APPLICATION NOTE

OZONE APPLICATIONS IN ATOMIC LAYER PROCESSING

BACKGROUND

Critical feature size in modern semiconductor devices has shrunk to the low nanometer (10-9 m) size scale. Fabricating small features demands atomically precise control over process and material parameters such as:

- deposition rates
- etch rates
- material composition
- interfacial planarity and purity
- geometrical shape and dimensions.

Legacy fabrication (i.e. chemical vapor deposition (CVD), physical vapor deposition (PVD), conventional epitaxy, and conventional plasma etch) are incapable of consistently delivering such precision. Therefore, device manufacturers have turned to Atomic Layer Processing (ALP). Atomic layer processes are self-limiting chemical reactions that occur in monolayers adsorbed on the surface of a substrate. 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 application note, the acronym ALE always refers to Atomic Layer Etch. Controlled deposition or etch In a monolayer-by-monolayer fashion is achieved through tight control of the sequential addition of reactive precursor molecules in a vacuum environment.

In an ALD process, first precursor molecules adsorb 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. Excess precursor material is then pumped away and a second precursor is introduced that reacts with the monolayer to produce a monolayer having the desired film composition. Byproducts of this reaction must be volatile so that they can be pumped away by the system. A thin film material is built up through many repetitions of this cycle.

ALE reactions are the reverse of ALD. In the first 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 precursor in the second reaction cycle. The product of the reaction between the agent and the chemically modified monolayer on the substrate surface must be volatile so that it can desorb from the substrate and be pumped away, effectively removing one monolayer of substrate material.

Ozone in Atomic Layer Processing

Ozone, O_3, is a uniquely effective oxidizer for atomic layer processing. It is a highly reactive, gaseous oxidizing agent with a well-established record as a very strong oxidant used in many industrial settings. Beginning in the 1990s, ozone was also employed as an oxidant in CVD reactions, particularly tetraethoxysilane/ozone (TEOS/O3) silicon dioxide thin film deposition processes [1] [2] [3].

The advent of ALP has created additional impetus for the adoption of ozone as an oxidizing agent in semiconductor thin film deposition processes. Ozone provides critical advantages over other oxidants for ALD when it comes to process behavior—thin film purity

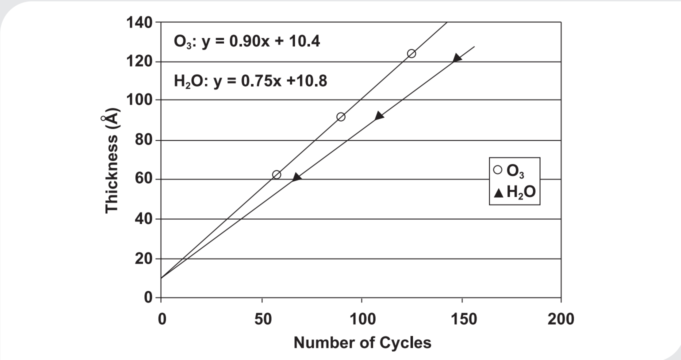

Figure 1 - Growth rate characteristics of O_3 vs. H_2O-based ALD processes for Al_2O_3 thin film deposition from TMA [4].

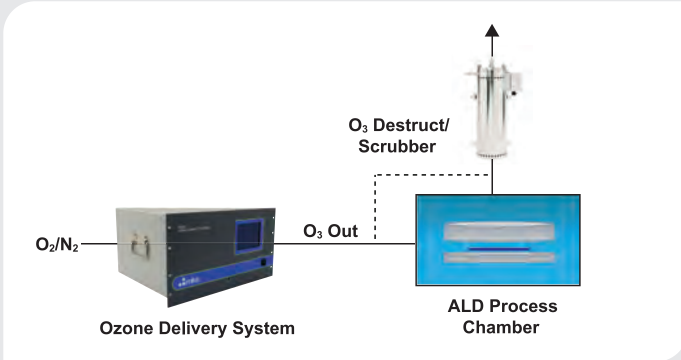

Figure 2 - ALD/O_3 deposition system delivering concentrations of ozone at flow rates that allow production throughputs.

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 [5] [6].

Advanced ALP requires oxidizers that can more effectively deliver oxygen to the substrate/thin film surface. O_2, O_3, H_2O, H_2O_2 and OH sources all fulfill this requirement; however, ozone offers particular advantages. Its high electrochemical potential compared to these other species (nearly twice that of molecular oxygen) ensures complete reaction of the surface monolayer, guaranteeing atomic precision in the control of film thickness and interface properties. High reactivity also ensures higher growth/etch rates in O_3-based ALP, reducing time in process (Figure 1). The volatility of ozone helps to reduce pump-down cycle times compared to low volatility species such as H_2O and H_2O_2, an additional aid in reducing process time. 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 the electrical properties such as gate leakage in insulator films. Al_2O_3 ALD films grown using ozone show superior electrical properties for charge injection, stability against flatband voltage shift, and leakage current density [7]. Unique, ozone-based ALD processes have been developed for high-k gate oxides and for 3D capacitor dielectrics that are not possible using other precursors [8] [9].

ALP/O_3 requires ozone delivery systems (Figure 2) that can deliver adequate concentrations of ozone at flow rates that allow production throughputs. For instance, DRAM applications such as ZrO/Al_2O_3/ZrO double layer high-k dielectrics require an ozone delivery system that can provide up to 20 slm of reagent gas at a concentration of 175 to 320 g/Nm_3 ozone. Other production processes may only need low flows of ozone precursor gas per chamber but require significantly higher concentrations than DRAM processes. ALP/O_3 for high-k gate dielectrics such as La_2O_3 in logic devices, for instance, employs 2 or 3 slm flows at 275 g/Nm_3 ozone concentration. 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 even higher than that used in high-k gate processes, up to 300 g/Nm_3. The continuing challenges for any ozone generator and/or delivery system are the simultaneous concentration and flow requirements driven by the application and by the OEM's system (i.e. chamber) design.

SOLUTION

MKS 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's flow and concentration requirements and the OEM's system requirements are the driving forces of ozone generator and delivery system technology development. MKS ozone generators and integrated delivery systems have a robust history of advancing ozone technology to fulfill these requirements. They 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 delivery flow. Figure 3 shows the steady increase of ozone output-based advances in MKS ozone generator technology. The AX8400 series generators, are highly configurable to meet moderate concentration requirements at gas flows up to ~250 g/hr.

The AX8415 and AX8410 generators target applications that require the highest concentrations in the highest flow regime. Designed to produce ultra-clean, high concentration, high flow ozone, the patented flow module design in the AX8400 series can provide concentrations up to 425 g/Nm_3 (27.1 wt%) and flow rates as high at 80 slm (see Figure 4). The AX8415 system is unique in its capability to be a direct replacement for an AX8407 generator within an MKS designed ozone system. This has obvious advantages for OEM system upgrades.

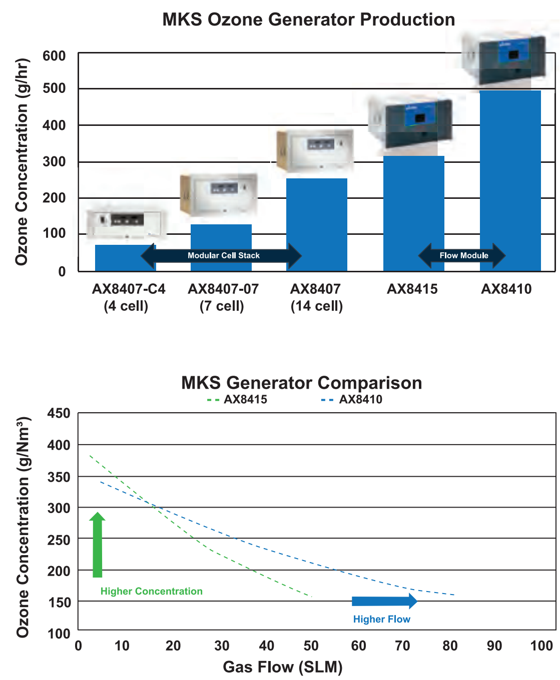

Figure 3 - Ozone output based on generator configuration.

MKS designs fully integrated ozone delivery systems that incorporate single or multiple generators to accommodate different ALP process requirements and OEM-specific tool configurations. For example, an oxide film process may require an ozone system configuration of three or four independent generators delivering 250 g/Nm_3 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_3 of ozone at 70 to 100 slm. The ozone system for a batch ALD

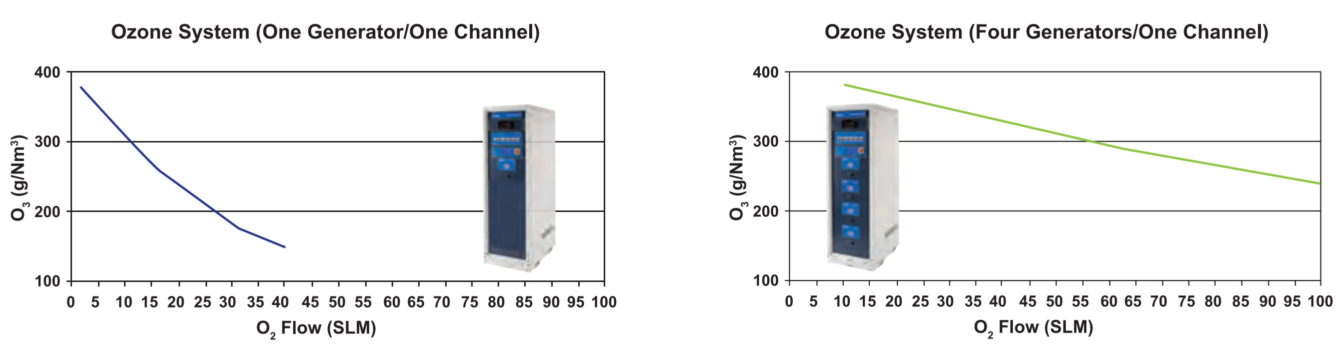

Figure 4 - Ozone output based on system configuration.

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 300g/ Nm_3 at 15 slm. The addition of another generator raises the output of the system to 300 g/Nm_3 at 30 slm. A four generator, single channel system, is thus capable of 300 g/Nm_3 at 60 slm. Ozone concentration remains constant with additional generators; however, the total amount of ozone produced is significantly increased. MKS ozone delivery systems do not use consumables or require chemical disposal, guaranteeing low operational costs. They have been reliability tested to >100,000 hours.

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

CONCLUSION

Atomic level processes are critical methodologies for continued advancement in the production of advanced semiconductor devices. Oxide dielectric material processes, especially, can experience significant benefits from the use of ozone, O_3, as the oxidizing precursor in ALD and ALE processes. The rapid and complete dissociation of ozone produces oxygen radicals, ensuring 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. Advanced MKS generators deliver the high concentrations and flows that are needed for the ALD and ALE production tools used in semiconductor device manufacturing. Versatile MKS ozone delivery systems feature close-loop process control and a single unit can service one to four process tools for significant savings in operational costs.

References

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