



# The Silicon Precursor Toolbox for Low-temperature Deposition

*White paper*

## INTRODUCTION

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The drive toward making electronics faster, denser, and cheaper continues unabated. Shrinking device dimensions and changes in structure place additional demands on the materials used in all steps of semiconductor processing, including depositing silicon nitride ( $\text{Si}_x\text{N}_y$ , or SiN) and silicon oxide ( $\text{SiO}_2$ ) films. With horizontal dimensions of transistors already near their lower limit, the path forward for Moore's Law requires building upward. Increasing use of FinFET transistor structures and 3D NAND memory devices is driving the move from planar coatings on horizontal surfaces to conformal coatings on vertical and topologically complex surfaces. Aspect ratios are growing to the point where conformal coating performance is becoming a potential roadblock.

Silicon nitride and oxide films serve two primary types of functions in semiconductor device fabrication. Some are used for patterning, and others are used for electrical insulation. Within these broad categories, each application comes with a slightly different set of challenges. In this white paper, we explain the role of precursors in depositing high-quality silicon-containing films under a wide range of challenging conditions.

## SILICON-CONTAINING FILMS USED FOR PATTERNING

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SiN and  $\text{SiO}_2$  function as disposable films for patterning layers in semiconductor devices. Self-aligned double and quadruple patterning, which is becoming increasingly common, is an effective method of creating extremely fine lines. This approach uses films deposited on the side-walls of patterned structures to circumvent the dimensional limitations of photolithography, fabricating narrower lines than individually patterned layers can achieve using 193 nm photolithography. The deposited side-wall layer is used as a mask to pattern underlying layers during subsequent etch steps. When the sacrificial layer is etched away, whether by a dry or wet etch process, the underlying layer has received the pattern at twice the spatial

density of the structure before deposition of the patterning film. With quadruple patterning, line widths are one-quarter of the width that would be possible without implementing multiple patterning steps.

There are two primary issues with these side-wall deposited films used for patterning. The first is etch selectivity and the second is step coverage, sometimes called conformality. Etch selectivity occurs when the film used for patterning resists etching in a specific environment while the layer below is receiving the desired pattern by etching more quickly. If the side-wall film is lacking resistance to this etch condition, then it will need to be deposited over a higher aspect ratio structure so that it is effectively thicker during the etch step. However, uniform deposition is more difficult over the higher aspect ratio structure. When the patterning function is complete, the layer needs to be easy to remove.

The composition and the density of the deposited film controls the etch selectivity. Excess hydrogen in the form of terminal Si-H, O-H, or N-H bonds tends to decrease the density of the film, making it susceptible to attack by both dry and wet etchant species. Carbon can be added to oxide or nitride films to increase their resistance to fluorine or HF attack, but terminal  $\text{CH}_3$  groups can be vulnerable to dry etchants that contain active oxygen. Silicon-rich nitrides have been used for enhanced resistance to HF wet etchants.

The second challenge is achieving appropriate step coverage during film deposition as aspect ratios increase. Ideally, all surfaces of each trench should be coated uniformly, but if the process and precursor are not properly matched and optimized, the film will preferentially coat the bottom and top surfaces before completely coating the sidewalls. To achieve a precise pattern transfer, the film's etch rate should be the same on the top and the sidewalls. Proper control of film deposition can create films with uniform step coverage and sufficient thickness, but as aspect ratios and the number of layers increase, it becomes more difficult to achieve a high-quality conformal coating.

## SILICON-CONTAINING FILMS AS ELECTRICAL INSULATION

SiN and SiO<sub>2</sub> films also function as electrical insulation in finished circuit designs, either in front-end-of-line (FEOL) applications, such as to isolate the gate from the source or drain in transistors, or further along in the fabrication process as dielectric layers, such as those used for the fully self-aligned via. In both cases, the films need to remain stable during subsequent processing steps, which may occur at relatively high temperatures.

The dielectric properties of silicon-containing films are critical to proper functioning of the chip. They must have a sufficiently high breakdown voltage and low leakage to reduce power consumption. Time-dependent dielectric breakdown (TDDB) is a special concern for FEOL dielectrics. The quality of the oxide layer is a critical factor in determining the risk of TDDB. As the distance between electrodes and thickness of the insulating layer decreases, the risk of TDDB increases and intrinsic oxide reliability becomes a greater issue.

In some applications, the dielectric constant ( $\kappa$ ) is also important. Materials with lower values of  $\kappa$  are used where there is a need to prevent cross-talk between conducting elements at higher frequencies. As devices shrink, this crosstalk can limit device performance. Low- $\kappa$  dielectrics have been widely adopted in the wiring layers but are just now becoming more common for the conformal dielectrics used to isolate the active devices.

## ADOPTION OF ATOMIC LAYER DEPOSITION

SiN and SiO<sub>2</sub> layers have historically been deposited using chemical vapor deposition (CVD) or plasma-enhanced chemical vapor deposition (PECVD). However, semiconductor manufacturers are now changing the fabrication process, taking advantage of atomic layer deposition (ALD) to create precise, ultrathin layers with good step coverage. The thermal ALD process was introduced first in DRAM capacitors and then gate dielectrics over a decade ago but is now migrating into more layers, following the trend toward three-dimensional (3D) devices with the need for

conformal film deposition. Deposition temperatures at or above 300°C (572°F) are typically required to produce good-quality oxide films using thermal ALD; temperatures at or above 500°C (932°F) produce good-quality nitride.

To protect previously deposited layers and structures from heat-induced degradation, however, ALD must sometimes be performed at lower temperatures. Common upper limits are 400–450°C (752–842°F) for FEOL and DRAM structures, 250°C (482°F) for alternative memory structures, and as low as 70–150°C (158–302°F) for covering photoresist structures. Thermal ALD is possible at temperatures as low as 200°C (392°F) for nitrides and 75°C (167°F) for oxides, but film quality is generally poor at low deposition temperature.

Plasma-enhanced ALD (PEALD) is one way to achieve sufficient deposition rates at lower deposition temperature. PEALD is not without drawbacks, however. The plasma activity often varies on the different regions of the structure. For example, the top, sidewall, and bottom of a structure may not have the same concentrations of activated species and levels of physical bombardment. This can result in deposited layers with non-uniform composition, density, and etching rate on the top, sidewall and bottom of the structure. Thermal ALD of silicon-containing films is gentler than PEALD, making it easier to deposit layers with uniform properties over the structure.

## THE IMPORTANCE OF PRECURSORS

The path toward depositing the best SiN or SiO<sub>2</sub> film for a particular application begins with selecting an appropriate chemical precursor. A wide variety of possible precursors exist, and researchers continue to develop new precursor molecules.

The strength of the bonds in the precursor affects the deposition of the silicon-containing film and helps to determine the chemical composition of the film. Some of the bonds break as the precursor reacts with the activated surface, and some of the bonds

remain in the oxide or nitride film. Table 1 lists bond energies of the atomic bonds in various commonly used precursors. Because some of the chemical bonds present in the precursor remain in the film, it is possible to engineer the chemical composition of the SiN or SiO<sub>2</sub> film by changing the precursor.

The bond energies of Si-Si bonds, Si-I bonds, and N-N bonds are relatively low compared to the other bonds in precursor molecules. These are bonds that we expect to be easier to break at low temperatures and so precursor containing them will saturate an activated surface more efficiently.

A wide variety of halosilane and organosilane precursors are available for low-temperature PEALD, with properties that depend on their chemical structure. Figure 1 shows the structures of some precursor molecules that have been tested for

low-temperature PEALD nitride deposition. Deposition rates depend on several factors, including the type of plasma used—some precursors are more effective with N<sub>2</sub> plasma, and others work better with NH<sub>3</sub>—and the deposition temperature. From this group of precursors, the amidosilanes require an N<sub>2</sub> plasma to reset the surface to an activated state and will not reset with NH<sub>3</sub> plasma. The chlorosilanes require an NH<sub>3</sub> plasma to reset the surface and will not reset with N<sub>2</sub> plasma.

SiNCH contains both low-energy N-N and Si-Si bonds, which contribute to its excellent low-temperature performance when used with N<sub>2</sub> plasma. SiNCH contains multiple methyl groups as well, allowing a significant level of carbon to be incorporated into the resulting film. The higher carbon level can provide the benefit of a lower dielectric constant for SiN films, as well as a lower etch rate for better etch selectivity.

Table 1: Bond energies of common atomic bonds present in silicon precursors, kJ/mole

Si-Si	Si-C	Si-H	Si-N	Si-O	Si-F
<b>327</b>	435	298	439	798	540
Si-Cl	Si-Br	Si-I	N-H	N-N	N=N
456	343	339	435	<b>264</b>	456

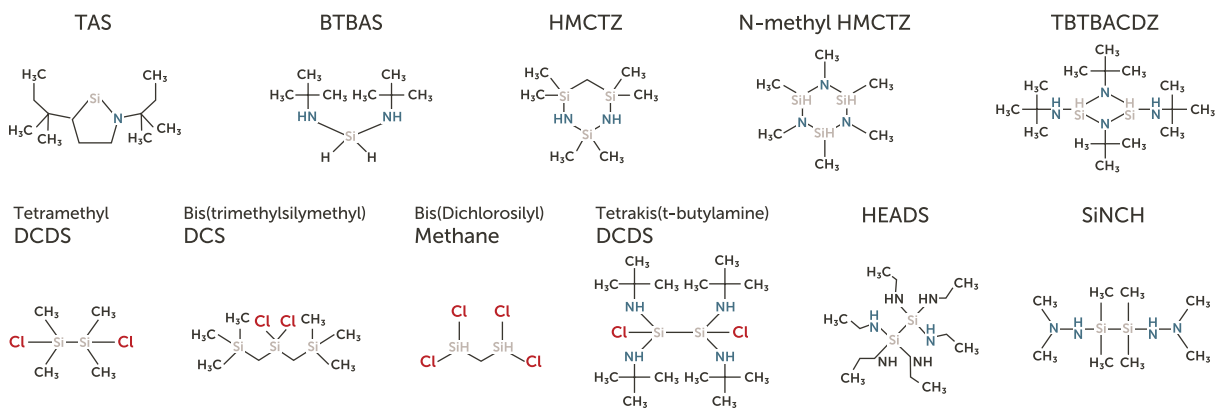


Figure 1. Chemical structure of various precursors for low-temperature nitride ALD.

Wet etch rate (WER) is a critical performance parameter for conformal coatings, and it is strongly dependent on precursor chemistry and the type of plasma used. In general, the WER is faster in films deposited with halosilane precursors than in films deposited with amidosilane precursors (Figure 2). For the results

in Figure 2, films were deposited under similar conditions for each precursor. In practice, the plasma conditions would be optimized for each precursor and application; etch rates can vary by over an order of magnitude by changing plasma conditions.

### Wet Etch Rates of PEALD Nitride Films

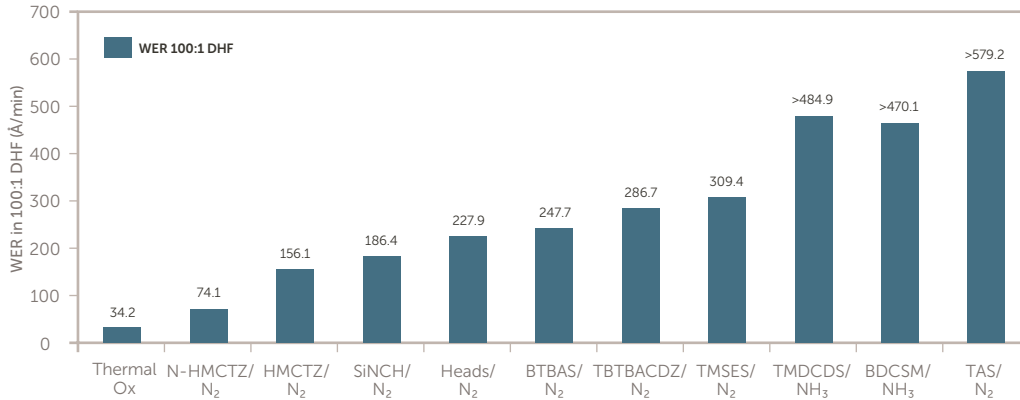


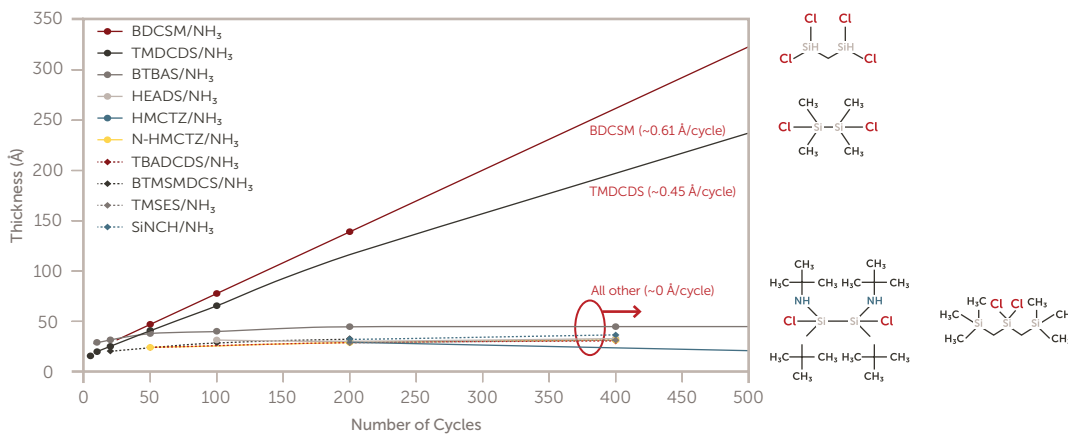
Figure 2. Wet etch rate when using various precursors for a fixed set of process conditions: 400°C 1 Torr 500W 1/5/5/2 sec.

### PRECURSORS WITH EXPOSED HALIDES

The effectiveness of various precursors in an  $NH_3$  plasma varies considerably, with many common precursors unable to achieve a manufacturable deposition rate. Tests of many possible precursors showed only two – bis(dichlorosilyl)methane (BDCSM) and 1,2-dichloro-tetramethyldisilane or tetramethyldichlorodisilane (TMDCDS) – that

demonstrated sufficiently high deposition rates (Figure 3). Both BDCSM and TMDCDS have exposed halides that accelerate SiN deposition on surfaces that have been activated using  $NH_3$  plasma. TMDCDS includes methyl and chlorine terminations, whereas BDCSM contains four exposed chlorine atoms per molecule.

### Silicon Nitride ALD Using $NH_3$ Plasma



(Process Condition: 60°C amp T / 400°C / 1 Torr / 500W RF / 1 sec Si / 3 sec  $NH_3$ )

Figure 3. Deposition thickness as a function of inverse temperature for ALD of various precursors with  $NH_3$  plasma.

Precursors with halide terminations are uniquely well-suited for SiN deposition using NH<sub>3</sub> plasma. Chlorine is the most common halide, but other halides such as iodine or bromine will be active for deposition at lower temperatures because both the Si-I and Si-Br bonds have lower bond energies than Si-Cl (Table 1).

## CATALYSTS FOR HALOSILANES

Adding catalysts during PEALD can enable deposition at lower temperatures or increase deposition rate. Chlorosilanes benefit from the addition of catalysts to accelerate the reaction. Basic (high-pH) catalysts, including ammonia and pyridine, have been used for this purpose since the early 2000s.

Recent studies have revealed improved process options. Amine catalysts can double the growth rate of SiN films deposited using halide precursors such as hexachlorodisilane (Si<sub>2</sub>Cl<sub>6</sub>) and tetrabromosilane (SiBr<sub>4</sub>). The data in Figure 4 demonstrate the effectiveness of the catalysts. The two datasets in the plot use the same halide and follow the standard processing flow for PEALD: Precursor pulse, purge, NH<sub>3</sub> plasma pulse, purge. The only difference between the two sequences is the addition of the amine catalyst during the precursor pulse step of the deposition process for Sequence B. The amine catalysts act by reducing the activation energy required for the reaction, increasing the rate at which the precursor reacts on the activated surface, resulting in much higher growth rates before saturation (during the first six seconds). In addition, the catalyst increases the number of active sites so that the growth per cycle is 2–3X higher than the uncatalyzed precursor pulse.

### PEALD Nitride

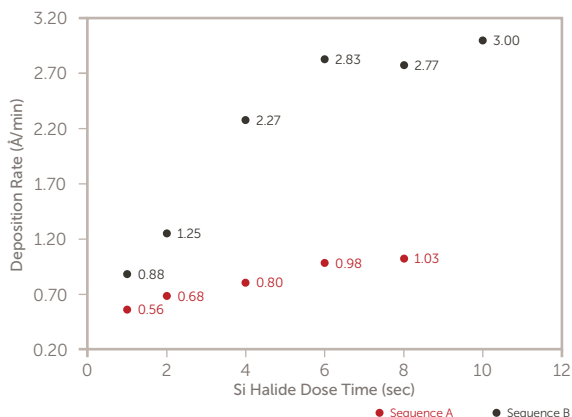


Figure 4. SiN growth rate as a function of Si halide dose time with and without an amine catalyst during the precursor pulse.

## PRECURSORS FOR OXIDE DEPOSITION

Amino disilanes such as hexakis(ethylamino)disilane (HEADS) and Tetramethylbis(dimethylhydrazino)disilane (SiNCH) are interesting alternatives to commonly used amino monosilanes. The relatively low bond energy of the active silicon-silicon bonds at the center of these molecules enables faster deposition at lower temperature. HEADS is a good choice for depositing SiO<sub>2</sub> at the lowest possible temperature. Its Si-N bonds are especially reactive on oxygen-rich surfaces, and when combined with the lower bond energy Si-Si bonds, it maintains a high deposition rate even at temperatures well below 200°C (392°F). Figure 5 shows the superior performance of HEADS at low temperature compared to other precursors when ozone is used as a co-reactant.

### Silicon Oxide Deposition Using Ozone

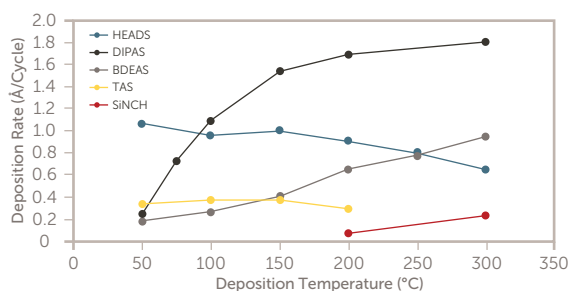


Figure 5. ALD deposition rate of oxide as a function of temperature for various precursors. 20 wt% ozone was used as a co-reactant. The weaker Si-Si bond of HEADS enables high deposition rates even at very low temperatures.

## THE PRECURSOR TOOLBOX

Because of the complexity involved in selecting an ideal precursor and the broad range of precursors available, developing a custom chemistry for each application is a time-consuming and expensive endeavor. The number of possible approaches to solve a single integration challenge can be overwhelming. In response, a precursor toolbox has been developed to help chip manufacturers find the best solution quickly.

The toolbox concept is a library of prescreened precursors that have been characterized over a wide range of conditions. The library includes recommendations for co-reactant and plasma selection, range of available deposition temperature, and potential catalysts. The specific precursors mentioned in this white paper are only examples.

Prescreening a wide variety of precursors enables chemical suppliers to react quickly to market demand. Developing a custom precursor for each niche application in response to a customer request takes too much time. Semiconductor device manufacturers can instead receive a short list of chemistries to evaluate and select the one they find works best for their application.

## SUMMARY

Increasing levels of vertical topography on finer structures and lower temperature budgets makes it harder to grow uniform layers of dielectric or patterning films that fulfill the performance demands necessary to produce reliable devices. This problem is not, however, insurmountable. Low-temperature deposition of SiO<sub>2</sub> and SiN with ALD and PEALD

can protect sensitive layers of the device from thermal damage while creating high-quality films. A toolbox approach to choosing the most appropriate precursor and plasma combination for a given application makes process development more efficient, benefiting semiconductor device manufacturers and their customers.

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