# Improved Uniformity through New Steam Delivery Method

By Jeffrey Spiegelman

Semiconductor, flat panel, solar, and optical devices all use oxide films as an essential feature. Uniformity of that oxide film is one of the factors that determines the yield of the device. Many films are now grown through a wet thermal oxidation process using water vapor rather than a dry oxidation process using oxygen gas. Advantages of water vapor over oxygen include:

- Faster growth rate for a given temperature, especially as the film thickness increases.
- Growth of oxide films at lower temperatures to reduce thermal stress on the device.
- Growth of selective oxidation where metallic films will degrade in the presence of oxygen but not water vapor.
- Improved uniformity, which is driven by growth rate, temperature and water vapor pressure within the tool.

The RASIRC® Steamer was designed to deliver water vapor into oxidation processes, replacing water bubblers, direct water injection, and pyrolytic torches. Starting with de-ionized water, the Steamer uses a non-porous hydrophilic membrane that selectively allows water vapor to pass through it. Membrane selectivity is significant, with water molecules passing through it 1,000,000 times faster than nitrogen molecules. In the vapor or steam phase all other molecules are greatly restricted, so water-borne contaminants such as dissolved gases, ions, total organic carbons, particles, viruses, bacteria, pyrogens, and metals can be removed. Total metals have been verified to less than 10 ppt (Ref. 1).

## Quick Review of Thermal Oxidation

*(Unless otherwise noted this information is excerpted from Prof. J. Salzman (Ref. 2)*

Oxidation is a process used in wafer fabrication. The goal of oxidation is to grow a high quality oxide layer on a silicon substrate. During oxidation a chemical reaction between the oxidants and the silicon atoms produces a layer of oxide on the silicon surface of the wafer. It is often the first step in wafer fabrication and will be repeated multiple times throughout the fabrication process.

Oxidation takes place in an oxidation tube. During the process, silicon reacts with oxidants to form silicon oxide layers. Typical operating temperature is between 800˚C and 1,200˚C. The oxide growth rate increases with temperature. Generally, this technique is used to grow oxides between 60Ǻ and 100,000Ǻ thick.

Thermal oxidation of silicon is divided into two classes:

- **Dry Oxidation**. Dry oxygen is introduced into the process tube where it reacts with silicon. Dry oxidation is a slow process that grows films at a rate between 140Ǻ and 250Ǻ per hour. It is only used in industry to grow thin oxides (<1000Å).

$$\text{Si (solid)} + O_2 \text{ (gas)} \quad \rightarrow \quad SiO_2 \text{ (solid)}$$

- **Wet Oxidation**. Water vapor is introduced into the heated oxidation tube. Because water molecules are smaller in size than oxygen molecules, they diffuse faster in silicon dioxide and the oxide growth rate increases. The wet oxidation growth rate is 1000Ǻ to 1200Ǻ per hour, so wet oxidation is the preferred method to grow thick oxides.

$$\text{Si (solid)} + H_20 \text{ (gas)} \quad \rightarrow \quad SiO_2 \text{ (solid)} + 2H_2$$

As a general principle, the amount of silicon consumed in the oxidation reaction is 45% of the final oxide thickness (Figure 1). For example, growing 10,000Å of oxide consumes 4,400Å of silicon.

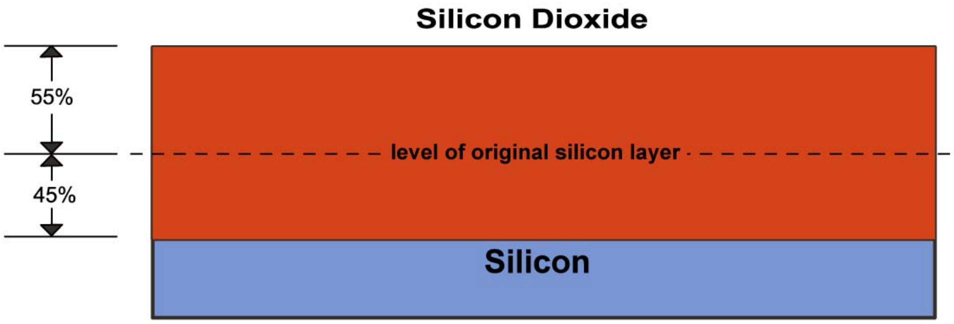

*Figure 1: Silicon Consumed in Oxidation Reaction*

## Linear Parabolic Model

The kinetics of $SiO_2$ growth has three steps. First, the oxidant ($H_2O$ or $O_2$) reacts with silicon atoms. Second, silicon atoms are consumed by the reaction and, finally, a layer of oxide forms on the silicon surface.

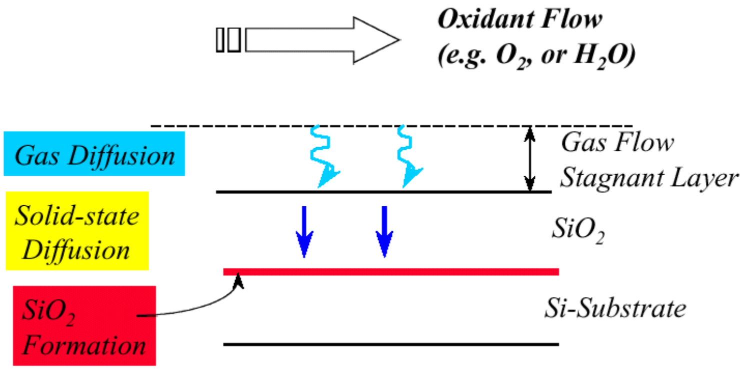

*Figure 2: Kinetics of $SiO_2$ Growth*

The Linear Parabolic Model developed by Deal and Grove (Ref. 3) demonstrates how silicon dioxide is grown on a silicon substrate during oxidation under both wet and dry conditions. The model identifies and defines two different stages in the oxidation of silicon:

- **Linear**. As the first phase in oxide growth, the Linear Stage refers to the chemical reaction resulting from the direct contact between the silicon and the oxidants at the surface of the wafer. The reaction is limited by the number of silicon atoms available to react with the oxidants. For approximately the first 500Å, the oxide grows linearly with time. From that point on, the reaction rate begins to slow down as a direct result of the silicon dioxide layer covering the silicon atoms. As the silicon dioxide layer grows, it eventually prevents the oxidants from coming in direct contact with the silicon atoms and the Parabolic Stage of oxidation begins. The reaction of the oxygen at the silicon/silicon dioxide interface limits the oxide growth in this stage.

- **Parabolic**. The Parabolic Stage of oxidation begins when approximately 1,000Å of silicon dioxide has been grown on the silicon substrate. At this point, the silicon atoms are no longer exposed to the oxidants and the oxidants begin to diffuse through the silicon dioxide in order to reach the silicon. The oxidation of silicon during this stage occurs at the silicon/silicon dioxide interface. As oxidation continues, the silicon dioxide layer thickens, and the distance the oxidants must travel to reach the silicon increases. The oxide growth rate is limited by the diffusion of the oxidants through silicon dioxide.

The details of the Deal-Grove Model are left to the reader. To summarize the portion relevant to our discussion, the growth rate depends on the concentration of oxidant at the oxidized surface to drive the oxidant through the oxide layer to get to the unoxidized silicon surface.

Henry's Law states that the concentration of an oxidant in the solid is proportional to the partial pressure of the oxidant in the surrounding gas. Increasing the water vapor pressure or oxygen pressure in the process gas environment will increase the oxidation growth rate.

*(1)*

$$P_G \uparrow \Rightarrow \frac{dX_{ox}}{dt} \uparrow$$

An increase in the water vapor pressure will directly increase the oxidation rate. Figure 3 shows how an increase in temperature or pressure increases the growth rate. The oxide thickness increases with both pressure and temperature.

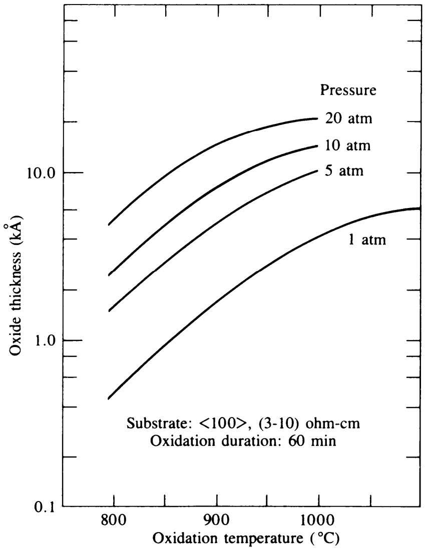

*Figure 3: Growth Rate Relative to Temperature and Pressure*

In practice, there are limitations to both temperature and operating pressures. While diffusion furnaces running above atmospheric pressure have been built, they are far more dangerous and become significantly more costly to purchase and operate. In general oxidation furnaces are run at atmospheric pressure.

## Steamer Test Results

RASIRC Steamers were installed and tested at five locations over the past two years. All installations were on horizontal furnaces that were dedicated to wet thermal oxidation, except for installation 5.

Installation 1. Steamer was installed on a six-inch tube furnace tube, replacing a water bubbler that used oxygen as a carrier gas.

Installation 2. Steamer was installed on an eight-inch furnace tube, replacing a direct water injection system that used an oxygen carrier gas to purge the vaporizer.

Installation 3. Steamer was installed on both a 150 mm and a 300 mm furnace, replacing pyrolytic torches that generated water vapor from combustion of oxygen and hydrogen.

Installation 4. Steamer was installed on a six-inch furnace, replacing a pyrolytic torch for thick oxide growth. The elimination of hydrogen from the process allowed the user to expand production and still remain within local fire ordinances.

Installation 5. Steamer was installed on a 300 mm vertical furnace to grow selective oxidation films in an oxygen free environment.

All customers expected the same or better film quality, but did not expect a change in oxidation growth rate or process uniformity.

Process recipe temperatures and run times were kept constant. The only changes made were installation of the Steamer and elimination of oxygen and/or hydrogen gas. The total amount of steam supplied was initially the same as the previous technology and then adjusted to maximize performance.

### Uniformity Testing: Installation 1: Bubbler Replacement

A six-inch horizontal furnace was operated at 1000˚C. Wafers were loaded at three locations within the tube. Run time was 104 minutes. By eliminating the oxygen and increasing the water vapor flow rate, the non-uniformity across the tube decreased from +/-3% to +/-0.2%.

| Water Vapor (slm) | Oxygen (slm) | Furnace Inlet | Furnace Middle | Furnace Rear | Uniformity (%) |
|---|---|---|---|---|---|
| 8.0 | 0.4 | 5275 | 5335 | 5275 | 1.1 |
| 8.8 | 0.0 | 5550 | 5595 | 5425 | 3 |
| 10.0 | 0.0 | 5630 | 5600 | 5550 | 1.4 |
| 11.2 | 0.0 | 5630 | 5620 | 5620 | 0.2 |

### Uniformity Testing: Installation 2: Vaporizer Replacement

Three separate runs were made of 8000Ǻ films. Previous customer requirements were +/-5%. Before installation of the Steamer, oxide thickness uniformity often exceeded the acceptance criteria, with film thickness failing to meet 95% of target. This required measurement of each wafer and reworking a partial load. The tighter uniformity eliminated rework for definitive oxide thickness.

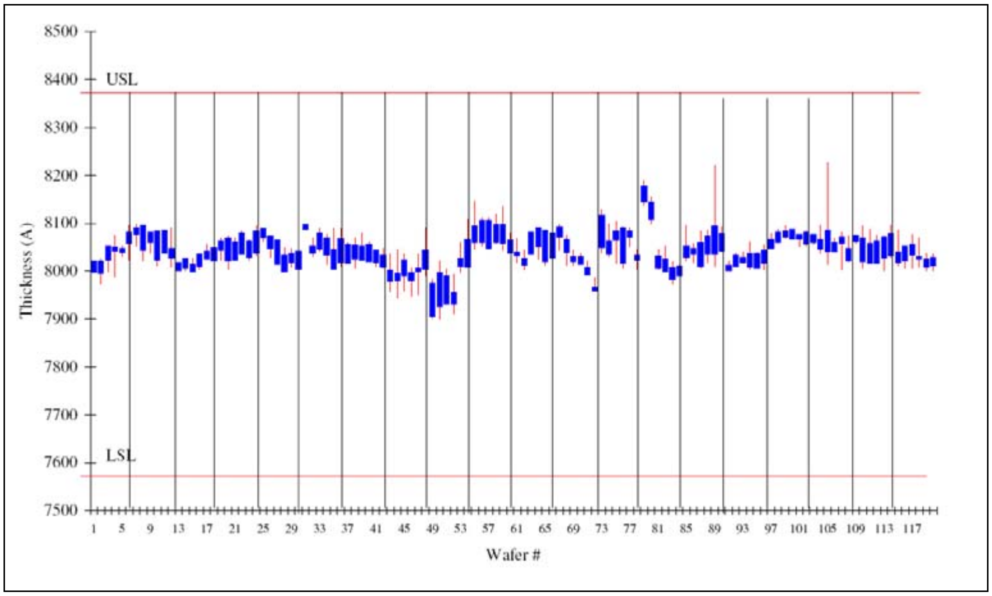

*Figure 4: Thickness Across Wafers*

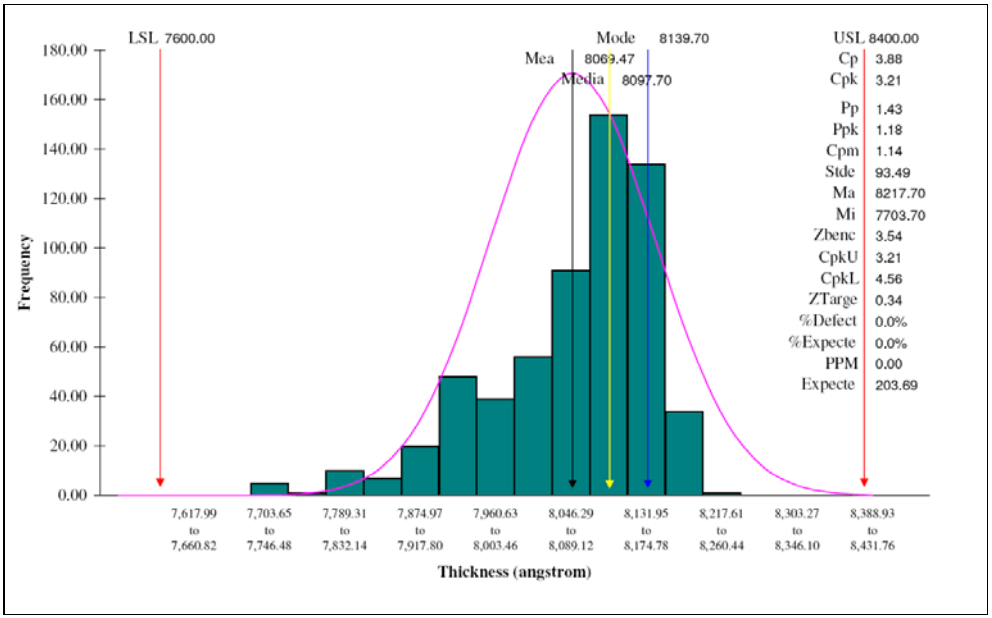

*Figure 5: Oxide Thickness Three Separate Lots of 175 wafers.*
*Wafers from each lot were tested randomly.*

## Uniformity Testing: Installation 3: Torch Replacement 150 mm and 300 mm

Data was collected from a six-inch furnace run at steam flow rate of 25 slm. This high flow rate was used to ensure water vapor pressure was equal across the furnace. The customer attributed the uniformity to the ability to control both temperature and water vapor pressure within the furnace.

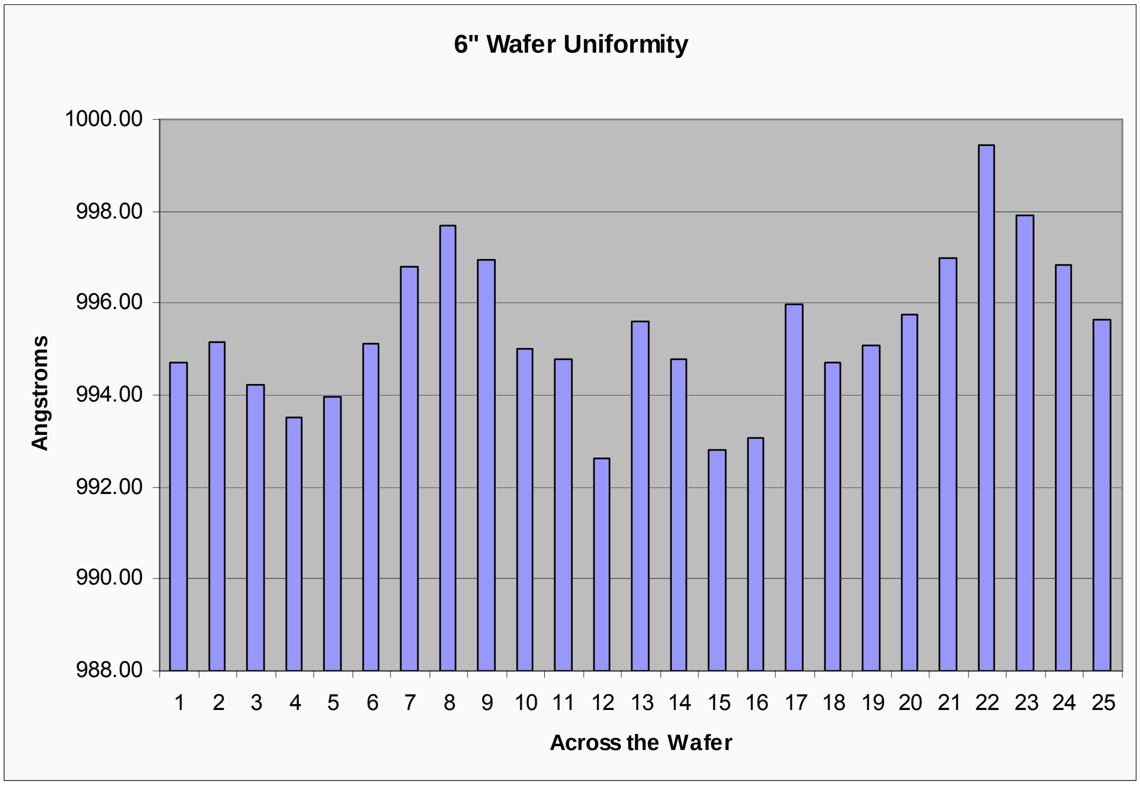

*Figure 6: Uniformity Across the 150 mm Wafer*

With the Steamer, this installation achieved the following uniformity:

| Average | Min | Max | Range | Std. Dev | Wafer Uniformity |
|---|---|---|---|---|---|
| 995.4 | 992.6 | 999.4 | 6.81 | 3.33 | 0.342 |

At the same installation, the 300 mm furnace had been running pyrolytic torches 300 mm. These furnace tubes measured 450 mm across. All torches were replaced with a high flow Steamers capable of generating 60 slm steam flow rates. While torches can generate these high flow rates, removing the excess heat (up to 2000˚C) from the pyrolytic combustion of hydrogen and oxygen becomes difficult and expensive as does the continued operating cost from the gas consumption.

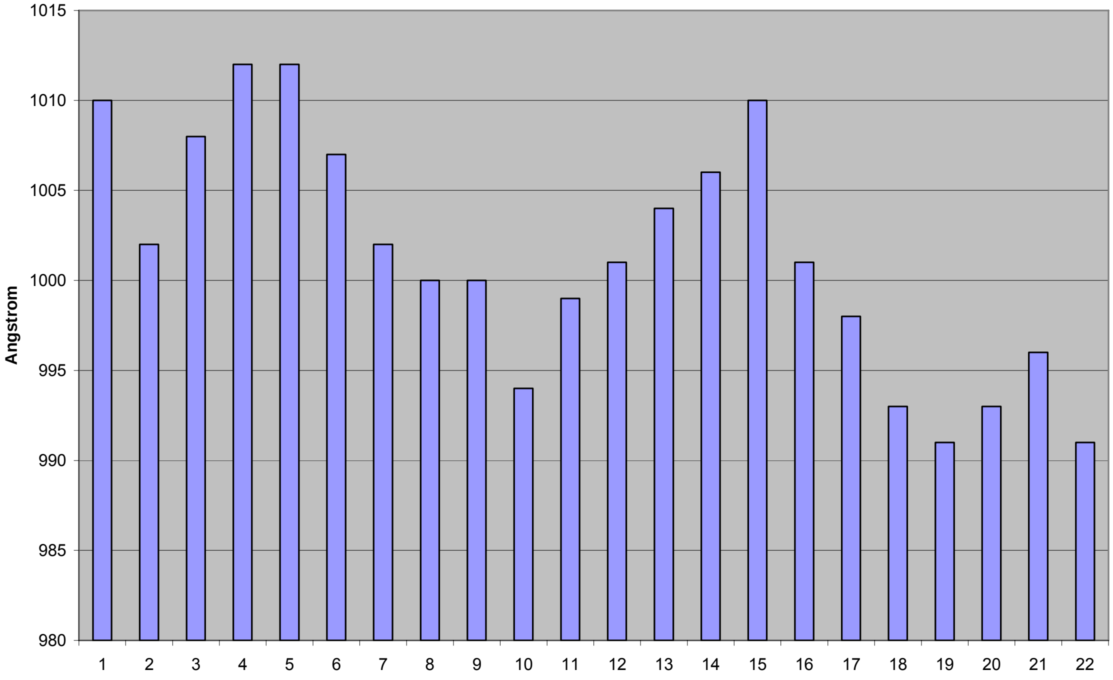

*Figure 7: Uniformity at 300mm*

With the Steamer, this installation achieved the following uniformity:

| Average | Min | Max | Range | Std. Dev | Wafer Uniformity |
|---|---|---|---|---|---|
| 1001.8 | 991 | 1012 | 20.9 | 6.53 | 1.05 |

## Uniformity Testing: Installation 4 : Thick Oxide Six-Inch Torch Replacement

Data from a thick oxide customer was included to demonstrate both thin and thick uniformity performance. This data is from the third run after initial installation. The tool is a six-inch horizontal furnace with a load size of 175 wafers. The run time was 14 hours and flow rate was 15 slm of steam. Overall average thickness was 26,973Å with a standard deviation of 49Å or 0.182%. Range was 185Å or 0.69%.

| | **Load** | | **Center** | | **Source** | | **Overall** |
|---|---|---|---|---|---|---|---|
| C | 26892 | 26937 | 26974 | 27006 | 27033 | 27005 | |
| T | 26925 | 26928 | 26951 | 26973 | 27008 | 26979 | |
| L | 26876 | 26920 | 26940 | 27019 | 27014 | 26978 | |
| F | 26891 | 26956 | 27011 | 27041 | 27061 | 27023 | |
| R | 26905 | 26954 | 27000 | 26976 | 27037 | 26970 | |
| Avg. | 26898 | 26939 | 26975 | 27003 | 27031 | 26991 | 26973 |
| Std. Dev. | 18.349 | 15.811 | 30.507 | 28.888 | 20.959 | 22.215 | 49.104 |
| S.D. % | 0.068 | 0.059 | 0.113 | 0.107 | 0.078 | 0.082 | 0.182 |
| Range | 49 | 36 | 71 | 68 | 53 | 53 | 185 |
| Range % | 0.18 | 0.13 | 0.26 | 0.25 | 0.20 | 0.20 | 0.69 |

## Uniformity Testing: Installation 5 Selective Oxidation

Growth of very thin oxide films is critical for metal gate formation. Previous torches had been used to growth these thin films, but oxygen in the oxidation gas can cause problems with uniformity. Because 100% combustion of oxygen is not possible, the user replaced their torch based system with a Steamer. They were able to growth films from 25.4Å to 26.5Å on 300mm vertical furnace.

| 300 mm Wafer | | | | |
|---|---|---|---|---|
| **X** | **Y** | **Top** | **Center** | **Bottom** |
| -147 | 0 | 26.25 | 25.61 | 25.45 |
| 0 | -147 | 25.95 | 25.91 | 26.13 |
| 0 | 0 | 25.42 | 25.72 | 25.37 |
| 0 | 147 | 26.54 | 26.06 | 25.00 |
| 147 | 0 | 26.09 | 25.82 | 25.95 |
| 73.5 | 73.5 | 25.73 | 25.82 | 25.46 |
| -73.5 | 73.5 | 25.60 | 25.82 | 25.15 |
| -73.5 | -73.5 | 25.44 | 25.56 | 25.59 |
| 73.5 | -73.5 | 25.55 | 25.76 | 25.77 |
| 73.5 | 0 | 25.49 | 25.70 | 25.52 |
| 0 | 73.5 | 25.58 | 25.74 | 25.21 |
| -73.5 | 0 | 25.50 | 25.65 | 25.34 |
| 0 | -73.5 | 25.61 | 25.62 | 25.65 |
| | Average | 25.75 | 25.75 | 25.51 |
| | S.D. | 0.35 | 0.13 | 0.31 |
| | S.D. % | 1.36% | 0.52% | 1.24% |
| | Uniformity | 2.18 | 0.095 | 2.21 |

## Discussion:

### Increased Growth Rate with Increased Partial Water Vapor Pressure

Users of the Steamer demonstrated increased oxide growth rate by increasing the partial pressure of water vapor while the operating pressure of the furnace remained fixed at atmospheric pressure. Similar increases in growth rate with increasing water vapor pressure had been reported by Geib Et.Al (Ref. 4).

While increasing water vapor flow rate to improve growth rates seems obvious, technical difficulties interfere with increasing the actual quantity of delivered water vapor when using:

- **Bubblers**. The water cannot be heated near boiling or uncontrolled flow will result. The carrier gas flow needs to be increased to increase the delivery rate, which can then slow the diffusion of water vapor to the surface. After the initial burst of steam, localized cooling causes the bubbler bulk operating temperature to droop leading to reduced water vapor flow.

- **Direct liquid injection systems**. Increasing flow rate leads to incomplete vaporization. This increases microdroplet formation, which increases nonuniformity and ionic contamination on the wafer. Oxygen is often needed to ensure complete vaporization in the furnace.

- **Torches**. Torches become larger and the thermal load from pyrolytic combustion of hydrogen and oxygen becomes more difficult to handle. There is also an increase in operating cost and safety issues. Torch cannot provide 100% water vapor due to accuracy limits of mass flow controllers.

Different facilities using different methods—a bubbler, vaporizer, and pyrolytic torch—all confirmed that a reduction in background oxygen gas and an increase in water vapor pressure resulted in increased oxide growth rate. This increase in water vapor pressure agrees with the Deal and Grove model for oxidation.

When the water vapor pressure is increased, the oxide growth rate is increased. According to the model of Deal and Grove, the growth rate of the oxide layer is directly related to the effective diffusion coefficient of the water molecules into the oxide layer and the equilibrium concentration in the immediate area. When a carrier gas is used to deliver water vapor, the carrier gas molecules generate a partial pressure. This partial pressure lowers the partial pressure of water vapor and slows the diffusion of water into the oxide film. The result is lower driving force and slower growth rate. For a given temperature and process pressure, oxide growth rates are fixed if the gas ratio is also constant. However, for a given operating temperature, this growth rate is not maximized until the water vapor pressure is equal to 100% of the operating pressure.

## Localized Effect and Uniformity

As long as oxygen is part of the process recipe the partial pressure within the furnace tube will not be uniform. At the gas entrance to the furnace tube there is a ratio of partial pressure of oxygen to water vapor. As the water molecules travel towards the exit of the tube they are absorbed into the oxide film at a much faster rate than the oxygen molecules. The oxide growth results in the gradual reduction in water molecules relative to the oxygen molecules. This localized reduction in water molecule concentration slows the available oxidation reaction and the growth rate as the exit of the furnace is reached. A typical slower growth at the exit of the furnace and front to back non-uniformity can be seen which requires adjusting the localized temperature within the furnace. By eliminating the oxygen gas, the water vapor pressure stays relatively constant and film uniformity improves across the furnace.

## Summary

Replacement of previous water vapor delivery systems with the RASIRC Steamer resulted in significant increase in oxide growth rate and improvement in uniformity throughout the furnace.

For a given temperature and process pressure, the oxide growth rate is not maximized until the water vapor pressure is equal to 100% of the operating pressure.

If oxygen makes up part of the process recipe during wet oxidation, it will slow the overall growth rate by reducing the water vapor partial pressure. The oxygen gas will also lead to non-uniform growth throughout the furnace tube, since as the water is consumed from front to back of the furnace, the partial pressure of oxygen increases, and the partial pressure of water decreases. This difference in water partial pressure leads to variability in the oxide growth rate and non-uniformity throughout the furnace tube.

## About RASIRC

RASIRC develops products that purify and deliver ultra pure liquids and gases, with a primary focus on water vapor. RASIRC dryers, humidifiers and steam generators are of critical importance for many applications in the semiconductor, pharmaceutical, medical, biological, fuel cell, and power industries. Custom systems are available upon request.

## References

1) "Alternative Method and Device to Purify and Deliver Water Vapor" by Jeffrey J. Spiegelman and Russell J. Holmes. SPWCC February, 2006

2) "Microelectronic Processing Oxidation" by J. Salzman. PowerPoint Presentation. Microelectronics Processing Course January 2002

3) Deal B. E. and Grove A. S. 1965 *J. Appl. Phys*. 36 3770

4) Geib, K.M., Choquette K.D., Hou H.Q., and Hammons, B.E. "Fabrication issues of oxide-confined VCSELS". Center for Compound Semiconductor Technologies. San dia National Laboratories