High Performance Optical Waveguides based on Boron and Phosphorous doped Silicon Oxynitride

Fei Sun*, Alfred Driessen, Kerstin Wörhoff
Integrated Optical Micro Systems group, MESA+ Research Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT

Silicon oxynitride (SiON) is a highly attractive material for integrated optics, due to its excellent properties such as high transparency, adjustable refractive index and good stability. In general, the growth of SiON layers by plasma enhanced chemical vapor deposition (PECVD) is followed by a high temperature annealing step in order to remove hydrogen and to achieve low propagation losses in the 1.5-μm wavelength window. The high annealing temperature (>1100°C) required for sufficient hydrogen removal induces, however, side effects like significant inter-layer diffusion and micro-cracks resulting in deterioration of the device performance.

In this paper compositional and optical properties of as-deposited and annealed boron (B) and phosphorous (P) doped SiON layers were investigated. The doped layers have been fabricated by introducing PH3 and B2H6 gaseous precursors into the PECVD process. Hydrogen contents of the samples have been studied by Fourier transform infrared (FTIR) spectroscopy. Compared to undoped film, a 50% reduction of the hydrogen content was measured in as-deposited P-doped SiON layers. Further reduction down to the FTIR detection limit was achieved upon annealing at temperatures as low as 700°C.

Besides hydrogen reduction the reflow properties of B and P doped SiON are also highly relevant for the realization of low-loss integrated optical circuits. Reactively ion etched channel waveguides have been reflowed applying a temperature of 900°C. Significant reduction of the sidewall roughness has been confirmed by scanning electron microscopy.

Keywords: Silicon oxynitride, optical waveguides, reflow, boron and phosphorus doping, sidewall roughness reduction

1. INTRODUCTION

Silicon oxynitride (SiON) is an amorphous material with excellent electrical, optical and mechanical properties being attractive for a large range of application fields1-5. The refractive index of the CVD-grown SiON layers can be adjusted from 1.46 (silicon dioxide, SiO2) to 2.01 (silicon nitride, Si3N4). Particularly attractive for optical applications is the high transparency of silicon oxynitride over a large wavelength range, from visible to infrared. These advantages have made SiON a widely applied material for photonic devices and integrated optical platforms1-5.

Chemical vapor deposition (CVD) is the most commonly applied method for the fabrication of SiON layers. Highly uniform thin films can be reliably deposited by means of reaction between different precursors with the aid of high temperature and/or plasmas. By adjusting the ratio between the different precursors, the atomic concentration of different elements within the SiON layer, and its corresponding refractive index, can be adjusted very conveniently. However, the application of hydrogen-containing precursors, such as SiH4 and NH3, in the deposition process, inherently results in the incorporation of Si-H and N-H bonds in the layers. The vibrational overtones of these bonds cause optical absorptions6,7 in the wavelength range around λ=1.5μm, being relevant for the 3rd telecom window. The hydrogen content in the layers can be reduced by high-temperature annealing8,9. The annealing temperature required for sufficient hydrogen removal is, however, as high as 1100°C. Since at such high annealing temperatures several undesired side effects, like interface diffusion, shrinkage and eventually layer cracking5,8, occur, the fabrication of hydrogen-free SiON layers at significantly reduced temperatures developed into one of the main research challenges in this field.

Furthermore, the fabrication processes of SiON-based channel waveguides, such as lithography and etching, will inevitably result in roughness on the channel sidewalls. This sidewall roughness is known to induce increased...
propagation losses through scattering. Since the amount of channel waveguide loss is decisive for the level of device complexity, which can be fabricated on a chip at an acceptable total loss value, the reduction of the sidewall roughness is highly-relevant for future applications of SiON technology.

By the introduction of boron (B) and/or phosphorous (P) into the SiON fabrication process, the above-mentioned research challenges can be addressed. The dopant incorporation will shift the bonding preferences and weaken the chemical bonds in the layers. Thus, the possibility of hydrogen bonds formation is expected to be reduced, and the required annealing temperature for further hydrogen removal will be decreased. Based on the considerably lower melting points of boron and phosphorus oxides, as compared to high melting temperature for SiON compounds, reflow of the B and P-doped layers at sufficiently low temperatures is expected. Consequently, the sidewall roughness of channel waveguides based on B and P-doped SiON will be reduced by the reflow process.

In this paper, boron and phosphorus-doped SiON layers with different B and P concentrations are deposited, followed by annealing of the samples at varied temperatures. The properties of the as-deposited and annealed layers are characterized and the measurement results are discussed. The reflow behavior and sidewall roughness reduction of channel waveguides are investigated as well.

2. EXPERIMENTAL DETAIL

A plasma enhanced chemical vapor deposition (PECVD) process has been applied for the fabrication of the SiON layers for the presented study. All the depositions were carried out in a load-lock-equipped Oxford Plasmalab System 133 PECVD reactor. The layers were deposited on p-type <100> oriented 100-mm silicon wafers at a substrate temperature of 300 °C, a chamber pressure of 26.7 Pa and a power of 60W (187.5kHz). Silane (2% SiH₄ diluted in N₂) and nitrous oxide (N₂O) served as precursors for undoped SiON layers. The B- or P-doping is realized by the introduction of diborane (5% B₂H₆ diluted in Ar) and phosphine (5% PH₃ diluted in Ar) into the deposition process.

<table>
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<tr>
<th>Samples</th>
<th>Flow Rates (sccm)</th>
<th>SiH₄/N₂</th>
<th>N₂O</th>
<th>B₂H₆/Ar</th>
<th>PH₃/Ar</th>
<th>Time (m:s)</th>
<th>Thickness (nm)</th>
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<tr>
<td>UD</td>
<td>480 340 0 0</td>
<td>998.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B20</td>
<td>480 340 20 0</td>
<td>1037.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>B40</td>
<td>480 340 40 0</td>
<td>1005.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B60</td>
<td>480 340 60 0</td>
<td>1032.9</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>B80</td>
<td>480 340 80 0</td>
<td>1009.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B100</td>
<td>480 340 100 0</td>
<td>998.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P05</td>
<td>480 340 0 5</td>
<td>959.2</td>
<td></td>
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<td></td>
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<tr>
<td>P10</td>
<td>480 340 0 10</td>
<td>982.6</td>
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<tr>
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<td>480 340 0 20</td>
<td>998.6</td>
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</tr>
<tr>
<td>P30</td>
<td>480 340 0 30</td>
<td>1000.1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P40</td>
<td>480 340 0 40</td>
<td>1003.7</td>
<td></td>
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</tbody>
</table>

Table I summarizes the flow rates of the different precursors for samples fabricated with varied boron or phosphorus concentrations. For our studies we have deposited an undoped sample (UD) and two series of doped SiON layers. The B- and P-doped SiON films have been fabricated by introduction of B₂H₆/Ar and PH₃/Ar at flow rates of 20-100 sccm and
5-40 sccm, respectively. The deposition time of all samples was set for a layer thickness around 1µm. The layer thickness of the as-deposited samples has been measured by spectroscopic ellipsometry (Woollam, M44) and is added to Table I as well.

After deposition the samples were annealed in nitrogen ambient. In the presented work, annealing experiments at temperatures from 600°C to 1100°C have been carried out. The duration of annealing was set to be 3 hours because the refractive index and thickness of the SiON layers become stable after 3 hours annealing, according to our previous study.10

In order to examine the reflow properties of the doped SiON samples and the sidewall roughness reduction of channel waveguides, B/P doped SiON layers were deposited on Si wafers with an 8-µm-thick thermal oxide layers which serve as the bottom claddings of waveguides. After fabrication of channel waveguides, reflow experiments were carried out at 900°C for 21 hours. The effect of the reflow has been evaluated by scanning electron microscope (SEM) images taken on channel waveguides before and after the reflow.

3. CHARACTERIZATION AND DISCUSSION

3.1 Refractive index variation

Figure 1 shows the refractive index of the as-deposited layers as a function of PH₃ and B₂H₆ flow. The refractive index of the B-doped SiON layers increases with the B₂H₆/Ar flow rates. For P-doped SiON layers, however, no monotonous change of the refractive index with PH₃/Ar flow rate was observed. At low flow rates the refractive index decreases; a minimum of refractive index was measured at PH₃/Ar = 5sccm. From previous studies on BPSG (= boron and phosphorous-doped SiO₂), it is well-known that the refractive index of BPSG increases upon addition of phosphorous while it decreases with the incorporation of boron.11,12 Our observations on the refractive index behavior of doped SiON films clearly deviate from the doping effects in BPSG. The main difference is the presence of nitrogen bonds in the SiON layers. Thus, the above-mentioned effects can probably be attributed to the difference in elemental composition of the base material, the occurrence of bonds between nitrogen and the introduced dopants, and the variation of layer densities. A detailed study is currently under investigation.

![Figure 1. Refractive index of as-deposited SiON layers as a function of the B₂H₆/Ar and PH₃/Ar flow rates](image)

The change of the refractive index of all samples as a function of the annealing temperature is shown in Figure 2. As can be seen, the refractive index of the undoped sample (UD) decreases with the annealing temperature until a minimum at 800°C is reached and slightly increases at temperatures beyond that value. For the B-doped samples, however, the refractive index decreases monotonously with temperature (Figure 2(a)). The index change with temperature also becomes larger for samples grown at higher flow rates of B₂H₆. For the P-doped SiON layers, similar changes of refractive index to that of the undoped sample were observed (Figure 2(b)). However, when the annealing temperature went to 1000°C and higher, some samples (P30 and P40 at 1000°C, P20 at 1100°C) became opaque and could not be
measured anymore. Scanning electron microscopy (SEM) showed that air voids and bubble-like structures were formed in these layers (Figure 3). This observation could be attributed to the formation of $P_2O_5$ clusters within the layers and their violent boiling or sublimation at high temperatures\textsuperscript{13}. Even for the P-doped SiON samples which did not become opaque at these high annealing temperatures (P05 and P10), the abrupt decrease of the refractive index indicates sudden changes in the layers; the clarification of which needs further detailed research. For the study presented in this paper we concluded from these first annealing results that the 900°C annealing temperature can be handled as a safe temperature limit for further annealing and reflow studies.

![Figure 2](image1.png)

Figure 2. Refractive index changes of (a) B-doped and (b) P-doped SiON layers as a function of annealing temperature

![Figure 3](image2.png)

Figure 3. SEM image of P20 after annealing at 1100°C for 3 hours in N$_2$ ambient.

### 3.2 Composition of the doped SiON layers

The as-deposited samples were characterized by X-ray Photoelectron Spectroscopy (XPS) to obtain the atomic concentrations of Si, N, O, B and P in the layers. As can be seen from the measurement results of B-doped SiON layers shown in Figure 4(a), with the increase of $B_2H_6$/Ar flow rate from 0 to 80 sccm, the atomic concentrations of B and N increase, together with the decrease of O and Si concentration. The change of the N and O concentrations of the B-SiON layers explains the increase of the refractive index which was measured by spectroscopic ellipsometry. For sample B100, however, the concentrations of all the elements change unexpectedly toward the opposite direction, which is not in line with the refractive index measurement and needs further detailed investigation. In case of the P-doped SiON layers shown in Figure 4(b), the concentrations of Si and N decrease while that of O increases, with the flow rate of PH$_3$/Ar. The concentration of phosphorus in the layers increases with PH$_3$/Ar flow rates from 0 to 20sccm, while decreases upon further increase of the phosphine flow. The refractive index variation of P-SiON layers at lower PH$_3$/Ar flow rate
(0–20sccm) can be attributed to the competition of two opposite contributions from P increase (index increase) and N decrease (index decrease). For P-doped SiON layers grown at higher PH3/Ar flow rate (20–40sccm), the refractive index change can not be solely explained by the measured element concentrations.

![Figure 4](image_url)

Figure 4. Atomic concentrations as a function of dopant precursor flow rates measured by XPS: (a) B-doped SiON layer and (b) P-doped SiON layer.

### 3.3 Hydrogen content in doped SiON layers

Fourier Transform Infrared (FTIR) spectroscopy has been used to determine the bond configuration and the hydrogen concentration of the samples. Figure 5(a) shows the full FTIR spectra of the as-deposited undoped sample where the positions of absorption peaks corresponding to Si-H stretching (around 2250cm⁻¹), N-H stretching (around 3350cm⁻¹) and O-H stretching (around 3550cm⁻¹) are indicated. No Si-H peaks were observed in the FTIR spectrum within the detection limit. The absorption peaks attributed to stretching of N-H is more prominent. Figure 5(b) shows the N-H and O-H peaks more clearly, after baseline correction of the FTIR spectrum.

![Figure 5](image_url)

Figure 5. FTIR spectra of the as-deposited undoped sample with indication of the absorption peaks corresponding to the Si-H stretching, N-H stretching and O-H stretching positions: (a) full spectra and (b) N-H and O-H absorption peaks after baseline correction.
Quite similar to the case of the undoped sample, the Si-H peaks in the FTIR spectra of all the other B- and P-doped SiON samples are too weak to be detected. Furthermore all detected O-H peaks are small compared to the N-H peaks. Therefore, we only consider the change of N-H peak for simplicity. The N–H bond concentration can be estimated by the method of Lanford and Rand$^6$, using the following expression

\[
[N - H] = \frac{1}{2.303 \times \sigma_{N-H}} \times \int_{\text{band}} \alpha(\omega)d\omega
\]

where $\sigma_{N-H}$ is the absorption cross-section for the N–H bonds, $\int_{\text{band}} \alpha(\omega)d\omega$ is the normalized absorption area of the band, and $\alpha = \frac{2.303}{A}$ is the absorption coefficient, $A$ being the absorbance and $t$ the film thickness.

The calculated N-H concentrations in all the as-deposited samples are shown in Figure 6. The N-H bond concentration in the P-doped SiON layers decreases with increasing PH$_3$/Ar flow rate. Compared to the undoped sample, a 50% reduction of N-H bonds was measured in the P40 layer. On the contrary the N-H concentrations in the B-doped SiON films increase with the flow rate of B$_2$H$_6$/Ar and are even higher than in the undoped sample.

![Figure 6. N-H concentration of SiON films as a function of the B$_2$H$_6$/Ar and PH$_3$/Ar flow rates.](image)

Figure 7 shows the effects of the annealing temperature on the N-H absorption peak in the FTIR spectra of three samples: undoped (Figure 7(a)), B-doped samples B100 (Figure 7(b)) and P-doped sample P10 (Figure 7(c). All curves are baseline-corrected and a vertical offset is applied to each curve for the ease of comparison between different curves. With increasing annealing temperature reduction of the N-H-related absorption peak can be clearly observed for all samples. When comparing, however, the doped and undoped samples we can conclude that hydrogen is more effectively removed in the doped samples. For the P-doped SiON films no hydrogen-related absorption peak was detected (within the detection limit) after annealing at 900°C.
The N-H concentrations in all boron- and phosphorus-doped samples treated at various annealing temperatures have been calculated with Equation (1). The results are presented in Figure 8. As can be seen from Figure 8(a), although B-SiON layers contain more N-H bonds than the undoped sample (Figure 6), more rapid reductions of N-H bonds with increasing annealing temperatures have been observed. For the P-doped SiON layers, the N-H elimination can be achieved by thermal annealing significantly more efficient. After annealing at temperatures as low as 700°C, the N-H concentrations in the P30 and P40 layers have been reduced close to the detection limit (Figure 8(b)).

3.4 Reflow of doped SiON channel waveguides

As discussed above, some severe side effects, such as bubble-like structure and abrupt decrease of refractive index occur in P-doped SiON layers when annealing temperatures above 900°C are applied. Therefore, we chose 900°C as the reflow temperature. The waveguide core layers were deposited on Si wafers with 8-µm thick thermal oxide layers using the same recipes shown in Table 1. Before fabrication of channel waveguides by lithography and reactive ion etching, the layers were annealed at 900°C for 3 hours to remove hydrogen and to obtain dense B- and P-doped SiON films. The channel waveguides were intentionally over-etched into the thermal oxide layers in order to allow for the roughness comparison between the sidewalls of doped and undoped materials. Reflow of all samples was carried out at 900°C for 21 hours in N₂. The effect of the reflow was evaluated from SEM images.
Figure 9. SEM images of P-doped SiON channel waveguide based on P40 recipe: (a) before reflow and (b) after reflow at 900°C for 21 hours in N₂ ambient.

From the SEM images we can conclude that reflow was only observed in waveguides based on the P-doped recipes. Figure 9 shows the SEM images of a channel waveguide fabricated with the P40 recipe before and after reflow. As can be seen from Figure 9(a), the sidewall roughness of the as-etched P-doped SiON channel waveguide on top of the over-etched lower oxide layer is comparable. After reflow treatment, significantly smoother sidewalls are achieved in the P-doped channel waveguide (Figure 9(b)). Meanwhile, the cross-sectional shape of the channel waveguide changed too, which calls for further investigations on the reflow process to achieve sidewall roughness reduction and control over the channel geometry simultaneously.

4. CONCLUSION

B- and P-doped SiON layers have been fabricated by introducing 5% B₂H₆/Ar and 5% PH₃/Ar, respectively, into the gas precursors of the PECVD process. The as-deposited and annealed layers were characterized by spectroscopic ellipsometry, X-ray Photoelectron Spectroscopy and Fourier transform infrared spectroscopy, in order to measure the refractive indices, element concentrations and N-H bond concentrations, respectively. Although an increased amount of N-H bonds was measured in the as-deposited B-doped SiON layers, they could be reduced more easily by thermal annealing. Even more pronounced N-H elimination was observed in P-doped SiON layers. The N-H absorption peak in the FTIR spectrum was reduced to the detection limit after annealing at a temperature as low as 700°C. First reflow results of P-doped SiON channel waveguides and the reduction of sidewall roughness have been demonstrated after thermal treatment at 900°C. These results are very promising for the development of extremely low-loss doped SiON waveguide technology for a large range of application fields in integrated photonics.

5. ACKNOWLEDGEMENT

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