |
| 22 | wait        |    | 5     |
| 23 | goto        | 12 | G     |
| 24 | flow        | 0  | 20    |
| 25 | flow        | 1  | 40    |
| 26 | MFCvalve    | 3  | 0     |

## Fiji System

### ZrO<sub>2</sub> grown with Tetrakis(Dimethylamido)Zirconium(Zr(NMe<sub>2</sub>)<sub>4</sub>) and plasma O<sub>2</sub>

**Precursors:** (Zr(NMe<sub>2</sub>)<sub>4</sub>) CAS# = 19756-04-8  
plasma O<sub>2</sub>

**Heaters:** ALD Valves: 16=17=150°C  
(Zr(NMe<sub>2</sub>)<sub>4</sub>) = 75°C

**Gas Flows:** Argon Carrier (Flow 0) = 30sccm  
Argon Plasma(Flow 1) = 100sccm

Pick a temperature and use these values in the recipe shown on the right.

| Temperature (C) | A   | B   | C   | D   | E   | F  | G           |
|-----------------|-----|-----|-----|-----|-----|----|-------------|
| 90              | 90  | 90  | 90  | 90  | 120 | 30 | ~1.2A/cylce |
| 150             | 150 | 150 | 150 | 150 | 30  | 20 | ~1A/cycle   |
| 200             | 200 | 200 | 200 | 200 | 5   | 20 | ~0.9A/cylce |
| 250             | 250 | 250 | 250 | 250 | 5   | 20 | ~0.9A/cylce |

If Fiji system is equipped with a turbo pump and APC valve, set the APC valve so the system pressure is 200mTorr when the door purge is 50sccm, the carrier Ar is 60sccm, and the plasma Ar is 200sccm.

|    | Instruction | #  | Value |
|----|-------------|----|-------|
| 0  | flow        | 0  | 20    |
| 1  | flow        | 1  | 40    |
| 2  | heater      | 12 | A     |
| 3  | heater      | 13 | B     |
| 4  | heater      | 14 | C     |
| 5  | heater      | 15 | D     |
| 6  | stabilize   | 12 |       |
| 7  | stabilize   | 13 |       |
| 8  | stabilize   | 14 |       |
| 9  | stabilize   | 15 |       |
| 10 | wait        |    | 600   |
| 11 | MFCvalve    | 3  | 1     |
| 12 | flow        | 0  | 30    |
| 13 | flow        | 1  | 100   |
| 14 | wait        |    | 20    |
| 15 | pulse       | Zr | 0.25  |
| 16 | wait        |    | E     |
| 17 | flow        | 3  | 20    |
| 18 | plasma      |    | 300   |
| 19 | wait        |    | F     |
| 20 | plasma      |    | 0     |
| 21 | flow        | 3  | 0     |
| 22 | wait        |    | 5     |
| 23 | goto        | 12 | G     |
| 24 | flow        | 0  | 20    |
| 25 | flow        | 1  | 40    |
| 26 | MFCvalve    | 3  | 0     |

## Fiji System

### HfO<sub>2</sub> grown with Tetrakis(Dimethylamido)Hafnium(Hf(NMe<sub>2</sub>)<sub>4</sub>) and H<sub>2</sub>O

#### 200°C Thermal Recipe:

Precursors: (Hf(NMe<sub>2</sub>)<sub>4</sub>) CAS# =19962-11-9  
H<sub>2</sub>O (unheated)

Growth rate = 0.95Å/cycle

**Heaters:** Chamber: 12=13=14=15=200°C  
ALD Valves: 16=17=150°C  
(Hf(NMe<sub>2</sub>)<sub>4</sub>) = 75°C

**Flows:** Argon Carrier (Flow 0) = 40sccm  
Argon Plasma (Flow 1) = 200sccm

#### ALD Pulses:

H<sub>2</sub>O (Valve 0) 0.060s, wait 15s  
Hf(NMe<sub>2</sub>)<sub>4</sub> (Valve 1) 0.250s, wait 15s

|    | Instruction | #   | Value     | Comments           |
|----|-------------|-----|-----------|--------------------|
| 0  | flow        | 0   | 20        | Heat TDMAHf to 75C |
| 1  | flow        | 1   | 40        |                    |
| 2  | heater      | 12  | 200       |                    |
| 3  | heater      | 13  | 200       |                    |
| 4  | heater      | 14  | 200       |                    |
| 5  | heater      | 15  | 200       |                    |
| 6  | stabilize   | 12  |           |                    |
| 7  | stabilize   | 13  |           |                    |
| 8  | stabilize   | 14  |           |                    |
| 9  | stabilize   | 15  |           |                    |
| 10 | wait        |     | 600       |                    |
| 11 | flow        | 0   | 60        |                    |
| 12 | flow        | 1   | 200       |                    |
| 13 | wait        |     | 20        |                    |
| 14 | pulse       | Hf  | 0.25      | Pulse TDMAZr       |
| 15 | wait        |     | 10        |                    |
| 16 | pulse       | H2O | 0.06      | Pulse H2O          |
| 17 | wait        |     | 10        |                    |
| 18 | goto        | 14  | ~1A/cycle | GPC ~1A/cycle      |
| 19 | flow        | 0   | 20        |                    |
| 20 | flow        | 1   | 40        |                    |

**90°C Thermal Recipe:**

Precursors: (Hf(NMe<sub>2</sub>)<sub>4</sub>) CAS# =19962-11-9  
H<sub>2</sub>O (unheated)

Growth rate = ~1Å/cycle

**Heaters:** Chamber: 12=13=14=15=90°C  
ALD Valves: 16=17=150°C  
(Hf(NMe<sub>2</sub>)<sub>4</sub>) = 75°C

**Flows:** Argon Carrier (Flow 0) = 40sccm  
Argon Plasma (Flow 1) = 200sccm

**ALD Pulses:**

H<sub>2</sub>O 0.06s, wait 120s  
Hf(NMe<sub>2</sub>)<sub>4</sub> 0.25s, wait 120s

|    | Instruction | #   | Value     | Comments           |
|----|-------------|-----|-----------|--------------------|
| 0  | flow        | 0   | 20        | Heat TDMAHf to 75C |
| 1  | flow        | 1   | 40        |                    |
| 2  | heater      | 12  | 90        |                    |
| 3  | heater      | 13  | 90        |                    |
| 4  | heater      | 14  | 90        |                    |
| 5  | heater      | 15  | 90        |                    |
| 6  | stabilize   | 12  |           |                    |
| 7  | stabilize   | 13  |           |                    |
| 8  | stabilize   | 14  |           |                    |
| 9  | stabilize   | 15  |           |                    |
| 10 | wait        |     | 600       |                    |
| 11 | flow        | 0   | 60        |                    |
| 12 | flow        | 1   | 200       |                    |
| 13 | wait        |     | 20        |                    |
| 14 | pulse       | Hf  | 0.25      | Pulse TDMAHf       |
| 15 | wait        |     | 120       |                    |
| 16 | pulse       | H2O | 0.06      | Pulse H2O          |
| 17 | wait        |     | 120       |                    |
| 18 | goto        | 14  | ~1A/cycle | GPC ~1A/cycle      |
| 19 | flow        | 0   | 20        |                    |
| 20 | flow        | 1   | 40        |                    |

## Fiji System

### TiO<sub>2</sub> grown with Tetrakis(Dimethylamido)Titanium (Ti(NMe<sub>2</sub>)<sub>4</sub>) and H<sub>2</sub>O

Precursors: Ti(NMe<sub>2</sub>)<sub>4</sub> (TDMAT), CAS# =3275-24-9, heated to 75°C and H<sub>2</sub>O (unheated)

**Common Heaters:** ALD Valves=150°C  
Precursor Delivery=150°C  
Ti(NMe<sub>2</sub>)<sub>4</sub> Precursor=75°C

**Flows:** Argon Carrier (Flow 0) = 60sccm  
Argon Plasma (Flow 1) = 200sccm

#### 250°C Thermal Recipe:

Growth rate 0.40 Å/cycle

**Heaters:** Reactor 1&2=250°C  
Chuck=250°C  
Trap=250°C

#### ALD Pulses:

H<sub>2</sub>O (Valve 0) 0.06s, wait 5s.  
Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 5s.

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 1200  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | wait        |   | 60    |
| 4  | pulse       | 0 | 0.06  |
| 5  | wait        |   | 5     |
| 6  | pulse       | 2 | 0.1   |
| 7  | wait        |   | 5     |
| 8  | goto        | 4 | m     |
| 9  | flow        | 0 | 20    |
| 10 | flow        | 1 | 20    |

#### 200°C Thermal Recipe:

Growth rate 0.37 Å/cycle

**Heaters:** Reactor 1&2=200°C  
Chuck=200°C  
Trap=200°C

#### ALD Pulses:

H<sub>2</sub>O (Valve 0) 0.06s, wait 10s.  
Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 5s.

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 1200  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | wait        |   | 60    |
| 4  | pulse       | 0 | 0.06  |
| 5  | wait        |   | 10    |
| 6  | pulse       | 2 | 0.1   |
| 7  | wait        |   | 5     |
| 8  | goto        | 4 | m     |
| 9  | flow        | 0 | 20    |
| 10 | flow        | 1 | 20    |

### 150°C Thermal Recipe:

Growth rate 0.43 Å/cycle

**Heaters:** Reactor 1&2=150°C  
Chuck=150°C  
Trap=150°C

### ALD Pulses:

H<sub>2</sub>O (Valve 0) 0.06s, wait 30s.  
Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 30s.

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 1800  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | wait        |   | 60    |
| 4  | pulse       | 0 | 0.06  |
| 5  | wait        |   | 30    |
| 6  | pulse       | 2 | 0.1   |
| 7  | wait        |   | 30    |
| 8  | goto        | 4 | m     |
| 9  | flow        | 0 | 20    |
| 10 | flow        | 1 | 20    |

### 100°C Thermal Recipe:

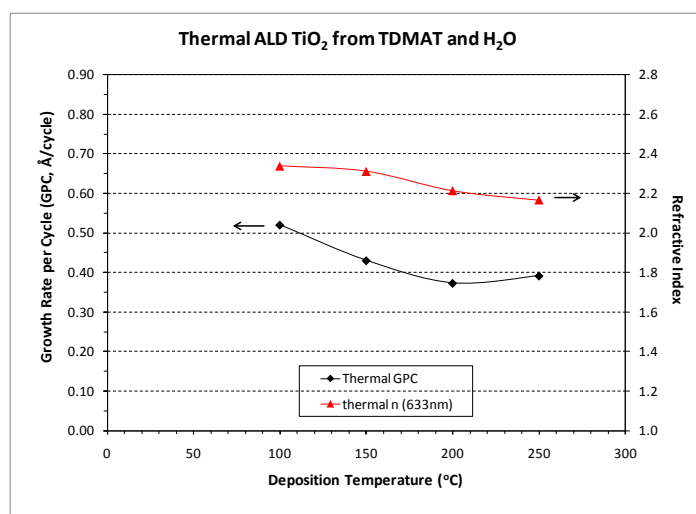
Growth rate 0.52 Å/cycle

**Heaters:** Reactor 1&2=100°C  
Chuck=100°C  
Trap=100°C

### ALD Pulses:

H<sub>2</sub>O (Valve 0) 0.06s, wait 60s.  
Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 60s.

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 3600  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | wait        |   | 60    |
| 4  | pulse       | 0 | 0.06  |
| 5  | wait        |   | 60    |
| 6  | pulse       | 2 | 0.1   |
| 7  | wait        |   | 60    |
| 8  | goto        | 4 | m     |
| 9  | flow        | 0 | 20    |
| 10 | flow        | 1 | 20    |



**Note.** The TDMAT peak at 0.1s pulse is very small and may become invisible on the pressure chart sometimes.

## Fiji System

### ZrO<sub>2</sub> grown with Tetrakis(Dimethylamido)Zirconium(Zr(NMe<sub>2</sub>)<sub>4</sub>) and H<sub>2</sub>O

#### 200°C Thermal Recipe:

Precursors: (Zr(NMe<sub>2</sub>)<sub>4</sub>) CAS# = 19756-04-8  
H<sub>2</sub>O (unheated)

Growth rate = 1.02Å/cycle

**Heaters:** Chamber: 12=13=14=15=200°C  
ALD Valves: 16=17=150°C  
(Zr(NMe<sub>2</sub>)<sub>4</sub>) = 75°C

**Flows:** Argon Carrier (Flow 0) = 30sccm  
Argon Plasma (Flow 1) = 100sccm

#### ALD Pulses:

H<sub>2</sub>O 0.060s, wait 10s  
Zr(NMe<sub>2</sub>)<sub>4</sub> 0.250s, wait 10s

If Fiji system is equipped with a turbo pump and APC valve, set the APC valve so the system pressure is 200mTorr when the door purge is 50sccm, the carrier Ar is 60sccm, and the plasma Ar is 200sccm.

|    | Instruction | #   | Value |
|----|-------------|-----|-------|
| 0  | flow        | 0   | 20    |
| 1  | flow        | 1   | 40    |
| 2  | heater      | 12  | 200   |
| 3  | heater      | 13  | 200   |
| 4  | heater      | 14  | 200   |
| 5  | heater      | 15  | 200   |
| 6  | stabilize   | 12  |       |
| 7  | stabilize   | 13  |       |
| 8  | stabilize   | 14  |       |
| 9  | stabilize   | 15  |       |
| 10 | wait        |     | 600   |
| 11 | flow        | 0   | 30    |
| 12 | flow        | 1   | 100   |
| 13 | wait        |     | 20    |
| 14 | pulse       | Zr  | 0.25  |
| 15 | wait        |     | 10    |
| 16 | pulse       | H2O | 0.06  |
| 17 | wait        |     | 10    |
| 18 | goto        | 14  | x     |
| 19 | flow        | 0   | 20    |
| 20 | flow        | 1   | 40    |

### 90°C Thermal Recipe:

**Precursors:** (Zr(NMe<sub>2</sub>)<sub>4</sub>) CAS# =19756-04-8  
H<sub>2</sub>O (unheated)

*Growth rate = ~1Å/cycle*

**Heaters:** Chamber: 12=13=14=15=90°C  
ALD Valves: 16=17=150°C  
(Hf(NMe<sub>2</sub>)<sub>4</sub>) = 75°C

**Flows:** Argon Carrier (Flow 0) = 30sccm  
Argon Plasma (Flow 1) = 100sccm

### ALD Pulses:

H<sub>2</sub>O 0.06s, wait 120s  
Hf(NMe<sub>2</sub>)<sub>4</sub> 0.25s, wait 120s

If Fiji system is equipped with a turbo pump and APC valve, set the APC valve so the system pressure is 200mTorr when the door purge is 50sccm, the carrier Ar is 60sccm, and the plasma Ar is 200sccm.

|    | Instruction | #   | Value |
|----|-------------|-----|-------|
| 0  | flow        | 0   | 20    |
| 1  | flow        | 1   | 40    |
| 2  | heater      | 12  | 90    |
| 3  | heater      | 13  | 90    |
| 4  | heater      | 14  | 90    |
| 5  | heater      | 15  | 90    |
| 6  | stabilize   | 12  |       |
| 7  | stabilize   | 13  |       |
| 8  | stabilize   | 14  |       |
| 9  | stabilize   | 15  |       |
| 10 | wait        |     | 600   |
| 11 | flow        | 0   | 30    |
| 12 | flow        | 1   | 100   |
| 13 | wait        |     | 20    |
| 14 | pulse       | Zr  | 0.25  |
| 15 | wait        |     | 120   |
| 16 | pulse       | H2O | 0.06  |
| 17 | wait        |     | 120   |
| 18 | goto        | 14  | x     |
| 19 | flow        | 0   | 20    |
| 20 | flow        | 1   | 40    |

## Expo Mode HfO<sub>2</sub> on Fiji using tetrakis(dimethylamino)hafnium (TDMAH) and H<sub>2</sub>O

Temperature (TDMAH) = 95°C, precursor line #2; unheated H<sub>2</sub>O on precursor line #0

Purge flows = 140 (plasma) + 40 (carrier) sccm

Expo flows = 60 (plasma) + 20 (carrier) sccm

Reactor, chuck and trap temperature = 175°C

Expo time = 60 sec (line 9, 19)

Purge = 90 sec (line 13, 23)

|    |           |   |      |
|----|-----------|---|------|
| 0  | wait      |   | 1800 |
| 1  | flow      | 0 | 40   |
| 2  | flow      | 1 | 140  |
| 3  | wait      |   | 30   |
| 4  | stopvalve |   | 0    |
| 5  | pulse     | 2 | 1.5  |
| 6  | wait      |   | 1    |
| 7  | flow      | 0 | 20   |
| 8  | flow      | 1 | 60   |
| 9  | wait      |   | 60   |
| 10 | flow      | 0 | 40   |
| 11 | flow      | 1 | 140  |
| 12 | stopvalve |   | 1    |
| 13 | wait      |   | 90   |
| 14 | stopvalve |   | 0    |
| 15 | pulse     | 0 | 0.12 |
| 16 | wait      |   | 1    |
| 17 | flow      | 0 | 20   |
| 18 | flow      | 1 | 60   |
| 19 | wait      |   | 60   |
| 20 | flow      | 0 | 40   |
| 21 | flow      | 1 | 140  |
| 22 | stopvalve |   | 1    |
| 23 | wait      |   | 90   |
| 24 | goto      | 4 | x    |
| 25 | flow      | 0 | 10   |
| 26 | flow      | 1 | 20   |

# Multicomponent Materials

- ALD films are deposited in cycles  $\sim 0.1\text{nm/cycle}$   $\rightarrow$  deposition of multi-component materials

## Doped material

|   |                          |
|---|--------------------------|
| 0 | pulse Zinc precursor     |
| 1 | wait/purge               |
| 2 | pulse water              |
| 3 | wait/purge               |
| 4 | Repeat 0-3 20x           |
| 5 | pulse Aluminum precursor |
| 6 | wait/purge               |
| 7 | pulse water              |
| 8 | wait/purge               |
| 9 | Repeat 0-8 30x           |

**ZnO Cycle  
Repeated 20x**

**1 Al<sub>2</sub>O<sub>3</sub>  
cycle**

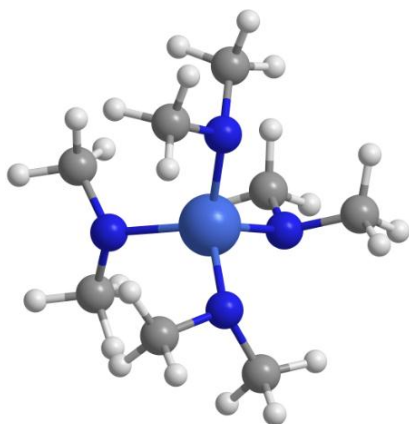
## Nanolaminate

|    |                                        |
|----|----------------------------------------|
| 0  | pulse Zirconium precursor              |
| 1  | wait/purge                             |
| 2  | pulse water                            |
| 3  | wait/purge                             |
| 4  | Repeat 0-3 50x ( $\sim 5\text{nm}$ )   |
| 5  | pulse Aluminum precursor               |
| 6  | wait/purge                             |
| 7  | pulse water                            |
| 8  | wait/purge                             |
| 9  | Repeat 5-8 50x ( $\sim 5\text{nm}$ )   |
| 10 | Repeat 0-9 10x ( $\sim 100\text{nm}$ ) |

**ZrO<sub>2</sub> Cycle  
Repeated 50x**

**Al<sub>2</sub>O<sub>3</sub> Cycle  
Repeated 50x**

**Precursors:**



Tetrakis(dimethylamido)titanium, TDMAT,  $\text{Ti}(\text{NMe}_2)_4$

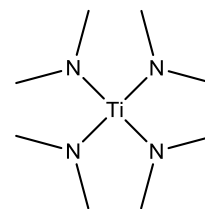
CAS#: 3275-24-9

Heated to 75°C

$\text{N}_2$  gas, Electronic grade 99.999+%

Optionally,  $\text{H}_2$  gas, Electronic grade 99.999+%

Optionally,  $\text{NH}_3$  gas, Electronic grade 99.999+%



All recipes for 250°C

For lower temperatures, longer plasma times will be required.

For higher temperatures, shorter purge times will be required to minimize thermal decomposition of the precursor.

APC Settings: For systems with APC throttle valves, the valve is set to different positions for the TDMAT pulse and the plasma steps. To determine the appropriate valve position, set the Ar flow through the precursor manifold (MFC0) to 60sccm, the Ar flow through the plasma source (MFC1) to 200sccm, and turn on the door purge (~50sccm Ar). Determine the APC valve position that establishes a reactor pressure of 200mTorr. The valve position for the plasma step is full open, ie 100.

**No turbo pump, N<sub>2</sub> only:**

|    | Instruction | #         | Value | Comments                                                                                    |
|----|-------------|-----------|-------|---------------------------------------------------------------------------------------------|
| 0  | flow        | 0         | 20    | Standby flows during thermal equilibrium                                                    |
| 1  | flow        | 1         | 40    |                                                                                             |
| 2  | heater      | 12        | 250   |                                                                                             |
| 3  | heater      | 13        | 250   | Set trap temperature                                                                        |
| 4  | heater      | 14        | 250   | Set reactor zone 1 temperature                                                              |
| 5  | heater      | 15        | 250   | Set reactor zone 2 temperature                                                              |
| 6  | stabilize   | 12        |       | Set chuck temperature                                                                       |
| 7  | stabilize   | 13        |       | Wait for temperatures to stabilize                                                          |
| 8  | stabilize   | 14        |       |                                                                                             |
| 9  | stabilize   | 15        |       |                                                                                             |
| 10 | wait        |           | 7200  | Time to pump away any residual H <sub>2</sub> O or O <sub>2</sub> from sample introduction* |
| 11 | MFCvalve    | 2         | 1     | Open N <sub>2</sub> pneumatic valve                                                         |
| 12 | flow        | 0         | 60    | Set Ar carrier process flow                                                                 |
| 13 | flow        | 1         | 200   | Set Ar plasma process flow                                                                  |
| 14 | flow        | 2         | 50    | Set N <sub>2</sub> plasma process flow                                                      |
| 15 | wait        |           | 10    | Give MFCs time to stabilize                                                                 |
| 16 | pulse       | 75C TDMAT | 0.2   | TDMAT pulse. Put ALD valve position in # column.                                            |
| 17 | wait        |           | 6     | TDMAT purge                                                                                 |
| 18 | plasma      | 300       |       | N <sub>2</sub> /Ar plasma on                                                                |
| 19 | wait        | 20        |       | 20s of N <sub>2</sub> /Ar plasma                                                            |
| 20 | plasma      |           | 0     | Plasma off                                                                                  |
| 21 | wait        |           | 5     | Purge reaction products                                                                     |
| 22 | goto        | 16        | y     | Set # of cycles. ~0.6Å /cycle on silicon                                                    |
| 23 | flow        | 0         | 20    | Set flows to standby levels.                                                                |
| 24 | flow        | 1         | 40    |                                                                                             |
| 25 | flow        | 2         | 0     |                                                                                             |
| 26 | MFCvalve    | 2         | 0     | Close N <sub>2</sub> pneumatic valve                                                        |

\* Reduce to 3600 if using a load lock

Refractive Index: ~2.1 @ 632nm (300 Å Film)

**No turbo pump, N<sub>2</sub> and H<sub>2</sub> (or NH<sub>3</sub>):**

|    | Instruction | #         | Value | Comments                                                                                    |
|----|-------------|-----------|-------|---------------------------------------------------------------------------------------------|
| 0  | flow        | 0         | 20    | Standby flows during thermal equilibrium                                                    |
| 1  | flow        | 1         | 40    |                                                                                             |
| 2  | heater      | 12        | 250   |                                                                                             |
| 3  | heater      | 13        | 250   | Set trap temperature                                                                        |
| 4  | heater      | 14        | 250   | Set reactor zone 1 temperature                                                              |
| 5  | heater      | 15        | 250   | Set reactor zone 2 temperature                                                              |
| 6  | stabilize   | 12        |       | Set chuck temperature                                                                       |
| 7  | stabilize   | 13        |       | Wait for temperatures to stabilize                                                          |
| 8  | stabilize   | 14        |       |                                                                                             |
| 9  | stabilize   | 15        |       |                                                                                             |
| 10 | wait        |           | 7200  |                                                                                             |
| 11 | MFCvalve    | 2         | 1     | Time to pump away any residual H <sub>2</sub> O or O <sub>2</sub> from sample introduction* |
| 12 | MFCvalve    | 4         | 1     | Open N <sub>2</sub> pneumatic valve                                                         |
| 13 | flow        | 0         | 60    | Open H <sub>2</sub> (or NH <sub>3</sub> ) pneumatic valve                                   |
| 14 | flow        | 1         | 200   | Set Ar carrier process flow                                                                 |
| 15 | flow        | 2         | 50    | Set Ar plasma process flow                                                                  |
| 16 | wait        |           | 10    | Set N <sub>2</sub> plasma process flow                                                      |
| 17 | pulse       | 75C TDMAT | 0.2   | Give MFCs time to stabilize                                                                 |
| 18 | wait        |           | 6     | TDMAT pulse. Put ALD valve position in # column.                                            |
| 19 | plasma      | 300       |       | TDMAT purge                                                                                 |
| 20 | wait        |           | 10    | N <sub>2</sub> /Ar plasma on                                                                |
| 21 | flow        | 4         | 20    | 10s of N <sub>2</sub> /Ar plasma                                                            |
| 22 | wait        |           | 5     | Add in some H <sub>2</sub> (or NH <sub>3</sub> )                                            |
| 23 | flow        | 4         | 0     | for 5s                                                                                      |
| 24 | wait        |           | 5     | Remove H <sub>2</sub> (or NH <sub>3</sub> )                                                 |
| 25 | plasma      |           | 0     | 5s more Ar/N <sub>2</sub> plasma                                                            |
| 26 | wait        |           | 5     | Plasma off                                                                                  |
| 27 | goto        | 17        | y     | Purge reaction products                                                                     |
| 28 | flow        | 0         | 20    | Set # of cycles. ~0.6Å/cycle on silicon                                                     |
| 29 | flow        | 1         | 40    | Set flows to standby levels.                                                                |
| 30 | flow        | 2         | 0     | Close gas pneumatic valves                                                                  |
| 31 | MFCvalve    | 2         | 0     |                                                                                             |
| 32 | MFCvalve    | 4         | 0     |                                                                                             |

\* Reduce to 3600 if using a load lock

Refractive Index: 2.1 @ 632nm (300 Å Film)

**Load lock, turbo pump/throttle valve, N<sub>2</sub> only:**

|    | Instruction | #         | Value | Comments                                                                                   |
|----|-------------|-----------|-------|--------------------------------------------------------------------------------------------|
| 0  | APC         |           | 100   | Open throttle valve                                                                        |
| 1  | flow        | 0         | 20    | Standby flows during thermal equilibrium                                                   |
| 2  | flow        | 1         | 40    |                                                                                            |
| 3  | heater      | 12        | 250   | Set trap temperature                                                                       |
| 4  | heater      | 13        | 250   | Set reactor zone 1 temperature                                                             |
| 5  | heater      | 14        | 250   | Set reactor zone 2 temperature                                                             |
| 6  | heater      | 15        | 250   | Set chuck temperature                                                                      |
| 7  | stabilize   | 12        |       | Wait for temperatures to stabilize                                                         |
| 8  | stabilize   | 13        |       |                                                                                            |
| 9  | stabilize   | 14        |       |                                                                                            |
| 10 | stabilize   | 15        |       |                                                                                            |
| 11 | wait        |           | 1800  | Time to pump away any residual H <sub>2</sub> O or O <sub>2</sub> from sample introduction |
| 12 | MFCvalve    | 2         | 1     | Open N <sub>2</sub> pneumatic valve                                                        |
| 13 | flow        | 0         | 60    | Set Ar carrier process flow                                                                |
| 14 | flow        | 1         | 200   | Set Ar plasma process flow                                                                 |
| 15 | flow        | 2         | 50    | Set N <sub>2</sub> plasma process flow                                                     |
| 16 | APC         |           | #     | See APC note on front page                                                                 |
| 17 | wait        |           | 10    | Give MFCs time to stabilize                                                                |
| 18 | pulse       | 75C TDMAT | 0.2   | TDMAT pulse. Put ALD valve position in # column.                                           |
| 19 | wait        |           | 6     | TDMAT purge                                                                                |
| 20 | flow        | 1         | 400   | Increase plasma Ar flow                                                                    |
| 21 | APC         |           | 100   | Reduce residence time for plasma step                                                      |
| 22 | plasma      | 300       |       | N <sub>2</sub> /Ar plasma on                                                               |
| 23 | wait        |           | 20    | 20s of N <sub>2</sub> /Ar plasma                                                           |
| 24 | plasma      |           | 0     | Plasma off                                                                                 |
| 25 | flow        | 1         | 200   | Return plasma Ar to precursor pulse flow rate                                              |
| 26 | APC         |           | #     | See APC note on front page                                                                 |
| 27 | wait        |           | 5     | Purge reaction products                                                                    |
| 28 | goto        | 18        | y     | Set # of cycles. ~0.6Å /cycle on silicon                                                   |
| 29 | flow        | 0         | 20    | Set flows to standby levels.                                                               |
| 30 | flow        | 1         | 40    |                                                                                            |
| 31 | flow        | 2         | 0     |                                                                                            |
| 32 | MFCvalve    | 2         | 0     | Close gas pneumatic valves                                                                 |
| 33 | APC         |           | 100   | Open throttle valve                                                                        |

Refractive Index: 2.1 @ 632nm (300 Å Film)

**Load lock, turbo pump/throttle valve, N<sub>2</sub> and H<sub>2</sub>(or NH<sub>3</sub>):**

|    | Instruction | #         | Value | Comments                                                                                   |
|----|-------------|-----------|-------|--------------------------------------------------------------------------------------------|
| 0  | APC         |           | 100   | Open throttle valve                                                                        |
| 1  | flow        | 0         | 20    | Standby flows during thermal equilibrium                                                   |
| 2  | flow        | 1         | 40    |                                                                                            |
| 3  | heater      | 12        | 250   | Set trap temperature                                                                       |
| 4  | heater      | 13        | 250   | Set reactor zone 1 temperature                                                             |
| 5  | heater      | 14        | 250   | Set reactor zone 2 temperature                                                             |
| 6  | heater      | 15        | 250   | Set chuck temperature                                                                      |
| 7  | stabilize   | 12        |       | Wait for temperatures to stabilize                                                         |
| 8  | stabilize   | 13        |       |                                                                                            |
| 9  | stabilize   | 14        |       |                                                                                            |
| 10 | stabilize   | 15        |       |                                                                                            |
| 11 | wait        |           | 1800  | Time to pump away any residual H <sub>2</sub> O or O <sub>2</sub> from sample introduction |
| 12 | MFCvalve    | 2         | 1     | Open N <sub>2</sub> pneumatic valve                                                        |
| 13 | MFCvalve    | 4         | 1     | Open H <sub>2</sub> pneumatic valve (or NH <sub>3</sub> )                                  |
| 14 | flow        | 0         | 60    | Set Ar carrier process flow                                                                |
| 15 | flow        | 1         | 200   | Set Ar plasma process flow                                                                 |
| 16 | flow        | 2         | 50    | Set N <sub>2</sub> plasma process flow                                                     |
| 17 | APC         |           | #     | See APC note on page 1.                                                                    |
| 18 | wait        |           | 10    | Give MFCs time to stabilize                                                                |
| 19 | pulse       | 75C TDMAT | 0.2   | TDMAT pulse. Put ALD valve position in # column.                                           |
| 20 | wait        |           | 6     | TDMAT purge                                                                                |
| 21 | flow        | 1         | 400   | Increase plasma Ar flow                                                                    |
| 22 | APC         |           | 100   | Reduce residence time for plasma step                                                      |
| 23 | plasma      | 300       |       | N <sub>2</sub> /Ar plasma on                                                               |
| 24 | wait        |           | 10    | 10s of N <sub>2</sub> /Ar plasma                                                           |
| 25 | flow        | 4         | 20    | Add in some H <sub>2</sub> (or NH <sub>3</sub> )                                           |
| 26 | wait        |           | 5     | for 5s                                                                                     |
| 27 | flow        | 4         | 0     | Remove H <sub>2</sub> (or NH <sub>3</sub> )                                                |
| 28 | wait        |           | 5     | 5s more Ar/N <sub>2</sub> plasma                                                           |
| 29 | plasma      |           | 0     | Plasma off                                                                                 |
| 30 | flow        | 1         | 200   | Return plasma Ar to precursor pulse flow rate                                              |
| 31 | APC         |           | #     | See APC note on page 1.                                                                    |
| 32 | wait        |           | 5     | Purge reaction products                                                                    |
| 33 | goto        | 19        | y     | Set # of cycles.                                                                           |
| 34 | flow        | 0         | 20    | Set flows to standby levels.                                                               |
| 35 | flow        | 1         | 40    |                                                                                            |
| 36 | flow        | 2         | 0     |                                                                                            |
| 37 | MFCvalve    | 2         | 0     | Close N <sub>2</sub> pneumatic valve                                                       |
| 38 | MFCvalve    | 4         | 0     | Close H <sub>2</sub> (or NH <sub>3</sub> ) pneumatic valve                                 |
| 39 | APC         |           | 100   | Open throttle valve                                                                        |

Refractive Index: 2.1 @ 632nm (300 Å Film)

Process Notes:

To minimize film impurities, we recommend point of use gas purifiers for the Ar, N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> gas lines on the Fiji to remove any trace quantities of O<sub>2</sub> and H<sub>2</sub>O. A variety of products exist for this application. Cambridge NanoTech has successfully utilized the Entegris Gatekeeper line of products on the systems in our laboratories.

Part # CE35KFSK4R, hydride gas purifier 35KF1 ¼ FS.

<http://www.entegris.com/Resources/Images/15183.pdf>

Prefilled cylinders of Ti(NMe<sub>2</sub>)<sub>4</sub> compatible with Fiji™ ALD reactors available from:

**Strem Chemicals**

<http://www.strem.com/catalog/v/98-4015/77/>

**Sigma-Aldrich**

[http://www.sigmaaldrich.com/catalog/ProductDetail.do?N4=669008|ALDRICH&N5=SEARCH\\_CONCAT\\_PNO|BRAND\\_KEY&F=SPEC](http://www.sigmaaldrich.com/catalog/ProductDetail.do?N4=669008|ALDRICH&N5=SEARCH_CONCAT_PNO|BRAND_KEY&F=SPEC)

## Fiji System

### TiO<sub>2</sub> grown with Tetrakis(Dimethylamido)Titanium (Ti(NMe<sub>2</sub>)<sub>4</sub>) and Plasma O<sub>2</sub>

Precursors: Ti(NMe<sub>2</sub>)<sub>4</sub> (TDMAT), CAS# =3275-24-9, heated to 75°C and Plasma O<sub>2</sub>

**Common Heaters:** ALD Valves=150°C  
Precursor Delivery=150°C  
Ti(NMe<sub>2</sub>)<sub>4</sub> Precursor=75°C

**Flows:** Argon Carrier (Flow 0) = 60sccm  
Argon Plasma (Flow 1) = 200sccm

**250°C Plasma Recipe:**  
Growth rate 0.52 Å/cycle

**Heaters:** Reactor 1&2=250°C  
Chuck=250°C  
Trap=250°C

**ALD Pulse:**  
Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 5s.

**Plasma:**  
Power 300Watts  
Oxygen (Flow 3) 30sccm, flow 20s, wait 5s

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 1200  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | MFCValve    | 3 | 1     |
| 4  | wait        |   | 60    |
| 5  | pulse       | 2 | 0.1   |
| 6  | wait        |   | 5     |
| 7  | flow        | 3 | 30    |
| 8  | plasma      |   | 300   |
| 9  | wait        |   | 20    |
| 10 | plasma      |   | 0     |
| 11 | flow        | 3 | 0     |
| 12 | wait        |   | 5     |
| 13 | goto        | 5 | m     |
| 14 | flow        | 0 | 20    |
| 15 | flow        | 1 | 20    |
| 16 | MFCValve    | 3 | 0     |

### 200°C Plasma Recipe:

Growth rate 0.51 Å/cycle

**Heaters:** Reactor 1&2=200°C  
Chuck=200°C  
Trap=200°C

### ALD Pulse:

Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 10s.

### Plasma:

Power 300Watts  
Oxygen (Flow 3) 30sccm, flow 20s, wait 5s

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 1200  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | MFCValve    | 3 | 1     |
| 4  | wait        |   | 60    |
| 5  | pulse       | 2 | 0.1   |
| 6  | wait        |   | 10    |
| 7  | flow        | 3 | 30    |
| 8  | plasma      |   | 300   |
| 9  | wait        |   | 20    |
| 10 | plasma      |   | 0     |
| 11 | flow        | 3 | 0     |
| 12 | wait        |   | 5     |
| 13 | goto        | 5 | m     |
| 14 | flow        | 0 | 20    |
| 15 | flow        | 1 | 20    |
| 16 | MFCValve    | 3 | 0     |

### 150°C Plasma Recipe:

Growth rate 0.52 Å/cycle

**Heaters:** Reactor 1&2=150°C  
Chuck=150°C  
Trap=150°C

### ALD Pulse:

Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 30s.

### Plasma:

Power 300Watts  
Oxygen (Flow 3) 30sccm, flow 20s, wait 5s

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 1800  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | MFCValve    | 3 | 1     |
| 4  | wait        |   | 60    |
| 5  | pulse       | 2 | 0.1   |
| 6  | wait        |   | 30    |
| 7  | flow        | 3 | 30    |
| 8  | plasma      |   | 300   |
| 9  | wait        |   | 20    |
| 10 | plasma      |   | 0     |
| 11 | flow        | 3 | 0     |
| 12 | wait        |   | 5     |
| 13 | goto        | 5 | m     |
| 14 | flow        | 0 | 20    |
| 15 | flow        | 1 | 20    |
| 16 | MFCValve    | 3 | 0     |

### 100°C Plasma Recipe:

Growth rate 0.59 Å/cycle

#### Heaters:

Reactor 1&2=100°C

Chuck=100°C

Trap=100°C

#### ALD Pulse:

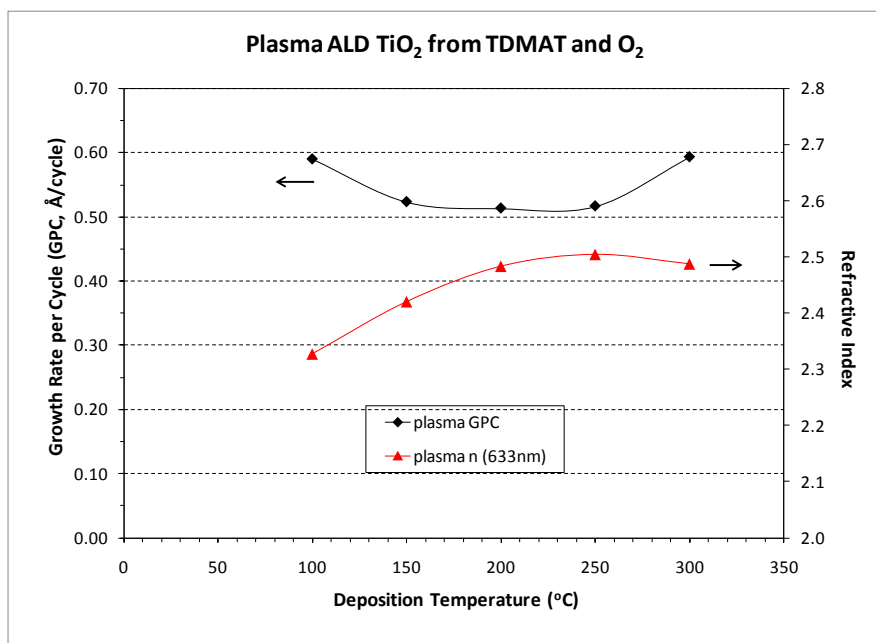
Ti(NMe<sub>2</sub>)<sub>4</sub> (Valve 2) 0.10s, wait 60s.

#### Plasma:

Power 300Watts

Oxygen (Flow 3) 30sccm, flow 20s, wait 10s

|    | Instruction | # | Value |
|----|-------------|---|-------|
| 0  | wait        |   | 3600  |
| 1  | flow        | 0 | 60    |
| 2  | flow        | 1 | 200   |
| 3  | MFCValve    | 3 | 1     |
| 4  | wait        |   | 60    |
| 5  | pulse       | 2 | 0.1   |
| 6  | wait        |   | 60    |
| 7  | flow        | 3 | 30    |
| 8  | plasma      |   | 300   |
| 9  | wait        |   | 20    |
| 10 | plasma      |   | 0     |
| 11 | flow        | 3 | 0     |
| 12 | wait        |   | 10    |
| 13 | goto        | 5 | m     |
| 14 | flow        | 0 | 20    |
| 15 | flow        | 1 | 20    |
| 16 | MFCValve    | 3 | 0     |



**Note.** The TDMAT peak at 0.1s pulse is very small and may become invisible on the pressure chart sometimes.