

# OZONE APPLICATIONS FOR ATOMIC LAYER PROCESSING

Chris Le Tiec, Fellow  
MKS Instruments

## Why is Atomic Layer Processing Needed?

Critical feature size in modern semiconductor devices has shrunk to the low nanometer ( $10^{-9}$  m) size scale. As Figure 1 shows, volume production of semiconductor devices has moved to design rules with sub-10 nm feature sizes for logic and sub-20 nm sizes for memory chips. To put this scale in a relevant context, the van der Waals radius,  $r_w$ , of a silicon atom ( $r_w$  is half the distance between two like atoms in contact but not bonded to each other) is roughly 0.2 nm. This means that the current design rules are at atomic scales. Fabricating such small features thus demands atomically precise control over process and material parameters such as deposition rates, etch rates, material composition, interfacial planarity and purity, and geometrical shape and dimensions. Legacy techniques for film deposition and etch processes in device fabrication (i.e. chemical vapour deposition (CVD), physical vapour deposition (PVD), conventional epitaxy, and conventional plasma etch) are incapable of consistently delivering such precision. For this

reason, device manufacturers have turned to Atomic Layer Processing (ALP). Techniques in this category add or subtract material a single atomic layer at a time. Processes that deposit material to form thin films are collectively known as Atomic Layer Deposition (ALD) while those that remove material are known as Atomic Layer Etch (ALE). The latter acronym should not be confused with Atomic Layer Epitaxy (ALE) an acronym for ALD that has been employed in European publications. In this paper, the acronym ALE always refers to Atomic Layer Etch.

## THE CHEMICAL AND PHYSICAL BASIS FOR ALP

Atomic layer processes are generally considered self-limiting chemical reactions that occur in monolayers adsorbed on the surface of a substrate. Deposition reactions proceed by creating one monolayer at a time to produce a highly conformal thin film while etch reactions subtract material one monolayer at a time. Controlled deposition or etch in a monolayer-by-monolayer fashion is achieved through sub-nanometer control of the

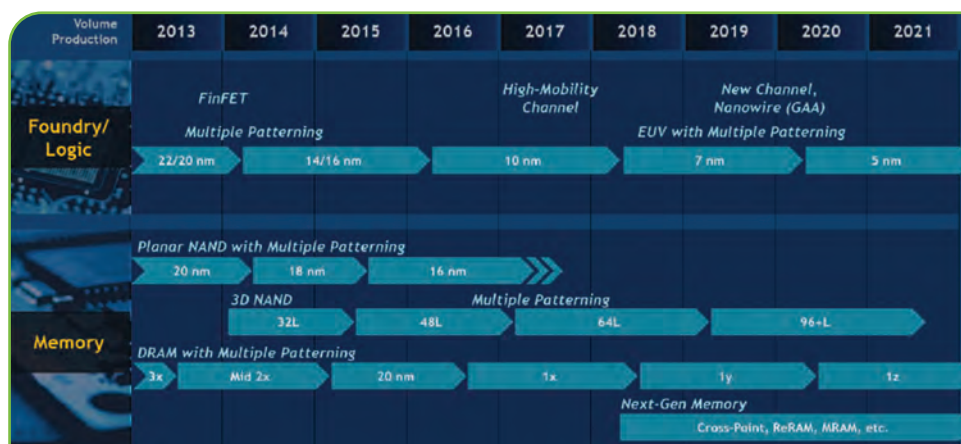


Figure 1 - Device scaling requirements needed to meet the SIA roadmap.

sequential addition of reactive precursor molecules in a vacuum environment. In an ideal deposition reaction, the first precursor molecule adsorbs as a self-limited monolayer on the substrate surface, bound to that surface by either strong dipolar or van der Waals interactions or, most often, by covalent chemical bonds. After excess precursor material is pumped away, a reacting agent is introduced which reacts with the monolayer to produce the desired film composition. By-products of this reaction must be volatile so that they can be pumped away by the system. A thin film of product material is built up through many repetitions of this cycle.

Atomic layer etch reactions are basically the reverse of atomic layer deposition reactions. In the first half-reaction cycle of an ALE process, a precursor is introduced that adsorbs as a monolayer on the substrate surface and reacts with that surface modifying its chemical nature. This chemical change makes the monolayer reactive with a second agent in the next half-reaction cycle. The product of the reaction between the agent and the chemically modified monolayer on the substrate surface must be volatile. It desorbs from the substrate and is pumped away, effectively removing one monolayer of substrate material.

There is an ALP website sponsored by Eindhoven University of Technology (<https://www.atomiclimits.com/>) that provides excellent databases detailing the chemistries of ALD and ALE processes and appropriate literature citations. The databases can be found at the following URLs:

ALD - <https://www.atomiclimits.com/alddatabase/>

ALE - <https://www.atomiclimits.com/aledatabase/>

## ATOMIC LAYER DEPOSITION

The earliest discussion of the concept of layer-by-layer material deposition is usually credited to the PhD thesis of Russian researcher V. B. Aleskovskii in 1952. The first literature reports on the method were published in the 1960s by Prof. S. I. Kol'tsov and others at the Leningrad

Technological Institute [1] [2] [3] [4] [5]. These reports used the term Molecular Layering (ML) for the technique. Early work in Russia has been extensively catalogued in a review by Malygin [1].

Finnish researchers were the first to bring ALD to practical use, developing and employing the technique for applications in electroluminescent displays in the 1970s. The first ALD patent was issued in 1977 to Finnish researchers T. Suntola and J. Antson for the production of compound semiconductor thin films [6]. Much of the development of ALD in the 1980s occurred in Finland, with the focus continuing to be on the development of electroluminescent displays. ALD deposition systems were also first commercialized in Finland (1988) by the company Microchemistry (acquired by ASM International in 1999 to form ASM Microchemistry Oy). A number of reviews on the history of atomic layer processing before the 2000s are available [1] [7] [8] [9] [10].

The atomically precise control of film thickness and chemical composition, the sharp, well-ordered interfaces between film and substrate, coupled with the fact that ALD films achieve 100% conformal coverage led to increased interest in ALD for microelectronics fabrication as device feature sizes shrank into the nanometer range in the late 1990s and early 2000s. Since then, continued reduction in device size in combination with the advent of 3D features and advances in ALD process equipment have made this an essential tool in achieving reliable production of nanoscale semiconductor devices.

### A Representative Process: ALD of Aluminum Oxide

Aluminum oxide is a high-k dielectric that is used as an insulating film in both DRAM and MOS-FET applications and the deposition of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is often used as a model system for ALD [11]. ALD of  $\text{Al}_2\text{O}_3$  thin films requires a sequence of exposures of a substrate to, first, a volatile Al-source, then to a volatile oxidant. Volatile sources of metals are typically either halides or metal organic compounds. Volatile aluminum alkyls,  $\text{AlR}_3$  (R = organic group), are excellent precursors for the ALD

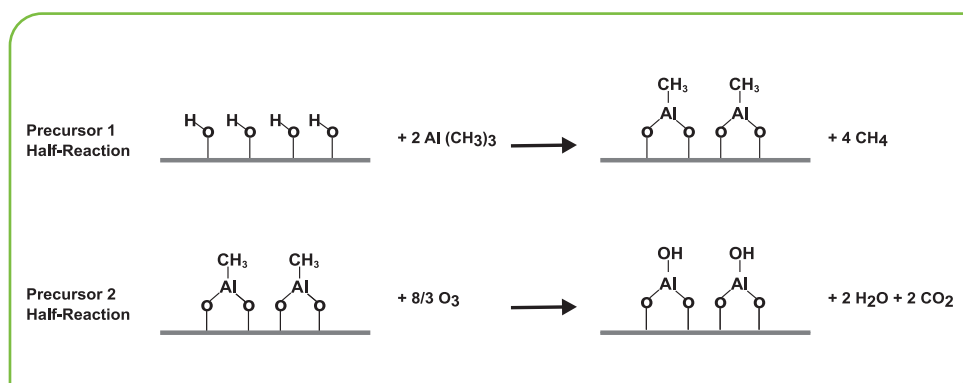


Figure 2 - Chemical reactions that occur in the ALD of aluminum oxide from trimethyl aluminum [24].

or aluminum oxide and the overall ALD reaction for the deposition of  $\text{Al}_2\text{O}_3$  from trimethylaluminum ( $\text{Al}(\text{CH}_3)_3$ ) and ozone ( $\text{O}_3$ ) can be written as:



The monolayer deposition occurs as two half-reactions, illustrated in Figure 2.

In the first cycle of the ALD  $\text{Al}_2\text{O}_3$  process, the substrate is exposed to a saturation concentration of Precursor 1 (trimethylaluminum). Trimethylaluminum reacts with the surface hydroxyl (OH) groups that are present on the substrate. This reaction produces a chemisorbed aluminum alkyl moiety shown as the product of the Precursor 1 half-reaction in Figure 2, after which excess gaseous aluminum alkyl and reaction product methane are pumped away. In the second cycle of the ALD process the substrate is exposed to ozone,  $\text{O}_3$  which reacts with the aluminum alkyl bonds ( $\text{Al}-\text{CH}_3$ ) in the surface monolayer, regenerating the hydroxylated substrate surface and producing water and carbon dioxide by-products that are pumped away. These two cycles are repeated until the desired thickness of aluminum oxide is produced on the substrate surface.

One of the key advantages of ALD is shown in Figure 3. This micrograph illustrates the near 100% conformal step coverage over severe surface topographies that is achievable using ALD. Other advantages include

extremely low in-process particulate contamination (since reactive precursors are not both present in the gas phase), sharply defined film interfaces, and atomically precise control over film thickness and chemical composition.

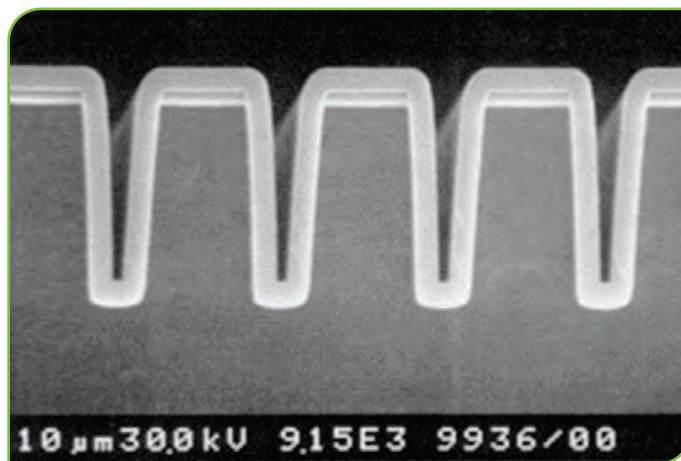


Figure 3 - 50 nm of  $\text{Al}_2\text{O}_3$  deposited by ALD (from Beneq [26]).

## ATOMIC LAYER ETCHING

Atomic layer etching, ALE, removes material one layer at a time using sequential surface reactions. The methodology for ALE is less well-developed than that of ALD as it was long considered too slow to be of use in production settings. However, progress in nanoscale device fabrication is expected to require effective ALE techniques. A recent review by Kanarik et al [12] provides a compelling case for the further development of advanced ALE techniques as a critical methodology for nanoscale fabrication.

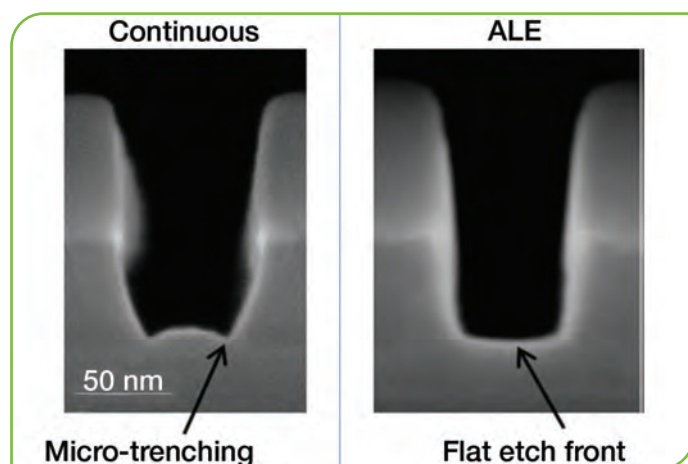


Figure 4 - A comparison of the results of conventional continuous reactive ion etch (RIE) with ALE processing under comparable process conditions [27].

ALE offers distinct advantages for nanoscale processing, including atomic-scale precision, extreme uniformity and directionality, fully anisotropic etching, and smooth residual surfaces. Figure 4 shows a comparison of etching results using conventional RIE vs. ALE. Clear advantages can be seen in the fully vertical walls and lack of micro-trenching in the ALE process. The fully anisotropic nature of ALE is particularly important when dealing with the very high aspect ratio features common in nanoscale devices (Figure 5).

#### A Representative Process: ALE of Titanium Nitride

Titanium nitride, TiN, finds use in a number of semiconductor applications, including as anti-reflective coatings, barrier layers [13], and electrode material in some CMOS devices (e.g. plasmonic Schottky barrier photodiodes [14]). A two-step thermal atomic layer etching process has been developed for TiN that oxidizes the titanium from the +3 state in TiN to +4 in  $\text{TiF}_4$ . The need for oxidation of the Ti arises from the fact that the Ti (+3) atoms in TiN are co-coordinatively unsaturated which leads to intermolecular bridging and low volatility whereas Ti (+4) compounds are co-coordinatively saturated which limits intermolecular interactions and significantly enhances volatility. As noted, volatility is necessary for effective removal of etch products during ALE.

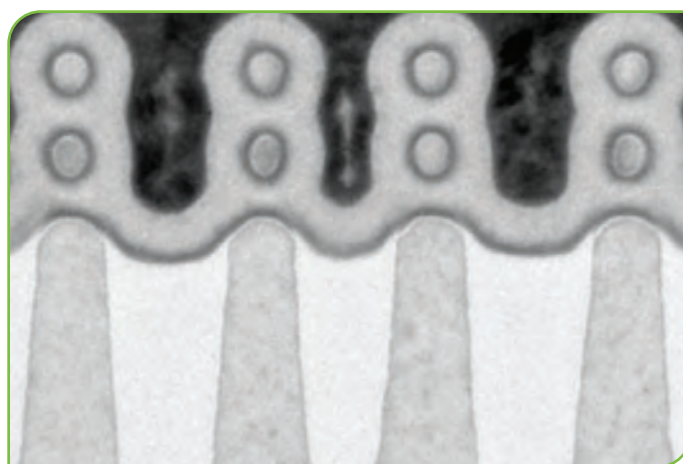


Figure 5 - Highly anisotropic etching for nanowires. (Photo: IMEC)

Figure 6 shows the process for ALE of TiN films. The graph on the right in Figure 6 shows the highly selective nature of TiN ALE in the presence of other insulators. The process employs a two-step reaction scheme to produce volatile  $\text{TiF}_4$  since HF cannot directly fluorinate TiN. Conventional oxidizers such as  $\text{O}_2$  or  $\text{H}_2\text{O}$  cannot oxidize TiN, so the TiN film is first oxidized with the very strong oxidant, ozone, at  $250^\circ\text{C}$ , to produce a monolayer of titanium dioxide ( $\text{TiO}_2$ ) and volatile by-products. This raises the oxidation state of titanium in the surface monolayer from +3 to +4. The half-reaction for the first step of the process can be written:



In the second step of the process, the  $\text{TiO}_2$  monolayer is fluorinated using HF, again at  $250^\circ\text{C}$ , producing volatile  $\text{TiF}_4$  and  $\text{H}_2\text{O}$  as by-products that can be easily pumped away. The half-reaction for this step of the process can be written:



This two-step cycle is repeated until the desired degree of etch has been achieved. As with conventional etch, mass spectral or optical end-point detection methods can be employed to determine when the etch process is complete. Similar ALE processes can be deployed for the etching of other metal nitrides (e.g. TaN) as well as for metal carbides and sulfides.



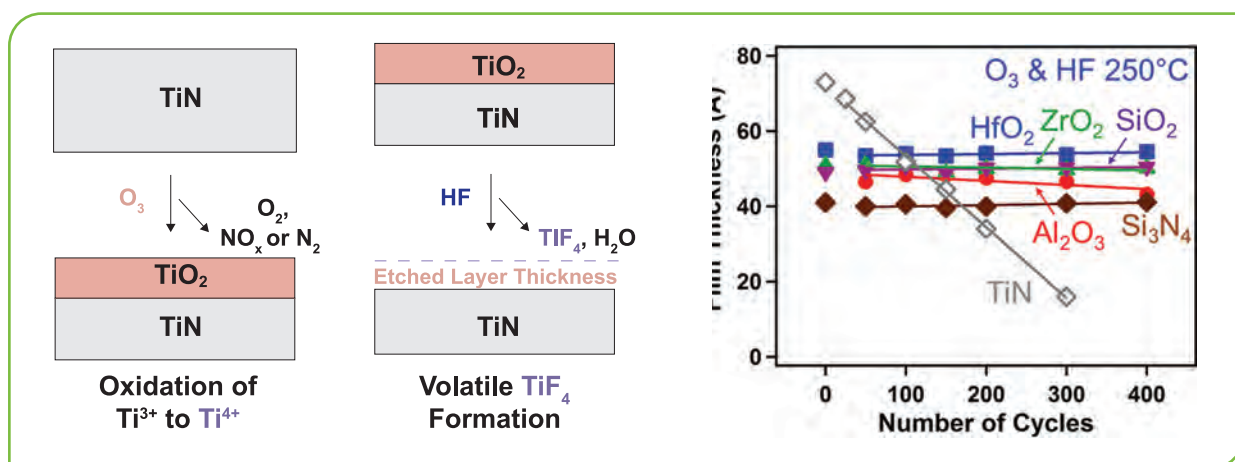


Figure 6 - ALE of titanium nitride [25].

## OZONE IN ATOMIC LAYER PROCESSING

The examples used above to illustrate ALD and ALE processes also demonstrate the unique utility of ozone,  $O_3$ , as an effective oxidizer for atomic layer processing. Ozone is a highly reactive, gaseous oxidizing agent with a well-established record as a very strong oxidant in many industrial settings. The first ozone generators were developed over 150 years ago [15]. Since that time, ozone has found wide use as a much safer and environmentally friendly alternative to more corrosive and toxic oxidants. Today, ozone is commonly used for water treatment, medical disinfection, pharmaceutical system disinfection, agricultural storage, and many other industrial applications.

Over the past 30 years, ozone has found increasing use in semiconductor device manufacturing where it is now commonly deployed in wafer cleaning and resist-stripping applications under an aqueous and gaseous form [16]. Beginning in the 1990s, ozone was also employed as a co-reagent in CVD reactions, particularly for tetraethoxysilane/ozone (TEOS/ $O_3$ ) silicon dioxide thin film deposition processes [17] [18] [19]. TEOS/ $O_3$  chemistries' low thermal budget and self-planarizing characteristics were important in ULSI (Ultra Large-Scale Integration) fabrication processes. TEOS/ $O_3$  processes were commercialized

by several semiconductor equipment suppliers and are commonly used in device fabrication.

The advent of ALD as a viable production methodology has created additional impetus for the adoption of ozone as an oxidizing agent in semiconductor thin film deposition processes. Ozone has critical advantages over alternate reactive agents in ALD processing when it comes to process behavior, thin film purity, and operational safety. Distinct advantages in process chemistries (e.g. high reaction rates) are attributable to ozone's high chemical potential. Further benefits in reagent purity and safety come from the fact that ozone has limited chemical stability and therefore it must be generated at the point-of-use. Point-of-use generation means that it cannot be shipped or stored for long periods of time, avoiding contamination that can occur during transportation and storage. As well, the relative instability of ozone means that it is an eco-friendly precursor since excess material can be easily decomposed back to oxygen using simple catalytic or thermal destruction units [16] [20].

Advanced ALD processes require oxidizers that can more effectively deliver oxygen radicals to the substrate/thin film surface.  $O_2$ ,  $O_3$ ,  $H_2O$ ,  $H_2O_2$  and OH radical sources all fulfill this requirement; however, ozone offers particular

advantages for ALD processing. Its high electrochemical potential compared to these other species (nearly twice that of molecular oxygen) ensures complete reaction of the surface monolayer on a growing film. This guarantees atomic precision in the control of film thickness and interface properties. High reactivity also ensures higher growth rates in O<sub>3</sub>-based ALD processes, reducing time in process (Figure 7). The high volatility of ozone helps to reduce pump down cycle times compared to low volatility species such as H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, an additional aid for shorter time in process. The lack of hydrogen or other non-oxygen atoms in ozone ensures that the oxide stoichiometry will be devoid of OH moieties and other contaminants, improving electrical properties of the film such as gate leakage and sheet resistance (Rs). Al<sub>2</sub>O<sub>3</sub> ALD films grown using ozone show superior electrical properties for charge injection, stability against flat band voltage shift, and leakage current density [21]. Detailed discussions of the advantages of ozone for ALD can be found in References [22] and [23]. Ozone-based atomic layer deposition processes have been developed for high-k gate oxides and for 3D capacitor dielectrics that are not possible using other precursors.

A simplified schematic for an ALD/O<sub>3</sub> process configuration is shown in Figure 8. Major OEMs such as Tokyo Electron, ASM, Applied Materials, LAM Research, Jusung, and Hitachi Kokusai as well semiconductor device manufacturers

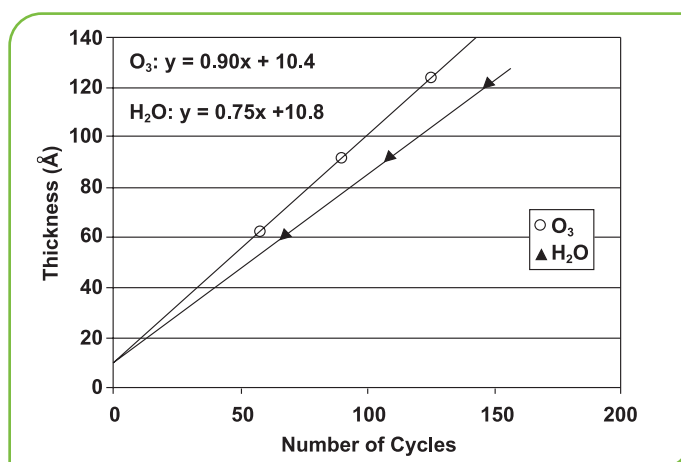


Figure 7 - Growth rate characteristics of O<sub>3</sub>- vs. H<sub>2</sub>O-based ALD processes for Al<sub>2</sub>O<sub>3</sub> thin film deposition from TMA [29].

and foundries have developed proprietary ALD/O<sub>3</sub> processes. These are carried out in different reactor designs using different energy sources and gas flow configurations, depending on the equipment manufacturer and fabrication process requirements (Figure 9).

The nature of ALD and ALE processes guarantees that ALP/O<sub>3</sub> deposition/etch uniformities will be excellent with <1% variation across large substrate diameters. Step coverage for ALD and directionality/anisotropic etch for ALE is better than 95% with the most rugged topographies on substrate surfaces. In-process added particle defects will be near zero. Throughput for ALD

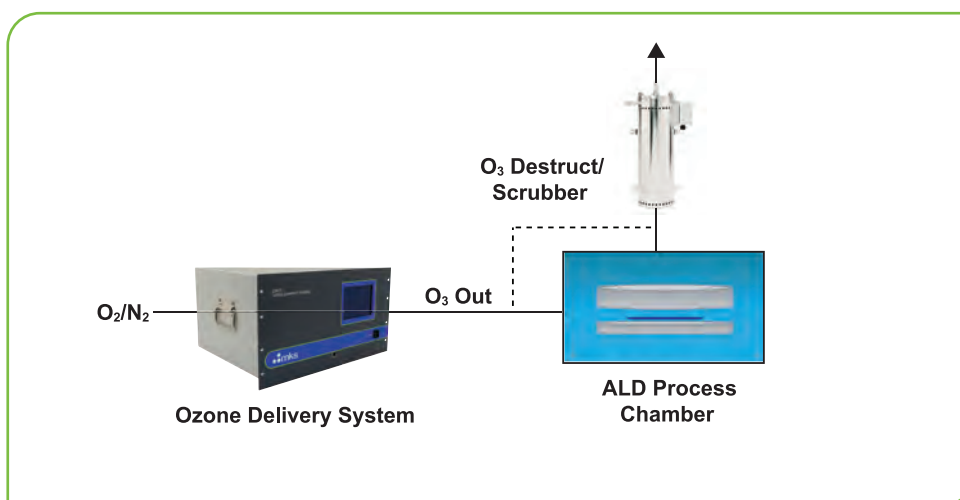


Figure 8 - Basic components of an ALD/O<sub>3</sub> deposition system.

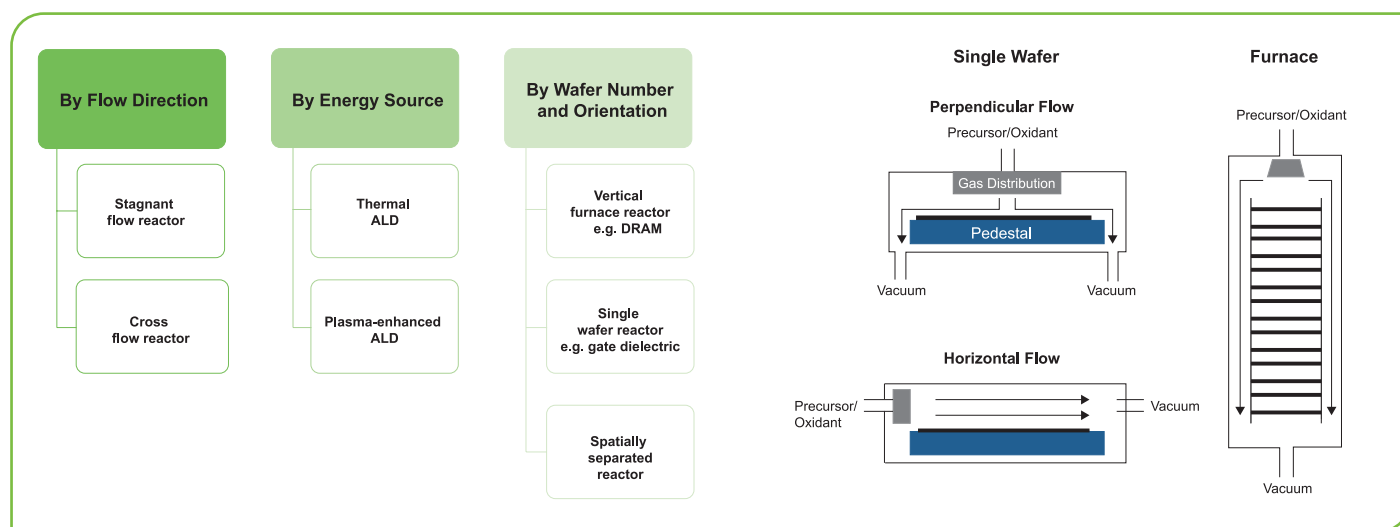


Figure 9 - ALD reactor categories with different reactor configurations.

and ALE reactors is typically greater than 25 wafers/hr. The size of the ozone delivery system for different reactor designs depends on the process and equipment requirements. Ozone provides similar advantages in ALE processing as those described for ALD.

### Ozone Application Space in ALP

Figure 10 shows the overall application space for ALD technology with the application space for ozone-based ALP/O<sub>3</sub> processes circled. These circled categories highlight the breadth of the application space for ALP/O<sub>3</sub>

in semiconductor and photovoltaic device manufacturing. Figure 11 shows some specific microelectronic applications of ALD/O<sub>3</sub> technology.

Ozone delivery systems are used with ALD equipment to produce a variety of critical dielectric films in microelectronics fabrication. ALD/O<sub>3</sub> is used for the deposition of ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> films in DRAM capacitors; the method is employed for SiO<sub>2</sub> deposition in deep holes and Al<sub>2</sub>O<sub>3</sub> in VNAND devices. Figure 12 shows a cross-section of a 3D NAND structure along with

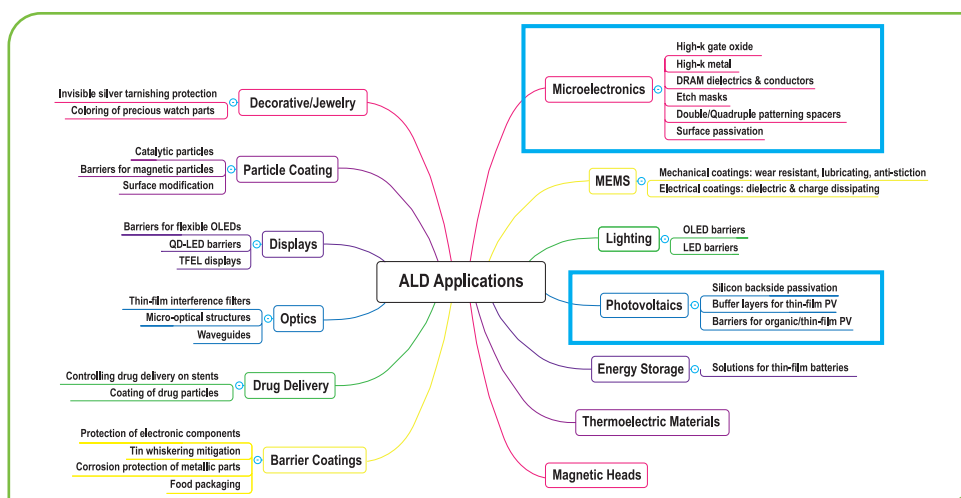


Figure 10 - ALD application space with ozone applications called out [28].

## 2.1 Overview – Application

- Device shrinkage
- 3D structure with high aspect ratio
- Low temperature's technology



Atomic Layer Deposition

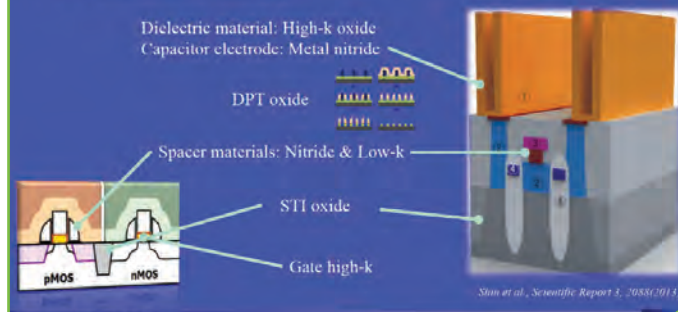


Figure 11 - Some application areas for ALP/O<sub>3</sub> thin film deposition processes. (ALD 2015 Workshop)

different processes employed in its fabrication. ALD is used extensively in the fabrication of this device with ALD/O<sub>3</sub> processes used for critical oxide layers. 64L 3D NAND structures have a deep hole aspect ratio(A/R) of 100:1; planned 3D NAND structures will have even more severe aspect ratios. The expectations for future 3D NAND designs call for ever-increasing numbers of layers with ever-greater aspect ratios for deep holes. The only deposition technology that can deal with topographies having such aspect ratios is ALD, with ALD/O<sub>3</sub> being the only option of in-hole dielectric deposition.

While less spectacular in terms of difficult topographies, current logic device designs call for increased use of ALP in their fabrication. Logic devices employ ALD/O<sub>3</sub> processes for the formation of high-k dielectrics such as ZrO<sub>2</sub>, HfO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and La<sub>x</sub>Al<sub>y</sub>O in, for instance, gate oxide applications. While these gate dielectric films can be produced using different oxidants, studies have shown that the use of O<sub>3</sub> for oxidation improves the electrical properties by improving interfacial properties and eliminating contamination, especially by hydroxyl (OH) moieties.

ALD/O<sub>3</sub> processes for DRAM, VNAND, and logic devices require ozone generating systems that can deliver adequate concentrations of ozone at flow rates that

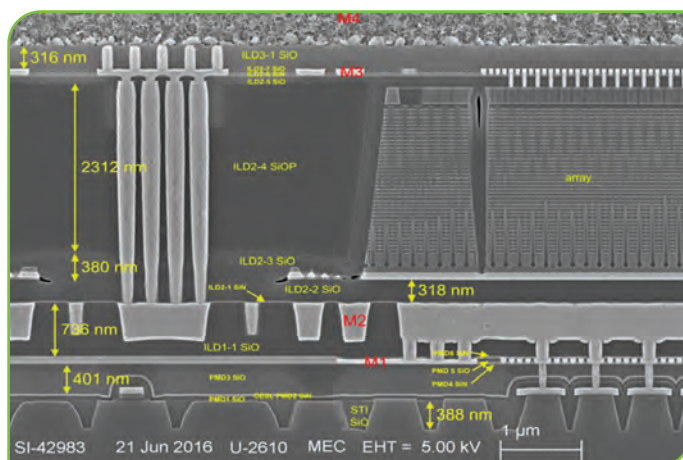


Figure 12 - 32L 3D NAND Flash memory. (IC Knowledge)

support production throughput needs. For DRAM applications such as ZrO/Al<sub>2</sub>O<sub>3</sub>/ZrO double layer high-k dielectrics, this means an ALD system needs to deliver up to 20 slm of gas having an ozone concentration of 175 to 320 g/Nm<sup>3</sup>. Production processes for high-k gate dielectrics such as La<sub>2</sub>O<sub>3</sub> in logic devices, only need 2 to 3 slm of ozone precursor gas per chamber, with precise dosage of ozone in the range of 5% wt per slm. A typical 3D NAND process requires similar precursor flows to those in DRAM production; however, the concentration of ozone in the precursor gas can be higher than that used in high-k gate processes, ranging between 150 to 300 g/Nm<sup>3</sup>. The continuing challenges for any ozone generator and/or delivery system are the simultaneous concentration and flow requirements driven by the application and the OEM's system (i.e. chamber) design.

Back Oxide - 1 Oxidation	Thermal SiO
Back SiN ALD Deposition	ALD SiN
Back Oxide - 2 Deposition	ALD SiO
Floating Gate Si ALD Deposition	ALD Si
SiN/SiO/Si E/B	Plasma Etch SiN/SiO/Si Isotropic
Strip + DI Rinse	SPM + APM + DIR
Pre-Cleaning	DHF + DIR
Tunnel Oxide - 1 ALD Deposition	ALD SiO



## OZONE GENERATORS AND DELIVERY SYSTEMS

ALD and ALE processes are the primary applications demanding continued advances in ozone technology. As noted above, simultaneously meeting the application flow and concentration requirements and the OEM's system design requirements are the driving forces of ozone generator and system technology development. MKS' product portfolio of ozone generators and integrated systems have a robust history of advancing ozone technology to fulfill these requirements.

All MKS ozone generators employ the dielectric barrier discharge method for ozone production. Over time, advances in discharge cell architecture have increased ozone concentration while broadening the range of ozone production and ensure that the real estate aspect is state of the art. Figure 13 shows the steady increase of ozone output-based advances in MKS' ozone generator technology. MKS Instruments AX8400 series of ozone generators, for example, are generators that are highly configurable to meet flow requirements up to about 250 g/hr. MKS' AX8415 and AX8410 generators target applications requiring the highest concentrations and highest flow regimes in a compact form factor.

The AX8415 and AX8410 are designed to produce ultra-clean, high concentration ozone. MKS' patented ozone cell design introduced in models AX8415 and AX8410 is able to support ozone delivery in concentrations up to 425 g/Nm<sup>3</sup> (27.1 wt%) and with flow rates as high as 80 slm (see Figure 14). MKS Instruments recognizes customers continually need to optimize their installed base longevity therefore the newer generator designs allow an ease of integration with the AX8415 generator a direct replacement for the AX8407 generator in an MKS designed ozone system.

MKS Instruments designs products to meet the ozone delivery application requirements of equipment manufacturers, providing fully integrated ozone delivery systems that incorporate single or multiple generators, with integrated ozone monitoring and safety devices as well as optional ozone destruct. The systems are designed using proprietary and adapted materials to meet semiconductor environmental and quality standards.

As an example, an oxide film process may require an ozone system configuration of three or four independent generators delivering 250 g/Nm<sup>3</sup> of ozone at 5 to 10 slm to a three or four chamber ALD tool. Another example is a 25 to 50 wafer vertical batch reactor that might need 180 to 200 g/Nm<sup>3</sup> of ozone at 70 to 100 slm. The ozone system for a batch ALD application needs the support of a multiple generator ozone system with a single output, or one-channel. Each additional generator in a system extends the flow range for a given concentration. For example, a single AX8415 generator generates an ozone concentration of 300 g/Nm<sup>3</sup> at 15 slm. The addition of another generator raises the output of the system to 300 g/Nm<sup>3</sup> at 30 slm. A four generator, single channel system, is thus capable of 300 g/Nm<sup>3</sup> at 60 slm. The ozone concentration remains constant with additional generators; however, the total amount of ozone produced is significantly increased.

MKS supplies ozone delivery systems to all OEMs producing ALP equipment. MKS ozone delivery systems are used with vertical furnaces, spatial ALD tools, and chamber deposition systems. Each ozone delivery system has its' specific application requirement aligned to the main process tool's requirements to ensure the end user is capable of depositing the highest quality thin-film or removing the specific atomic layer.

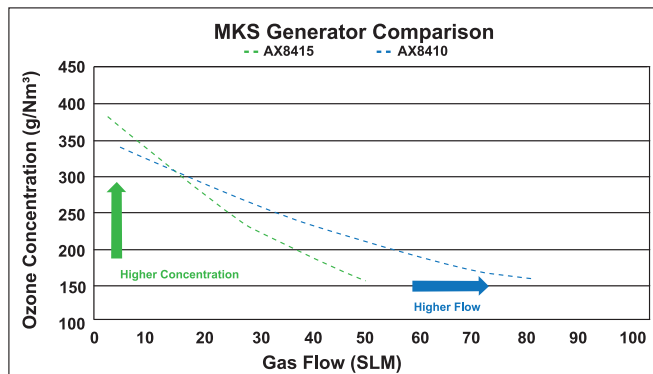
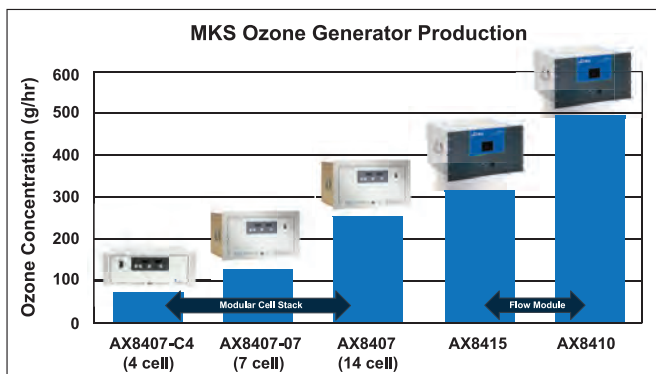


Figure 13 - Ozone output based on generator configuration.

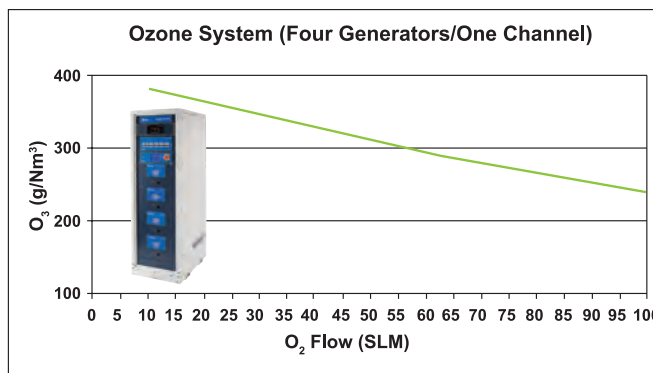
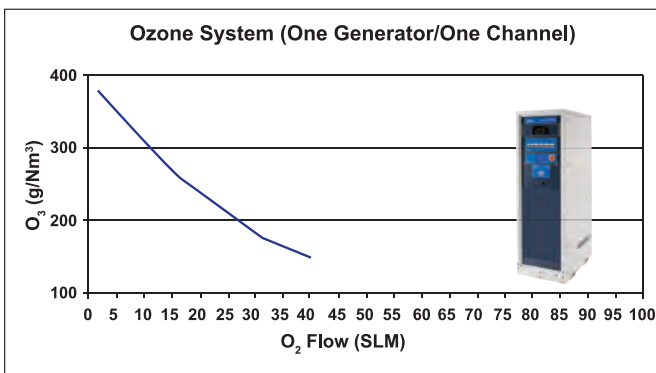


Figure 14 - Ozone output based on system configuration.

## CONCLUSION

Atomic level processing, ALD and ALE, is a critical methodology for continued advancement in the production of advanced semiconductor devices. Oxide dielectric material processes especially can experience significant benefits using ozone,  $O_3$ , as the oxidizing precursor in ALD and ALE processes. The rapid and complete dissociation of ozone to produce oxygen radicals ensures the uniform production of an oxide monolayer on substrate surfaces. The fact that ozone contains no hydrogen ensures that the oxide films will be free of hydroxyl species that degrade electrical characteristics. On-site generation of precursor ozone

avoids the contamination that can occur during storage and transportation. Finally, ozone is easily decomposed, reducing safety and environmental concerns.

MKS Instruments is the world leader in ozone generation and delivery systems and supplies ozone systems to all leading OEM ALD tool manufacturers. MKS' generators deliver the high concentrations and flow rates needed for the ALD and ALE production tools used in semiconductor device manufacturing. MKS' versatile ozone delivery systems feature closed-loop process control and a single unit can service one to four process tools for significant savings in operational costs.

## REFERENCES

- [1] A. A. Malygin, V. E. Drozd, A. A. Malkov and V. M. Smirnov, "From V. B. Aleskovskii's "Framework" Hypothesis to the Method of Molecular Layering/Atomic Layer Deposition," *Chemical Vapor Deposition*, vol. 21, pp. 216-240, 2015.
- [2] S. I. Kol'tsov, *J. Appl. Chem. USSR*, vol. 38, p. 1352, 1965.
- [3] S. I. Kol'tsov, *J. Appl. Chem. USSR*, vol. 42, p. 1023, 1969.
- [4] S. I. Kol'tsov and V. B. Aleskovskii, *Russ. J. Phys. Chem.*, vol. 42, p. 630, 1968.
- [5] S. I. Kol'tsov, G. B. Kuznetsova and V. B. Aleskovskii, *J. Appl. Chem. USSR*, vol. 40, p. 2644, 1967.
- [6] T. Suntola and J. Antson, "Method for Producing Compound Thin Films". USA Patent 4,058,430, 25 November 1977.
- [7] G. N. Parsons, J. W. Elam, S. M. George, S. Haukka, J. Hyeongtag, W. M. M. (. Kessels, M. Leskela, P. Poodt, M. Rital and S. M. Rossnagel, "History of atomic layer deposition and its relationship with the American Vacuum Society," *J. Vac. Sci. Technol. A.*, vol. 31, no. 5, pp. 50818-1 - 50818-11, 2013.
- [8] R. L. Puurunen, "A Short History of Atomic Layer Deposition: Tuomo Suntola's Atomic Layer Epitaxy," *Chemical Vapor Deposition*, vol. 20, pp. 332-344, 2014.
- [9] "Virtual Project on the History of ALD (VPHA) overview," [Online]. Available: <http://www.vph-ald.com/>. [Accessed 28 01 2020].
- [10] A. e. al., "Review Article: Recommended reading list of early publications on atomic layer deposition Outcome of the "Virtual Project on the History of ALD"," *J. Vac. Sci. Technol. A*, vol. 35, no. 1, pp. 010801-1 - 010801-13, 2017.
- [11] S. M. George, "Atomic Layer Deposition: An Overview," *Chemical Reviews*, vol. 110, pp. 111-131, 2010.
- [12] K. J. Kanarik, S. Tan and R. A. Gottscho, "Atomic Layer Etching: Rethinking the Art of Etch," *J. Phys. Chem. Lett.*, vol. 9, pp. 4814-4821, 2018.
- [13] C. Lee and Y.-L. Kuo, "The Evolution of Diffusion Barriers in Copper Metallization," *JOM*, vol. 59, no. 1, pp. 44-49, 2007.
- [14] J. Gosciniaik, F. B. Atar, B. Corbett and M. Rasras, "CMOS-Compatible Titanium Nitride for On-Chip Plasmonic Schottky Photodetectors," *ACS Omega*, vol. 4, pp. 17223-17229, 2019.
- [15] W. Siemens, *Poggendorff's Ann. Phys. Chem.*, vol. 102, p. 66, 1857.
- [16] C. Gottschalk and J. Schweckendiek, "Using dissolved ozone in semiconductor cleaning applications," *Micromagazine*, vol. 3, no. March, p. 81, 2004.
- [17] K. Fujiino, Y. Nishimoto, N. Tokumasu and K. Maeda, *J. Electrochem. Soc.*, vol. 140, p. 2922, 1993.
- [18] T. Homma, M. Suzuki and Y. Murao, *J. Electrochem. Soc.*, vol. 140, p. 3591, 1993.

- [19] T. K. Whidden and S. Y. Lee, "In Situ Fourier Transform Infrared Spectroscopy near the Substrate in Tetraethoxysilane/Ozone Chemical Vapour Deposition," *Electrochem. and Solid State Lett.*, vol. 2, no. 10, pp. 527-530, 1999.
- [20] H. Sundstrom and C. Gottschalk, "The Evolution of Ozone Subsystems," *Semiconductor International Equipment Components and Subsystems Supplement*, pp. 2-6, September 2006.
- [21] J. B. Kim, D. R. Kwon, K. Chakrabarti, C. Lee, K. Oh and J.-H. Lee, "Improvement in  $\text{Al}_2\text{O}_3$  dielectric behavior by using ozone as an oxidant for the atomic layer deposition technique," *J. Appl. Phys.*, vol. 92, no. 11, pp. 6739-6742, 2002.
- [22] H. Sundstrom, "Ozone as the Oxidizing Precursor in Atomic Layer Deposition," *EuroSemi*, December 2005. [Online]. Available: <https://www.johnmorrisgroup.com/Content/Attachments/121136/TechZ141.pdf>. [Accessed 03 02 2020].
- [23] P. O. Oviroh, R. Akbarzadeh, D. Pan, R. A. M. Coetzee and T.-C. Jen, "New development of atomic layer deposition: processes, methods, and applications," *Science and Technology of Advanced Materials*, vol. 20, no. 1, pp. 465-496, 2019.
- [24] R. G. Gordon, "ALD Precursors and Reaction Mechanisms," in *Atomic Layer Deposition for Semiconductors*, C. S. Hwang and C. Y. Yoo, Eds., New York, Springer, 2014, pp. 15 - 46.
- [25] Y. Lee and S. M. George, "Thermal Atomic Layer Etching of Titanium Nitride Using Sequential Self-Limiting Reactions: Oxidation to  $\text{TiO}_2$  and Fluorination to Volatile  $\text{TiF}_4$ ," *Chemistry of Materials*, vol. 29, pp. 8202-8210, 2017.
- [26] Beneq, "The Future of Moisture Protection is Here," Beneq, 2019. [Online]. Available: <https://beneq.com/en/thin-films/blog/future-moisture-protection-here>. [Accessed 30 Jan 2020].
- [27] C. G. N. Lee, K. J. Kanarik and R. A. Gottscho, "The grand challenges of plasma etching: a manufacturing perspective," *Journal of Physics D*, vol. 47, p. 273001 (9 pp), 2014.
- [28] H. J. Lim, "ALD Technologies and Applications in Semiconductor Device Fabrication," in *Samsung Electronics ALD Workshop*, 2015.
- [29] J. Niinisto, M. Putkonen, L. Niinisto, K. Arstila, T. Sajavaara, J. Lu, K. Kukli, M. Ritala and M. Leskela, " $\text{HfO}_2$  Films Grown by ALD Using Cyclopentadienyl-Type Precursors and  $\text{H}_2\text{O}$  or  $\text{O}_3$  as Oxygen Source," *Journal of the Electrochemical Society*, vol. 153, no. 3, pp. F39 - F45, 2006.