

Fabrication and characterization of PECVD phosphorus-doped silicon oxynitride layers for integrated optics applications

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Phosphorus-doped silicon oxynitride layers ($n = 1.48 - 1.59$) have been deposited by a Plasma Enhanced Chemical Vapor Deposition (PECVD) process from 2% SiH_4/N_2 , N_2O , NH_3 and PH_3 gaseous mixtures. The refractive indices of the deposited layers were found to increase by adding PH_3 gas to the process. A slight variation in refractive index was observed in low refractive indices layers due to moisture absorption. Fourier transform infrared spectroscopy showed a significant reduction (40% –100%) in N-H bonds concentration for the P-doped silicon oxynitride, as compared with that for the undoped samples. These results are very promising for applications in low-loss integrated optical devices.

Introduction

Plasma Enhanced Chemical Vapor Deposition (PECVD) for silicon oxynitride (SiON) layers results in a flexible material for optical waveguides. Because of the hydrogenated precursors, the as-deposited SiON layers contain a large amount of hydrogen bonds as N-H and Si-H with stretching modes around 3340 cm^{-1} and 2280 cm^{-1} , respectively. Consequently, their overtones contribute to the absorption losses around 1510 and 1500 nm wavelength, respectively. Since this wavelength region is of particular interest for the third telecommunication window, the hydrogen content of the SiON layers has to be reduced significantly. It is known from literature that hydrogen can be eliminated from SiON layers by heat treatment at $1150\text{ }^\circ\text{C}$ [1,2]. Nevertheless, annealing at this high temperature for a long time period (several hours) leads to an undesired impurity diffusion and to an unwanted strong increase of the stresses, which might result in micro-cracks in the materials [2]. One of the means of reducing the hydrogen content in the as-deposited PECVD SiON layers is the introduction of phosphorus doping. In this paper we will summarize our results on the fabricating of P-doped SiON layers.

Experimental

The undoped and P-doped SiON layers studied in this work were deposited on p-type $\langle 100 \rangle$ oriented 4" Si substrates in a parallel-plate PECVD reactor (Oxford system 133 PECVD). All the studied samples were deposited at a substrate temperature of $350\text{ }^\circ\text{C}$, a chamber pressure of 1050 mTorr and RF power of 20 W with 13.56 MHz frequency applied to parallel plates of 210 mm diameter. The deposition conditions are given in table 1. The phosphorus doped SiON layers were deposited by adding 50 sccm of 5% PH_3/Ar to the gas mixture of sample 1 to 5, see table 1. The refractive index and thickness of the layers were determined by spectroscopic ellipsometry. The measurement error is approximately $\pm 2 \times 10^{-3}$ in refractive index and $\pm 0.1\%$ in layer thickness. The thickness non-uniformity represents the difference between the maximum and the minimum over a $70 \times 70\text{ mm}^2$ area and 15×15 points on a 4" wafer.

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Table 1: Gas flow rates and refractive index for undoped silicon oxynitride layers

Sample	Gas flow rates (sccm)			Refractive index n @ 632.8
	2%SiH ₄ /N ₂	N ₂ O	NH ₃	
1	600	600	0	1.481
2	600	480	0	1.488
3	600	600	25	1.498
4	600	360	50	1.536
5	600	240	50	1.570

The bonding configuration and the hydrogen concentration of the layers were determined with a Digilab FTS-575C Fourier transform infrared (FTIR) spectrometer. The absorption bands were measured 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 similar 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 [3].

Results and discussion

Refractive index characterization

PECVD phosphorus doped SiON layers were deposited by adding phosphine, PH₃, to the gas mixture. Fig. 1 shows a comparison between the refractive indices of undoped and P-doped PECVD SiON layers (1 to 5). The refractive index inhomogeneity is less than 0.002 and the thickness non-uniformity was found to be in the range 0.8 - 2% for the entire layers. It appeared that the refractive indices of all undoped layers have increased by adding PH₃ to the process as shown in Fig. 1. As the refractive indices of the phosphorus oxide, P₂O₅ and silicon oxide, SiO₂ are 1.51 and 1.46 respectively, an increase in index would be expected when incorporating P₂O₅ into SiON. The observed result from Fig. 1 is in agreement with this expectation.

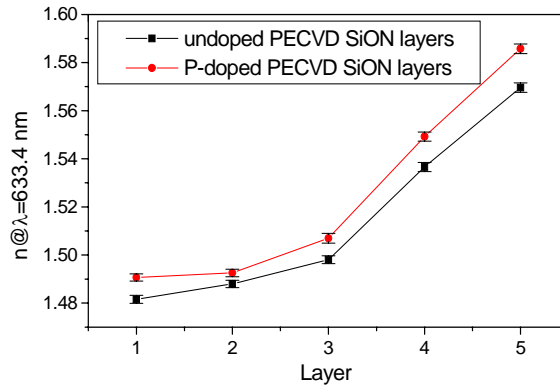


Figure 1: Refractive index of thin (~200 nm) undoped and P-doped SiON layers measured with a spectroscopic ellipsometer.

To check the stability of the P-doped SiON layers with time, a comparison was made between a refractive index measured immediately after deposition and some days later; see figure 2. A slight change in refractive indices was observed for low refractive index layers. This can be attributed to the well-known phenomena of moisture absorption

within the P-doped SiO₂ layers [4], which is usually described by the following scheme:
 $(-\text{Si-O})_3\text{P=O} + \text{H}_2\text{O} \rightarrow (-\text{Si-O})_3\text{P(OH)}_2$

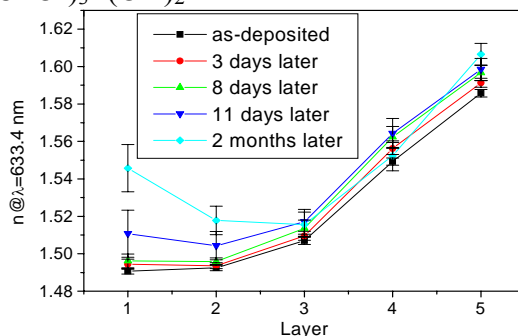


Figure 2: Refractive index of P-doped SiON layers as function of storage time in a cleanroom environment

In the following section this explanation is confirmed by direct measurements of the P=O bonds by infra-red absorption spectroscopy.

FTIR characterization

Fourier transform infrared spectroscopy was performed on undoped and P-doped PECVD SiON layers (1 to 5) to obtain information about the compositional and vibrational properties of the deposited layers. For the FTIR measurement all layers with thickness of 1.2 μm were deposited on p-type <100> oriented 4" silicon substrates. The FTIR absorption spectra of the layers are shown in Figure 3. The observed vibrational modes are presented in table 2.

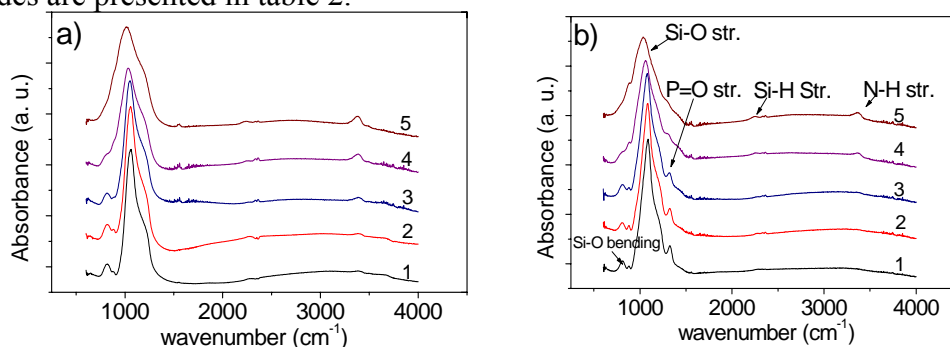


Figure 3: FTIR spectra of undoped SiON layers (a) and P-doped SiON layers (b)

Table 2: Infrared vibrations observed in undoped and P-doped PECVD silicon oxynitride layers

Vibration type	Peak frequency (cm ⁻¹)										Ref.
	Undoped layers					P-doped layers					
	1	2	3	4	5	1	2	3	4	5	
Si-O bending	821	820	817	-	-	807	807	809	-	-	[1,4]
Si-O stretching	1063	1056	1049	1032	1013	1035	1058	1080	1084	1087	[1,2]
P=O stretching	-	-	-	-	-	1326	1324	1320	1302	-	[4]
Si-H stretching	2277	2277	2268	2259	2251	2276	2275	2265	2258	2251	[1,2]
N-H stretching	3380	3381	3385	3385	3385	-	-	3368	3370	3374	[1,2]

All samples show a dominant absorption feature around 1050 cm⁻¹. Absorption due to the P=O stretching around 1325 cm⁻¹ is observed in the P-doped layers. The P=O peak increases in the layers with lower refractive indices, which is in line with the slight change of these layers with time. The absorption bands of N-H and Si-H bonds are of

special interest for optical applications, since their overtones contribute to absorption losses around 1510 and 1500 nm wavelength, respectively. The absorption due to N-H stretching modes is observed in the regions $3300 - 3400 \text{ cm}^{-1}$ in all undoped layers. A significant reduction in N-H bonds concentration was observed for the P-doped SiON layers, as compared with that for the undoped samples. Moreover P-doped SiON layers 1 and 2 have been deposited without the presence of N-H bonds (see fig. 4a and table 3). The absorption due to Si-H stretching modes is observed in the regions $2150 - 2300 \text{ cm}^{-1}$ and remains unchanged in all samples (Fig. 4b).

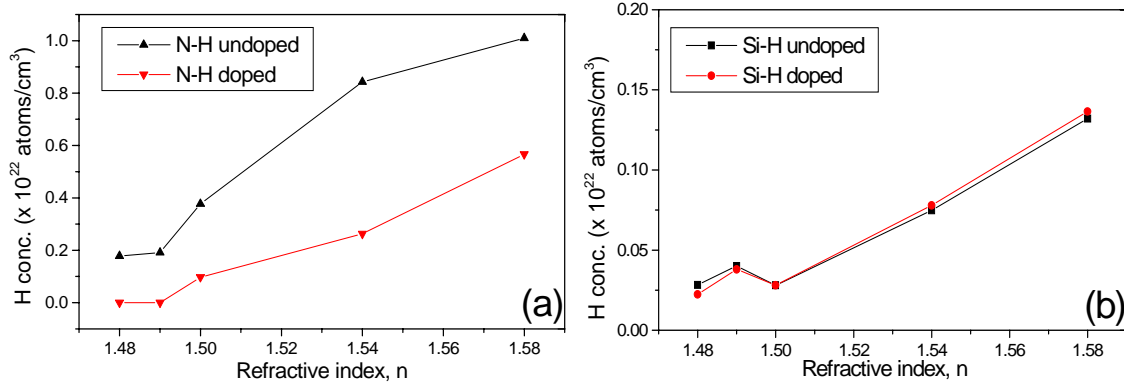


Figure 4: N-H bonds (a) and Si-H bonds concentration (b) for undoped and P-doped SiON layers

Table 3: The percentage reduction of N-H bonds concentration of the undoped layers as compared with the P-doped SiON layers

Sample	Refractive index n @ 632.8	N-H bond concentration ($\times 10^{21}$ atoms/cm ³)	Percentage decrease in N-H concentration (%)
1	1.481	1.779	100
2	1.488	1.913	100
3	1.498	3.7676	74
4	1.536	8.4271	69
5	1.570	10.1002	44

Conclusion

By admitting phosphine, PH_3 , to the gas mixture in the PECVD process we have fabricated P-doped Silicon oxynitride layers with various compositions ($n = 1.48 - 1.59$) having good uniformity and reproducibility. The refractive index of the deposited layers was found to increase by adding PH_3 gas to the process. A significant reduction in N-H bonds concentration was observed for the P-doped SiON layers, as compared with that for the undoped samples. Moreover, low refractive index P-doped PECVD SiON layers have been deposited without the presence of N-H bonds.

References

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