PROBLEM
Many of the advanced oxide deposition processes required in modern semiconductor device manufacture benefit from the use of highly reactive ozone gas as an oxidant. Especially, ozone has proven advantages over other oxidants in processes such as shallow trench isolation (STI) and atomic layer deposition (ALD).

As device geometries continue to shrink, the development of oxide processes for STI and DRAM trench capacitor fabrication which employ high ozone flows are expected to prove advantageous. In the case of STI processes for smaller geometries, uniform trench coverage and "pinch off" of the high K oxide at the top of the trench are a problem. A sub-atmospheric pressure chemical vapor deposition approach that employs high ozone concentrations has been found to increase deposition rates and produce a more uniform oxide growth that helps to alleviate this issue. DRAM trench capacitor processes employ ALD Al₂O₃ to ensure 100% surface conformality in these very high aspect ratio structures.

This Application Note describes a new high flow, high concentration ozone generator for use in these advanced processing environments.

BACKGROUND
Ozone (O₃) is an unstable, gaseous allotrope of oxygen that is produced when O₂ molecules are exposed to a high voltage electrical discharge. It is the strongest commercially available oxidant; its high electrochemical potential (2.08 eV vs. 1.23 eV for the oxygen molecule) results in high reaction rates when ozone is used as an oxidant in a variety of chemistries. Ozone reactions with target molecules are extremely rapid, occurring through either direct reaction with the O₃ molecule or through the liberation of highly reactive atomic oxygen radicals.

Ozone has been recognized as an effective industrial oxidant for many years; it has a long history of use in water purification that goes back well over a century. It is ideally suited for use in safety- and environmentally-conscious industries such as semiconductor device manufacture. It can be easily generated on-site, thus avoiding the cost and safety issues that are associated with transportation and storage of strong oxidants. Excess ozone from a process is destroyed using catalytic destruction, further assuring environmental compliance. As well, any fugitive ozone released from the process rapidly decomposes to oxygen under ambient conditions.

The use of high concentrations of ozone in SACVD STI processes for aggressive topographies has enabled both geometry shrinkage and significant process simplification. Early STI processes such as HDP-CVD required multiple deposition/etch steps with the usual concomitant risks to process yields engendered by process complexity. These processes have been found to be no longer effective for STI gap fill at the <65 nm technology node. SACVD high flow ozone/TEOS based STI gap fill processes have been developed and these have proven successful for <65 nm gap fill.

ALD processes are especially well-suited for depositing advanced high-K dielectric film such as Ta₂O₅, HfO₂, ZrO₂, etc. on the severe topographies present in modern device geometries. These processes have certain prerequisites for successful application. First, the deposited film must be of high purity, especially, they must have low hydroxyl contamination[1]; the presence of significant concentrations of hydroxyl in these films leads to poor leakage current characteristics. Secondly, the reactants used in the process must be highly volatile since ALD processes require very rapid reaction/purge cycles to maintain commercial throughput. Finally, reaction rates in the process must be extremely high, again to maintain adequate throughput. Ozone's chemical composition, high volatility and the rapid reaction rate of ozone-based oxidations make ozone especially advantageous in ALD high-K oxide thin film processes. Other oxidants such as water, hydrogen peroxide and oxygen all fail to fulfill one or more of the prerequisites outlined above. In terms of film purity, ozone introduces no hydrogen to the process and hence cannot produce hydroxyl moieties in the oxide film (note, however, that other reactants in the system may contribute hydrogen). The high electrochemical potential of ozone results in high overall reaction rates in ALD processes that are significantly higher than can be achieved with other oxidants and this in turn contributes to rapid reaction/purge cycles. The fact that ozone is a gas allows it to be rapidly purged from ALD chambers, contributing further to rapid reaction/purge cycles.

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MKS Instruments’ SEMOZON® AX8407 has been the industry-leading high concentration, high flow ozone generator employed in many semiconductor and other industrial applications. The AX8407 has been employed, either as a standalone unit or integrated into a rack system in semiconductor ozone applications that include SACVD TEOS/Ozone, Ta2O5 CVD, photosist strip, wafer cleaning, contaminant removal, surface conditioning, oxide growth, and ALD.

Figure 1 shows the operational space of the AX8407. The ozone concentration and flow ranges available using this generator have been appropriate for the process requirements of existing STI and ALD processes. Recently, however, advances in STI gap fill and ALD processes for low nanometer geometries have produced a need for ozone generators having concentration and flow ranges beyond those of the AX8407.

**SOLUTION**

In response to the industry demand for ozone concentrations and flows beyond those supplied by the AX8407, MKS Instruments has developed the SEMOZON® AX8410 PRIME ozone generator (Figure 2). Figure 3 shows the dramatic expansion in process space possible when using the AX8410 PRIME as compared with that of the AX8407.

The AX8410 PRIME provides a dramatic improvement over the ozone production capability of the AX8407. Where the AX8407 generator produced ozone concentrations of 238 g/Nm³ at input O₂ flows of 20 SLM with 17°C cooling water, the AX8410 PRIME exceeds this ozone concentration at input oxygen flows up to 35 SLM (Figure 3). Figure 3 shows that the AX8410 PRIME can be operated with input oxygen flows up to 80 SLM, greatly expanding the available process window for STI gap fill and ALD processes. It is also noteworthy that the increased operational window achieved in the AX8410 PRIME was achieved with no loss in ozone generation capability at lower flows. Furthermore, the increased operational window in the AX8410 PRIME does not require extreme chilling of cooling water. Higher ozone concentrations can be achieved in the AX8407, however, this requires that the cooling water have a temperature of 5°C at the inlet. AX8410 PRIME, by comparison, not only produces greater output, but does so at nominal 17°C cooling water temperature, eliminating any dependence on chilled water for enhanced performance.
The improvement in performance in the AX8410 PRIME is achieved through the use of an innovative small and efficient ozone cell design. Smaller, more efficient cells free valuable chassis real estate for integration of a robust 10 kW power supply. Special attention was paid to the materials of construction of the revised ozone cell to reduce process contamination, increase the mechanical reliability of the cell structure and to incorporate anti-degradation technology that extends the ozone-producing life of the generator. Whether integrated into a rack mounted system or used as a stand-alone unit, the AX8410 PRIME features the flexibility of AX8407 while simultaneously enabling advanced STI and ALD applications and much greater process throughput.

The AX8410 PRIME is certified to meet the following standards:

- CE Safety (EN61010-1)
- CE EMC (EN 61326-1)
- NRTL (UL/ CSA 61010-1)
- Semi F47 Voltage Sag Immunity
- RoHS compliant

**CONCLUSION**

The AX8410 PRIME, the newest member of the MKS family of ozone generators, represents the next generation in ozone producing technology. It combines cutting edge cell design with a robust power train to produce significantly greater operating range than previous ozone generators. This, in turn, enables greater flexibility in advanced process development for semiconductor device fabrication and other applications.

**REFERENCES**

For more information on MKS Instruments, link to our web site http://www.mksinst.com/index.aspx

For a general catalog of MKS ozone generators and subsystems, follow this link: http://www.mksinst.com/docs/UR/OzoneGeneration-DS.pdf

**Additional Application Notes of Interest**

- Ozone/TEOS CVD Oxide Deposition Using DLI
- Ozone as the Oxidizing Precursor in Atomic Layer Deposition
- Ozone Data Conversion Tables