Improved Oxide Growth Rate and Uniformity through New Steam Delivery Method

By

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Oxidation of silicon is a common and frequent step in the manufacture of integrated circuits (IC). The success or failure of the IC manufacturer often depends on the ability to grow a uniform oxide film quickly and repeatedly. Water vapor is commonly used to grow oxides. RASIRC has developed a new device to deliver water vapor to oxidation furnaces.

The RASIRC Steamer was designed to replace water bubblers, direct water injection, and pyrolytic torches for the delivery of water vapor into oxidation processes. 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 contaminants in water 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. Reference (1).

Test results were collected from installations at three different fabs. Each Steamer installation replaced a different form of water vapor delivery. Expected benefits were lower cost, improved safety, and reduced film contamination. These expectations were met, and unexpected improvements in uniformity and growth rate were also reported during wet thermal oxidation of silicon wafers.

The following article will review the thermal oxidation process for silicon, present the field results for the Steamer installations, and then discuss the results.

Thermal Oxidation

(Unless otherwise noted this information is excerpted from Prof. J. Salzman (reference 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 reaction silicon reacts with oxidants to form silicon oxide layers. Typical operating temperature is between 900˚C and 1,200˚C. The oxide growth rate increases with temperature.

Generally, this technique is used to grow oxides between 60Å and 100,000Å thick.

Thermal oxidation of silicon is divided into two classes – dry and wet.

- Dry Oxidation

  Si (solid) + O_2 (gas) → SiO_2 (solid)
- Wet Oxidation

  Si (solid) + $H_2$0 (gas)→ SiO_2 (solid) + $2H_2$

Dry Oxidation

During 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 140 and 250Å/hour. It is only used in industry to grow thin oxides (<1000Å).

Wet Oxidation

During 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 1000 to 1200 Å/hour, so wet oxidation is the preferred method to grow thick oxides.

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

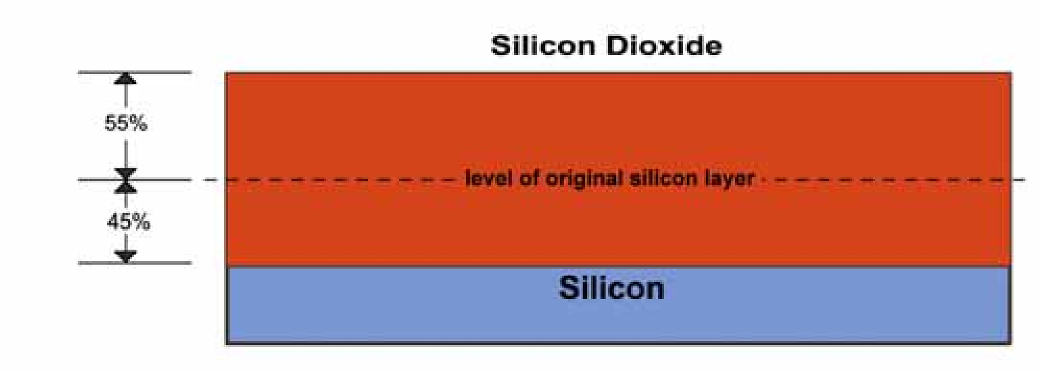


Figure 1

Linear Parabolic Model

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

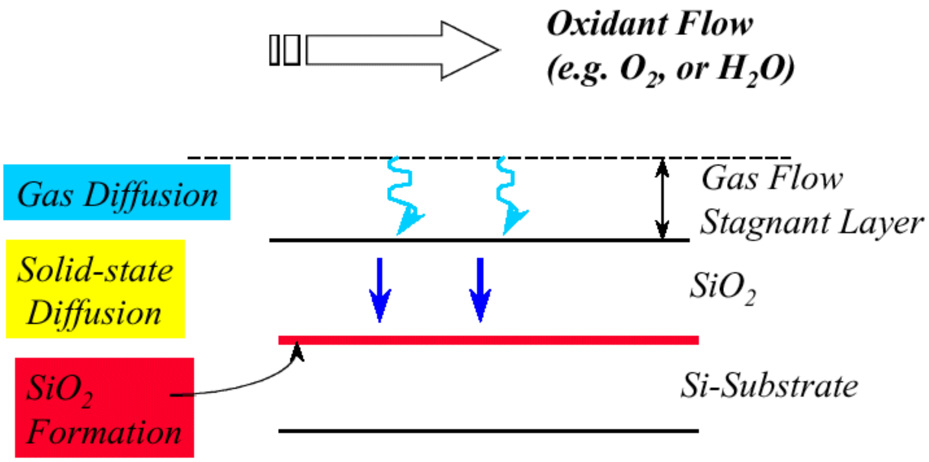


Figure 2

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 and Parabolic.

Linear (first) Stage of Oxidation

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 500 Å, 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 (second) Stage

The Parabolic Stage of oxidation begins when approximately 1,000 Å 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.

$$P_G \uparrow \Rightarrow \frac{dX_{ox}}{dt} \uparrow \qquad (1)$$

An increase in the water vapor pressure will directly increase the oxidation rate. Many researchers have reported increased growth rate with increased water pressure. Choe, et.al. (Ref 4) reported a four-fold increase in AlAs oxide growth rate with increased water vapor pressure and no carrier gas at 440˚C.

Figure 3 shows how an increase in temperature or pressure increases the growth rate. The oxide thickness increases with both pressure and temperature.

In practice, there are limitations to both temperature and operating pressures. Operating temperatures are kept below 1200˚C due to limitations of the equipment and thermal effects on materials. While diffusion furnaces running above atmospheric pressure have been built, they are far more dangerous and become significantly more costly to purchase and operate. Most commonly oxidation furnaces are run at atmospheric pressure.

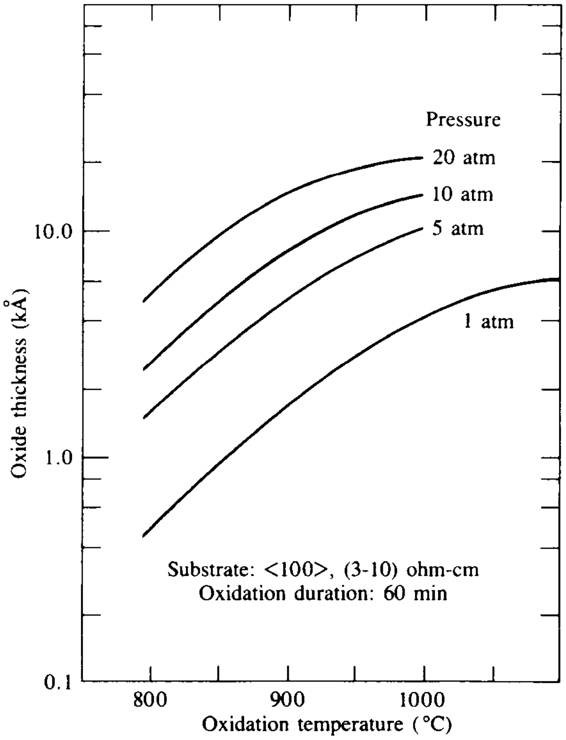


Figure 3

Steamer Test Results

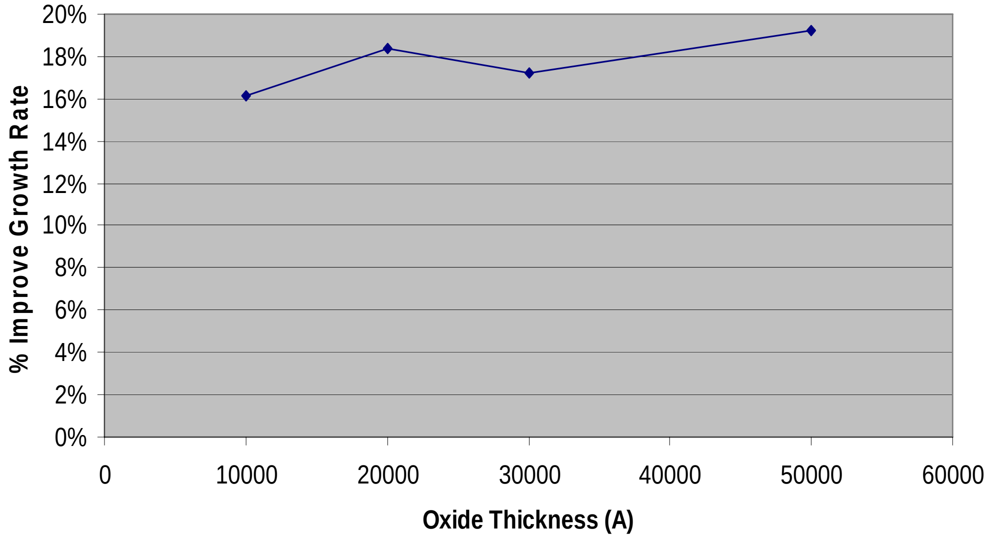
RASIRC Steamers were installed at three separate locations. All three installations were horizontal furnaces that were dedicated to wet thermal oxidation. The first Steamer installation was on a 6” tube furnace tube that replaced a water bubbler that used oxygen as a carrier gas. The second Steamer was installed on an 8” furnace tube and replaced a direct water injection system that used an oxygen carrier gas to purge the vaporizer. The third installation was on a 300 mm furnace and replaced a pyrolytic torch that generated water vapor from combustion of oxygen and hydrogen. The elimination of hydrogen from the process allowed the user to expand production and still remain within local fire ordinances. 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 the elimination of oxygen and/ or hydrogen gas and installation of the Steamer. Total amount of steam supplied was initially the same as the previous technology and then adjusted to maximize performance.

Growth Rate

Installation 1

The furnace was operated at 1000˚C. Initial results from replacing the bubbler with the Steamer generated a consistent improvement of greater than 16%.

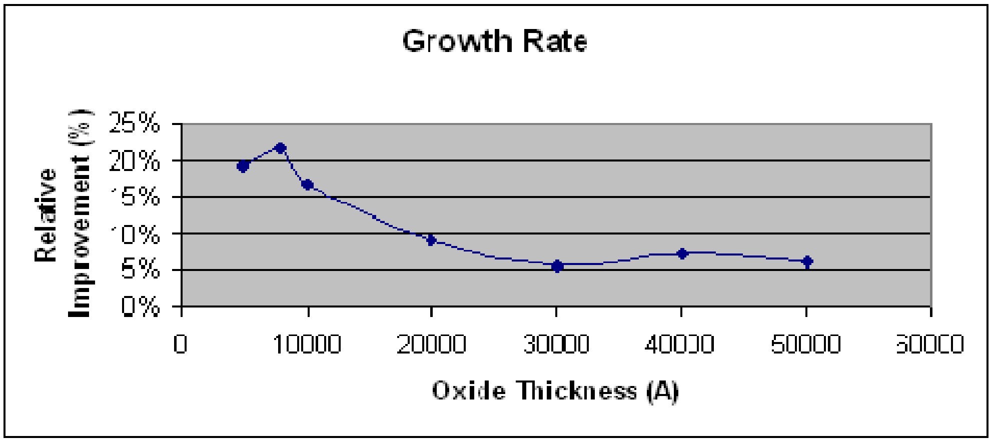


The recipe was then changed to eliminate the oxygen flow of 1 slm. Wafers were loaded at three locations within the tube. Run time was 104 minutes.
By eliminating the oxygen purge the growth rate improved by 7% on 50,000Å film.

Installation 2

At the second installation, the Steamer was attached to an eight inch horizontal furnace. The Steamer replaced an existing de-ionized water direct injection system running at 8 grams/minute. The oxygen purge through the injector was also eliminated. Multiple lots of 130 wafers were run through the furnace for different periods of time. Every fifth wafer was measured to get an average growth rate along the furnace tube and from run to run. The results were compared to film grown with water injection versus the Steamer.

Thin films reported better than 20% increase in growth rate. This rate slowed to greater than 5% at thickness above 3000Å.



Installation 3

The 300 mm furnace was operated at 900˚C. The pyrolytic torch was replaced with a RASIRC Steamer. Flow rate was 30 slm of steam. Time to grow the 1000Å film was reduced from 32 minutes to 28 minutes, representing an increase in growth rate of 7%.

Uniformity

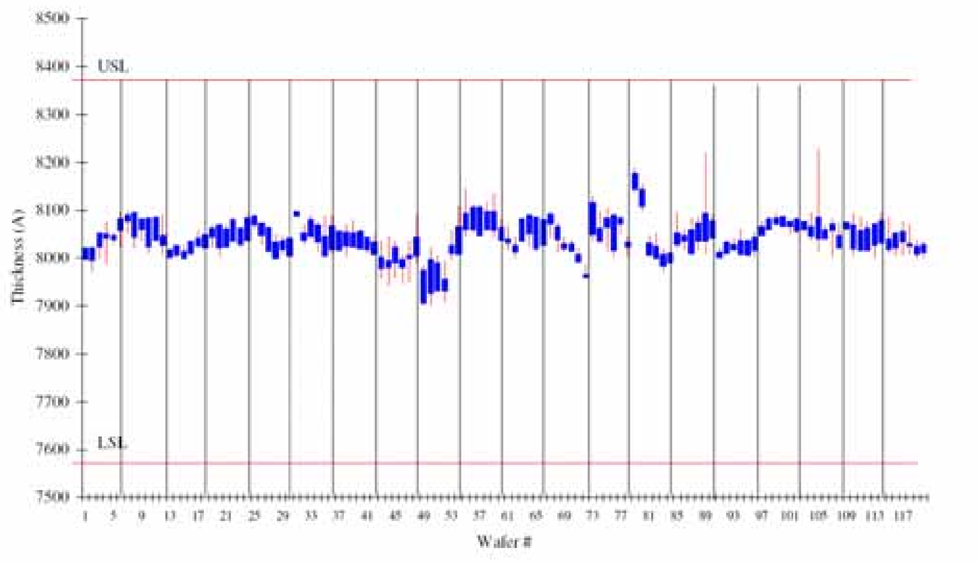
Installation 1

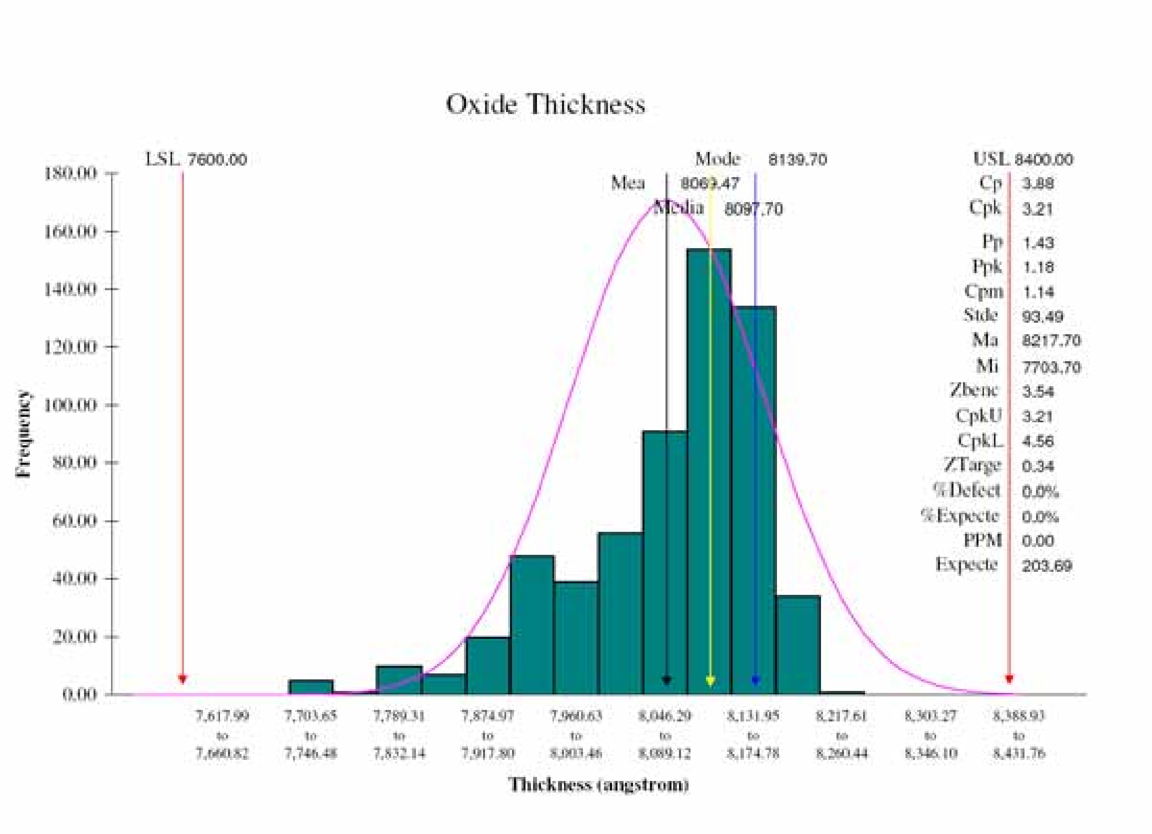
A six inch horizontal furnace was operated at 1000˚C. Wafers were loaded at three locations within the tube. Run time was 104 minutes. By eliminating the oxygen and increasing the water vapor flow rate, the non-uniformity across the tube decreased from +/-3% to +/-0.2%.

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

Installation 2

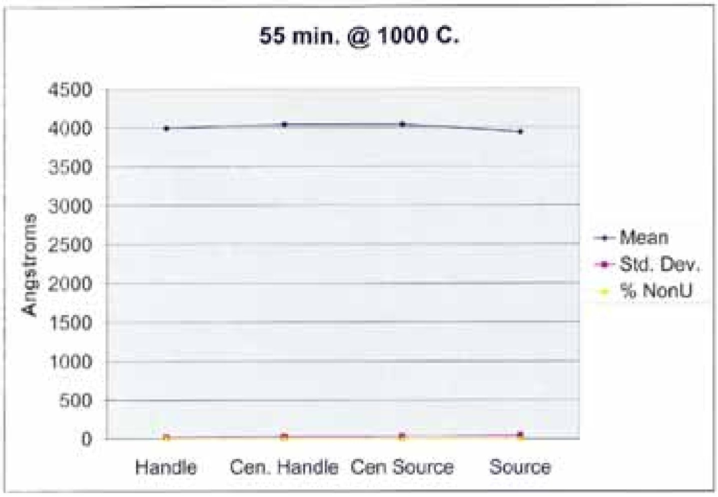
Three separate runs of where made of 8000Å films. Previous customer requirements were +/-5%. Before installation of the Steamer, oxide thickness uniformity often exceeded the acceptance criteria with film thickness failing to meet 95% of target. This required measurement of each wafer and reworking a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

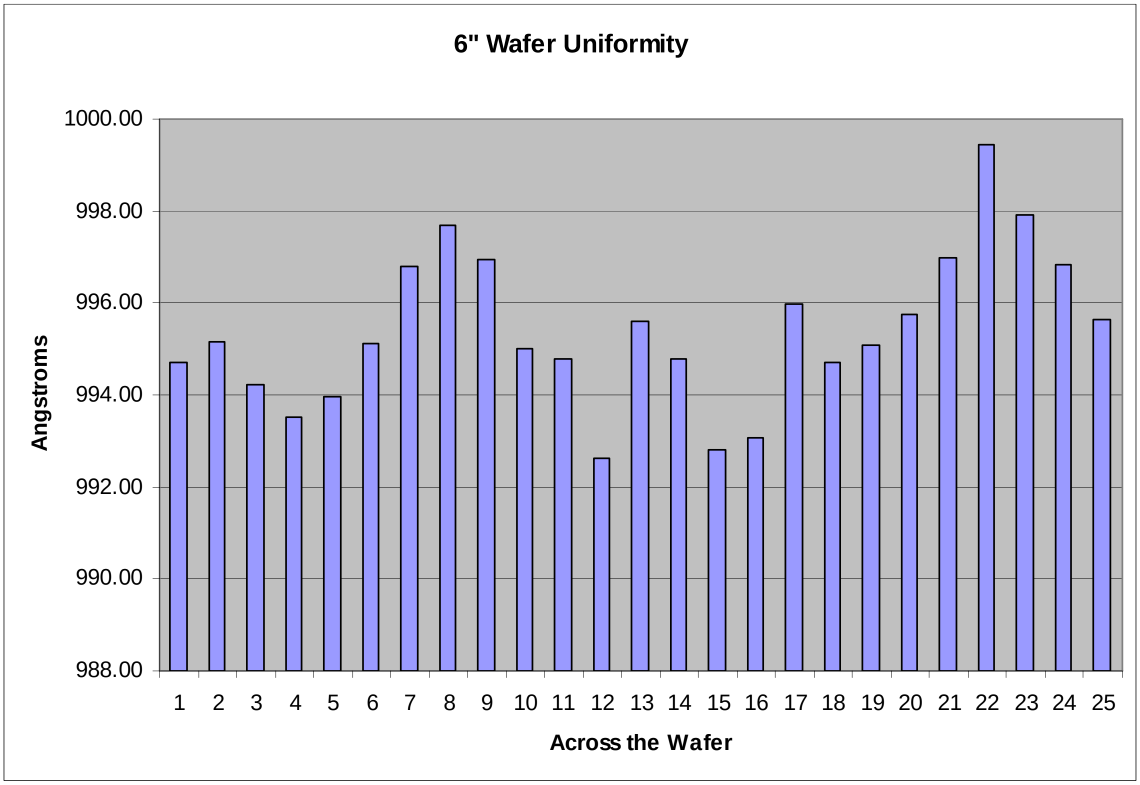




Installation 3

Initial data collected on the 300mm tool.





The steamer was moved from the 300mm tool to the 8" furnace for additional tests. Uniformity was Average 995.410, Min 992.63, Max 999.43, Range 6.809, Std. Dev 3.325, and Wafer Uniformity 0.342000.

Discussion:

Increased Growth Rate with Increased Partial Water Vapor Pressure

Users of the Steamer demonstrated increased growth rate while keeping operating pressure fixed at atmosphere and increasing the partial pressure of water vapor. Similar increases in growth rate with increasing water vapor pressure had been reported by Geib Et.Al (ref 5).

While increasing water vapor flow rate seems obvious to improve growth rates, technical difficulties interfere with increasing the actually quantity of delivered water vapor. For bubblers, the water cannot be heated near boiling or uncontrolled flow will result. The carrier gas flows needs to be increased to increase the delivery rate which can then slow the diffusion of water vapor to the surface. With direct liquid injection systems, increasing flow rate leads to incomplete vaporization. This increases micro droplet formation, which increases non-uniformity and ionic contamination on the wafer. 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.

Three different facilities using three 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 an increase 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

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. Leading to a typical slower growth at the exit of the furnace and front to back non-uniformity as can be seen in the uniformity results from installation 1.

As long as oxygen is part of the process recipe the partial pressure within the furnace tube will not be uniform. By eliminating the oxygen gas, the water vapor pressure stays relatively constant and film uniformity improves across the chamber.

Conclusion

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

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