

# Nitrous Oxide-Based Progressive Silicon Oxynitridation in Furnaces of Different Dimensions

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## ABSTRACT

As integrated device technologies enter the deep sub-half micron regime, there is a need for a corresponding reduction in the thickness of the dielectrics too. After formation of the dielectric film, maintenance of its characteristics during subsequent processing is also a necessity. Due to the less attractive characteristics of silicon dioxide (which has so far been the material of choice) for dielectrics less than about 100 Å thick, new materials have to be explored as dielectrics. In this regard, silicon oxynitrides have shown promising characteristics. This study deals with the progress of oxynitridation of silicon in nitrous oxide with increasing time at 900°C and 1 atm in two furnaces of different dimensions. It is found that both the nitrogen incorporation and removal processes occur very differently in the two reactors studied, thus depicting the effect of reactor scaling factors on the amount and concentration profile of nitrogen in the oxynitride film. A qualitative growth model is proposed to explain the observations. Besides, the effect of reaction kinetics and transport phenomena on silicon oxynitridation are also discussed.

**Keywords:** Silicon, Oxynitride, Dielectric, Oxide, and Microelectronics.

## INTRODUCTION-BACKGROUND

Silicon dioxide has been the main dielectric material in integrated circuits. But its properties appear to be less attractive in the ultra-thin regime (less than about 100Å)[1,2]. Thus, other dielectric materials are being sought after for Ultra Large Scale Integration (ULSI) applications. In this regard, silicon oxynitride has been attracting attention for over a decade now. Compared to the oxide, the silicon oxynitride exhibits better properties such as enhanced radiation hardness, higher barrier properties to boron penetration from the p<sup>+</sup> gate layer during the subsequent high temperature processing step, increased stress stability, lesser charge trapping, larger charge to breakdown ratio, and substantial growth rate retardation with time that facilitates the fabrication of ultra-thin films[1-14]. Also, it is easier to control the growth rate of these films, thanks to their self-limiting growth kinetics, due to nitrogen incorporation too[13-14]. There are some issues, however, which need to be well understood before this material could be effectively used for microelectronic applications.

In this study, we focus on how the amount and profile of N incorporation depend on reactor configuration and design in the oxynitride film growth from pure N<sub>2</sub>O. The effect of furnace geometry and dimensions and, hence, scaling factors on N solid phase concentration profiles in oxynitrides is reported. This is important in the design and scaling up of oxynitridation processes as well as in the implementation of any desired N concentration profile in a silicon oxynitride film.

## EXPERIMENTAL

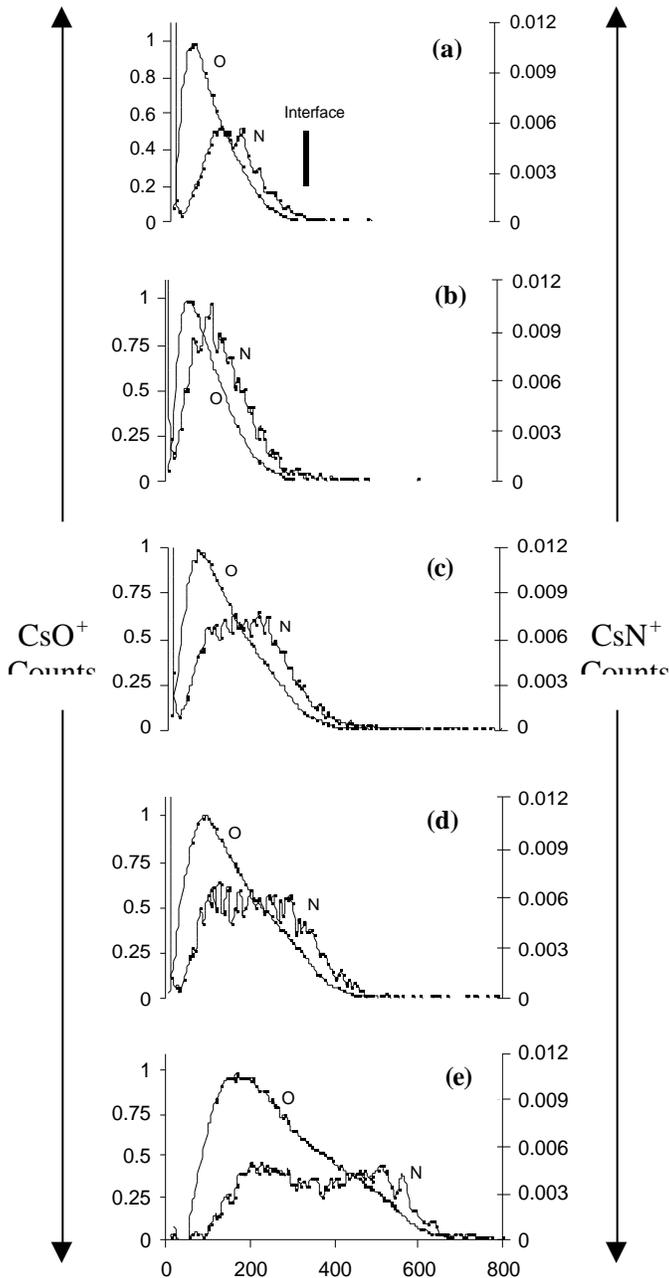
All films were grown at 900°C and 1 atm, with a feed gas flow rate of 2 standard liters per minute (slpm) of N<sub>2</sub>O (AGA, 99.5%) for 15 to 160 min. The resulting film thickness was approximately between 50 and 200Å. Two horizontal furnaces were used for the experiments: one is a Lindberg/Blue STF55346C system, named Furnace I from now on, and it is 3-in. in diameter with a total length of 36 in., out of which the middle 24 in. are heated. The other system, named Furnace II, is custom-made, 2-in. in diameter with a total length of 20 in., out of which 12 in. are heated. The temperature in both furnaces is controlled within ±2°C. A CAMECA IMS 5f secondary ion mass spectrometer (SIMS) was used for determining the Si, O, and N depth profiles in the oxynitride films. Sputtering was done with a 5.5 keV Cs<sup>+</sup> primary beam. Counts of secondary species, namely CsSi<sup>+</sup>, CsO<sup>+</sup>, and CsN<sup>+</sup>, were monitored to determine the depth profiles of Si, O, and N, respectively. A Gaertner single wavelength ellipsometer was also used to measure the film thickness.

## RESULTS AND DISCUSSION

### Furnace I (large diameter)

The SIMS depth profiles of silicon oxynitride films grown for 15, 30, 90, 120 and 150 min are shown in Figure 1. The CsO<sup>+</sup> and CsN<sup>+</sup> normalized secondary ion counts (ordinate) are direct measures of the O and N concentrations, respectively, while the sputtering time (abscissa) is linearly related to film depth as measured from the top surface. The dielectric/Si interface is approximately located at the point where the O curve starts to become almost parallel to the horizontal axis. The experiments presented here were repeated, and practically identical N concentration profiles were obtained for the same conditions, at all times.

After 15 min of oxynitridation, the N concentration peaks in the bulk, a bit closer to the dielectric/Si interface than to the top surface (Figure 1a). Its profile is broader than the sharp peak reported for oxynitrides grown by rapid thermal processing (RTP) [15,19], but is in agreement with studies in which a furnace was utilized[12-15]. It is seen that the oxynitride film consists of an O-rich layer near the top surface and a N-rich layer close to the interface. The SIMS Si profile (not shown here) shows a 'dip' in the Si concentration as the N concentration (close to the dielectric/Si interface) decreases, after which the Si concentration level becomes constant indicating that the substrate has been reached. This dip in the Si profile suggests bonding of Si with N and not with O, close to the interface[20], an observation supported by previous X-ray photoelectron spectroscopic(XPS) studies, too[19,21].



## Sputtering Time (sec)

Figure 1: SIMS depth profiles for films grown after 15 (a), 30 (b), 90 (c), 120 (d), and 150 min (e) in furnace I (3-in. in diameter), at 900°C, 2 slpm of N<sub>2</sub>O, and 1atm. The dielectric/Si interface in all the cases can be approximately located at the point where the O curve starts to become almost parallel to the horizontal axis, as indicated by the thick vertical line shown only in (a).

The N concentration profile resulting from 30 min of oxynitridation depicts a near doubling of the N peak concentration ( $N_{\text{peak}}$ ) without any substantial change in the peak position, accompanied by a slight increase in the film thickness (Figure 1b). Oxynitridation for 60 min is seen to result in very little additional N incorporated into the film, if any. A 90 min oxynitridation results in a rather substantial decrease in the  $N_{\text{peak}}$  (Figure 1c), indicating partial removal of N from the location it was previously incorporated at. It is important to note here that the flatter and broader N concentration profile obtained in the 90-minute growth run is comprised of two parts: (i) N inserted close to the dielectric/Si interface during the latter 30 minutes (approximately at 200-300 s on the abscissa), and (ii) previously incorporated N some of which has been removed during the last 30 minutes of processing (at about 100-200 s on the abscissa).

For longer oxynitridation times (e.g., 120 min), as the dielectric/Si interface moves deeper into the Si substrate, more N is incorporated closer to the new interface, accompanied by a continuous and gradual removal of previously inserted N (Figure 1d). The addition of more N closer to the new interface leads to a broadening of the profile with increasing oxynitridation time, as it is shown more dramatically in the 150-minute profile (Figure 1e). In fact, Figure 1e shows a dip almost in the middle of the N profile, thus separating it into 2 parts: the left part (at about 100-300 s on the abscissa) consisting of “left-over” nitrogen as a result of the gradual and continuous removal of the N incorporated early on during growth, and the right part (at about 400-600 s on the abscissa) which includes N inserted during the latter stages of the growth (e.g., here, after 120 minutes). This trend could be further studied to see whether a longer single oxynitridation processing step yields a bimodal N concentration profile, with two N peaks in the dielectric film, one near the top surface and the other near the dielectric/Si interface. Such a bimodal N profile has been obtained elsewhere with successive oxynitridation/oxidation processing steps[22,23].

## Furnace II (small diameter)

For dielectric films grown in furnace II, the SIMS O and N depth profiles of different samples with increasing oxynitridation times are shown in Figure 2. The 30-minute N concentration profile (Figure 2a) is about the same as the corresponding one obtained for furnace I (Figure 1a). After additional 30 minutes of growth, both processes, namely removal of previously incorporated N and N incorporation

closer to the interface, are seen to occur (Figure 2b). For the 90 min oxynitridation, Figure 2c shows that almost all incorporated N early on is now removed resulting in a sharper peak very close to the interface (Figure 2c) *in contrast* to the 90-minute N concentration profile obtained in furnace I (Figure 1d). The depth profiles after and 120 minutes (Figure 2d) of growth also show the N concentration peaking very close to the interface, in agreement with results reported by Singhvi and Takoudis[13]. These N profiles are *unlike* the broadened ones observed in furnace I for similar processing times.

Three additional differences between the N profiles probed in the two furnaces may also be pointed out. First, after 30 minutes of oxynitridation, the  $N_{\text{peak}}$  is slightly higher in the larger diameter reactor (furnace I); for longer processing times too, it appears to remain higher in furnace I than in furnace II. Second, the N removal rate closer to the top surface of the film is much higher in furnace II than in furnace I. Third, the dielectric film is seen to be thicker in the smaller diameter reactor (furnace II). In both furnaces, N is incorporated closer to the interface (though much more dramatically in the smaller diameter system), thereby suggesting that N does not replace O atoms in the bulk Si-O bonds[15].

These findings underline the effect of furnace scale up, linear velocity, and gas phase reactions on the oxynitridation process. The level and profile of the N concentration in the silicon oxynitride film are apparently affected by such factors. Both the incorporation and removal of N are observed to occur at different rates and at different growth stages in the two reactors studied. A possible reason for this may lie in interfacial strain relieving considerations. If N relieves strain at the Si/SiO<sub>2</sub> interface (and is therefore incorporated near that region), then its removal would be thermodynamically favorable only when incoming NO (surmised as the source of N incorporation[14]) is unable to diffuse through the N rich interfacial layer to react with the substrate Si. This proposition is supported by the fact that in both the furnaces, N removal is witnessed only after N concentration in the film reaches its peak value (i.e. after which, perhaps, it is able to block the diffusion of incoming NO towards the substrate).

Since N appears to play a critical role in the performance of silicon oxynitrides as future promising dielectrics, optimized furnace dimensions, flow rates, and heating elements of the reactors may have to be determined for desired pre-specified optimal N incorporation.

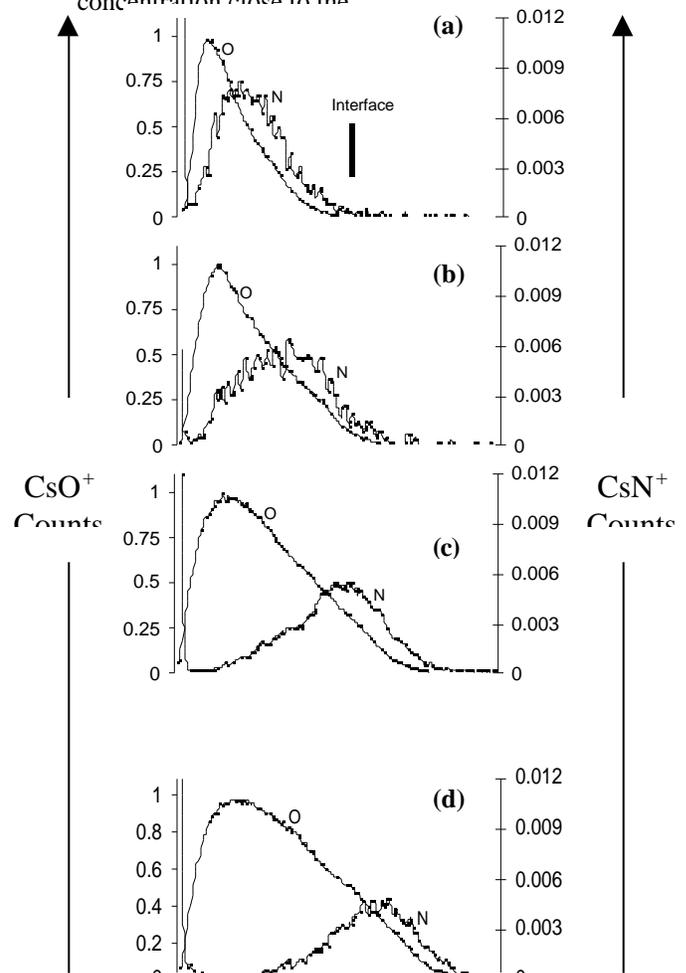
## Growth Model

From the results discussed above, a qualitative silicon oxynitride growth model is proposed the following points of which are noteworthy:

- 1) In the initial period (here, 15 minutes) of growth, both O and N incorporation take place with the O profile being closer to the top surface of the film. This is followed by retardation of oxidation reaction by the N incorporated in the solid phase. In the next 15 minutes of growth, the incorporated N retards the oxidation reaction gradually but more intensely, thus resulting in a sharp decrease of the growth rate, in agreement with other studies too (e.g., Tang *et al.*[16]). The growth

rate retardation seems to be proportional to the N concentration in the film.

- 2) Since the N removal process is either apparently absent (furnace I) or significantly lower than the incorporation rate (furnace II), the highest value of  $N_{\text{peak}}$  is reached after about 30 minutes of processing in nitrous oxide, also in agreement with Tang *et al.*[16] who suggested that most N in the oxynitride film is incorporated during the early stages of the process. This may have important implications on the development of optimal ultra-thin silicon oxynitridation processes, since further oxynitridation (a) can result in a decreased  $N_{\text{peak}}$  that may not be effective in forming a barrier for B penetration, for example, (b) may yield a higher N concentration in the bulk as observed in furnace I (thus, perhaps, degrading device performance[15]), and (c) can result in an increased film thickness, possibly outside the desired ultra-thin thickness regime.
- 3) Up to about 60 min of oxynitridation, the slowed down oxidation reaction as well as the N incorporation process continue. At later times, the N removal rate close to the top surface increases and proceeds in tandem with the N incorporation process closer to the interface. In the meantime, the oxidation reaction continues at even slower rate. For longer processing times, the N removal rate close to the top surface is clearly different in the two different furnace systems. This suggests that although solid state diffusion may be thought of as one of the plausible mechanisms for the removal of N close to the top surface as well as the increase of the incorporated N concentration close to the



## Sputtering Time (sec)

Figure 2: SIMS depth profiles for films grown after 30 (a), 60 (b), 90 (c), and 120 min (d) in furnace II (2-in. in diameter) at 900°C, 1atm, and 2 slpm of N<sub>2</sub>O.

interface, such a mechanism is clearly a minor contributor in these systems, if it is at all.

Different process-property relationships may, therefore, be implemented depending on the desired nitrogen concentration profile in silicon oxynitride films.

## Design Considerations

Since substantial variations are observed in N incorporation in the films grown in the two systems studied, a close look at the differences in reaction kinetics and transport phenomena occurring in such furnaces is now called for.

The residence time of the gases before reaching the wafers in furnace I can be calculated to be 10.6 s, resulting in a flow velocity of 2.9 cm/s; the corresponding values for furnace II are 2 s and 6.5 cm/s. Assuming the half-life of N<sub>2</sub>O decomposition to be equal to 2 s at 900°C as calculated by Tobin *et al.*[14], N<sub>2</sub>O is almost fully decomposed in furnace I before reaching the wafers, while this is not the case for furnace II. This leads to a lower NO content in furnace II and, hence, lesser N concentration in the film when compared with furnace I (Figures 1 and 2). But whether the lowering of NO content in the gas is equally reflected in the decreased solid-phase concentration of N or not, depends on how strongly the oxynitridation process is NO diffusion-limited at the conditions under study, and what the role of NO is in the growing dielectric films. Since O<sub>2</sub> has been suggested as the source of N removal from the oxynitride films[e.g., 18], it is possible that the rate of N removal is a function of the available O<sub>2</sub> and/or the N concentration in the film. The amount of O<sub>2</sub> available for N removal may differ in both the furnaces because of the difference in the extent of N<sub>2</sub>O decomposition, the O<sub>2</sub> mass transfer rate to the substrate surface, and the O<sub>2</sub> diffusion resistance in the solid film due to different film thickness. Therefore, N is being incorporated and removed at different rates in the two different oxynitridation reactors.

The gas-phase chemistry in a furnace can also be strongly affected by heat transfer[24]. As the feed gas enters the furnace at room temperature, it is heated through heat transfer from the furnace walls. A higher value of the heat transfer coefficient increases the rate of gas heating from the reactor walls, resulting in faster dissociation of N<sub>2</sub>O. The exothermic nature of the dissociation reaction may lead to additional heating of the gas[24]. But the higher value of the coefficient helps to dissipate the heat from the gas to the outside environment too. Whether a heat accumulation occurs or not in the gas mixture depends upon the amounts of heat released and dissipated. As the volume of furnace I is higher than that of

furnace II, the amount of N<sub>2</sub>O present in a furnace at a particular time is higher in furnace I. This leads to more heat released in furnace I as a result of the dissociation reaction. Further, since the gas-phase composition is different in the two furnaces as explained above, the heat transfer coefficient is also different, thus resulting in varied rates of gas heating/cooling. Besides, the heat transfer through the reactor walls depends upon the gas residence time. A more detailed study quantifying the above mentioned heat transfer effects is being pursued.

## SUMMARY-CONCLUSION

We have studied the behavior of N incorporation and removal processes with time in two furnaces of different dimensions at 900°C and 1 atm. At the growth conditions probed, the furnace dimensions and geometry appear to play a vital role, especially in identifying the position and the critical growth time at which the N removal starts/picks up. The N concentration profile is found to start (irrespective of the reactor dimensions used in the two furnaces of this study) with a peak in the bulk, closer to the dielectric/Si interface. But as silicon oxynitridation progresses, furnace dimensions are seen to have a strong effect on the N concentration profile movement as well as further incorporation of N into the thin film. To explain the observations, a qualitative model of progression of oxynitridation with time is thus proposed. Besides, results are also discussed in the context of furnace heat transfer effects, gas-phase chemistry, and our recent work suggesting O<sub>2</sub> as the source of N removal from oxynitrides[18]. Because the presence of nitrogen is critical for satisfactory performance of silicon oxynitrides, these findings can help to establish fundamental knowledge-driven process-property relationships for ultra thin dielectrics in current and future microelectronic applications. This is very important in order to design and scale up the oxynitridation process in different furnaces and to tune in any desired nitrogen concentration profile in a silicon oxynitride film with properties of specific interest.

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