Precursors For Atomic Layer Deposition Of High-k Dielectrics

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Insulators with high dielectric constants (k) play several critical roles in modern semiconductor devices, including capacitors that store memory bits in DRAMs, decoupling filter capacitors protecting microcircuits from undesired noise, and insulating gates from channels in transistors. Scaling of semiconductor devices to follow Moore's Law past the 65 nm node will require higher-k insulators to maintain capacitance on smaller devices. At the same time, complex structures, such as deep trenches and rough pedestals, have been introduced to keep the available capacitor areas from shrinking too rapidly. Thus any future higher-k dielectrics must be produced uniformly within the increasingly narrow spaces in these structures. Furthermore, higher-k dielectrics must meet stringent requirements for low leakage currents and stability during processing and in use. All these objectives must be met by a reliable, production-worthy and cost-effective process that produces uniform results over 300 mm wafers. Finally, the material and process must integrate seamlessly into conventional semiconductor process flows.

To achieve ALD's unique characteristics and to be suitable as a practical vapor deposition process, ALD precursors must have specific properties.

Until recently, silicon dioxide was almost universally used as the dielectric in microelectronics. Despite its relatively low dielectric constant (k~4), SiO_2 has served remarkably well as the MOSFET gate dielectric due to both its unique interface properties with Si and simple processing. SiO_2 has already been replaced by aluminum oxide (k~8) in DRAMs, tantalum oxide (k~20) in decoupling filters and silicon oxynitride (k~6) in transistor gates. Developing acceptable higher-k replacements for these materials is a complex challenge. The leading candidates under investigation are metal oxides based on HfO_2 and include ternaries, such as hafnium aluminates, silicates and oxynitrides, as well as quaternaries such as Hf aluminates and silicates containing nitrogen. Other metal oxides being considered include those based on zirconium, lanthanum and praseodymium.

A successful dielectric deposition method must deposit contamination-free films of these new materials with precise, uniform thicknesses over large areas and aggressive topologies while remaining cost effective. ALD has already demonstrated these capabilities for deposition of Al_2O_3 in current mass-production of DRAMs. ALD is a vapor deposition process based on sequential self-terminating surface reactions where the precursors are injected separately in pulses added to a flowing carrier gas separated by a purge of excess precursor vapor. Each pulse and purge sequence constitutes an ALD half-cycle. Ideally, each half-cycle results in one additional atomic monolayer of material and then the reaction stops even if more precursor vapor arrives at the surface. This self-terminating character results in ALD's uniformity, conformality and precise thickness control. In practice, the deposition per cycle is usually half of a monolayer or less. Several excellent reviews[1-4] provide an overview of ALD while this article aims to summarize the principles that determine precursor properties to aid precursor selection.

To achieve ALD's unique characteristics and to be suitable as a practical vapor deposition process, ALD precursors must have specific properties. They must be sufficiently volatile (at least about 0.1 Torr equilibrium vapor pressure at a temperature at which they do not decompose thermally). Furthermore, they should vaporize rapidly and at a reproducible rate, conditions that are usually met for liquid precursors, but not for solids. For self-terminating surface reactions, precursors must not self-react, including decomposing on the surface or in the gas phase. Precursors must also be highly reactive toward the other precursor previously attached to the surface, resulting in relatively fast kinetics and thus lower ALD temperatures and cycle times. Furthermore, the byproducts must be volatile and thus easily purged in order to prepare for the subsequent half-cycle. Moreover, byproducts should not be corrosive to prevent non-uniformities due to film etching and corrosion of the tool. Precursors having exothermic reactions with their complementary precursor tend to produce pure films because the ligands are completely removed. A large thermodynamic driving force also usually allows low deposition temperatures, resulting in the smooth, amorphous films needed for gate dielectrics.

ALD precursors for metal oxides are generally classified as metal precursors and oxygen sources. Metal precursors

(ML_n) generally contain one metal atom M bound to n ligands L and can be categorized by the types and number of atoms directly bound to the metal center. (see Figure 1). Selecting precursors with all of the desired properties has not been straightforward because relatively little data is available, and detailed ALD chemistry has not been well understood. The dominant ALD reactions forming high-k metal oxides appear to be ligand-exchange reactions[5] (see Figure 2). When water is used as the oxygen source, as is common in ALD of high-k dielectrics, ligand-exchange involves breaking the metal-ligand bonds of the precursor and an O-H bond, and forming an M-O bond and a L-H bond. The strengths of the bonds that dissociate and form during the ALD reactions directly determine the thermodynamics of the reaction and, less directly, influence the rates of reaction. Precursors with strong L-H bonds (again, when H_2O is used as the oxygen source) and weak M-L bonds have strongly exothermic reactions, tending to make pure, amorphous films at low temperatures. Furthermore, unwanted side reactions will be less likely, and the process will usually be faster. However, the metal-ligand bond must be sufficiently strong for the precursor to be stable.

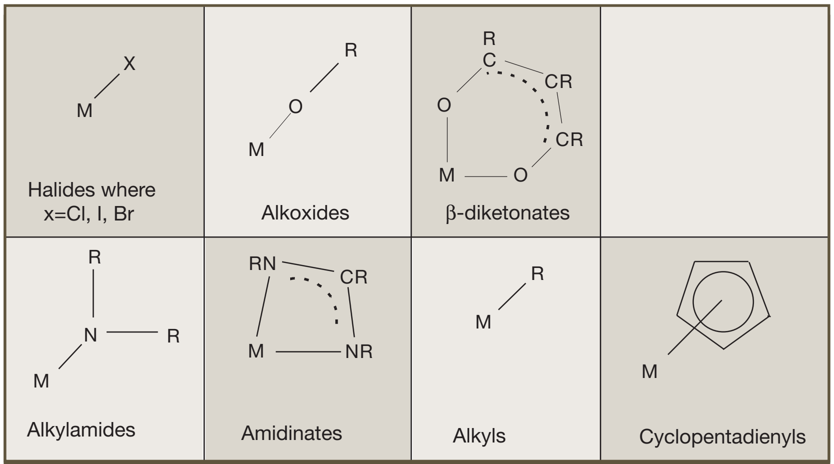

Figure 1: Precursor types. The R's represent alkyl groups consisting of carbon and hydrogen, such as methyl (CH_3) or ethyl (C_2H_5).

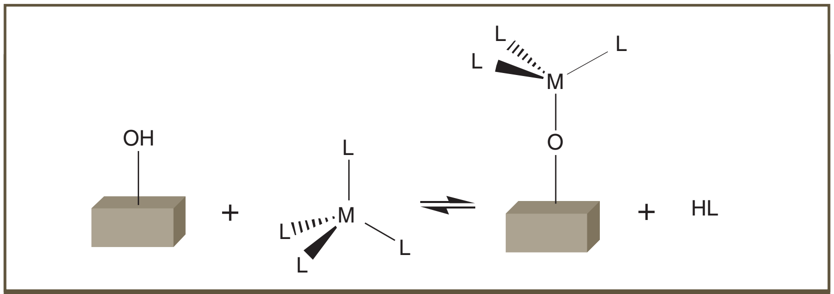

Figure 2: Schematic of a ligand exchange reaction for a ML_4/H_2O ALD process.

Another important precursor property is its size. Ligands are attracted to each other through weak van der Waals interactions and thus bulky ligands generally lower precursor volatility. However, bulky ligands can also shield the metal center from bonding interactions between precursors, thereby increasing precursor volatility. Because of these competing effects there may be an optimum ligand size that maximizes the precursor volatility. Large ligands can also restrict the packing density of precursors in the saturated precursor monolayer. However, more complete ligand exchange reactions during precursor exposure reduce the number of ligands remaining in the monolayer, increasing the monolayer density.

The metal halides consist of a metal atom directly bonded to halogen atoms (F, Cl, Br or I), for example $HfCl_4$. Unfortunately, metal halides are usually solids with low volatilities except, for example, $TiCl_4$, which is a liquid at room temperature and a relatively successful ALD precursor for TiO_2 and TiN. On the other hand, the metal chlorides have strong M-Cl bonds, resulting in high activation barriers, ALD temperatures and Cl contamination of HfO_2, which causes failure after the required anneal. The high ALD temperature may also lead to low observed deposition per cycle due to reduction of active OH surface sites. Furthermore, the metal chlorides produce HCl as a byproduct, which etches the film leading to non-uniform film thicknesses, and corrodes reactors. The metal chlorides are the most thoroughly investigated high-k precursors. Fluorides of Zr, Hf and La are not suitable for ALD because they have very low volatility, and HF is a corrosive and hazardous byproduct. Transition metal bromides and iodides do not offer significant advantages over the chlorides.

Metal precursors with oxygen bonded to the metal include alkoxides ($M\text{-}(O\text{-}C\text{-}R)_n$), such as hafnium tert-butoxide, $Hf(OC_4H_9)_4$, where each alkoxo ligand is bound to the metal atom through one O atom, and ß-diketonates ($M{=}(O_2C_3R_3)_n$, such as $Zr(thd)_4$, where each diketonato ligand is bound to the metal through two metal-oxygen bonds (the ligand "chelates" the metal center). Alkoxide precursors already possess M-O bonds and consequently, ligand exchange reactions with water maintain the same number of M-O and O-H bonds. Thus these reactions have little enthalpic driving force. The strong dative bonds between the metal center and surface OH groups and the alkoxo O atom and surface metal atoms lead to strongly bound intermediates. Consequently, alkoxide precursors require relatively high ALD temperatures. Alkoxo ligands must also be relatively bulky to achieve sufficient volatilities and low melting points because the M-O-R structure of the alkoxide does not screen the metal center from interacting with the oxygen atoms of nearby precursors. Alkoxides can deposit both a metal atom and oxygen atom in a single step when alternated with a second metal precursor – for example, a

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metal chloride. However, the kinetics of these reactions are relatively slow, and some chloride impurity remains in the product films.

ß-diketonates are common precursors for CVD and have been investigated for ALD of metal oxides. Because they already possess two M-O bonds per ligand, water does not react with these precursors. Strong oxidizers, such as ozone, are required to break the strong carbon-to-oxygen bonds, but carbon contamination remains, leading to increased leakage currents. Furthermore, ß-diketonates generally have low volatilities and slow vaporization kinetics because they are solids.

Precursors with nitrogen bonded to the metal include metal alkylamides ($M(NR_2)_n$), such as hafnium dimethylamide, $Hf(N(CH_3)_2)_4$ and metal amidinates ($M(N_2CR_3)_n$), such as lanthanum N,N'-diisopropylacetamidinate, where each amidinate ligand chelates the metal center through two M-N bonds. Alkylamido precursors have relatively weak M-N bonds and strong byproduct N-H bonds, lowering the ALD temperature, although sufficiently strong M-N bonds that the precursors are stable at the normal temperatures at which they are used. Alkylamides are reactive to both water and ammonia, enabling nitrogen incorporation into oxide films and even growth of metal nitrides without a plasma. Furthermore, the ligands of alkylamides are particularly good at preventing neighboring precursors from bonding to the metal center, and so alkylamides have high volatilities as well as low melting points, so most are liquids at room temperature.

ALD of oxides of lanthanum and other lanthanide metals, such as praseodymium, has been difficult because of the low volatility and stability of most of their compounds. Lanthanide amidinates are the most volatile lanthanum compounds known, although they are solids. Because the amidinato ligand chelates the metal center, they are thermally stable, yet have the high and self-limited reactivity to water vapor needed for ALD.

Organometallic precursors have metal atoms bound directly to carbon, including alkyls $M(C_xH_y)_n$, such as trimethylaluminum, $Al(CH_3)_3$; and cyclopentadienyls, such as dicyclopentadienyldimethylhafnium, $Hf(C_5H_5)_2(CH_3)_2$ (a mixed ligand precursor). Alkyls have not been studied extensively for high-k ALD, except for ALD of Al_2O_3 using $Al(CH_3)_3$. Alkyls are vulnerable to decomposition to metal hydrides and metal alkenes making many of them impractical for ALD. Metal cyclopentadienyls ($M(C_5H_5)_n$ or $M(C_p)_n$) are being explored for metal ALD, but not extensively for high-k ALD. C_p ligands are good electron donors and metal cyclopentadienyls bound to good metal electron acceptors are relatively stable.

So we come to the bottom line. Which precursor is most suitable for high-k ALD? The answer depends on which metal compound you are depositing. Aluminum oxide is usually deposited from trimethylaluminum and water or ozone, while aluminum nitride is made more easily from aluminum dimethylamide, $Al_2(N(CH_3)_2)_6$, and ammonia. For ALD of hafnium oxide and hafnium oxynitride, hafnium ethylmethylamide, $Hf(N(CH_3)(C_2H_5))_4$, is a good liquid precursor, combining high reactivity toward water, ozone and ammonia, with sufficient volatility and stability.[6,7] Amidinates, such as lanthanum N,N'-diisopropylacetamidinate, show a unique high reactivity to non-oxidized silicon surfaces, which allows growth without a low-k interlayer on a silicon surface. Addition of some aluminum oxide to lanthanum oxide provides excellent environmental stability. The high band offset of lanthanum aluminate has allowed very low leakage currents to be obtained for ALD lanthanum aluminate films on silicon.[8]

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Biographies

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Charles Musgrave is an assistant professor of chemical engineering at Stanford University. He is known for his use of quantum chemical methods to determine the detailed chemical mechanisms important in various semiconductor processes, including ALD.

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Roy Gordon is professor of chemistry at Harvard University. His group has introduced a number of new precursors and processes for ALD of metals, metal nitrides and metal oxides that are being developed for applications in the semiconductor industry.