

Influence of phosphorus doping on hydrogen content and optical losses in PECVD silicon oxynitride

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PECVD Phosphorus-doped silicon oxynitride layers ($n=1.5$) were deposited from N_2O , 2% SiH_4/N_2 , NH_3 and 5% PH_3/Ar gaseous mixtures. Chemical bonds were determined by Fourier transform infrared spectroscopy. N–H bond concentration of the layers decreased from 3.29×10^{21} to $0.45 \times 10^{21} \text{ cm}^{-3}$, as the 5% PH_3/Ar flow rate increased from 0 to 60 sccm. A simultaneous decrease of O–H related bonds was also observed within the same phosphine flow range. The optical loss of slab-type waveguides at $\lambda=1505 \text{ nm}$ was found to decrease from 14.1 to 6.2 dB/cm as the 5% PH_3/Ar flow rate increased from 0 to 30 sccm, respectively. Moreover, the optical loss values around $\lambda=1400$ and 1550 nm were found to decrease from 4.7 to below 0.2 dB/cm and from 1.8 to 1.0 dB/cm respectively. These preliminary results are very promising for applications in low-loss integrated optical devices.

Introduction

Silicon oxynitride (SiON) layers applied in optical waveguiding structures have attracted large interest because of low absorption in the visible and a broad range in the index of refraction between 1.45 (SiO_2) and 2 (Si_3N_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]. For application in the 3rd telecommunication window, plasma enhanced chemical vapor deposition (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 [1, 2]. The hydrogen content of as-deposited SiON layers can be reduced significantly by heat treatment at $1150 \text{ }^\circ\text{C}$. 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 micro-cracks. One of the means of reducing the hydrogen content in the as-deposited PECVD SiON layers is the introduction of phosphorus doping [3]. In this paper we will summarize our results on the fabrication of P-doped SiON layers and the influence on the hydrogen content and the optical losses.

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 powered at a frequency of 13.56 MHz, via an automatic matching unit, which matches the impedance of the generator to that of the process chamber to ensure maximum power transfer. The upper electrode is also functioning as a showerhead for the gases inlet. The system is integrated with a load-lock wafer transporter, allowing fast system pump-down.

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All layers were deposited on p-type <100> oriented 100 mm silicon wafers at a substrate temperature of 350 °C, a chamber pressure of 1050 mTorr and RF power of 20 W. The details of the deposition parameters are given in Table I.

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

Sample	Gas flow rate			
	N ₂ O (sccm)	2% SiH ₄ /N ₂ (sccm)	NH ₃ (sccm)	5% PH ₃ /Ar (sccm)
P-00	600	600	25	0
P-10	600	600	25	10
P-30	600	600	25	30
P-60	600	600	25	60

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 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 [4].

The Phosphorus concentration of the layers was determined using Rutherford backscattering spectrometry (RBS). The RBS measurements, were performed with a He⁺ beam with energy $E = 2.0 \text{ MeV}$, charge $Q = 20 \text{ } \mu\text{C}$, current $I = 20 \text{ nA}$ and detection angle of 15° and analyzed using RUMP software.

For optical loss measurements, all layers have been deposited on thermally oxidized silicon wafers. The thickness of the thermal oxide has been chosen sufficiently thick so that the silicon substrate does not influence the modes. The measurement was performed on the fundamental mode using the sliding prism method [5]. The measurement limit of this method is approximately 0.2 dB/cm.

Results and Discussion

Figure 1 show the phosphorus concentration determined by RBS, the refractive index (n) obtained by spectroscopic ellipsometry and the density in g/cm^3 of the PECVD SiON layers with increasing P-doping. The atomic phosphorus concentration increases 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 the SiO₂ ($n = 1.457$) and the undoped SiON layer under study ($n = 1.505$).

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. The densities of the P-doped SiON layers was 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. 1b).

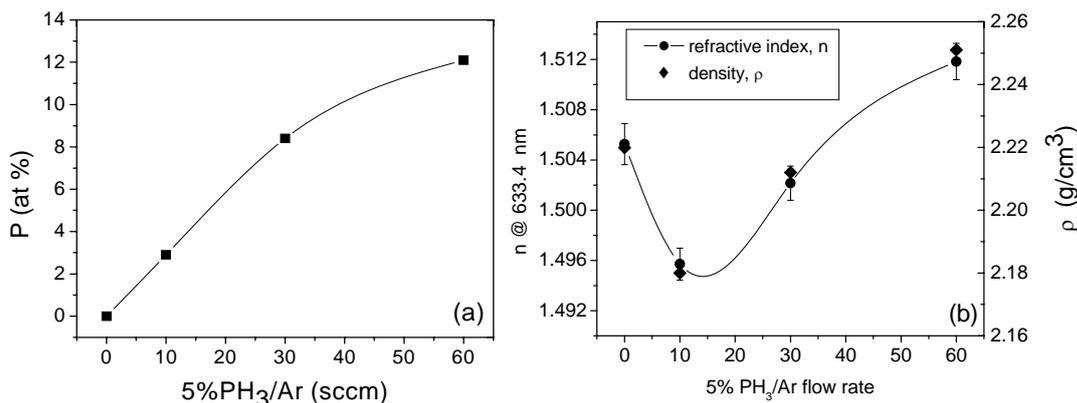


Figure 1: Phosphorus concentration as measured by RBS (a) and refractive index \bullet - and density \blacklozenge (b) of the layers studied in this work as a function of PH₃ (5% in Ar) flow ratio.

Figure 2 shows the FTIR spectrum of the phosphorus-doped PECVD SiON layers (P-10, P-30 and P-60) in comparison with the undoped layer (P-00). The dominant feature in these spectra, a broad Si-O stretching mode around 1050 cm⁻¹ could be observed in all samples. The absorption around 1320 and 1400 cm⁻¹ are assigned to the vibrational modes of the P=O and P-N peak respectively. As expected, this absorption becomes more pronounced with increasing PH₃ flow rate.

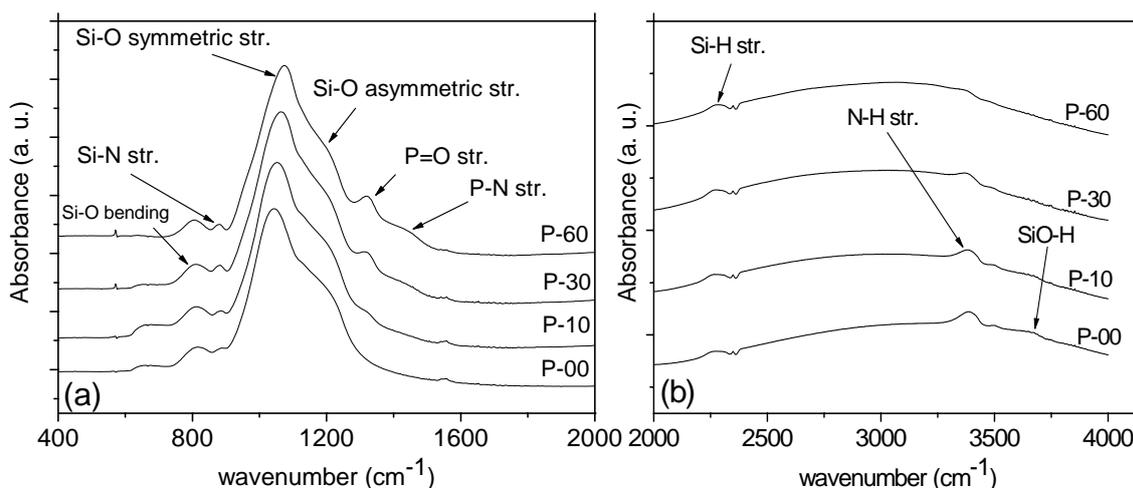


Figure 2: FTIR spectra of PECVD SiON layers from 400 to 2000 cm⁻¹ (a) and from 2000 to 4000 cm⁻¹ (b) with increasing P-doping

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 [1]. 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 [4], see figure 3a. A significant reduction in N-H bonds concentration was observed for increasing P-doping (figure 2b and 3a). This corresponds well with the loss measurements obtained from undoped and P-doped SiON layers (figure 4b). The peak loss at 1505 nm wavelength is reduced from 14.1 dB/cm for undoped samples to 6.2 dB/cm for the doped samples (PH₃/Ar = 30 sccm). 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 1.0 dB/cm respectively, what makes P-doped SiON waveguides material very

promising for applications in low-loss integrated optical devices. It should be mentioned that the bond strength of P-N (617.1 KJ/mol) > Si-N (470KJ/mol) > N-H (339 KJ/mol) [3]. 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, as can be clearly seen in figure 2. In this way, one can understand at least qualitatively the reduction of N-H bonds with increasing PH₃ flow rate (see figure 3).

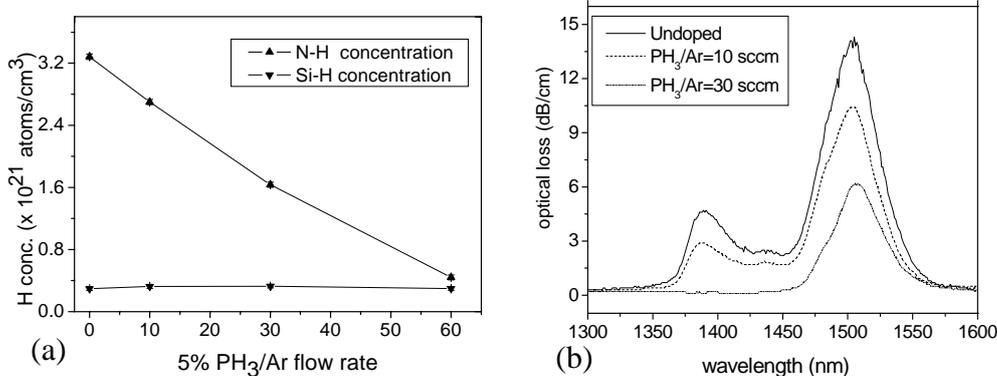


Figure 3: N-H and Si-H bonds concentration (a) and optical loss as a function of wavelength (b) of the as-deposited P-doped SiON layers as a function of the 5% PH₃/Ar flow rate.

The simultaneous decrease in the optical loss around $\lambda=1400$ nm can be attributed to the elimination of OH related group, since the phosphorus oxygen bonds (599.1 KJ/mol) are favorable to be formed in the reaction than hydrogen oxygen bonds (427.6 KJ/mol).

Conclusions

The bonded hydrogen in PECVD SiON is predominantly in the form of N-H bonds. A significant reduction in N-H and O-H bonds concentration was observed for the P-doped SiON layers, when compared to undoped samples. The optical loss of slab-type waveguides at $\lambda=1505$ nm was found to decrease from 14.1 to 6.2 dB/cm as the 5%PH₃/Ar flow rate increased from 0 to 30 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 1.0 dB/cm respectively.

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