

# Low Temperature (LT) Thermal ALD Oxides Using Ozone Process

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## **Low Temperature ALD Overview**

Atomic Layer Deposition (ALD) is a powerful nanofabrication technique capable of depositing highly-conformal coatings for a variety of applications. ALD is based on a modified chemical vapor deposition (CVD) process, in which the overall chemical reaction is split into two sequential, self-limiting, half reactions. This allows for sub-nanometer precision in material thickness, which can be controlled with a resolution of ~1 Angstrom. Due to the self-limiting nature of the surface chemical reactions, ALD processes enable excellent uniformity when coating high aspect ratios (above 2000:1), allowing for 3-dimensional engineering of complex nanostructured architectures. The atomically-precise tuning of surfaces and interfaces afforded by this process create numerous opportunities in the fields of semiconductor devices and memory, energy conversion and storage, MEMS/NEMS, catalysis, and other emerging areas.

The coating of thermally fragile substrates by ALD may provide exciting new applications of ALD in diverse areas ranging from food packaging to microelectronics to biomaterials. For example, thin ALD films may serve as gas diffusion barriers in food packaging and extend shelf life by decreasing oxygen diffusion or slowing the escape of CO<sub>2</sub> from pressurized containers. ALD coatings on polymers may also be important as gas diffusion barriers for flexible electronic devices or organic light emitting diodes (OLEDs).

## **Characterization of LT ALD Al<sub>2</sub>O<sub>3</sub> Films**





Growth rate versus temperature study shows that growth rate stabilized at the window of 150 C and higher. At temperatures below 150C the growth rate increased with lowering temperature. This is due to the insufficient removal of excessive surface-adsorbed material, most probably oxygen

The growth rate did not change when lengthening the purging time of ozone from 5s to 20s. Normally 5s was used. This is much shorter than purging of water at the same 60 C.

ALD processes commonly employ water as the oxidant. However at low temperature water is very sticky and hard to purge away, resulting in parasitic CVD growth. More powerful and more readily purged oxidants such as ozone and plasmas have been tested and used in low temperature ALD. Arradiance has incorporated both approaches into our process library.

# **Experimental Method: GEMStar and Ozone system**



Ozone system



The growth rate decrease by 10% when lengthening the purging time of TMA from 20s to 40s. This is due to an increased removal of excessive surfaceadsorbed chemicals.

# **Surface Roughness and Uniformity**

Some typical films developed for LT ALD oxide films on GEMStar 8": Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub> etc. A typical AFM of TiO<sub>2</sub> is presented here and shows smoother and lower crystallinity film at lower temperature.

A typical non-uniformity data over 8" are presented below for LT Al<sub>2</sub>O<sub>3</sub> process.

0.99A/cy 1.00 A/cy 0.99 A/cy

0.99 A/cy

Uniformity of LT Al<sub>2</sub>O<sub>3</sub> film by ozone over 8": 0.55% (1 $\sigma$ ) Reactants: TMA and  $O_3$ Deposition temperature: 60 C

GEMStar-8 system is designed for extreme surface area, high aspect ratio structures: Multi-channel precursor delivery system isolates & distributes precursors combine with a tapered exhaust to provide exceptional nanofilm uniformity.

Metrology Interface for QCM, ellipsometry, FTIR, OES and room for up to six high capacity precursor cylinders (up to 4 heated) with 2 independent gas lines, maximizes system productivity. The hot wall design allows stacks of multi-wafers or samples to improve the through put and reduce the cost per device.

Arradiance specifies a durable ozone system (~10% ozone concentration) as an option for LT ALD. The ozone system is engineered into one of the gas ports of GEMStar with the majority of output of ozone going to the ozone destruct. We use  $N_2$  buffered  $O_2$  to generate higher concentration of ozone. This system shows advantage to reduce ALD oxide cycle time at low temperature.

All the organometallic precursors can be obtained through pre-loaded Arradiance bottle by Strem.

ALD process temperature typically range between 60 to 200C.

# **Characterization of LT ALD Al<sub>2</sub>O<sub>3</sub> Films**



Uniformity of LT TiO<sub>2</sub> film by ozone over 8": 1.1% (1 $\sigma$ ) Reactants: TDMATi and O<sub>3</sub> Deposition temperature: 100C



The rms for ALD TiO<sub>2</sub> at 150C is 6 nm for 50nm film

The rms for ALD TiO<sub>2</sub> at 100C is 2nm for 50nm film

### Summary

By using LT ozone process, we have achieve d:

1. Better film barrier and optical properties realized with Ozone as compared to water;

#### Saturation curve versus ozone



Saturation studies shows that the growth saturates at 100 ms dosing of



ozone. In subsequent runs a 200 ms ozone dose was used.

The linear growth shows the typical ALD behavior of LT Al<sub>2</sub>O<sub>3</sub> process with growth rate of 1.0A/cy.

2. Excellent uniformity (~1%) demonstrated for TiO<sub>2</sub>, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films 3. Low temperature deposition, using Ozone as oxidant, exhibited linear growth at 60C 4. Full integration of Ozone source with GemStar user interface allows for fully automated processing

#### References

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