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To cite this article: V Christiano and S G dos Santos Filho 2015 IOP Conf. Ser. Mater. Sci. Eng. 76 012002

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Physical characterization of ultrathin silicon oxynitrides grown by Rapid Thermal Processing aiming to MOS tunnel devices

V. Christiano\(^1\) and S. G. dos Santos Filho\(^1\)

\(^1\)University of São Paulo: LSI/PSI/EPUSP – São Paulo, Brazil.

E-mail: veronica@lsi.usp.br

Abstract. Oxynitrides were grown in a homemade Rapid Thermal Processor (RTP) using a low mass quartz carrier, to obtain thin oxynitrides over large areas of 3 inches silicon p-type wafers. Layers with thickness varying from 0.97 to 2.39 nm with uniformity better than 0.4%, were obtained at 700 and 850°C, in a mixed ambient of nitrogen and oxygen (4N\(_2\):3O\(_2\) in volume). The nitrogen concentration was obtained with the aid of X-ray photoelectron spectroscopy (XPS) and was 0.6 at%. On the other hand, the Si/O ratio in the oxynitride was approximately 1.9, indicating an almost stoichiometric SiO\(_2\) with a small amount of nitrogen. In addition, using the \(^{16}\)O(α, α) elastic-scattering signal at 3.039 MeV, the planar concentration of oxygen was 5.5x10\(^{15}\) cm\(^{-2}\) for the oxynitride grown at 850°C during 40s.

1. Introduction
The fabrication of metal-oxide-semiconductor (MOS) structures is a matter of increasing attention due to the aggressive downsizing, which also means thickness increasingly smaller. The main challenge to obtain efficient MOS tunnel devices is the achievement of high-quality uniform ultrathin dielectrics with small defect density and high dielectric strength [1-2]. Silicon oxynitrides grown by rapid thermal processing (RTP) are reported as interesting dielectrics for MOS devices, owing to their high quality of physical and electrical characteristics [1,3]. The incorporation of nitrogen during the film growth by RTP has been reported as beneficial for MOS devices due to the small amount of nitrogen distributed close to the oxynitride/silicon interface, which is responsible for a decrease of the leakage current, and an increase of the resistance to boron penetration [4].

In this work, it is shown the physical characterization of SiO\(_2\)N\(_x\) films grown in a homemade RTP using a low mass quartz carrier, considering different processing conditions (temperature, processing time and environment).

2. Experimental
Si wafers were chemically cleaned by RCA cleaning [5]. The recipe used for the RCA cleaning consisted of two baths: (a) 400 ml H\(_2\)O + 25 ml NH\(_4\)OH (38%) + 175 ml H\(_2\)O\(_2\) (37%) and (b) 400 ml H\(_2\)O + 100 ml HCl (38%), heated at 90°C, for 15 min. Between each bath, the wafers were immersed in deionized (DI) water for 5 min. Finally, it was performed a dip in fluoridric acid, in the proportion 80:1 (80 H\(_2\)O + 1 HF(49%)), for 100 s, at room temperature and, other immersion in DI water for 3
min. Immediately after the cleaning, the wafers were oxidized by RTP at the temperatures of 700 or 850°C as shown in the following.

2.1. Homemade RTP

The homemade RTP using a low mass quartz carrier is composed by a cover at the end of the furnace, made in quartz, with a hole to allow the quartz rod introduction. In addition, a quartz carrier for samples of 3 inches is fixed at the end of the quartz rod inside the furnace (see figure 1).

![Schematic view of the homemade RTP.](image)

The rapid thermal processing was performed by the quick entry of the wafer into the furnace till its center position, ensuring the natural increase of the temperature till a plateau. The quartz carrier, for 3 inches wafers, was made using three thin brackets welded on the quartz rod in order to assure low thermal mass in contact with the wafer, so that, temperature uniformity was better than 4% [7].

2.2. Silicon oxynitrides grown

The growth procedure to obtain the silicon oxynitrides (SiO$_x$N$_y$) were:

- The wafer was positioned in the beginning of the furnace during 5 min in ultrapure nitrogen for the wafer achieve initial temperatures of 495°C (figure 2a) or 600°C (figure 2b) for the furnace previously calibrated at 700°C or 850°C, respectively.
- The gas flow was turned on 5 s before starting the RTP. The wafers were processed in ultrapure N$_2$+O$_2$ ambient (4N$_2$:3O$_2$, in volume).
- The quartz rod was pushed in 5 s until the wafer could reach the center position of the furnace, to be processed during 10, 20, 40, 80 and 160 s, for 700 and 850°C.
- After the oxidation, the removal of the samples was during 5s, where the quartz rod was pulled until the wafer could reach the front position of the furnace and then, the oxygen flow was turned off.
- The wafer was maintained during 5 min. at the beginning of the furnace before its removal to the ambient of the clean room.

Figures 2a and 2b show temperature profiles starting with an increasing ramp, followed by the temperature plateau. The processing time is measured from the initial temperature of 495°C or 600°C till to the soak temperature of 700 or 850°C, respectively. In addition, it is important to point out that it takes 6 and 9s to achieve ninety percent of the soak temperature, respectively, for 700 or 850°C.
2.3. Physical Characterization

The silicon oxynitride thicknesses were estimated by an ellipsometer (Autoel IV), using a wavelength of 6.328 nm. All the values of thickness in the results and discussion correspond to the arithmetic average of nine points spaced 2 cm from each other, along of the three inches wafers.

X-ray photoelectron spectroscopy (XPS) was employed to obtain the nitrogen concentration in the thin silicon oxynitrides by means of a UNI-SPECS UHV commercial spectrometer with an Mg X-ray source. The composition of the surface was determined considering the relative ratios of the peaks for Si 2p, O 1s and N 1s in the spectra, taking into account the atomic sensitivity factors [6].

RBS spectra were taken under normal incidence of a He$^+$ beam and with a scattering angle of 80° using an accelerator Pelletron - Tanden, model 55 DH/NEC. The $^{16}$O($\alpha$, $\alpha$) elastic-scattering signal was observed at 3.039 MeV, which presents an enhanced sensitivity for oxygen detection (also known as oxygen resonance [7]). The planar concentration of oxygen was extracted from $^{16}$O($\alpha$, $\alpha$) elastic-scattering signal at 3.039 MeV from the relation of areas of the oxygen signal for a given measured sample and a reference sample with a well-known planar concentration of oxygen, as follows [7]:

$$N_O = \frac{A_O}{A_R} \frac{\Omega Q_{RBS} \sigma_R \Gamma}{\left[\varepsilon_0^R\right]} \tan^{-1} \left( \frac{N_R \left[\varepsilon_0^R\right]}{\Gamma} \right) \left[ \frac{\Omega Q_{RBS} \sigma_R \Gamma}{\left[\varepsilon_0^R\right]} \right]$$

Where $A_O$ is the area of the oxygen peak of the measured sample, $A_R$ is the area under the oxygen peak of the reference sample, $\Omega$ is the solid angle for measurement, $Q_{RBS}$ is the particle flux or the integrated charge of the backscattered He$^+$ beam from the sample, $\sigma_R$ is the cross section at the resonance energy, $\Gamma$ is the half-width of the oxygen peak, $\left[\varepsilon_0^R\right]$ is the stopping cross section of the incident beam at the resonance energy for the measured sample and $\left[\varepsilon_0^R\right]$ is the stopping cross section of the incident beam at the resonance energy for the reference sample.

3. Results and discussions

At first, oxynitrides were grown at 700 and 850°C in a mix of pure N$_2$ and O$_2$ (4:3). The processing times were 10, 20, 40, 80 and 160 s. The graphs of thickness as a function of the processing time are shown in figure 3.

The samples processed at 700°C exhibited a rapid initial oxidation starting from the processing time of 10 s with a growth rate of 0.12 nm/s and becomes approximately constant and equal to 0.0025 nm/s in the range of 40 to 160 s. This last situation can be modeled by an oxynitridation
process dominated by surface reaction according to the model of Deal and Grove [8]. On the other hand, the rapid initial oxidation can be formerly associated to an enhanced rate due to the increasing ramp of the temperature profile since the temperature profile is not enough to saturate at a plateau.

For samples processed at 850°C, an approximately linear growth rate of 0.08 nm/s was observed in the range of 10 to 80s followed by a tendency of being quadratic for processing times higher than 80 s. In this case, the rapid initial oxidation must be occurred for the processing time lower than 10 s and the growth rate became constant in the range of 10 to 80 s where the oxynitridation process is possibly dominated by surface reaction according to the model of Deal and Grove [8].

In addition, the oxynitrides films grown with thickness in the range of 0.97 to 2.39 nm, as shown in figure 3, presented uniformity better than 0.4% in large areas of 3 inches silicon wafers.

XPS analysis allows one to obtain the atomic concentration at the surface region (around 4 nm in depth) for samples with thin layers besides to give the local chemical structure, from the signals associated to the chemical elements in these samples [8-10]. Figure 4 shows the XPS spectra where it is indicated the signals for N 1s and O 1s in expanded horizontal scale. The O 1s signal is mainly due to oxygen bonded to silicon (O-Si) at 532.6 eV, and the N 1s signal is compounded of nitrogen bonded to oxygen (N-O) at 402.4 eV, both pointing to the formation of SiO$_x$N$_y$ grown by RTP. Based on the spectra exhibited in figure 4, the atomic concentration of nitrogen is 0.6% and the Si/O ratio in the oxynitride is approximately 1.9, which means an almost stoichiometric SiO$_2$ with a small amount of nitrogen.

Figures 5a and 5b shows, respectively, the RBS spectra for the SiO$_2$ reference and for the oxynitride grown at 850°C during 40s, both at the oxygen resonance-energy of 3.039 MeV. Using the areas under the oxygen peaks for the oxynitride (A$_O$) and for the 20nm-thick SiO$_2$ reference (A$_R$), the total planar concentration of the oxynitride was calculated from equation (1) and resulted 5.5 x 10$^{15}$ cm$^{-2}$.

**Figure 3.** Average thickness as function of the RTP time for 700 and 850°C.

**Figure 4.** O 1s XPS spectra for the sample oxynitrided at 850°C during 40s.
4. Conclusions
Thin silicon oxynitrides have been grown in a homemade RTP using a low mass quartz carrier. The thicknesses were in the range of 0.97 to 2.39 nm with uniformity better than 0.4% in large areas of 3 inches silicon wafers. The samples processed at 700°C exhibited a rapid initial oxidation starting from the processing time of 10 s with a growth rate of 0.12 nm/s and becomes approximately constant and equal to 0.0025 nm/s in the range of 40 to 160 s. This situation was modeled by an oxynitridation process dominated by surface reaction. For samples processed at 850°C, an approximately linear growth rate of 0.08 nm/s was observed in the range of 10 to 80 s. XPS presented O 1s signal mainly due to oxygen bonded to silicon (O-Si) at 532.6 eV, and the N 1s signal of nitrogen bonded to oxygen (N-O) at 402.4 eV, both pointing to the formation of SiO$_x$N$_y$ grown by RTP. On the other hand, the atomic concentration of nitrogen is 0.6 at% and the Si/O ratio in the oxynitride is approximately 1.9, which means an almost stoichiometric SiO$_2$ with a small amount of nitrogen. In addition, the planar concentration of oxygen was extracted from $^{16}$O($\alpha$, $\alpha$) elastic-scattering signal at 3.039 MeV for the oxynitride grown at 850°C during 40 s and resulted 5.5 x 10$^{15}$ cm$^{-2}$.

5. Acknowledgements
The authors would like to thank CNPq for the financial support and Laboratório de Espectroscopia de Fôtoelétrons from UNESP-Araraquara for the XPS measurements.

References
[1] Depas M, van Meirhaeghe R L, Laflère W H and Cardon F 1993 Microelect. Eng. 22 61
[2] Chang K-M, Yang W-C, Chen C-F and Hang B-F 2004 J. Electroch. Soc. 151 F118
[3] Lu Z H, Tay S P, Cao R and Pianetta P 1995 Appl. Phys. Lett, 67 2836
[4] Xu Y et al 2014 J. Appl. Phys. 115 033502
[5] Kern W and Puotinen D A 1970 RCA Rev. 31 187
[6] Scofield J H 1976 J. Electron Spectrosc. and Related Phenomena 8 129
[7] Mezey G 1976 Ion Beam Surface Layer Analysis vol 1, ed O Meyer (New York: Plenum Press)
[8] Deal B E and Grove A S 1965 J. of Appl. Phys. 36 3770–78
[9] Wagner C D, Riggs W M, Davis L E, Moulder J F and Mullenberg G E 1979 Handbook of x-ray photoelectron spectroscopy (Minnesota: Perking-Elmer Corporation)
[10] Kawase K, Tanimura J, Kurokawa H, Kobayashi K, Teramoto A, Ogata T and Inoue M 1999 Materials Science in Semiconductor Processing 2 225
[11] Green M L, Gusev E P, Degraeve R and Garfunkel E L 2001 J. of Appl. Phys. Reviews 90 2057