XPS study of nanoscale SiO$_x$N$_y$ layers synthezised by plasma immersion implantation of nitrogen

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Abstract. Plasma immersion implantation (PII) of nitrogen into Si was used to prepare nanoscale SiO$_x$N$_y$ layers. The SiO$_x$N$_y$ layers were synthesized in a cycle of PII followed by a high-temperature treatment in O$_2$ ambient. Nitrogen was implanted into the Si substrate with energy of 2 keV and a fluence in the range of $10^{16} - 10^{18}$ cm$^{-2}$. The implanted structures were subjected to a high-temperature annealing at 1050 ºC for 10 or 20 minutes in dry oxygen at atmospheric pressure. X-ray photoelectron spectroscopy (XPS) revealed the chemical bonds and surface layer composition. The atomic concentrations of the SiO$_x$N$_y$ constituents were obtained. By a combination with a sputter experiment the N concentration was found to be about 2.6 at. %. The low N content is due to the nitrogen escaping from Si during the oxidizing annealing. The thickness of the SiO$_x$N$_y$ layer for the highest implantation fluence did not exceed 10 nm as revealed from ellipsometric and XPS data analyses.

1. Introduction
Silicon oxynitride SiO$_x$N$_y$ thin layers have found different applications in the semiconductor industry. They have been used as a substitute for SiO$_2$ gate oxide layers to reduce the gate leakage and boron penetration through the oxide and to adjust the threshold voltage. Nanoscaled SiO$_x$N$_y$ layers have also found applications as a low-defect interface layer between a Si substrate and high-$k$ layers deposited over it. Resistance to oxidation and a lower mechanical stress are other important properties of the SiO$_x$N$_y$ layers. The large flexibility in tuning the refractive index between 1.46 of SiO$_2$ and 2.0 of Si$_3$N$_4$ is important for use in optical communication devices. An attractive opportunity of major significance is the possibility to integrate electronic and optical components on the same Si chip.

The growth of ultrathin oxynitride layers by plasma ion implantation (PII) of nitrogen into Si, followed by thermal processing in an oxidizing ambient, has been reported for different electronic and optoelectronic applications [1-3]. Recently, we suggested that the presence of N in the Si promotes the formation of Si-Si bonds during the synthesis of SiO$_x$N$_y$ in an O$_2$ ambient [4]. Clustering of the Si-Si bonds can result in the formation of nanoparticles. Different N concentrations and distributions...
through the oxide can be achieved using a variety of processing conditions, such as implantation energy and fluence, annealing temperature and ambient. A better knowledge of the structural properties of the grown SiO$_x$N$_y$ layers is required in view of process development and engineering and for process control.

The optical and structural properties of SiO$_x$N$_y$ have been thoroughly studied mainly in the form of CVD deposited layers [5,6]. Information has been obtained on the chemical bonds and their concentration in dependence of the deposition parameters, such as gas flow ratio and temperature [7]. The formation of Si nanocrystals has also been discussed [8, 9]. The results reported have mostly been related to films containing hydrogen and the latter’s effect on the film’s properties [10, 9]. In our study, the deposition in a PII module allowed us to produce hydrogen-free oxides.

The problem of finding the chemical content and composition of SiO$_x$N$_y$ layers can be approached by different methods. In the present study, X-ray photoelectron spectroscopy (XPS) as a non-destructive method was applied to identify the different bonds, such as Si-O and Si-N in the SiO$_x$N$_y$ matrix. By combining it with a sputtering technique, we gathered information about the distributions through the SiO$_x$N$_y$ thickness. The characterization was completed by using spectroscopic ellipsometry (SE).

2. Experimental details

The experiments were carried out on Cz-grown Si(100) p-type wafers with a resistivity of $5 \sim 8$ ohm cm. The first step of the processing was bombardment by atomic nitrogen (N$^+$) and molecular (N$_2^+$) ions into a shallow Si surface region by plasma-beam ion immersion (PII) implantation in a planar plasma reactor. The implantation of nitrogen ions was implemented at normal incidence at energy of 4 keV and a fluence within the $10^{16} \sim 10^{18}$ cm$^{-2}$ interval. The second step was elimination of the possible surface contamination through a short dip in diluted HF. As the last step, the implanted Si substrates were thermally annealed in a conventional furnace at 1050 °C for 10 minutes and 20 minutes in a dry oxygen environment at atmospheric pressure. The ellipsometric measurements were performed on a variable-angle spectroscopic ellipsometer (J.A. Woollam Co.).

The depth profiles of the implanted ions were derived using the SRIM simulation code based on a Monte-Carlo method for different annealing durations taking into account the diffusion of the implanted species.

The composition of the layers was identified by XPS. The XPS measurements were carried out with PHI Quantera equipment working at the low residual pressure of $10^{-7}$ Pa and using monochromatic Al-K$\alpha$ radiation (1486.6 eV). The charging effect was minimized by using dual beams (electrons and Ar ions) as a neutralizer. The binding energy positions were obtained with a precision of 0.2 eV.

3. Results and discussion

The thickness of the SiO$_x$N$_y$ synthesized layers as obtained from the SE measurements varied between 10 nm and 40 nm with the N$^+$ fluence (figure 1). A reduction of the oxidation rate was observed as the N concentration in the Si substrate increased. The analysis based on the Deal-Grove model pointed to a complicated kinetics with diffusion and surface oxidation rates determined by the implantation defects and the nitrogen species [11]. The oxidation of the implanted Si was mainly determined by the oxidant diffusion through the already formed oxide layer. The thickness of the layers was determined using the ratio of the areas of the XPS peaks of the oxide to the substrate Si 2p peaks upon sputtering [12, 13]. A very good agreement with the SE thickness data was found, as illustrated in figure 1 for a fluence of $10^{18}$ cm$^{-2}$.

The XPS study yielded information on the bonding arrangements of silicon, oxygen, and nitrogen atoms and the relative elemental atomic content. Figure 2 shows photoemission spectra from SiO$_x$N$_y$ layers grown in Si implanted with the highest fluence of $10^{18}$ cm$^{-2}$.

The oxygen spectra for the different fluences closely resemble each other, illustrated by the spectrum in figure 2a for $10^{18}$ cm$^{-2}$ fluence. The Si2p core level spectrum in figure 2b shows two separate components in the range 98 – 107 eV. The main part located at 103.5 eV is ascribed to Si$^{4+}$.
oxidation state in silicon oxide and/or nitride [14]. The low energy peak at 99.2 eV indicates Si-Si bonds usually taken as substrate contribution. However, the much smaller intensity of this peak has been interpreted as originating from nanosized Si clusters in the grown layer. The N1s emission shows a multicomponent behavior as evident in figure 2c. The deconvolution reveals peaks at about 398.6 eV and 400 eV characteristic for Si-O-N bonding in different configuration usually assigned to N(SiO3)_{x}, O–N–Si2.

Analyzing the contributions of the different atoms in the SiO\textsubscript{x}N\textsubscript{y} composition, we can trace the evolution of the layer structure as the N\textsuperscript{+} fluence and the annealing time are increased. The results for the atomic concentrations are presented in figure 3. It can be seen that at the annealing time of 10 minutes, the nitrogen content progressively increases at the expense of oxygen as the N\textsuperscript{+} fluence is increased. Thus, the composition progresses from SiO\textsubscript{x}N\textsubscript{y} with very low N content, nearly SiO\textsubscript{2}, to a layer with a fourfold increase of the N concentration. Nevertheless, the N concentration of 2 at. % at a fluence of 10\textsuperscript{18} cm\textsuperscript{-2} still can be estimated as low. At the longer annealing time of 20 minutes, the N concentration has a nearly constant value at a very low level so that the film composition approaches SiO\textsubscript{2}.

A similar tendency of an increase in the N content with the ion fluence was detected by the spectroscopic ellipsometry investigation, where the volume fraction of the Si\textsubscript{2}N\textsubscript{3} component was found to vary from 3 vol. % to 16.8 vol. %, in spite of the 5,5-fold increase against the 4-fold one in the atomic

![Figure 1. Thickness of the synthesized layers as a function of the N\textsuperscript{+} PII fluence.](image1)

![Figure 2. Binding energy of N1s, Si2p and O1s core levels in layers formed into Si implanted at a N\textsuperscript{+} fluence of 10\textsuperscript{18} cm\textsuperscript{-2}.](image2)

![Figure 3. Relative concentrations of the different atoms in the SiO\textsubscript{x}N\textsubscript{y} layer as a function of the N\textsuperscript{+} fluence.](image3)
fractions above in figure 3b. However, one should bear in mind that, in the present XPS study, the photoemission originates from the ~5 nm top surface layer, while the ellipsometric data refers to the total layer volume. The implantation of the ions follows a depth profile in the Si substrate with a low concentration near the surface. Diffusion and escape of N are quite possible during the oxidation in the annealing cycle.

The SiOxNy layers were characterized using XPS depth profiling in a sputtering cycle with sputter rate of about 2.5 nm/min. The resulting depth distribution for a 10-nm layer is given in figure 4a. It shows a decreasing concentration mainly due to N escape from the 10 nm layer. The total concentration obtained by integrating the ion distribution in figure 4a over the whole layer amounts to 2.6 at. %.

A flattened implantation profile during annealing was inferred by modelling the implantation profile while taking the diffusion into account, as is evident in figure 4b. It can be seen that the two profiles, the measured and the modelled, differ by the in-depth distributions.

The density of N atoms in the volume of the sputtered film studied as calculated from the profile in figure 4a amounts to $1.2 \times 10^{22}$ cm$^{-3}$. The density obtained from the simulated profile in figure 4b for the same volume is $3.1 \times 10^{22}$ cm$^{-3}$, which is of the same order of magnitude, albeit slightly higher. The differences in the calculated and the measured nitrogen distributions imply that, most probably, the diffusion is not the only process contributing to nitrogen migration during SiOxNy synthesis.

4. Conclusions
XPS investigation of SiOxNy layers synthesized by high-temperature annealing in O$_2$ ambient of plasma-beam nitrogen ion implanted Si substrates revealed peaks characteristic for Si-O-N bonding in different configurations. The atomic concentrations of the Si, O and N were determined. The nitrogen distribution in the synthesized layer was obtained revealing decreasing in-depth concentrations. This was compared with the flat distribution obtained by SRIM modelling and taking into account the nitrogen diffusion during oxidizing annealing. The layers were identified as containing SiOxNy with a low N content of 2.6 at. %.

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