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Silicon Nitride and Silicon Oxide Thin Films by Plasma ALD

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Introduction

Silicon nitride, silicon dioxide and silicon oxynitride ultra thin films are becoming increasingly important in the manufacture of semiconductor devices. Si3N4 films at Si/SiO2 interfaces decrease interface traps and improve hot carrier immunity and improve the reliability and performance of conventional SiO2 gate oxides. Silicon nitride layers grown by low pressure chemical vapour deposition (LPCVD) at a wafer temperature of 700 °C are known to have a high interface and bulk trap density [1]. It has been reported that ALD Si3N4 films show promise in lowering interface trap property probably due to the low thermal budget of the deposition process [2].

This work focuses on SiO2/SiNx thin films grown by plasma ALD using different process parameters. Spectroscopic Ellipsometer (SE), AES, SEM, and electrical measurement were used for characterisation of the physical, chemical and optical properties of the as-deposited SiO2 and SiNx thin films.

Experimental Results and Discussion

The SiOx and SiNx layers were prepared using two amino-silane sources (BTBAS, 3DMAS). The films were characterised using both in situ and ex situ spectroscopic ellipsometry. Good film uniformity across 100mm wafers with a thickness variation of not more than ±0.5% was readily achieved for all the as-deposited films.

SiO_2

3DMAS SiO_2 films were grown using an O_2 plasma. Deposition rates of 1.0 Å/cycle were obtained at 300°C (Fig. 3). The growth rate was found to be relatively insensitive to temperature over the 100°C to 400°C range, see Fig. 4. The refractive index of the films determined by SE was about 1.43.

BTBAS The SiOx layers were deposited at growth rates of 1.2-1.4 Å per cycle at a temperature of 290°C have been obtained, see Fig. 5. Figure 6 shows the influence of deposition temperature on the growth rate, uniformity over a 4" wafer and refractive index of SiOx..

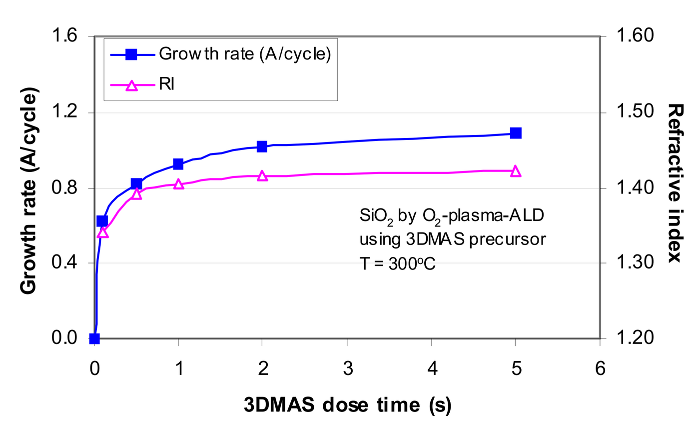


Figure 3 (left) thickness and refractive index saturation curve of 3DMAS.

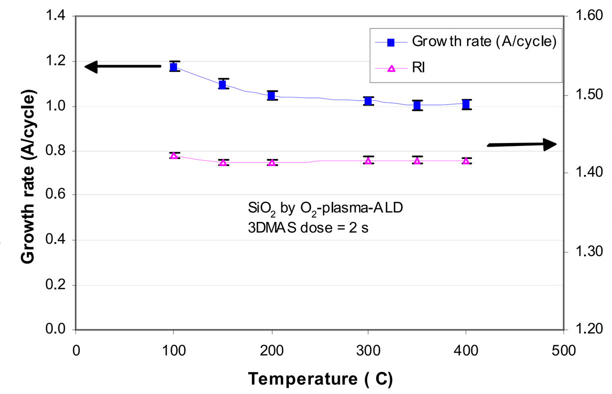


Figure 4 (right) growth per cycle and refractive index against deposition temperature for SiO_2 deposited with 3DMAS.

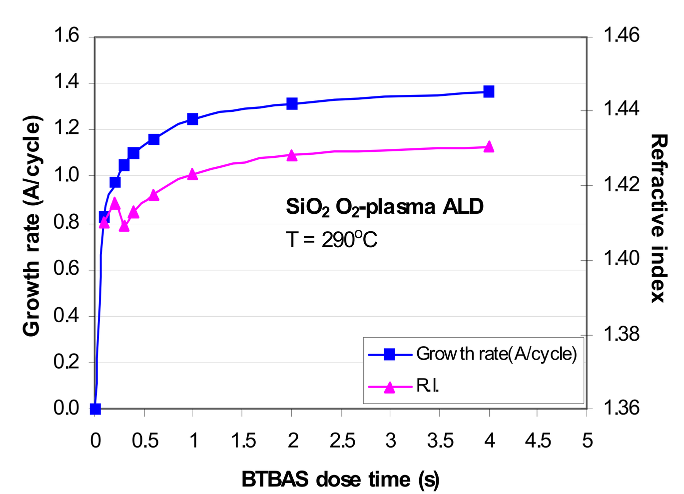


Figure 5 (left) growth rate and refractive index of SiOx using BTBAS and O_2-plasma at 290 ºC.

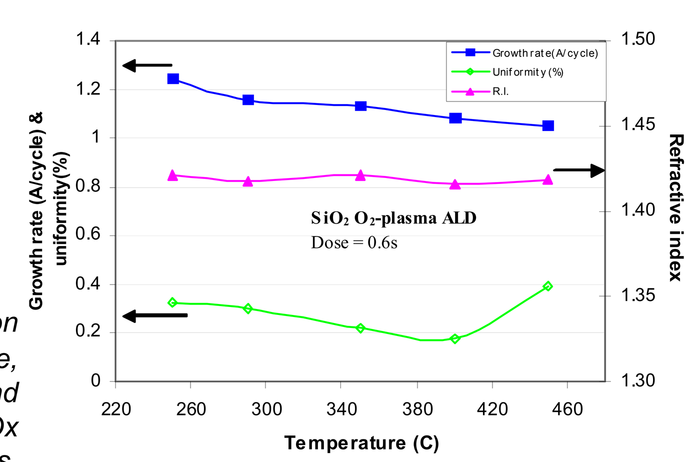
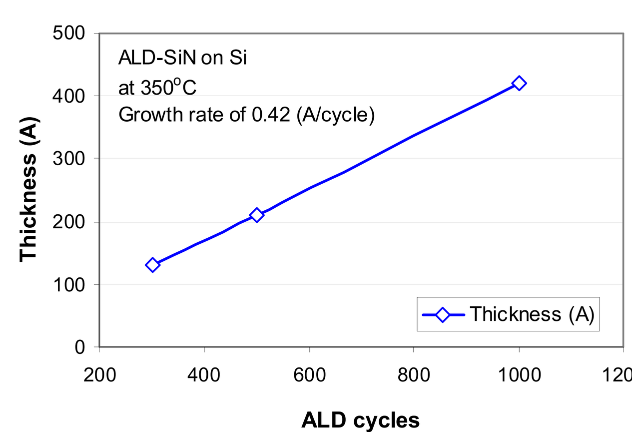


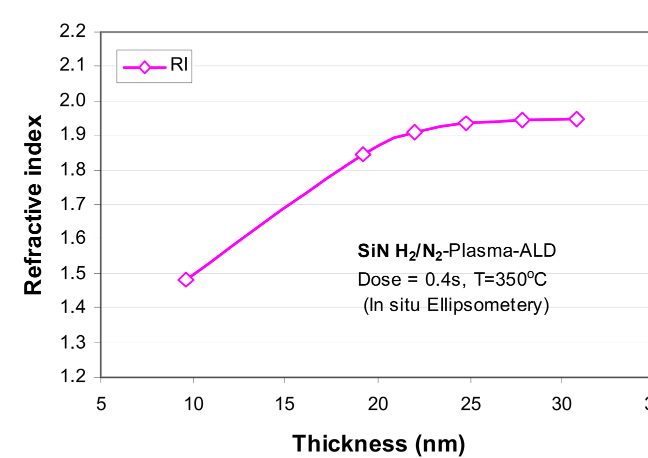
Figure 6 (right) deposition temperature on the growth rate, uniformity on 4" wafer and refractive index of ALD-SiOx films.

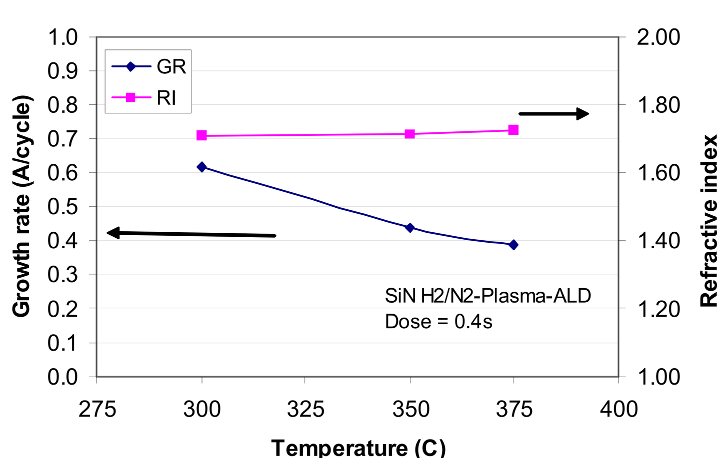
SiN_x

The ALD SiN_x thin films were grown using a N_2/H_2-plasma with 3DMAS. Deposition rates of 0.4 Å per cycle were obtained at a temperature of 350°C. The refractive index of the SiNx film obtained by spectroscopic ellipsometry (SE) is as high as 1.950. The details of ALD behaviour using 3DMAS and N2/H2-plasma are shown in Figs.7-10. Figure 10 shows what is believed to be an artefact of the ellipsometer model in that ultra thin films are fitted to give low refractive index.

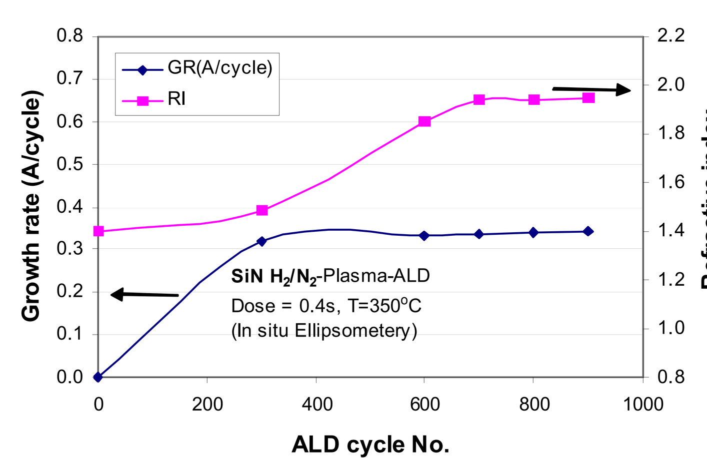


Figures 7 and 8 (left), SiNx by plasma-ALD using 3DMAS, (top) thickness vs ALD cycles (bottom) GPC and R.I. vs deposition temperature.





Figures 9 - 10 (right), ALD-SiNx (top) GPC & R.I. vs cycle numbers (bottom) RI vs thickness



Experimental set-up

The Oxford Instruments FlexAL® remote plasma ALD reactor, described in detail in Ref [3], was used for this work. A schematic and photograph of the reactor are included below in figures 1 and 2.

- Remote plasma and thermal ALD capabilities within a single system
- Enables low temperature ALD processes by using plasma
- Maximum flexibility in the choice of materials and precursors
- Ability to handle small wafer pieces up to 200 mm wafers
- Built in ports for in-situ diagnostics e.g. ellipsometry, RGA, etc

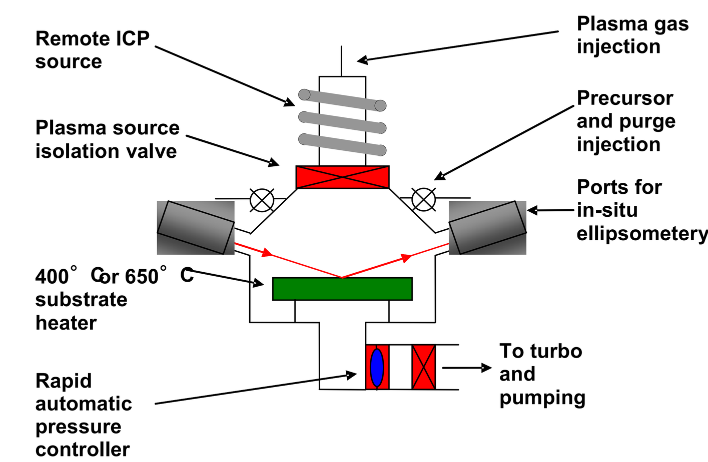


Figure 1 (left), schematic of the FlexAL® reactor.

Figure 2 (right), photograph of the FlexAL® reactor

Surface and Composition Analysis

AES and SEM were used for characterisation of the composition and surface of the SiO2 and SiNx layers. Figure 11 shows the AES profile of ALD SiO2 layer deposited using BTBAS at 290oC. It confirms the ALD film has uniform Si/O ratio of almost exactly 2:1 and with very low impurities (C < 2% and N <2%). Figure 12 is an AES of ALD SiNx layer deposited using 3DMAS at 350oC. It shows that the ratio of N/Si in the SiNx film is around 1.1 and the carbon in the film is in a range of 5-10 atomic %. The oxygen (< 3% in the bulk) is observed mainly at the surface and interface of SiN/Si substrate (the wafers were not HF dipped). The spectrum data from AES analysis of SiN are shown in Fig. 12.

Wet etch rates in buffered hydrogen fluoride solution were found to be comparable to our PECVD films at similar deposition temperatures (see fig 13).

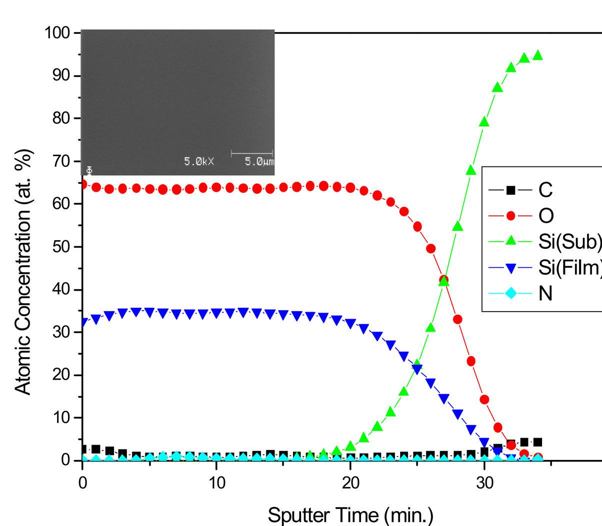


Figure 11(left), AES of ALD-SiO2 layer (31 nm) deposited using BTBAS at 290 ºC

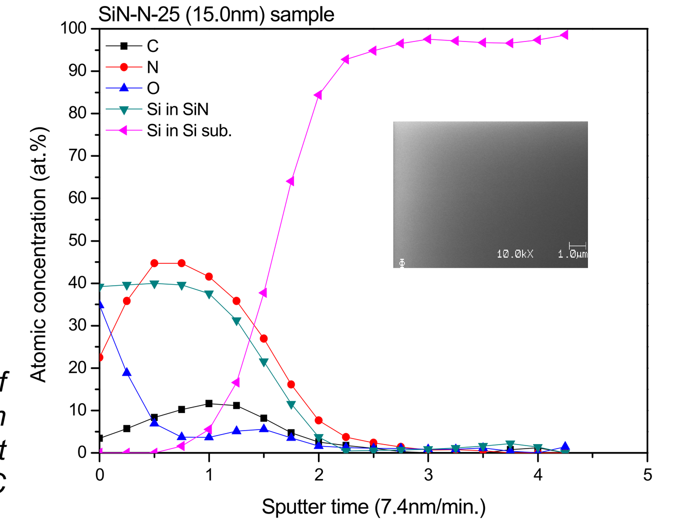


Figure 12 (right), AES of ALD-SiNx layer (15 nm deposited using 3DMAS at 350 ºC

Film	Precursor	Deposition temperature (°C)	Wet etch rate (nm/min)
SiNx	3DMAS	350	7.7
SiO2	3DMAS	300	148
SiO2	BTBAS	290	98
Thermal SiO2	Si oxidation	1100	60

***Figure 13** (left), wet etch rates of SiNx and SiO_2 dipped in 10:1 BHF solution. A thermal SiO_2 wafer was dipped alongside for reference.*

Conclusions and Future Work

We reported that SiO_2 and SiNx thin films were grown by using remote plasma enhanced ALD. SiO_2 films have uniform Si:O ratio almost 2:1 with very low impurities (C and N less 2%). The ratio of N:Si in the SiNx film is around 1.1:1 and oxygen (< 2% in the bulk) is observed mainly at the surface and interface of SiN/Si substrate. A significant amount of care is needed in obtaining such low oxygen contamination in ALD SiNx films since the preferential reaction of 3DMAS is always with oxygen containing molecules. The carbon in the film is in a range of 5-10 at.%. Future work includes electrical measurement of the ALD-films and anneal process of the ALD-films to improve the as-deposited layers with slightly low refractive index for SiO_2 and an improvement of ALD process to reduce carbon impurity in the SiNx thin films is on going.

References
1.Yun Wu, Huicai Zhong, Jeremias Romero, Cyrus Tabery, Cristina Cheung, Brian MacDonald, Jay Bhakta, Arvind Halliyal, Fred Cheung, and Robert Ogle, Journal of The Electrochemical Society, 150 (12) G785-G789 (2003).
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