# Ozone as the Oxidizing Precursor in Atomic Layer Deposition

With nanometric semiconductor processing pushing on to the atomic level, atomic layer deposition techniques become more attractive and are already seeing some application. A precursor capable of supplying reactive oxygen is a key requirement for high-K gate oxide deposition. Among the many alternatives, ozone has distinct advantages. By **Hans Sundstrom, MKS Instruments Inc., USA**.

Throughout the past decade, Atomic Layer Deposition (ALD) (Figure 1) has gained acceptance as a promising technology for advanced thin film deposition. ALD has a number of advantages over conventional CVD in next generation semiconductor device manufacturing [1]. It enables precise control of the deposited material thickness and composition over the large areas and aggressive topologies that are typically found in advanced device fabrication. The temperature requirements for ALD processes are, in general, lowered relative to conventional CVD, thus making the technology compatible with the industry trend toward lower processing temperatures. The unique surface chemical nature of ALD processes broadens the range of available precursors for thin film deposition processes. The fact that ALD reactions occur solely at the substrate surface is the determining factor in the control of film stoichiometry in the ternary and quaternary oxide systems of advanced dielectric films, a control that is very difficult or impossible to achieve using conventional CVD approaches. Finally, both particulate and chemical contamination issues are more easily controlled in ALD processing [2,3].

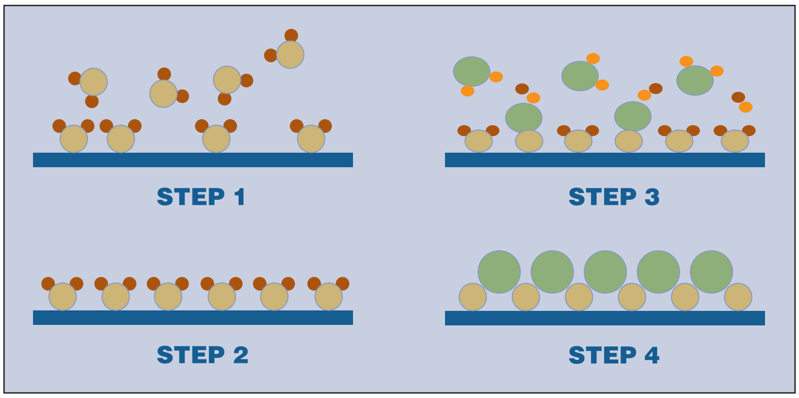
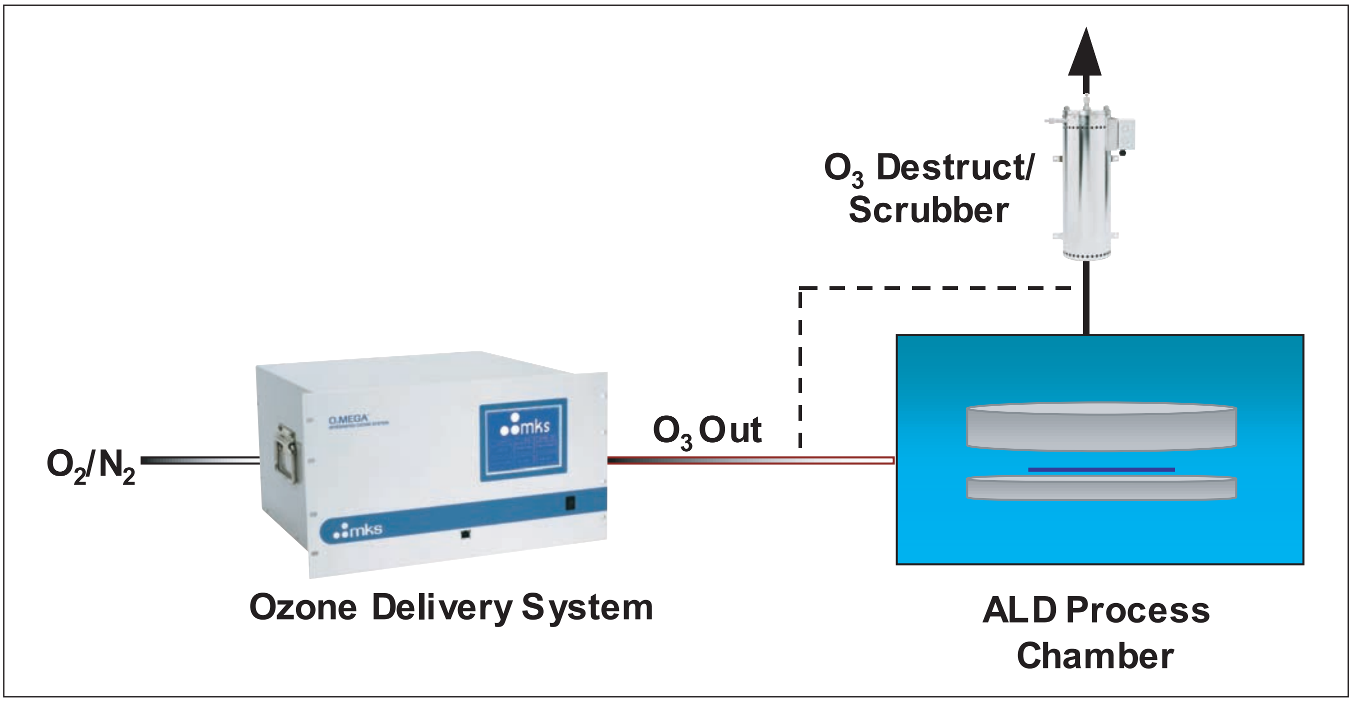



Figure 1: The ALD Process Sequence: A typical four step process making up an ALD cycle. Steps 1 and 2 depict the creation of the initial film generated from the reaction between the primary precursor and the substrate material. Steps 3 and 4 depict the generation of the desired final film created by the reaction between the initial film and a reactant precursor material

ALD may be used in the deposition of a broad scope of thin films, including binary, ternary and quaternary oxides for advanced gate and capacitor dielectrics. ALD is also an excellent process choice for depositing metals such as Cu and W for electro deposition seed layers, transition metal nitrides such as TiN and TaN for Cu interconnect barriers and noble metals for FRAM and DRAM capacitor electrodes.

ALD processing is particularly effective in the formation of DRAM capacitor structures. ALD offers a unique advantage in the formation of the dielectric layer in DRAM trench capacitors. The aspect ratios in these structures have become so severe that conventional CVD cannot provide the step coverage that is needed. ALD is inherently 100% conformal, providing a unique solution to this problem. Production processes that employ ALD for the formation of $Al_2O_3$ capacitor dielectrics have been implemented in DRAM fabs around the world by companies such as Infineon, Samsung and Hynix [4]. ALD is also employed extensively for the development of new high-K materials for gate oxides to replace $SiO_2$. Process




development for low Equivalent Oxide Thickness dielectric films that exhibit reduced leakage as compared with $SiO_2$ is nearing completion. Processes for $HfO_2$, $ZrO_2$ and other high-K materials, including ternary and quaternary oxides such as hafnium aluminates, silicates and oxynitrides have been reported [5-8].

The formation of gate oxide and high-K dielectric films by ALD requires the use of a precursor capable of supplying reactive oxygen at the growing film surface. Precursors that fulfill this requirement include $O_2$, $H_2O_2$, "OH radical", $H_2O$ and $O_3$ (Ozone). Ozone has distinct advantages over the alternative oxidizing precursors in the ALD of advanced dielectric films. The high electrochemical potential of ozone (Table 1) results in fast reaction rates at relatively low temperatures. Ozone is highly volatile, shortening purge times between cycles. These two factors result in a significant advantage in process throughput when ALD processes employ ozone rather than the less volatile or less reactive oxidants such as water, hydrogen peroxide or oxygen. The absence of hydrogen in the ozone molecule results in a reduced risk of hydrogen and hydroxyl contamination in the growing film (hydrogen or hydroxyl groups may still be available through the second precursor). Comparative studies on $Al_2O_3$ films formed by ALD using ozone vs. ALD using water have shown that lower levels of leakage current are present in films formed using ozone [9]. Hydroxyl contamination is also thought to give rise to problems such as film delamination during anneal. Oxide films by ALD using ozone as the oxidizing precursor can be produced at low processing temperatures and exhibit high breakdown voltages, low defect densities, good adhesion properties, and therefore are thermally stable. [10]

Ozone offers further process and safety advantages over the other reactive oxidants listed in Table 1 in that it can be reliably generated at the point of use. Transportation and storage are primary sources of contamination in process reagents and point of use generation of the ozone precursor results in extremely low contaminant levels in the ALD process and film. Figure 2 shows a typical equipment PFD (Process Flow Diagram) for ozone-based ALD processing. The current generation of ozone generators such as the MKS AX8561 depicted in Figure 2 can supply ozone concentrations of up to 20 wt% (300 g/m3) at flow rates ranging from 0.5 to 5 SLM. An ALD process gas switching arrangement directs the ozone that is created in the generator either to the process chamber or to a bypass leading to an ozone scrubber. Bypass and process effluent

Fig 2: Ozone delivery System.
Source: MKS Instruments

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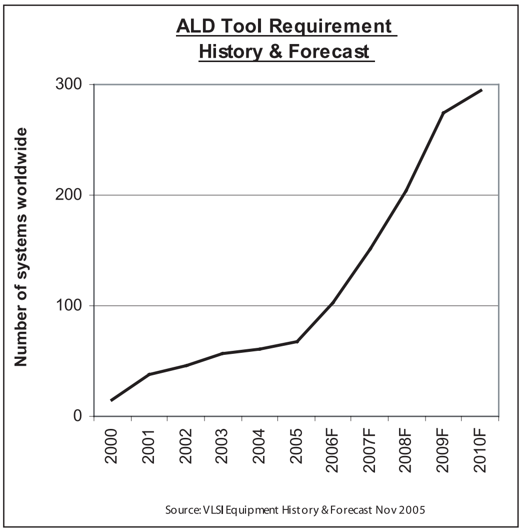


Figure 3. ALD tool market growth, history and yearly forecast

ozone can be easily decomposed back to oxygen by catalytic or thermal means. Ozone is a safe and eco-friendly "green" precursor since the product of its decomposition is simply oxygen - $2O_3 \rightarrow 3O_2$ . The ability to generate ozone at the point of use and the chemical and toxicologically benign nature of ozone decomposition products results in significant cost savings since there is no need for transportation, storage and chemical disposal of the spent oxidizer.

Ozone is being developed as the preferred oxidizing precursor for numerous ALD thin film applications, precisely because of the advantageous properties discussed above. As noted, it is already employed in production ALD processes for the formation of $Al_2O_3$ capacitor dielectric layers in advanced DRAMs. Ozone/ALD of $Al_2O_3$ is also finding application in MEMS structures as abrasion resistant coatings on actuators and in disk drives where ozone/ALD $Al_2O_3$ is being used as a Reader isolation layer on recording heads. Ozone/ALD processing is also being used to produce $Al_2O_3$ films for gate stack dielectrics. $HfO_2$ and $ZrO_2$ [5], $Ta_2O_5$ [11] and $La_2O_3$ [12] films by ozone/ALD are also under development for gate dielectric applications. $HfO_2$ films, which have a significantly higher dielectric constant than alumina, appear to be on the verge of production application at this point. Metal films may also be deposited by ozone/ALD. Copper seed layers have been produced by first depositing CuO using ozone/ALD, followed by in-situ chemical reduction of copper oxide to elemental copper using alcohols or $H_2$ plasma.[13].

| Oxygen Source | Symbol | Electrochemical Potential (V) |
|---|---|---|
| Hydroxyl Radical | OH* | 2.80 |
| Ozone | $O_3$ | 2.08 |
| Hydrogen Peroxide | $H_2O_2$ | 1.78 |
| Oxygen | $O_2$ | 1.23 |

Table 1. The electrochemical potential of selected oxidizing agents

ALD processing is rapidly becoming the technology of choice for thin film deposition on advanced device structures as is attested by the rapid growth in the ALD tool market (Figure 3). The application of ozone as an oxidizing precursor in ALD processing, with its inherent advantages for wafer throughput, process/film contamination, thin film properties, safety and chemical handling and disposal costs will be a major factor in the continued growth of this market.

*MKS Instruments is the world's leading supplier of process control solutions that improve productivity in semiconductor and related advanced manufacturing. With extensive process knowledge and proven technology leadership, MKS is well suited to provide ALD OEM's and end-users with high value solutions that optimize process performance, reduce costs and provide greater ROI. For more information on additional ALD solutions from MKS please visit http://mksinst.com/pdf/ALDps.pdf*

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