Extra Low-temperature SiO_2 Deposition Using Aminosilanes

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High quality SiO_2 thin films were grown by atomic layer deposition using a newly considered silicon precursor, SAM24, an aminosilane, with an ozone/oxygen mixture. SAM24 is a liquid and has sufficient volatility (with a vapor pressure of 2 Torr at R.T.) and is therefore easy to deliver into the reactor. Deposits obtained exhibit a very good thickness control when deposited as low as 100 ºC and up to 400 ºC at 1 Torr in a hot wall reactor.

Introduction

Atomic layer deposition (ALD) is a well suited technique to meet stringent uniformity, conformality, thickness and composition control requirements of semiconductor manufacturing, in particular at the gate, capacitor, and low-k/copper interface levels. Suitable precursors need to be smartly designed or identified, synthesized at effective costs and stable at ordinary temperature as well as in delivery conditions. They also need to be combined with the relevant co-reactants at appropriate process conditions so as to pass the evermore demanding deposition tests in order to obtain the film properties dictated by the ITRS roadmap.

A number of attempts to deposit high quality silicon oxide (SiO_2) film at low temperature have been carried out by many research teams for applications to temperature sensitive device for the forthcoming device generation in MOS technology. Moreover, it is considered to use such a SiO_2 film together with the classic nitride layer as a double-sidewall spacer to reinforce the transistor performances. SiO_2 precursors can be used as well for Si doping in high-k film deposition.

Various methods and source materials have been considered: $SiCl_4$ + H_2O [1-5] possibly using an amine as a catalyst [6-7], or alternatively the Cl-free TEOS/ H_2O [8]. However, these silica films are found porous and hygroscopic as the result of the formation of Si-OH by the cleavage of Si-O-Si bonds. The presence of moisture has been proven to be detrimental to their insulating properties (the leakage current seems directly related to the O-H bond in the films), a critical parameter for the targeted application. This layer would be rather thin (10-100 Å-thick) and a good thickness control is important. Current silicon sources used in the semiconductor industry such as monosilane, or disilanes (disilane and hexachlorodisilane), either exhibit insufficient reactivity on the surface (no growth by ALD), or self decomposition, or tend to leave detrimental impurities (such as chlorine). Among newer and reactive silicon compounds are silanols such as TBOS (tris-tertiarybutoxysilanol $HOSi(OtBu)_3$), and TICS (tetrakis-isocyanatosilane $Si(NCO)_4$), but both suffer from being solids at room temperature.

In this paper, a novel precursor dubbed SAM24 was studied for ALD because of its high volatility, reduced steric hinderance and suitable number of amino ligands, as well as the absence of undesired elements in its chemical formula, minimizing the risk of their incorporation during the deposition process and its expected reactivity in ALD conditions. The deposition features of the corresponding high quality SiO_2 thin films are described in terms of deposition characteristics (deposition rate as a function of temperature, as a function of pulse time, as a function of purge time…) as well as in terms of film composition.

Experimental

The silicon substrates cut to the size of 10 cm x 2 cm were first cleaned in a 5% HF solution to remove the native oxide layer, then rinsed with deionized water and blown free of particles with dry nitrogen before they were loaded in the ALD reactor.

As illustrated in Figure 1, SAM24 is stored in a bubbler at room temperature from where vapors are carried out by 50 sccm of nitrogen. 8 percents of ozone are generated by passing 100 sccm of oxygen into an ozonizer (Ecodesign Inc.: ED-OG-R3Lt). The gaseous species are sequentially introduced either into a tubular reactor, consisting of a quartz tube heated by a conventional 3-zone furnace ($T_{reactor}$= 100-400 ºC), or sent to a bypass line and then decomposed in a detoxification unit. 150 sccm of nitrogen were continuously flown to effectively purge the reactor between the pulses. The pressure in the chamber was set 1 Torr was monitored by a Baratron gauge and controlled by a Butterfly valve.

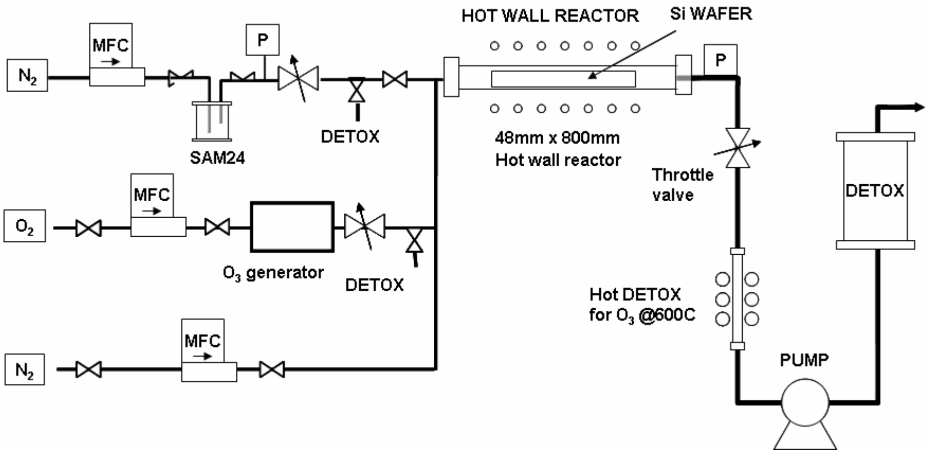


Figure 1: Schematic of the Atomic Layer Deposition set-up

The growth of SiO_2 films was performed on typical silicon wafers by alternating reactions between SAM24 pulses and O_3 pulses (Figure 2), while nitrogen was continuously flown in order to purge the reactor and maintain the pressure constant during the periods when no reactant is introduced. Pulse times for each reactant have been set to 5 seconds for the sake of simplicity as this duration exceeds the time needed for the surface saturation. Figure 2 exemplifies the ALD gas flow program for a SAM24 and O_3.

The film compositions were analyzed by an Auger Electron Spectrometer (Perkin Elmer, PHI650) allowing depth profile monitoring. The thickness, the refractive index and the etch rate were measured by a Spectroscopic Elipsometry (Horiba Jobin Yvon: UVISEL). The etch rate was measured by 0.1% HF. The measurements by Secondary Ion Mass Spectrometry of hydrogen, carbon and nitrogen were subcontracted.

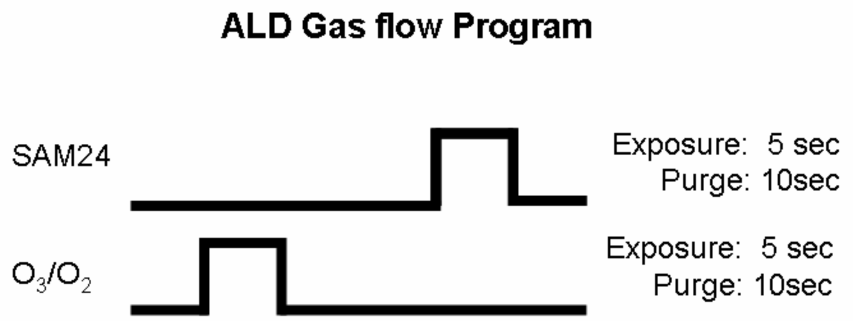


Figure 2: Example of ALD gas flow program

Results and discussion

Experiments were performed in order to determine films characteristics such as deposition rate, deposition temperature, and film quality and film composition. The deposition was performed on Si wafers cleaned by 0.5%HF. The SiO_2 film was obtained with excellent thickness uniformity in 600 mm-long reactor. A representative example, obtained at 300 ºC and at an operating pressure of 1 Torr is shown in figure 3.

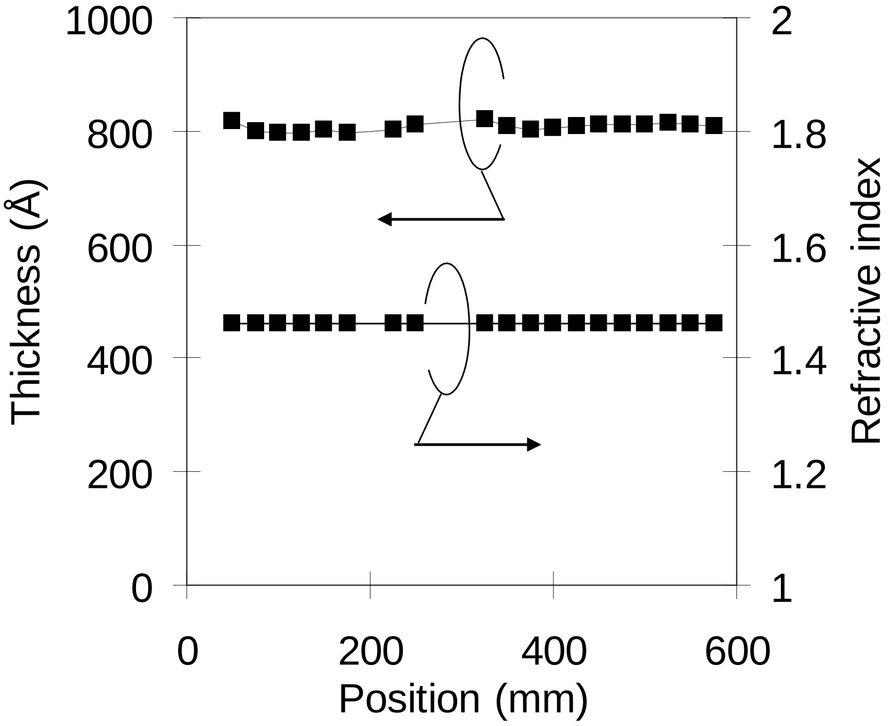


Figure 3: Typical result of thickness and refractive index for a typical SiO_2 film
Deposition temperature: 250°C. Number of cycles: 1500.
The thickness and the refractive index are constant all along the wafer stripe.

In order to demonstrate a self-limited growth, several sets of experiments were performed for measuring the deposition rate as a function of pulse time, at different deposition temperatures. Figure 4, with T_{dep}=250°C, exemplifies the growth characteristics observed at temperature ranging between 200 and 300°C. A plateau is typically reached after a pulse time 4 or 5 seconds.

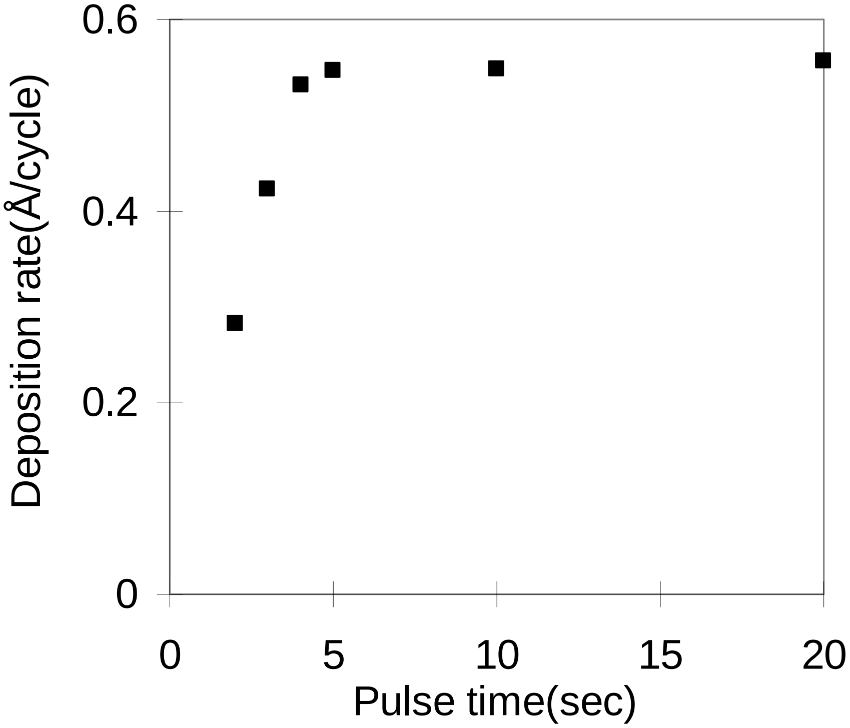


Figure 4: Deposition rate of SiO_2 film as a function of pulse time (T_{dep}= 250°C)
A plateau is reached after about 4-5 seconds of pulse time.

The influence of the nitrogen purge duration to evacuate reactive gaseous species into the reactor, and consequently the time needed to avoid parasitic CVD, was investigated. From our calculations, the residence time is about 0.76 second. Therefore one second should be enough to completely evacuate the chamber. Indeed, the deposition rate was experimentally found not sensitive to the purge time beyond 1 second (Figure 5).

The depositions between 100 and 400 ºC were carried out, and results are shown in figure 6. Deposition rate increases from 100°C to 200ºC, then reach a plateau at 200-300ºC, and finally decreases above 300 ºC. The evolution of the deposition rate vs. temperature seems to indicate a behavior where the adsorption of the reactants is low below 200 ºC and a desorption phenomenon above 300 ºC.

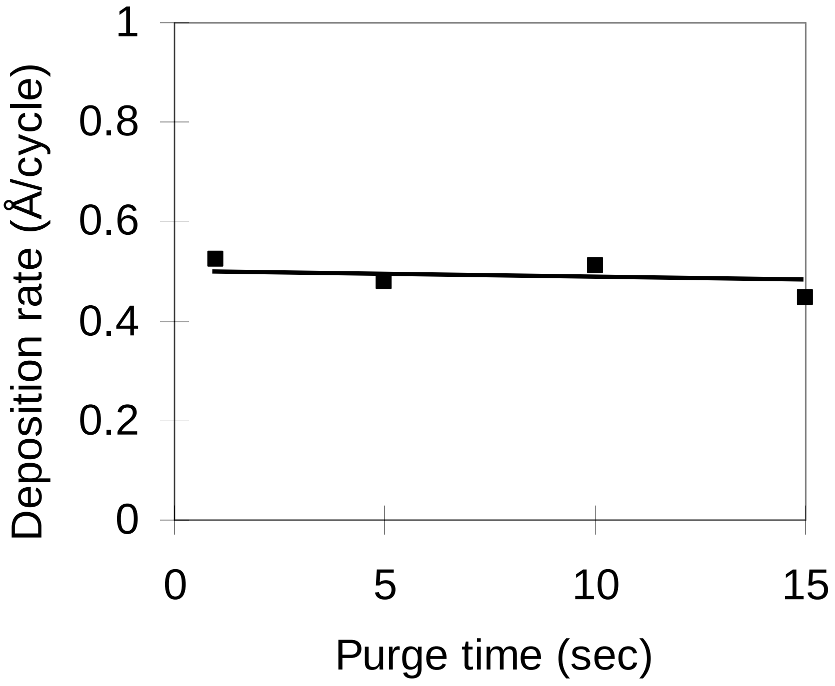


Figure 5: Deposition rate of SiO_2 film as a function of purge time.
The deposition time is found insensitive to purge time at T_{dep}= 250°C

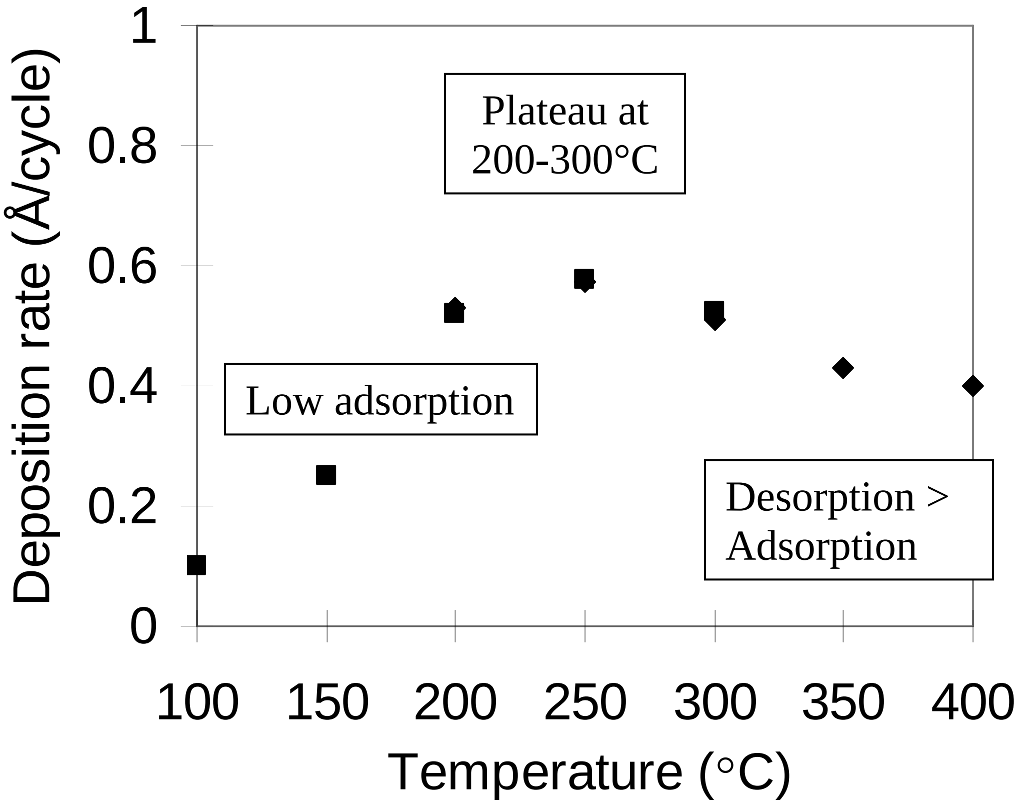


Figure 6: Deposition rate of SiO_2 film vs. process temperature

The deposited films did include neither nitrogen nor carbon according to in-depth analysis by Auger as shown in figure 7. In agreement with the expectations and the refractive index typical of stoichiometric silicon dioxide film, the film composition is found stable within the bulk of the film. The sharp interface between the silicon oxide and the iridium substrate suggests limited or no oxidation of the metal during the deposition process.

SiO_2 films deposited after 350, 600 and 900 cycles deposition tests exhibits no or negligible incubation time, as shown figure 8.

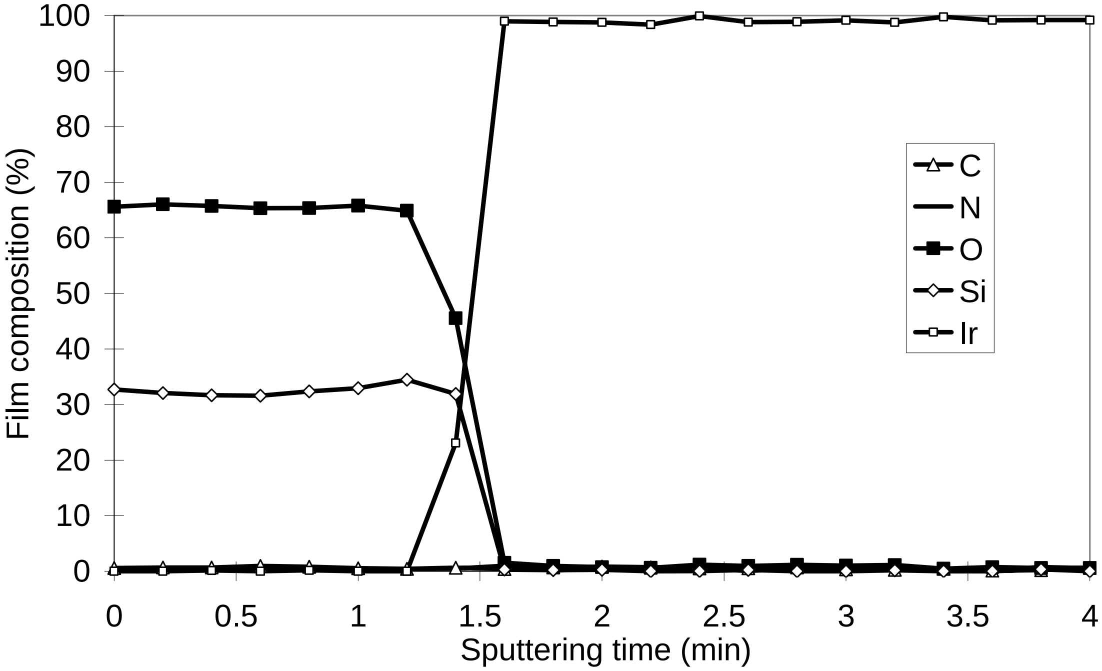


Figure 7: AES analysis of a SiO2 film deposited on an iridium substrate

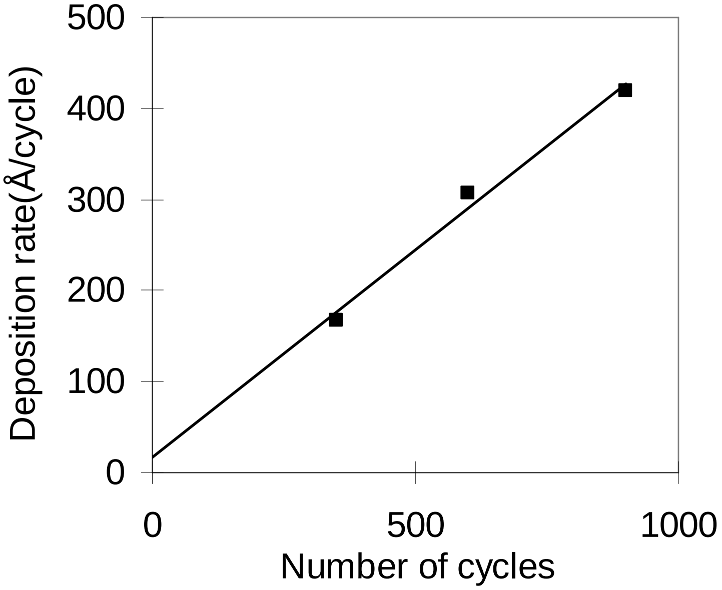


Figure 8: Number of ALD cycles vs thickness of the layer

The wet etch resistance was performed for the films deposited at 100 to 300 ºC by 0.1% HF, as shown figure 9. The temperature dependence was not observed on the etch resistance. The etch rate is typically ~50 Å/min in 0.1% HF, and is stable with deposition temperature.

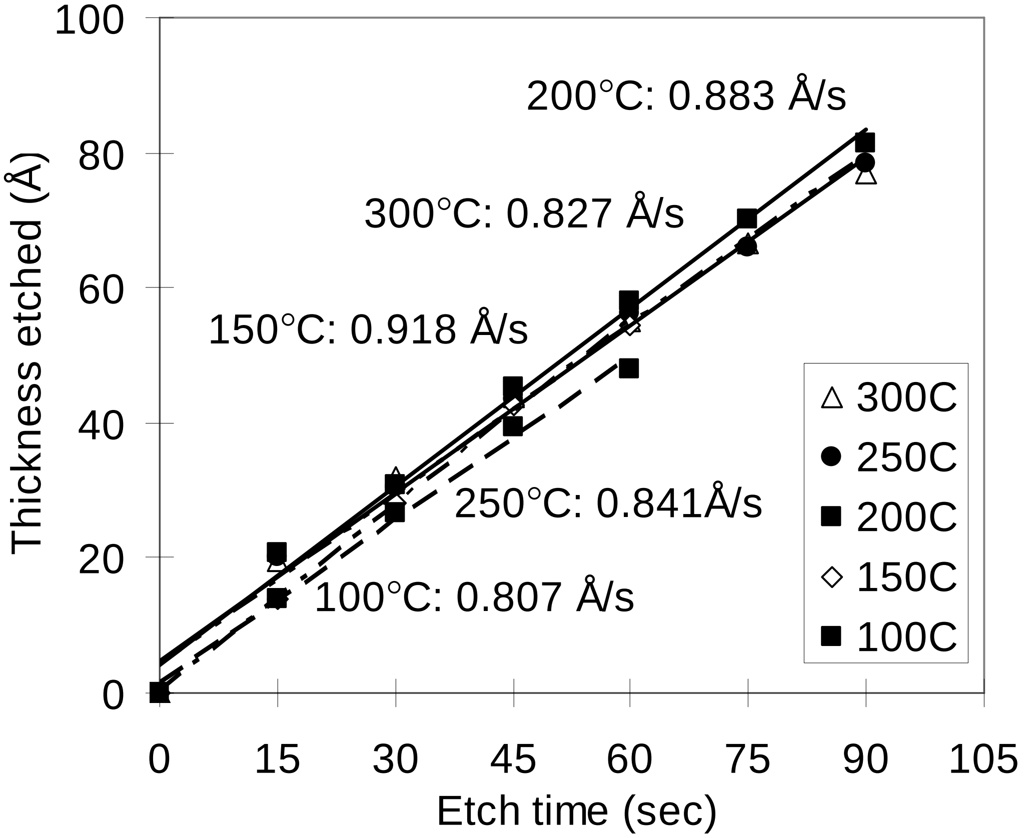
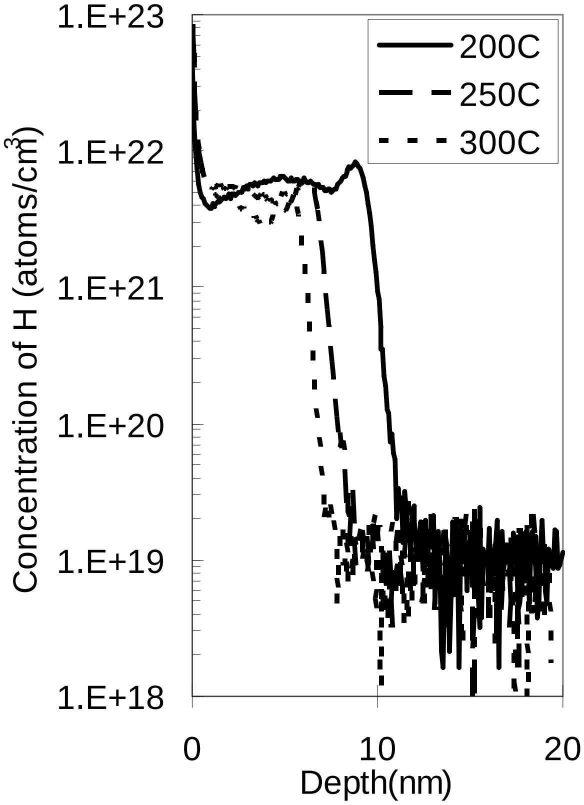


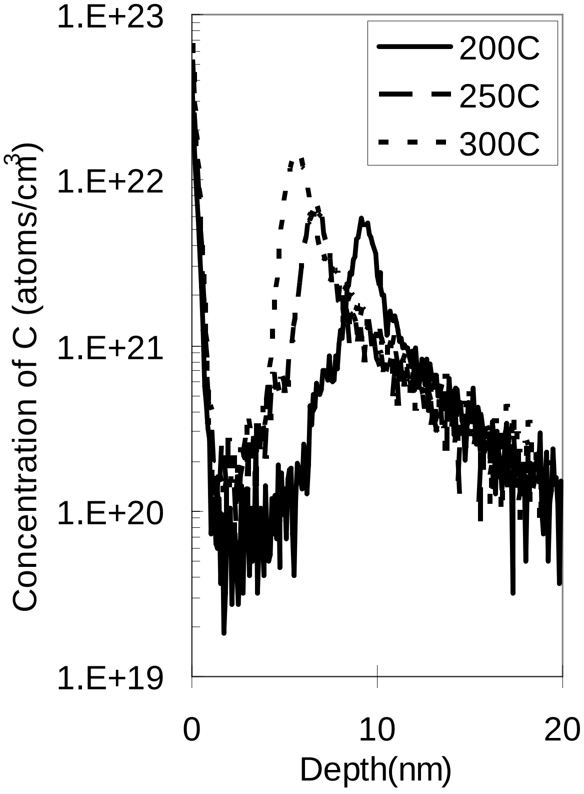
Figure 9: Wet etch resistance in 0.1% HF

In our experimental conditions, neither nitrogen nor carbon were detected by AES. A more sensitive technique such as SIMS is hence required to assess the impurity content in the film. The interface between SiO_2 is easily identified through a dramatic decrease of hydrogen content (figure 10a) or through the sharp peaks of carbon (figure 10b) and nitrogen (figure 10c). Very low carbon and nitrogen contents, close to the background level and to the level in the bulk of silicon substrate, are detected in the bulk and these amounts become only significant at the interface between SiO_2 and the substrate or at the surface for carbon.

(a) hydrogen



(b) carbon



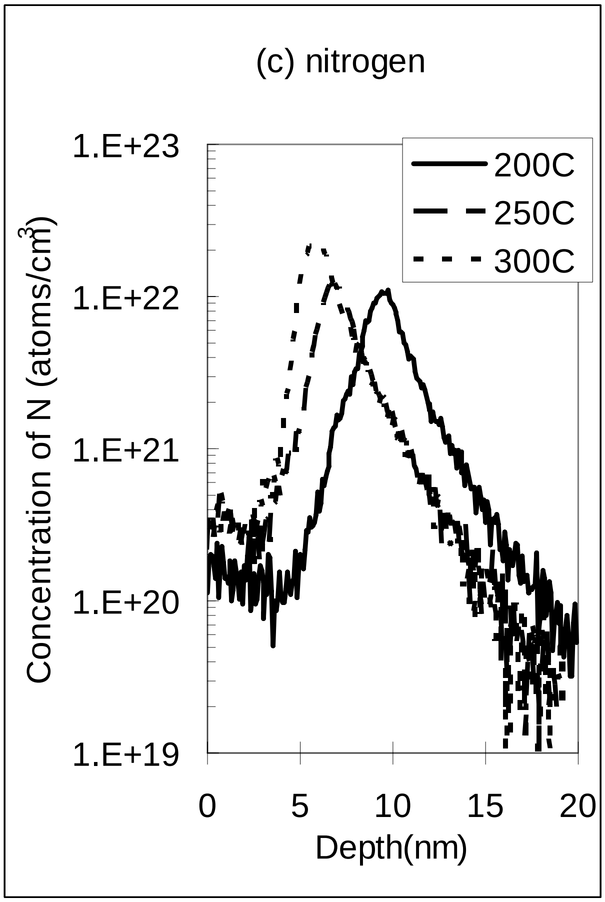


Figure 10: SIMS in-depth profile for (a) hydrogen, (b) carbon and (c) nitrogen contents in the SAM24-based SiO_2 films.

Conclusion

SAM24, a newly designed precursor for being volatile and having reduced steric hindrance with no undesirable elements, was studied for ALD. The experimental show that the deposition of SiO_2 using SAM24 can obtain superior results including:

1. Self limited growth characteristics between about 200 and 300°C (saturation at high pulse time, deposition rate unchanged after high purge time). This ALD process is characterized by an increasing deposition rate with temperature from 100 to 200°C and a slow reduction of the deposition rate from 300°C.
2. Stoichiometric films as shown by AES analyses and confirmed by the refractive index
3. High growth rate per cycle (~0.6 Å/cycle)
4. Low impurities incorporation in the deposited films, even at low temperature
5. Stable film properties and composition over a wide temperature range (wet etch rates change of ~10% or less for films deposited between 100 and 350°C).

Acknowledgments

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