Reduction of hydrogen-induced optical losses of plasma-enhanced chemical vapor deposition silicon oxynitride by phosphorus doping and heat treatment

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Plasma-enhanced chemical vapor deposition phosphorus-doped silicon oxynitride (SiON) layers with a refractive index of 1.505 were deposited from N2O, 2% SiH4/N2, NH3, and 5% PH3/Ar gaseous mixtures. The PH3/Ar flow rate was varied to investigate the effect of the dopant to the layer properties. We studied the compositions and the chemical environment of phosphorus, silicon, oxygen, nitrogen, and hydrogen in these layers by using x-ray photoelectron spectroscopy and Fourier transform infrared spectroscopy. The number of N–H and O–H bonds, which are responsible for optical losses around 1.55 and 1.3 μm, decreases in the as-deposited layers with increasing phosphorus concentration. Furthermore, the bonded hydrogen in all P-doped layers has been eliminated after annealing at a temperature significantly lower than required for undoped silicon oxynitride layers, that is to say 1000 °C instead of 1150 °C. The resulting optical loss in the entire third telecommunication window was well below 0.2 dB/cm, making P-doped SiON an attractive material for demanding integrated optics applications. © 2007 American Institute of Physics. [DOI: 10.1063/1.2423219]

I. 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 (n) between 1.45 (SiO2) and 2 (Si3N4). This versatility together with easy and reproducible deposition methods makes SiON an attractive material system that allows for compact and potentially low-cost integrated optics structures.4–6 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) technique.4,5,7

For application in the third telecommunication window, 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 and 2280 cm−1, respectively. Their first and second overtones at 1510 and 1500 nm, respectively, contribute substantially to the absorption in the stretching modes around 3400 and 2280 cm−1, respectively. The hydrogen content of as-deposited SiON layers can be reduced significantly by heat treatment at 1150 °C.5,8,9,11 Annealing, however, at this high temperature for several hours leads to undesired interface diffusion and to an unwanted strong increase of the stress in the layers that might result in microcracks. One of the means of reducing the hydrogen content in the as-deposited PECVD SiON layers is the introduction of phosphorus doping. In our previous work,12 we used N2O, 2% SiH4/N2, and 5% PH3/Ar gaseous mixtures for P-doped SiON deposition with an index of about 1.48. In the present work our challenge was to fabricate low-loss SiON waveguides with an increased index of about 1.5. For this we added ammonia as an additional processing gas.

In the following we first summarize our results on the PECVD deposition process of SiON layers with varying P doping. Thereafter an analysis is given of the as-deposited as well as annealed layers with respect to the hydrogen content and optical losses. We end up with some conclusions.

II. EXPERIMENTAL DETAILS

Undoped and P-doped SiON layers have been fabricated with an Oxford Plasmalab System 133 PECVD reactor. It consists of a process chamber in which two parallel plate electrodes of 210 mm diameter are placed horizontally with a spacing of 20 mm. The upper electrode is connected to a rf generator of 13.56 MHz via an automatic matching unit to ensure maximum power transfer. This electrode is also functioning as a showerhead for the gas inlet. The system is integrated with a load-lock wafer transporter, allowing fast system pump down.

Undoped and P-doped SiON layers were deposited on p-type (100) oriented 100 mm silicon wafers at a substrate temperature of 350 °C, a chamber pressure of 140 Pa, and rf power of 20 W. Optimized undoped SiON layers (P-00) could be obtained by gas mixtures of 600 SCCM of silane (2% SiH4 diluted in N2), 600 SCCM of nitrous oxide (N2O), and...
25 SCCM of ammonia (NH₃). Three types of phosphorus-doped layers P-10, P-30, and P-60 were deposited by adding 10, 30, and 60 SCCM of phosphine (5% PH₃ diluted in Ar) to the gas mixtures.

In order to determine the composition, density, and optical properties of the PEVCD layers, several depositions of P-00-, P-10-, P-30-, and P-60-type layers were carried out. The layer thickness and the index of refraction with an uncertainty of approximately 2 \times 10^{-3} and 0.1%, respectively, have been determined by spectroscopic ellipsometry (Wool-lam M44) on approximately 250 nm thin layers directly deposited on silicon wafers. Relatively thick layers (~1200 nm) deposited directly on silicon were used for the density and the atomic concentration measurements, whereas for the optical loss measurement sufficiently thick layers on thermally oxidized wafers were prepared.

The density \( [\rho (g/cm^3)] \) was determined by weighting the silicon wafer before and after deposition, while the film volume was deduced from the film thickness. The nature of the hydrogen bonds and the hydrogen concentration of the layers 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 transmission through the deposited layer and the silicon substrate with a spectral resolution of 4 cm⁻¹. The hydrogen concentration of the undoped and the doped layers was evaluated from the IR peak area of the N–H and Si–H peaks using the calibration factors from Lanford and Rand.

The atomic concentrations of Si, O, and N of the layers were determined by x-ray photoelectron spectroscopy (XPS) using a PHI Quantera scanning electron spectroscopy for chemical analysis (ESCA) microprobe. The compositions of the layers are determined from the ratio of the experimental core level areas, taking into account the sensibility coefficient of each element. The relative concentrations were determined to an accuracy of ~10% for silicon, oxygen, and nitrogen.

For optical loss measurements the thickness of the thermal oxide has been chosen sufficiently thick so that the silicon substrate does not influence the modes. The SiON layer was approximately 2.5 μm thick to ensure single mode propagation. The measurement was performed on the TE mode using the sliding prism method. The measurement limit of this method is approximately 0.2 dB/cm.

### III. RESULTS AND DISCUSSION

#### A. Characterization of as-deposited layers

In order to study the phosphorus-doping effect on the PEVCD SiON layer properties, a series of PEVCD P-doped SiON layers (P-10, P-30, and P-60) were deposited by adding 5% PH₃/Ar to the gas mixture. The as-deposited layers were analyzed and showed a refractive index inhomogeneity of less than 0.002 and a thickness nonuniformity of 1% for the entire layers.

Figure 1 shows the atomic concentration determined by XPS, the refractive index obtained by spectroscopic ellipsometry, and the density of the PEVCD SiON layers with increasing P doping. The atomic phosphorus concentration increases, as expected, with increasing PH₃/Ar gas flow rate. 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 that of SiO₂ (n=1.457) and of the undoped SiON layer under study (n=1.505).

In order to examine the origin of this initial deep decrease, the densities of the layers were determined. The densities of the P-doped SiON layers were found to have 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 [Fig. 1(b)].

With the XPS analysis the atomic concentration of the heavier elements in the layers could be determined. For the hydrogen concentration and bond energies FTIR spectroscopy has been used. Figure 2 shows FTIR spectra of the P-doped PEVCD SiON layers (P-10, P-30, and P-60) in

![FIG. 1. Properties of the layers studied in this work as a function of the PH₃ (5% in Ar) flow ratio: (a) atomic concentration as measured by XPS and (b) refractive index (○) and density (●).](image)

![FIG. 2. FTIR spectra ranging from 400 to 4000 cm⁻¹ of the PEVCD SiON layers under study with increasing P doping.](image)
The dominant absorption feature in these spectra, a broad peak around 1050 cm$^{-1}$, could be observed in all samples. This peak can be resolved into contributions by Si–O bending, Si–N$_1$ stretching, Si–N$_2$ stretching, Si–O symmetric stretching, P–O stretching, N–H bending, P–N stretching, Si–O asymmetric stretching, P=O stretching, and P=O stretching. For a quantitative analysis we used nonlinear curve fitting, assuming that the peaks have a symmetric Gaussian form. The deconvolution of the absorption spectra yields Gaussian peaks whose parameters are summarized in Table I (see also Fig. 3). The infrared peak positions are in good agreement with previous studies on undoped SiON and P-doped silica layers.$^{8,16–22}$.

Slight shifts were observed in all peak positions with increasing P doping (see Table I). The peak position around 1050 cm$^{-1}$ (the so-called Si–O peak, Fig. 2) is slightly shifting from 1042 to 1075 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.$^{23}$ This fact can be attributed to the increase in the electronegativity in the neighborhood of these bonds, since oxygen has higher electronegativity than nitrogen. Also in our case the XPS analysis, Fig. 1, shows a slight increase of the oxygen content with the PH$_3$ flow rate; this corresponds well with the energy shift.

The analysis presented in Table I shows that no P–O bonds were observed in sample P-10. This provides evidence that nearly no phosphorus oxide P$_2$O$_5$ and phosphate PO$_4$$^{5-}$ oxidation state, P with one P=O and three P–O single bonds are formed in sample P-10, although an increase in oxygen has been observed by XPS with respect to P-00. Moreover, the fitting results show an initial increase and decrease in Si–O and Si–N band areas, respectively [see Fig. 4(a)]. It is well known for SiON that the nitrogen atomic concentration is related by the following equation.$^{24}$:

$$3[N] = [\text{Si–N}] + [\text{N–H}].$$

(1)

Based on Eq. (1) and the preferred formation of Si–N bonds in comparison with N–H bonds, we suggest the configuration being the most probable nitrogen related bond configuration in the undoped SiON layers. This will not be the case when P is present in the reaction since P–N and P=O bonds are more favorable than N–Si and N–H bonds.

**TABLE I. 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>
</tr>
</thead>
<tbody>
<tr>
<td>Si–O bending</td>
<td>817 815 813 808</td>
</tr>
<tr>
<td>Si–N (1) stretching</td>
<td>882 883 881 879</td>
</tr>
<tr>
<td>Si–N (2) stretching</td>
<td>938 939 948 953</td>
</tr>
<tr>
<td>Si–O symmetric str.</td>
<td>1035 1051 1052 1034</td>
</tr>
<tr>
<td>P–O stretching</td>
<td>... ... 1085 1090</td>
</tr>
<tr>
<td>N–H bending</td>
<td>1135 1130 1128 1130</td>
</tr>
<tr>
<td>P–N stretching</td>
<td>... ... 1155 1151 1152</td>
</tr>
<tr>
<td>Si–O asymmetric str.</td>
<td>1174 1203 1197 1191</td>
</tr>
<tr>
<td>P–O stretching</td>
<td>... ... 1315 1318 1319</td>
</tr>
<tr>
<td>P–N stretching</td>
<td>... ... 1386 1397 1407</td>
</tr>
<tr>
<td>Si–H(N2Si)</td>
<td>2261 2261 2255 2254</td>
</tr>
<tr>
<td>Si–H(N3)</td>
<td>2305 2297 2280 2281</td>
</tr>
<tr>
<td>P–H stretching</td>
<td>... ... 2312 2308 2309</td>
</tr>
<tr>
<td>N–H–N str.</td>
<td>3368 3375 3343 3342</td>
</tr>
<tr>
<td>N–H stretching</td>
<td>3408 3411 3386 3382</td>
</tr>
<tr>
<td>H–O–H stretching</td>
<td>3497 3498 3489 3482</td>
</tr>
<tr>
<td>Si–OH--HOH</td>
<td>3604 3632 ... ...</td>
</tr>
<tr>
<td>Si–OH (1)</td>
<td>3672 3677 ... ...</td>
</tr>
<tr>
<td>Si–OH (2)</td>
<td>3749 3748 ... ...</td>
</tr>
</tbody>
</table>

FIG. 3. The broad IR absorption band between 700 and 1500 cm$^{-1}$ for sample P-30. It is well fitted with ten Gaussian-shaped absorption bands.

FIG. 4. Variation of the normalized absorption band area for PECVD SiON layers with increasing PH$_3$ flow rate: (a) silicon related bonds and (b) phosphorus related bonds.
as the bond strength of P–N (617.1 kJ/mol) > Si–N (470.0 kJ/mol) > N–H (339.0 kJ/mol). This indicates that the silicon and hydrogen bonds in

![diagram of silicon-nitrogen bond](image)

will be replaced by phosphorus. As a consequence, the free silicon radicals in the reaction chamber increase and Si–O bonds can increasingly be formed at low concentration of P radicals in the reaction chamber as seen for sample P-10, Fig. 4(a). Nevertheless, at higher P doping, P–O and P=O are more favorable to be formed. We also suggest that the most probable nitrogen related bond configuration in the P-doped SiON layers are

![diagram of nitrogen-phosphorus bond](image)

and

![diagram of silicon-phosphorus bond](image)

The increase in Si–O bonds agrees with the observed refractive index and density behavior of the P-doped PECVD SiON layers when only a small amount of PH3 is added. The increase in these parameters after adding more PH3 can be attributed to the increase in the phosphorus content and the simultaneous decrease in silicon content and Si–O bond concentration in the layers as confirmed by the XPS and FTIR measurements. With the increased P content, P2O5 can be formed in the SiON matrix as can be seen by the significant increase in the P–O bond concentration for sample P-60, see Fig. 4(b). The absorption around 1320 and 1400 cm⁻¹ in the FTIR spectra can be assigned to the vibrational mode of the P=O and P=O peak, respectively. As expected, this absorption becomes more pronounced with increasing PH3 flow rate [see Figs. 2 and 4(b)].

Another important feature that can be observed in all samples is the absorption due to N–H and Si–H stretching modes in the regions 3300–3450 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 loss 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, see Fig. 5(a).

A significant reduction in N–H bond concentration was observed for increasing P doping [Fig. 5(a)]. This corresponds well with the loss measurements obtained from undoped and P-doped SiON layers [Fig. 5(b)]. The peak loss at 1505 nm wavelength is reduced from 14.1 dB/cm for undoped samples to 3.5 dB/cm as the 5% PH3/Ar flow rate increased from 0 to 60 SCCM, respectively. Moreover, the optical losses around λ=1400 and 1550 nm were found to decrease from 4.7 to 0.2 dB/cm and from 1.8 to 0.7 dB/cm, respectively. This makes P-doped SiON a very promising waveguide material for applications in low-loss integrated optical devices. As mentioned before, the bond strength of P–N > Si–N > N–H and consequently P–N and P=O bonds are more likely to be formed instead of N–H bonds. 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, as can be clearly seen in Figs. 2, 4(b), and 5(a). In this way, one can understand at least qualitatively the reduction in N–H bonds with increasing PH3 flow rate [Fig. 5(a)].

The simultaneous decrease in the optical loss around λ =1400 nm can be attributed to the elimination of OH related group, since the P–O bonds (599.1 kJ/mol) are energetically more favorable than O–H bonds (427.6 kJ/mol).

**B. Effect of postdeposition annealing**

In order to study the effects of heat treatment to the hydrogen content and optical losses in P-doped SiON layers, the layers (P-00, P-10, P-30, and P-60) were annealed at four different temperatures of 600, 800, 900, and 1000 °C for 3 h in a nitrogen atmosphere. A typical example of the FTIR spectrum of as-deposited and annealed undoped (P-00) and P-doped (P-30) SiON layers is shown in Figs. 6(a) and 6(b). It appears that the N–H peak is eliminated after annealing at 1000 °C for the doped sample, while for the undoped sample most of the N–H bonds still remain. On the other hand, Si–H bonds have been eliminated from all samples after annealing at 900 °C. This effect can be attributed to the cross-linking between N–H and Si–H according to Si–H+N–H→Si–N+H2.11

![diagram of hydrogen bond concentration and optical loss](image)

**FIG. 5.** The hydrogen bond concentration and the optical loss of the as-deposited P-doped SiON layers as function of the 5% PH3/Ar flow rate: (a) N–H and Si–H bond concentration and (b) optical loss as a function of wavelength.
The analysis of the FTIR absorption data 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 Figs. 7a and 7b, respectively. It can be observed from Fig. 7 that the bonded hydrogen in all P-doped layers has been eliminated after annealing at 1000 °C, while undoped SiON layers require annealing at 1150 °C. Further, N–H bonds have been removed completely at 600 °C annealing temperature from layer P-60 that contains the highest phosphorus concentration. 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. It has been reported that the most common bonding orientations for P in borophosphosilicate glass (BPSG) layers are PO₄ with one P–O and three P–O single bonds, and P₂O₅ which could be the case in our layer when more phosphine is added to the process. It is well known that phosphorus oxides have weaker average bond strengths than silicon oxides resulting, for example, in a boiling point of P₂O₅ as low as 605 °C. Incorporation of phosphorus oxide in the SiON matrix will weaken the nearest neighbor bonds. This might explain the elimination of the N–H bonds at lower temperature for the P-doped SiON in comparison with the undoped layers. This corresponds also well with the optical loss measurements of the annealed undoped and P-doped SiON layers (see Fig. 8). It can be clearly seen that the optical loss is reduced to below 0.2 dB/cm after annealing at 1000 °C for the doped sample, while in the undoped sample the absorption peak around 1500 nm still remains.

IV. 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 was found to increase steadily 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. The bonded hydrogen is predominantly in the form of N–H bonds in PECVD SiON. A significant reduction in N–H and O–H bond concentrations was observed for the P-doped SiON layers, when compared to undoped samples. The optical loss of slab-type waveguides at λ=1505 nm was found to decrease from 14.1 to 3.5 dB/cm as the 5% PH₃/Ar flow rate in-
creased from 0 to 60 SCCM, respectively. Moreover, the optical loss values around $\lambda = 1400$ and 1550 nm were found to decrease from 4.7 to 0.2 dB/cm and from 1.8 to 0.7 dB/cm, respectively.

The annealing results show that the H bonds in the P-doped layers can completely be eliminated by annealing at 1000 °C. In that case, the optical losses in the entire third telecommunication window are reduced to below 0.2 dB/cm for slab-type P-doped SION waveguides with a refractive index around 1.505. It can therefore be concluded that this material is well suited for application in telecommunication devices.

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