DEPOSITION AND CHARACTERIZATION OF PECVD PHOSPHORUS-DOPED SILICON OXYNITRIDE LAYERS FOR INTEGRATED OPTICS APPLICATIONS

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Phosphorus-doped silicon oxynitride layers have been deposited by a Plasma Enhanced Chemical Vapor Deposition process from N$_2$O, 2% SiH$_4$/N$_2$ and 5% PH$_3$/Ar gaseous mixtures. The PH$_3$/Ar flow rate was varied to investigate the effect of the dopant to the layer properties. As-deposited and annealed (600, 800, 900 and 1000 °C) layers were characterized by Fourier transform infrared spectroscopy, Rutherford backscattering spectroscopy and spectroscopic ellipsometry. In this way the refractive index could be determined as well as the amount of hydrogen that is responsible for enhanced absorption in the 3rd telecommunication window around 1550 nm. The N-H bonds concentration was found to decrease with the phosphorus concentration. Furthermore the bonded hydrogen in the entire P-doped layers have been eliminated after annealing at 1000 °C, while undoped SiON layers require annealing at 1150 °C.

INTRODUCTION

Silicon oxynitride (SiON) layers applied in optical waveguiding structures have attracted large interest because of low absorption in the visible and near-infrared and a broad range in the index of refraction between 1.45 (SiO$_2$) and 2 (Si$_3$N$_4$). This versatility together with easy and reproducible deposition methods makes SiON an attractive materials system that allows for compact and potentially low-cost integrated optics structures (1,2). The deposition of these layers can be done by well-established standard silicon integrated circuit processing tools, such as plasma enhanced chemical vapor deposition (PECVD) or low pressure chemical vapor deposition (LPCVD) techniques (3). For application in the IR, PECVD SiON layers suffer from the incorporation of hydrogen, especially in the form of N-H and Si-H bonds with stretching modes around 3400 cm$^{-1}$ and 2280 cm$^{-1}$, respectively. Their first and second overtones at 1510 and 1500 nm respectively, contribute substantially to the absorption in the third telecommunication window around 1550 nm. The hydrogen content of as-deposited SiON layers can be reduced significantly by heat treatment at 1150 °C (1,2,4). Annealing, however, at this high temperature for a long time period (several hours) leads to undesired impurity diffusion and to an unwanted strong increase of the stress in the layers that might result in micro-cracks (2). Another reason for a heat treatment is the need of an improved smoothing topology and coverage of the device structure. Undoped SiON has a prohibitive high melting temperature whereas for doped-silica it is known that by controlling the dopant concentration of phosphorus, germanium or boron, a suitable
reflow temperature can be obtained (1,8). The technology of PECVD phosphorus-doped silica (PSG) layers has been studied for a long time and employed in integrated circuit manufacturing (5). There are numerous reports on the structural and optical prosperities of phosphorus-doped silica glass (5-8). The deposition and optical characterization of phosphorus-doped SiON, however, has to our knowledge not been reported previously, in the following we describe the PECVD deposition process of SiON layers with varying P-doping and analyze as-deposited as well annealed layers with respect to the hydrogen content and index of refraction.

EXPERIMENTAL DETAILS

Undoped and P-doped SiON layers were deposited on p-type <100> oriented 4” Si substrates in a parallel-plate PECVD reactor (Oxford system 133 PECVD). All studied samples were deposited at a substrate temperature of 350 °C, a chamber pressure of 1050 mTorr and RF power of 20 W at 13.56 MHz applied to the parallel plates of 210 mm diameter. Undoped SiON layers were deposited from appropriated gas mixtures of silane (2% SiH₄) diluted in N₂ and nitrous oxide (N₂O). Phosphorus doped SiON layers were deposited by adding different phosphine (5% PH₃ diluted in Ar) flow rates to the gas mixtures. The details of the deposition parameters are given in Table I.

Table I: Gas flow rates for undoped and P-doped silicon oxynitride layers

<table>
<thead>
<tr>
<th>Sample</th>
<th>2% SiH₄/N₂ (sccm)</th>
<th>5% PH₃/Ar (sccm)</th>
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<tbody>
<tr>
<td>P-00</td>
<td>600</td>
<td>0</td>
</tr>
<tr>
<td>P-10</td>
<td>600</td>
<td>10</td>
</tr>
<tr>
<td>P-20</td>
<td>600</td>
<td>20</td>
</tr>
<tr>
<td>P-30</td>
<td>600</td>
<td>30</td>
</tr>
</tbody>
</table>

The refractive index and the thickness of the layers were determined by spectroscopic ellipsometry with an uncertainty of approximately 2×10⁻³ in refractive index and 0.1% in layer thickness.

The nature of the hydrogen bonds and the hydrogen concentration of the layers with a thickness of ~1200 nm were determined with a Digilab FTS-575C Fourier transform infrared (FTIR) spectrometer. The measurements were carried out at room temperature in a nitrogen atmosphere by infrared transmission through the deposited layer and the silicon substrate with a resolution of 4 cm⁻¹. The background has been subtracted by using a silicon substrate identical to those used to deposit the layers. The hydrogen concentration of the undoped and the doped layers was evaluated from the IR peak area of the N-H and Si-H peak using the calibration factors from Lanford and Rand (9).

The atomic composition of the layers was determined using Rutherford backscattering spectrometry (RBS). The RBS measurements, were performed with a He⁺ beam with energy E = 2.0 MeV, charge Q = 20 μC, current I = 20 nA and detection angle of 15° and analyzed using RUMP software.
RESULTS AND DISCUSSION

As-deposited layers characterization

To study the phosphorus-doping effect on the layer properties, a series of PECVD P-doped SiON layers were deposited by adding 5% PH₃/Ar to the gas mixture. The gas flow rates of the 4 samples are given in Table I. The other process parameters were optimized to obtain a uniform layers thickness and refractive index. The as-deposited layers were analyzed and showed a refractive index in-homogeneity of less than 0.002 and a thickness non-uniformity of 1% for the entire layers. Figure 1 shows the atomic concentration determined by RBS and the refractive index (n) obtained by spectroscopic ellipsometry.

![Figure 1: Atomic concentration as measured by RBS (a) and refractive index (b) of the layers studied in this work as a function of PH₃ (5% in Ar) flow ratio.](image)

With increasing PH₃ gas flow rate the atomic phosphorus concentration increases linearly. The refractive index, however, increases only after an initial deep decrease. This decrease is unexpected as the index of refraction of phosphorus oxide, P₂O₅ is 1.51, substantially higher than the SiO₂ (n = 1.457) and the undoped SiON layer under study (n = 1.488). It is well-known that the refractive index of a layer is strongly influenced by its structure and composition. In particular, decreasing the layer density and the nitrogen content or increasing the oxygen content will result in a decreased refractive index value. We therefore performed a more detailed analysis of the density, the bonding configuration and the composition of the layers.

Regarding the density, one clearly can observe in figure 2 that the densities of the P-doped SiON layers follow the same trend as the refractive index indicating that the initially decreasing index of refraction is mostly caused by the reduced density of the slightly P doped layers.

Figure 3 shows the FTIR spectrum of the phosphorus-doped PECVD SiON layers (P-10, P-20 and P-30) in comparison with the undoped layer (P-00). The energy of the observed vibrational modes is presented in table II.
Figure 2: The density of the as-deposited layers as a function of 5% \( \text{PH}_3 \) in Ar flow ratio.

Figure 3: FTIR spectra of SiON layers with increasing P-doping.

Table II: Energy of the infrared vibrational modes observed in undoped and P-doped PECVD silicon oxynitride layers

<table>
<thead>
<tr>
<th>Vibration type</th>
<th>Peak frequency (cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O bending</td>
<td>P-00: 817, P-10: 813, P-20: 811, P-30: 809</td>
<td>(1,7)</td>
</tr>
<tr>
<td>Si-N stretching</td>
<td>P-00: 884, P-10: 884, P-20: 883, P-30: 882</td>
<td>(10)</td>
</tr>
<tr>
<td>Si-O stretching</td>
<td>P-00: 1051, P-10: 1062, P-20: 1069, P-30: 1073</td>
<td>(1,6,11)</td>
</tr>
<tr>
<td>P=O stretching</td>
<td>P-00: - , P-10: 1320, P-20: 1320, P-30: 1322</td>
<td>(5,7)</td>
</tr>
<tr>
<td>Si-H stretching</td>
<td>P-00: 2266, P-10: 2266, P-20: 2270, P-30: 2276</td>
<td>(1,10)</td>
</tr>
<tr>
<td>N-H stretching</td>
<td>P-00: 3387, P-10: 3383, P-20: 3382, P-30: 3381</td>
<td>(1,10)</td>
</tr>
</tbody>
</table>

The dominant feature in these spectra, a broad Si-O stretching mode around 1050 cm\(^{-1}\) could be observed in all samples. Its position shifts slightly from 1051 to 1073 cm\(^{-1}\) with increasing P doping. It has been reported that with increasing oxygen content, the position of the Si-O peaks shifts to high energies (11). This fact can be attributed to the increase of the electronegativity in the neighborhood of these bonds. Also in our case the RBS analysis, fig. 1.a shows a slight increase of the oxygen content with the \( \text{PH}_3 \) flow rate. This agrees with the observed refractive index behavior of the P-doped PECVD SiON layers when a small amount of \( \text{PH}_3 \) is added. The increase in the density and the refractive index of the layers after more \( \text{PH}_3 \) is added can be attributed to the increase in the phosphorus content in the layers with the \( \text{PH}_3 \) flow rate as confirmed by the RBS measurement. The absorption around 1320 cm\(^{-1}\) in the FTIR spectra can be assigned to the vibrational mode of the P=O peak. As expected, this absorption becomes more pronounced with increasing \( \text{PH}_3 \) flow rate.

Another important features that can be observed in all samples are the absorption due to N-H and Si-H stretching modes in the region 3300 – 3450 cm\(^{-1}\) and 2150 – 2300 cm\(^{-1}\) respectively. These modes influence largely the performance of devices for applications in optical telecommunication, since their overtones contribute to the optical losses at the third telecommunication window around 1550 nm. Therefore, the amount of N-H and Si-H bonds in the layers has been estimated by applying the N-H and Si-H absorption cross-sections as given by Lanford and Rand (9), see figure 4.
A significant reduction in N-H bonds concentration was observed for increasing P-doping, whereas the Si-H stretching modes remain unchanged in all samples. In order to explain the reduction of N-H bonds incorporation with increasing PH₃ flow rate at constant RF power, the following reactions for N₂O was proposed (12):

\[
\begin{align*}
N_2O & \rightarrow O + N_2 \quad [1] \\
N_2O + O & \rightarrow 2 \text{NO} \quad [2] \\
NO + O & \rightarrow \text{NO}_2 \quad [3]
\end{align*}
\]

The oxygen atom initially removed from N₂O by reaction [1] is used either for the layer formation or it can react with N₂O by equation [2] to form a NO radical, which gets absorbed in the layer as a source of nitrogen. Concurrent to [2], reaction [3] diminishes the amount of oxygen. When phosphine is added to the gas mixture, phosphorus is present in the layer and oxygen is bonded to phosphorus as P=O together with Si-O bonds. This agrees well with the results obtained from figures 1 and 3, where one can observe an increase in the oxygen content combined with a decrease in the nitrogen content from 3.0 at.% to 2.2 at.% It should be mentioned that the bond strength of P-N (617.1 KJ/mol) > Si-N (470 KJ/mol) > N-H (339 KJ/mol) (13). Therefore, the P-N is more favorable than the N-H bond. Hence the H atom bonded to nitrogen in the undoped layer will be replaced by a P atom when phosphine is added to the process. In this way, one can understand at least qualitatively the reduction of N-H bonds with increasing PH₃ flow rate (see figure 4).

**Annealing study**

In order to reduce the unwanted hydrogen bonds, the layers were annealed at four different temperatures of 600, 800, 900 and 1000 °C for 3 hours in a nitrogen atmosphere. The samples studied were deposited at identical conditions as mentioned in the previous section (samples P-00 to P-30). A typical example of the FTIR spectrum of as-deposited and annealed undoped and P-doped silicon oxynitride layers is shown in
figure 5 and 6. It can be clearly seen that both N-H and Si-H peaks are eliminated after annealing at 1000°C for the doped sample, while in the undoped sample the N-H bond still remains.

Figure 5: FTIR spectra (N-H peak) of undoped SiON layer, sample P-00 (a) and P-doped SiON layer, sample P-10 (b) for several annealing temperatures.

Figure 6: FTIR spectra (Si-H peak) of undoped SiON layer, sample P-00 (a) and P-doped SiON layer, sample P-10 (b) for several annealing temperatures.

The analysis of the FTIR absorption results in an estimate for the amount of N-H and Si-H bonds of the various as-deposited and annealed layers as is shown in figure 7 (a) and (b), respectively.

Figure 7: N-H concentration (a) and Si-H concentration (b) of layers (P-00 to P-30) with different PH₃ flow rate as a function of anneal temperature.
It can be observed from figure 7, that the bonded hydrogen in the entire P-doped layers has been eliminated after annealing at 1000 °C, while undoped SiON layers require annealing at 1150 °C to remove the hydrogen (2,4). Further, N-H bonds have been removed completely at 600 °C annealing temperature from layer containing 8.3 at.% of Phosphorus. The annealing temperature that required removing N-H is increasing when the phosphorus concentration decreases. This indicates that the elimination of the N-H bonds at lower annealing temperature is associated with the incorporation of phosphorus in the SiON matrix.

Finally, the refractive index and the relative thickness change have been measured as function of the annealing temperature as shown in figure 8.

Figure 8: Refractive index (a) and relative thickness change (b) of undoped and P-doped SiON layers (P-00 to P-30) as a function of anneal temperature.

From these results three steps in the annealing process can be clearly distinguished for P-doped PECVD SiON: First, at temperature of 600°C the hydrogen bonds are broken and reaction products are diffusing out of the layer. From the decrease of the refractive index while the layer starts to shrink in the lower temperature range, it might be concluded that not only hydrogen is removed, but also other species such as gaseous NH (14). Second, at temperatures above 600°C and below 900°C the material is sintered, which can be explained by the combination of increasing refractive index and shrinkage of the thickness. Third, in the case of the P-20 and P-30 samples the decrease in the refractive index again at annealing temperature above 900°C and the increase in layer thickness can be explained by the formation of voids in the layers, see SEM picture (figure 9).

Figure 9: Scanning electron microscope micrograph of a P-doped PECVD SiON layer (10 wt% P) annealed at 1100 °C for 4 hours in N₂ atmosphere.
CONCLUSIONS

Phosphorus-doped silicon oxynitride layers have been deposited by a PECVD process from 2% SiH4/N2, N2O, NH3 and 5% PH3/Ar gaseous mixtures. The phosphorus concentration in the film determined by RBS and FTIR spectroscopy was found to increase linearly with the phosphine flow rate. Special attention has been given to the presence of hydrogen bonds that lead to unwanted optical absorption in telecommunication applications. A significant reduction in N-H bonds concentration was observed for the P-doped SiON layers, when compared to undoped samples. The annealing results for the P-doped PECVD SiON layers show that the H bonds in the P-doped layers can completely be eliminated by annealing at 1000 °C.

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REFERENCES