Annealing of Si surface region modified by plasma immersion implantation of nitrogen

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Abstract. In the present work, the formation of a nano-scale Si surface layer is studied after high-temperature annealing of Si modified by shallow plasma immersion implantation of nitrogen with fluences of $10^{16}$ - $10^{18}$ cm$^{-2}$. The implanted profiles of the atomic ($\text{N}^+$) and molecular nitrogen ($\text{N}_2^+$) are modeled by SRIM for different annealing durations taking into account the diffusion process. The presence of Si-O and Si-N bonds is established by Fourier (FTIR) spectral analysis and spectroscopic ellipsometry (SE). The refractive index value measured at 632.8 nm varies between 1.46 and 1.59, corresponding to a low $y/x$ ratio. The models using VIS and IR ellipsometric data reveal formation of nanostructured SiO$_x$N$_y$ layer with Si inclusions.

1. Introduction
Silicon oxynitride films find different applications as an important dielectric material. It exhibits low absorbance and adjustable refractive index between 1.46 ($\text{SiO}_2$) and 1.9 ($\text{Si}_3\text{N}_4$) [1], being thus suitable for optoelectronic devices. Low-energy ion-implantation of nitrogen for formation of silicon nitride layers offers an alternative to the traditional CVD deposition methods with the advantage of ensuring clean conditions. By adjusting the implantation parameters and the post-implantation conditions, high-quality nanoscaled layers with easily controlled composition and thickness [2] can be produced.

The aim of the present study was to synthesize ultrathin SiO$_x$N$_y$ layers on the silicon surface with controllable nitrogen concentrations by using shallow nitrogen plasma implantation and subsequent annealing in oxidizing ambient.

2. Experimental details
The experiments were carried out on Cz-grown (100) p- and (111)n-type silicon substrates with resistivity of 5-8 Ohm.cm. The first step of the processing was the incorporation of nitrogen ions into the near surface Si region through plasma-beam ion immersion (PII) implantation technology. The $\text{N}^+$ ion beam with energy of 4 keV was directed at normal incidence with fluences ranging from...
$10^{16}$ to $10^{18}$ cm$^{-2}$. It should be noted that the implanted species are atomic nitrogen ($N^+$) and molecular ($N_2^+$) ions from the plasma. The implanted Si substrates were subjected to high-temperature furnace annealing at 1050 °C up to 20 min in dry oxygen O$_2$ ambient at atmospheric pressure.

The optical and structural properties of the synthesized Si$_{x}$O$_y$N$_z$ layers were studied in detail with spectroscopic ellipsometry (SE) in the visible (VIS-SE) and in the infrared (IR-SE) range and Fourier transform infrared (FTIR) transmission spectroscopy. The ellipsometric measurements were performed in the range 190–1700 nm at an angle of incidence of 70° on a J.A. Woollam Co. variable-angle spectroscopic ellipsometer. The infrared (IR) spectroscopic measurements were carried out using a Perkin-Elmer 1430 IR spectrophotometer in transmission mode at normal incidence. The spectra were collected in the spectral range from 400 to 4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ at room temperature. The depth profiles of implanted ions and vacancies 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.

3. Results and Discussion

The thickness and the refractive index of the layers synthesized on Si substrates were estimated from the VIS-SE ellipsometric data. Figure 1 shows the thickness and the refractive index values at a wavelength of 632.8 nm of the layers for implantation with different N$^+$ fluencies and different annealing durations. The refractive index reaches 1.59, corresponding to a low y/x ratio.

![Figure 1. Thickness (a) and refractive index (b) of the synthesized layers on n-Si (full symbols) and p-Si (empty symbols) as a function of N$^+$ PII implantation fluence.](image)

The process of Si$_{x}$O$_y$N$_z$ formation is determined to a high extent by the profile of the implanted nitrogens and the induced defects, such as vacancies and interstitials, N and Si. Taking into account that the plasma implantation ambient provides N$^+$ and N$_2^+$ ions; figure 2 presents the ion and the vacancy profiles obtained by the SRIM modeling. It is seen that the concentration of N atoms available for Si$_{x}$O$_y$N$_z$ formation changes substantially with the depth. For both N$^+$ and N$_2^+$, the concentration of vacancies is much higher than the concentration of the implanted nitrogen atoms. The results of SRIM modeling, given in figure 2, show the expected depth of nitrogen ion penetration with a maximum concentration located at 14.4 nm for N$^+$ and 8.3 nm for N$_2^+$ below the Si surface. It should be stated that for $10^{18}$ cm$^{-2}$, the concentrations corresponding to the profiles are close to a nitrogen content of $5.8\times10^{22}$ cm$^{-3}$ of stoichiometric Si$_3$N$_4$ over a substantial depth in the Si substrate [3].

The Si$_{x}$O$_y$N$_z$ layer formation is accomplished by formation of Si-N and Si-O bonds. The vacancies play an important role for diffusion of the oxidizing species and as available sites for N and/or Si atoms. It can be suggested that the local concentration ratio of the available atoms and vacancies will substantially determine the reactions leading to formation of Si$_{x}$O$_y$N$_z$, i.e., the degree of nitridation through the formed layer.

The high temperature synthesis can be alter the nitrogen implantation profile due to diffusion of N atoms. During annealing under oxidation conditions, nitrogen atoms already present in the Si network...
will compete with the diffusing oxygen to form Si-bond. The presence of oxygen can influence the impurity diffusion. The implanted nitrogen can be found mostly at interstitial position forming directly interstitial pairs, i.e., N-N dimers [4]. Only a very small amount of N goes to substitutional Si sites [4].

The N-N dimer was found to move with an activation energy of ~3 eV, a value very close to the experimentally found energy for diffusion of nitrogen in Si. We suggest that the N$_2$+ implants serve as a N-N dimmer precursor. Therefore, we examined the N$_2$ migration at the annealing temperature of 1050°C. The results from the simulation of the implantation profile in the Si substrate are plotted in figure 3 for annealing times of 10 and 20 min. For comparison, the as-implanted ion profile is also given. The simulation was performed using the implantation profile and standard diffusion equations with a diffusion coefficient $D = D_o \exp(-E_a/(kT))$, where $D_o = 0.87 \times 10^{-4}$ m$^2$s$^{-1}$ and the activation energy $E_a$ = 3.9 eV. The broadening of the profile is evident and the nitrogen concentration decreases in the whole implanted region, becoming substantially lower than the value of $5.8 \times 10^{22}$ cm$^{-3}$ for stoichiometric Si$_3$N$_4$ [3], substantiating the assumption for formation of SiO$_x$N$_y$ with low N content. Moreover, a contribution to this effect comes from the high outdiffusion of the implanted atoms because of the shallow plasma implantation. No results are shown in figure 3 for the N+ migration since the diffusion was found to proceed rapidly with a barrier of only 0.4 eV leading to flattened N profile at an insignificant low concentration level.

Information that SiO$_x$N$_y$ synthesis terminated with formation of Si-N and Si-O bonds was obtained from the IR spectra analysis. No bands connected to the Si–H (2170 cm$^{-1}$), N–H (3350 cm$^{-1}$) or O–H (3640 cm$^{-1}$) bonds were detected. The IR transmission spectra are shown in figure 4 in the range below 2000 cm$^{-1}$ since the main bands for SiO$_x$N$_y$ appear up to about 1400 cm$^{-2}$. Evidence of SiO$_x$N$_y$ formation is the broad band in the range of 650-1000 cm$^{-1}$, marked in figure 4, attributed to the stretching mode of Si-N bonds. This band is observed in all spectra; its intensity increases with the N fluence. A band related to Si-N stretching bonds in silicon nitride is known to appear within the 800-900 cm$^{-1}$ range with position and intensity depending on the y/x ratio in Si$_x$N$_y$ [5-7]. One should note that as the N fluence increases, the intensity of the 1096 cm$^{-1}$ band decreases because of the increased implantation damage and enhanced SiOx formation [8, 9]. The band becomes less pronounced and the full width at half height (FWHH) increases with the fluence as seen in the inset of figure 4. This is an indication that the structure of the synthesized layer becomes less ordered. The rocking mode of Si–O–Si bonds at 460 cm$^{-1}$ is also present, obviously independent of the ion fluence. This is reasonable, since this mode is not being influenced by structural changes [8]. The bending mode of the Si–O bond at 800 cm$^{-1}$ cannot be distinguished because it overlaps with the broad Si-N band. The band at 614 cm$^{-1}$ is typical for the
Si–Si bond vibration and is an indication for the presence of Si-Si clusters. These considerations allow estimation of the synthesized layer as silicon-rich SiOxNy with Si inclusions.

Additional information about the chemical composition and molecular vibrations is gained from ellipsometric measurements in the IR region. Figure 5 shows the spectra of the $\Psi$ angle for the studied layers. The $\Psi$ spectra in figure 5 a for 10 min annealing contain a feature at 1250 cm\(^{-1}\). The intensity of this peak decreases steadily with the ion fluence without the characteristic shift. It can be ascribed to the stretching LO-phonon vibration mode of Si-O-Si bonds. Due to the Berreman effect, this peak appears in the IR reflectance spectrum recorded at a proper incidence angle but it is not present in the normal incidence transmittance IR spectrum. The peak around 1250 cm\(^{-1}\) was found in native oxides and in thermal silica, as well as in SiOx [10]. A shoulder at about 1150 cm\(^{-1}\) is an indication of Si-N bond formation, as is typical for Si3N4 [11]. Upon prolonged annealing for 20 min, the $\Psi$ angle spectra change, as can be seen in figure 5 b. The shoulder at about 1150 cm\(^{-1}\) has become clearly pronounced, which evidences formation of Si3N4.

Conclusions

SiOxNy layers were synthesized by high temperature annealing in O\(_2\) ambient of plasma-beam nitrogen ion implantation for different durations. The FTIR analysis revealed the presence of Si–N bonds and SiOx depending on the implantation fluence. The refractive index was found to increase with the ion fluence up to 1.59, implying a low y/x ratio. The IR-SE analysis revealed a gradual increase of the Si3N4 fraction. The FTIR and VIS-SE experimental results, as well as the SRIM–based modeling, allowed us to identify the layers as nanostructured silicon-rich SiOxNy films with low N content.

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